Tables

Table 1
Historical Removal Actions and Investigations
Benning Road Facility RI/FS Project
3400 Benning Road, NE
Washington, DC 20019

Date	Incident / Investigation	Location	Activities
May-85	**PCB Cleanup**: Underground pipe leaked waste transformer oil containing PCBs.	Underground pipe leading from Kenilworth Transformer Shop (Current Building 56)	Removal of aboveground storage tank, associated piping, and excavation of PCB-contaminated material >5 ppm (approximately 288 cu ft)
Sep-88	**PCB Cleanup**: Soil contamination detected under concrete pad used to prepare off-line PCB capacitor banks for disposal in area formerly used to store used electrical equipment.	Parking lot located in the northeast portion of facility.	Removal of approximately 2500 cu ft (389 tons) of PCB-contaminated material (>5 ppm), including concrete slab.
1989-91	**UST Removals**: A total of 6 USTs were removed/closed in place during this period	550-gal #4 (south of bulk tank #1) 4,000-gal diesel (fuel island) 15K-gal #2 (est of Units 13 and 14) 2,000-gal used oil (Fleet Main.) 250-gal #4 10K-gal Diesel (Fuel Island)	All UST removals were inspected and approved for closure by the District.
Mar-91	**PCB Cleanup**: PCB capacitor leaked approximately 8 pounds onto concrete surface and seeped through expansion joints.	Concrete covered area located between Buildings 42 and 61	Approximately 126 cu ft PCB contaminated soil (>25 ppm PCBs) were removed and backfilled. Concrete replaced.
Apr-95	**PCB Cleanup**: PCB containing caulk and joint filler located inside cooling tower structures were found to be impacting the cooling tower concrete basins, sludge and water inside the basins, and soil adjacent to the basin's wall expansion joints. Pre-cleanup sediment sampling results from cooling tower blowdown discharge location upstream of Outfall 013 indicated no PCBs above 1 ppm.	Unit 15 and 16 cooling tower basins and surrounding soil	Approximately 185 cu ft of soil (>1-3 ppm) PCB was excavated. Old joint filler and caulk were removed and the expansion joints and basin were double washed and rinsed. The basin was encapsulated with concrete sealant after all rinse water was removed.
Sep-96 to Mar-97	**Intake Dredging**: Dredging of Station Intake for creation of wetlands	Generating station intake and points up- and downstream	Intake area in the Anacostia River was dredged and the dredge spoils were used to construct wetlands. Pre- and post-dredge sediment samples exhibited total PCBs of 119-934 ppb.
Apr-97	**USEPA Multi-media Inspection**: NPDES, RCRA and TSCA compliance inspection conducted by USEPA.	Entire facility	No compliance problems noted. PCBs at 0.25-3.13 ppm detected in residue samples from storm sewers inlets and outfalls. Elevated concentrations of heavy metals were also detected.
Dec-99	**Phase I Environmental Site Assessment**: conducted by PHI in anticipation of property transaction.	Entire facility	Recognized environmental concerns noted oil staining at two #4 and #2 fuel oil recirculation ASTs located east of the generating station. No concrete bottom noted in the containment areas.
Nov-03	**Salvage Yard Investigation**: Soil investigation was completed in area formerly used for storing used electrical equipment.	Salvage yard located west of Buildings 75 and 88	Approximately 296 cu ft of PCB contaminated material (>1 ppm) was removed from the site. TPH-DRO was detected, but were below DCDOH requirements upon final excavation.
Jun-09	**USEPA Site Inspection**: Site Inspection conducted during 2008 to determine further actions under CERCLA.	Former sludge dewatering area and the Anacostia River water and sediments	Metals, PAHs and PCBs were detected in the former sludge dewatering area and in Anacostia River sediments at concentrations exceeding the screening levels. USEPA links the historical discharges at the site to contamination found in river sediments.
Jan-10	**Phase I ESA**: conducted in connection with substation expansion.	18.5-acre area in the eastern and southern portions of the site that will be impacted by the substation expansion.	Conclusions noted potential for petroleum, metals and PCB impacts of subsurface soils and recommended sampling to develop proper health and safety and soils management procedures during construction.

Table 2
Landside Data Quality Objectives
Benning Road Facility
3400 Benning Road, N.E.
Washington, DC

DQO Step	Site-Specific Information
Step 1: State the Problems	Based on limited sediment sampling, PCBs, PAHs, and metals were detected at elevated levels in the Anacostia River in the vicinity of the Benning Road facility (the Site). Additional environmental assessment including soil and groundwater sampling is necessary at the Site to characterize environmental conditions, refine the CSM and to determine whether past or current conditions at the Site have caused or contributed to contamination of the river. This data is also needed to evaluate the potential for risk to human health and evaluate potential remedial alternatives.
Step 2: Identify the Decisions	1) Has the nature and extent of soil and groundwater contamination been adequately delineated? 2) Are potential target chemical concentrations detected in soil, groundwater or storm drain impacting the river currently or in the past? 3) Is the site-specific hydrogeology and volumetric flux of groundwater to the Anacostia River well understood in the context of the CSM? 4) Is the storm drain system and associated discharge to the Anacostia River at various outfalls well understood in the context of the CSM? 5) Are the target chemical concentrations in soil and groundwater at the Site greater than background concentrations? 6) Are the target chemical concentrations in soil or groundwater present at levels that indicate the potential for risk to human health or the environment?
Step 3: Identify Inputs to the Decision	The key inputs for making the required decisions are briefly summarized as follows: 1) Historical hydrogeological information, geotechnical information, analytical data and Site use/operations documentation. 2) Potential surface soil impacts will be evaluated by collecting 20 surface soil samples for PID and XRF instrument field screening. 3) Potential current or historic discharges from the storm drain system will be evaluated by sampling 5 sediment/residue and 5 water samples. Forensic analysis will be performed on up to 2 samples. 4) Five (5) HSA geotechnical soil borings and ERI will be performed to verify existing data and better characterize Site lithology and potential impacts, respectively. 5) 40 DPT soil borings with XRF field instrument screening and TPH/PCB aroclor analysis using on-site mobile laboratory will be performed to evaluate potential subsurface impacts. Discrete groundwater sampling at DPT locations will be performed to evaluate potential groundwater impacts. 6) HSA-installed monitoring wells, groundwater sampling, and aquifer testing will be performed following site-wide assessment to evaluate potential groundwater impacts and Site-specific hydrogeology. 7) A comprehensive analysis for VOCs, SVOCs, Metals, PCBs, Pesticides, Dioxin, and Furans will be performed selectively in the various media sampled to evaluate for these potential impacts.

Table 2
Landside Data Quality Objectives
Benning Road Facility
3400 Benning Road, N.E.
Washington, DC

DQO Step	Site-Specific Information
Step 4: Define the Study Boundaries	The Landside investigation includes Target Areas identified within the 77-acre Site (i.e. Benning Road Facility located at 3400 Benning Road, Northeast in Washington, DC). The Site is bordered by a DC Solid Waste Transfer Station to the north, Kenilworth Maintenance Yard (owned by the National Park Service, NPS) to the northwest, the Anacostia Avenue and Anacostia River to the west, Benning Road to the south and residential areas to the east and south (across Benning Road).
Step 5: Develop a Decision Rule	1) Historical information will be reviewed to identify potential sources of target chemicals and contamination at the Site. Past or current sources at the Site will then be evaluated using ERI followed by confirmatory soil and groundwater samples at target zones to delineate potential zones of impact and identify any continuing sources of contamination. 2) An evaluation will be performed which compares the analytical results to background to see if the concentrations are consistent with background concentrations. Should concentrations be less than or consistent with background concentrations, then this suggests no unacceptable risk attributable to the Site. 3) If the groundwater and soil concentrations of target chemicals are at or below the conservative human health screening values, then the potential source area will be recommended for no further evaluation. 4) If the soil or groundwater concentrations are above the screening values at a potential source area, the Site data will be further evaluated, including a fate and transport analysis of the target chemicals to characterize the potential impacts to the river.
Step 6: Specify Tolerable Limits of Decision Errors	The data quality indicators for screening and definitive data are defined in terms of the precision, accuracy, representativeness, completeness, and comparability (PARCC) parameters. The assessment of the data quality indicators is necessary to determine data usability and involves the evaluation of the PARCC parameters. To ensure the quality and integrity of the project data, the precision and accuracy of the analysis, the representativeness of the results the completeness of the data, and the comparability of the data to existing data will be evaluated. Data that meet the DQOs and fulfill project goals will be deemed acceptable. Data that do not meet objectives and goals will be reviewed on a case-by-case basis to ascertain its usefulness. To limit errors made based upon analytical data, the reporting limits (practical quantitation limits) for target analytes have been established at a level at least three times less than the action limit whenever technically feasible. In general, statistical analysis will not be used to determine decision error tolerance limits. Generally each sample will be used to make a decision.

Table 2
Landside Data Quality Objectives
Benning Road Facility
3400 Benning Road, N.E.
Washington, DC

DQO Step	Site-Specific Information
Step 7: Optimize the Design	The sampling design incorporates a progressive elimination approach using screening parameters to help focus the sampling and analysis for target chemical concentrations over the Site. The variability of data will have an effect on the sampling design. If necessary, the sample frequency and the analytical procedures may undergo changes to optimize the design. The design options, such as sample collection design, sample size and analytical procedures will be evaluated based on cost and ability to meet the DQOs.

Table 3
Waterside Data Quality Objectives
Benning Road Facility
3400 Benning Road, N.E.
Washington, DC

DQO Step	Site-Specific Information
Step 1: State the Problems	Based on limited sediment sampling, PCBs, PAHs, and metals were detected at elevated levels in the Anacostia River in the vicinity of the Benning Road facility (the Site). Additional sediment and surface water sampling is necessary to identify potential Site-related, near-Site and far-Site sources of COPCs in sediment and surface water and evaluate the potential for risk to human health and the environment.
Step 2: Identify the Decisions	1) Has the nature and extent of sediment contamination been adequately delineated? 2) Are the target chemical concentrations in surface sediments adjacent to the Site greater than upstream from the Site? 3) Are the target chemical concentrations in sub-surface sediments adjacent to the Site greater than upstream from the Site? 4) Are the target chemical concentrations in surface water adjacent to the Site greater than upstream from the Site? 5) Are detected concentrations in surface water or sediment present at levels that indicate the potential for risk to human health or the environment? 6) Is sedimentation in the portion of the Anacostia River in Study Area well understood in the context of the CSM? 7) Are the target chemical concentrations in sediment or surface water present at levels that indicate the potential for risk to human health or the environment?
Step 3: Identify Inputs to the Decision	The key inputs for making the required decisions are briefly summarized as follows: 1) PCBs and PAHs within the Anacostia River will be evaluated by sampling surface water and sediment (surface and sub-surface) from within the Waterside Investigation Area and background locations for laboratory analysis. 2) Inorganics within the Anacostia River will be evaluated by sampling surface water and surface sediment from within the Waterside Investigation Area and background locations for laboratory analysis of inorganics, hardness (water only), grain size (sediment only), TOC (sediment only), and SEM/AVS (sediment only). 3) VOCs, SVOCs, Pesticides, Dioxins, and Furans within the Anacostia River will be evaluated by sampling a sub-set of surface water and sediment (surface) samples from within the Waterside Investigation Area and background locations for laboratory analysis. 4) A sub-set of sediment samples will be collected and submitted for forensic laboratory analysis of PCBs and PAHs to differentiate between Site-related, near-Site and far-Site sources of COPCs.
Step 4: Define the Study Boundaries	The Benning Road facility is located at 3400 Benning Road, Northeast in Washington, DC. The Waterside investigation will primarily address sediment conditions within an area of the Anacostia River approximately 10 to 15 acres in size including approximately 2,500 linear feet to the south (approximately 700 feet south of the Benning Road Bridge) and 1,000 linear feet to the north of the Site's main storm water outfall area.

Table 3
Waterside Data Quality Objectives
Benning Road Facility
3400 Benning Road, N.E.
Washington, DC

DQO Step	Site-Specific Information
Step 5: Develop a Decision Rule	1) A benchmark comparison will be conducted to determine whether the sediment and surface water concentrations of organic and inorganic constituents adjacent to the site are above human health and ecological benchmarks, indicating the potential for risk. a. If the benchmark comparison indicates that adjacent concentrations are below human health and/or ecological benchmarks, then this suggests no unacceptable risk attributable to the site. b. If the benchmark comparison indicates that adjacent concentrations are above human health and/or ecological benchmarks, then additional investigation may be necessary. If the constituent concentrations are less than the sediment quality benchmarks, then those contaminants are not expected to contribute to total site risk. If the contaminant concentrations are greater than the sediment quality benchmarks, then further evaluation may be required. 2) A statistical evaluation will be conducted to determine whether the sediment and surface water concentrations of organic and inorganic constituents adjacent to the site are consistent with upstream conditions. a. If the statistical evaluation indicates that adjacent concentrations are less than or consistent with upstream concentrations, then this suggests no unacceptable risk attributable to the site. b. If the statistical evaluation indicates that adjacent concentrations are greater than upstream concentrations, then additional investigation may be necessary.
Step 6: Specify Tolerable Limits of Decision Errors	The data quality indicators for screening and definitive data are defined in terms of the precision, accuracy, representativeness, completeness, and comparability (PARCC) parameters. The assessment of the data quality indicators is necessary to determine data usability and involves the evaluation of the PARCC parameters. To ensure the quality and integrity of the project data, the precision and accuracy of the analysis, the representativeness of the results the completeness of the data, and the comparability of the data to existing data will be evaluated. Data that meet the DQOs and fulfill project goals will be deemed acceptable. Data that do not meet objectives and goals will be reviewed on a case-by-case basis to ascertain its usefulness. To limit errors made based upon analytical data, the reporting limits (practical quantitation limits) for target analytes have been established at a level at least three times less than the action limit whenever technically feasible. In general, statistical analysis will not be used to determine decision error tolerance limits. Generally each sample will be used to make a decision.

Table 4: Landside Data Collection Program
Benning Road Facility RI/FS Project
3400 Benning Rd, N.E.

Data Type	Data Use	Approximate Quantity	Methods
Surface Soil Samples (Phase I)			
Chemical analysis	Evaluation of surface soil quality	25 locations	TPH (8015), VOC (8260), PCB (8082), Metals, EPA 16 PAHs (8270)
		Up to 10 locations	VOCs (8260), SVOCs (8270), Pesticides, and Dioxins/furans
Forensic analysis	Evaluation of PCB and PAH origin and contribution	Up to 5 locations	PCB 680 Homologs and/or PCB 1668 Congeners, PAH fingerprinting
Storm Drain System (leading to Outfall 013) Sampling (Phase I)			
Water	Surface water discharge pathway	5 locations	PCBs (8082), PCB (608), EPA 16 PAHs (8270), dissolved and total Metals, VOCs (8260), TPH (8015), Pesticides
Sediment	Surface water discharge pathway	5 locations	PCBs (8082), PCB (608), EPA 16 PAHs (8270), Metals, VOCs (8260), TPH (8015), Pesticides
Forensic samples	PCB and PAH origin, site reference, surface water pathway	Up to 2 locations	PCB 680 Homologs, PCB 1668 B Congeners, PAH fingerprinting, dioxins/furans
Surface Geophysics (Phase I)			
Electrical Resistive Imaging (ERI)	Evaluation of subsurface geology, obstructions, NAPL plumes and optimization of soil boring and monitoring well placement	Up to 8 transects of 300-500 ft long	Geo Trax™ Survey
Soil Borings to 100 ft below grade (Phase I)			
Lithology	Subsurface geology	Continuous	Visual identification
PID Reading	Screening for VOCs	Continuous	Field methods
Geotechnical	Subsurface geology	25 samples (5 locations, and up to 5 samples per location)	ASTM Grain size and Atterberg limits
Geotechnical	Subsurface geology	10 Shelby tubes (5 locations and two samples per boring)	ASTM Permeability
Subsurface Soil and Groundwater Samples (Phase II)			
Direct Push (Geoprobe™) Borings to 5 ft below groundwater	Subsurface geology, identification of free phase oils	40 locations	Visual identification
VOC Vapor Screen	Rapid characterization, flexibility to field adjust sampling grid	Continuous	Photoionization Detector (PID) field instrument
Metals screen	Subsurface soil quality, rapid characterization, flexibility to field adjust sampling grid	120 samples (three depths at 40 locations)	X-Ray Fluorescence (XRF) field instrument
Soil chemical	Rapid characterization, flexibility to field adjust sampling grid	120 samples (three depths at 40 locations)	Mobile lab TPH (8015) and PCBs (8082)
Soil chemical	Metals confirmation/correlation	24 samples (20% of 120)	Metals (fixed lab)
Soil chemcial	Evaluation of subsurface soil quality	Up to 40 samples	VOCs (8260), PAHs (8270)
Soil chemical	Evaluation of subsurface soil quality	Up to 10 samples	Pesticides, SVOC (8270), dioxins/furans
Groundwater chemical	Evaluation of groundwater quality	40 locations	Mobile lab TPH (8015) and PCBs (8082)
Groundwater chemical	Evaluation of groundwater quality	40 locations	VOCs (8260), EPA 16 PAHs (8270), total and dissolved metals

Table 4: Landside Data Collection Program
Benning Road Facility RI/FS Project
3400 Benning Rd, N.E.

Groundwater chemical	Evaluation of groundwater quality	Up to 10 samples	Pesticides, SVOC (8270), dioxins/furans
Forensic analysis	Evaluation of PCB and PAH origin and contribution	Up to 5 soil/groundwater samples	PCB 680 Homologs, PCB 1668 Congeners, PAH fingerprinting
Monitoring Wells to the top of Arundel Clay (Phase III) *			
GW elevation monitoring	Determine depth to groundwater and groundwater gradient	TBD	Gauging
Aquifer testing	Evaluation of aquifer characteristics	TBD	Slug Testing
Chemical analysis	Evaluation of groundwater quality	TBD	VOC (8260), PCB (8082), dissolved and total Metals, EPA 16 PAHs (8270), SVOC (8270), pesticides
Chemical analysis	Evaluation of groundwater quality	TBD	Pesticides, dioxins/furans
Forensic analysis	Evaluation of PCB and PAH origin and contribution	TBD	PCB 680 Homologs and/or PCB 1668 Congeners, PAH fingerprinting
Civil Surveying			
Horizontal and vertical surveys	To locate all sampling points	All locations sampled in Phases I, II and III	GPS surveys

* Number and location of monitoring wells to be determined following evaluation of results from Phase I and Phase II.

Table 5: Waterside Data Collection Program
Benning Road Facility RI/FS Project
3400 Benning Rd, N.E.

Data Type	Data Use	Approximate Quantity	Methods
River Bottom Surveys (Phase I)			
Bathymetric survey	Understanding of depth of the water column and configuration of river bottom	Investigation area and background locations	USACE Hydrographic survey methods (Differential Geographic Positioning System, DGPS)
Utility Survey	Confirm utilities and other underwater obstructions	Investigation area and background locations	Side scan sonar
Surface Water Samples (Phase II)			
General chemistry	Evaluation of surface water quality near sediment-water interface	20 locations (10 transects + up to 10 background)	Field methods for measuring temperature, pH, turbidity, dissolved oxygen and conductivity
Chemical analysis	Surface water impacts	20 locations (10 transects + up to 10 background)	PCBs (8082), EPA 16 PAHs (8270), and Total and dissolved phase Metals (including hardness)
		Up to 10 locations	VOCs (8260), SVOCs (8270), Pesticides, and Dioxins/furans
Surface Sediment Samples (Phase II)			
Chemical analysis	Evaluation of surface sediment quality and background surface sediment quality	55 samples (45 near the site + up to 10 background)	PCBs (8082), Metals, EPA 16 PAHs (8270), AVS/SEM
		Up to 20 samples	VOCs (8260), SVOC (8270), Pesticides, and Dioxins/furans
Sediment characteristics	Evaluation of surface sediment quality and background surface sediment quality	55 samples (45 near the site + up to 10 background)	Total Organic Carbon (TOC), ASTM grain size
Forensic analysis	Evaluation of PCB and PAH origin and contribution	Up to 8 samples	PCB 680 Homologs and/or PCB 1668 Congeners, PAH fingerprinting
Subsurface Sediment Samples (phase II)			
Vibracore Borings (8 to 10 ft deep depending on refusal)	Sediment physical characteristics	55 samples (45 near the site + up to 10 background)	Visual identification
Chemical analysis	Evaluation of subsurface sediment quality and background surface sediment quality	165 samples (3 depths at 55 locations)	PCB (8082) and PAH16 (8270)
Forensic analysis	Evaluation of PCB and PAH origin and contribution	Up to 7 samples	PCB 680 Homologs and/or PCB 1668 Congeners, PAH fingerprinting
Geotech	Evaluation of subsurface sediment physical characteristics	Up to 20 samples	ASTM Grain size and TOC

Table 6
Summary of Calibration Frequency and Criterion for Field Instruments
Benning Road Facility
3400 Benning Road, N.E.
Washington, DC

Instrument	Calibration Frequency	Calibration Standards	Acceptance Criteria
pH meter	Initial: Each time instrument is turned on or upon erratic results	Two reference buffers which bracket expected sample values	Within ≤0.1 pH unit of true value
	Check: Every 15 samples and at the end of the day	pH 7 reference buffer	Within ≤0.1 pH unit of true value or instrument will be recalibrated
Specific conductivity meter	Initial: Each time instrument is turned on or upon erratic results	Two reference standards	Within 10% of true value
	Check: Every 15 samples and at the end of the day	Initial reference standard	Within 10% of true value or instrument will be recalibrated
DO meter	Initial: Each time the instrument is turned on or upon erratic results	Moist air	Within 5% of true value (based on altitude and temperature)
	Check: Every 15 samples and at the end of the day	Moist air	Within 5% of true value or instrument will be recalibrated
ORP meter	Initial: Each time instrument is turned on or upon erratic results	Two reference standards	Within 10% of true value
	Check: Every 15 samples and at the end of the day	Initial reference standard	Within 10% of true value or instrument will be recalibrated
Turbidity meter	Initial: Each time the instrument is turned on or upon erratic results	Two standards	Within 10% of true value
	Check: Every 15 samples or upon erratic results	Higher of initial reference standards	Within 10% of true value or instrument will be recalibrated
Temperature meter	Initial: Factory calibrated annually; no field calibration required.	NA	NA
	Check: Prior to use in field	Mercury bulb thermometer	Within 0.5°C of bulb thermometer or instrument will be replaced
Water Level Tape	Beginning, middle, and end of field program	Check against a manual water level measurement (steel tape)	Within 0.1 ft
PID	Initial: Each time the instrument is turned on or upon erratic results	Clean ambient air and compressed gas standard (isobutylene at 100ppm)	Within 5% of true value
	Check: Mid and end of the day	Compressed gas standard (isobutylene at 100 ppm)	Within 5% of true value
XRF	Initial: Each time the instrument is turned on or upon erratic results.	Use of certified reference standards/samples.	Within 2% of true value
	Check: Mid and end of the day	Initial reference standard	Within 2% of true value

Appendix A

Field Standard Operating Procedures

Project Operating Procedures
Benning Road Facility RI/FS Project

Site:
Benning Road Facility
3400 Benning Road, N.E.
Washington, DC 20019

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Contents

List of Acronyms

°C	degrees Celsius
CFR	Code of Federal Regulations
°F	degrees Fahrenheit
DI	Deionize
DIUF	deionized ultra-filtered water
DO	dissolved oxygen
eV	electron volts
GPS	Global Positioning System
HASP	Health and Safety Plan
IDW	investigation derived waste
LNAPL	Light Non-Aqueous Phase Liquid
MDS	Multi parameter Display System
mg/L	Milligrams per liter (parts per million)
MS/MSD	Matrix Spike / Matrix Spike Duplicate
mV	millivolts
NCR	Nonconformance Report
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards & Technology
ORP	Oxidation Reduction Potential
OSHA	Occupational Safety and Health Administration
oz	ounce
PDA	Personal Digital Assistant
PID	photoionization detector
POP	Project Operating Procedure
PPE	personal protective equipment
ppm	parts per million
Project	Benning Road RI/FS
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
RCRA	Resource Conservation and Recovery Act
RF	Outside Electronic Noise
SAP	Sampling and Analysis Plan
TOC	Top of Well Casing
µS/cm	microsiemen per centimeters
U.S. EPA	United States Environmental Protection Agency
UV	ultraviolet
VOCs	Volatile Organic Compounds
YSI	YSI Incorporated

Sediment Core Sampling – POP 005

1.0 Scope and Applicability

Selection and proper use of sediment sampling equipment is essential to the collection of accurate, representative sediment data that will meet the project Data Quality Objectives (DQOs). Most sediment collection devices are designed to isolate and consistently retrieve a specified volume and surface area of sediment, from a required depth below the sediment surface, with minimal disruption of the integrity of the sample and no contamination of the sample. The purpose of this document is to define the project operating procedure (POP) for collecting sediment cores using a vibracoring device.

This POP describes the equipment, field procedures, materials, and documentation procedures necessary to collect cores associated with the Benning Road Project using a vibracore.

2.0 Health and Safety Considerations

The health and safety considerations for the work associated with this POP, including physical, chemical, and biological hazards, are addressed in the site specific Health and Safety Plan (HASP; AECOM 2010) and associated task hazard analysis forms (THAs).

The health and safety considerations for the work associated with vibracoring include:

- The physical hazards of handling heavy equipment,
- Overhead lifting hazards using boat based winches and A-frames,
- Marine safety aspects of the program, and
- The specific chemical hazards related to the sediments.

Daily safety briefs will be conducted at the start of each working day before any work commences. These daily briefs will be facilitated by the Site Safety Officer (SSO) or his/her designee to discuss the day's events and any potential health risk areas covering every aspect of the work to be completed. Weather conditions are often part of these discussions. As detailed in the site specific HASP, everyone on the field team has the authority to stop work if an unsafe condition is perceived until the conditions are fully remedied to the satisfaction of the SSO.

If sampling from a boat, all sampling personnel must wear personal flotation devices (PFDs) when in the boat, and must follow all health and safety protocols for working in a boat presented in the project-specific health and safety plan. Care should be taken to avoid splashing when lowering the sampler and/or messenger into the water. Lifting the samplers into the boat, dumping its contents, and washing those contents may require leaning over the side of the boat. Care should be taken to keep the boat in proper balance at all times during sampling.

3.0 Interferences

Cross contamination may occur if the sediment samplers and associated equipment are not properly decontaminated between each use. Procedures for proper decontamination of field equipment are presented in POP 105-Decontamination of Field Equipment. Sampler-specific interferences are presented below.

Vibracoring methodologies can disrupt surface sediment, as well as consolidate/compact sediment layers and restrict the entry of soft horizons from entering the core tube thereby biasing profile results and confusing recovery information.

The Field Task Manager should continually monitor the core progression and ensure that the core sample is not vibrated excessively if the downward progression has ceased. Common interferences encountered during core driving include:

Interference	Possible Effect	Action Taken to Minimize Effect
Vibratory action	Consolidate/compact sediment during driving	Free fall the corer when possible and vibrate only as needed to advance the tube; use of a piston to improve recovery; establish minimum acceptance criteria
Loss of material out bottom	Less drive length achieved; gaps in retained sediment	Use core catcher
Blocking	Material doesn't enter core	Move off station and re-drive; establish minimum acceptance criteria

	tube or lessens recovery	
Angled entry	Drive length less than expected and fore-shortened	Make sure that wire line is vertical before core driving

4.0 Equipment and Materials

Sampler-specific equipment and supplies are listed below. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Personal protective equipment (PPE) and other safety equipment (refer to HASP);
- Sampling vessel;
- GPS or other positioning equipment;
- Vibracore device;
- Deployment equipment (e.g., A-frames, winches, generator);
- Decontaminated core tubes liners;
- Decontaminated stainless steel core catcher;
- Decontaminated stainless steel core cutter;
- Core storage racks to hold cores vertical and cold during temporary storage on-board coring vessel;
- Waterproof logbooks, pens, and labels;
- Core collection log
- Permanent marker or grease pencil;
- Line with weight and 0.1 foot increments indicated
- Tape measure and ruler;
- Tubing;
- Core tube caps;
- Electrical or duct tape;
- Cell phone
- Nitrile gloves
- Polarized sunglasses
- Sample containers, labels, and preservatives
- Personal flotation devices (PFDs), if sampling from a boat
- Chest waders, if sampling on foot
- Surveyor rod or weighted line, if sampling on foot
- Camera; and
- Decontamination equipment/supplies (POP 012- Decontamination of Field Equipment).

5.0 Procedures

Depending on the characteristics of the site being investigated, sediment core samples may be collected from a boat, or by sampling personnel in waders. In all instances, sediment sampling should begin from the most downstream location and proceed to the most upstream location. If sediment samples are collocated with surface water samples, the surface water sample should be collected prior to the sediment sample in order to avoid increased turbidity from displaced sediment. Regardless of the type of sediment sampling equipment used, documentation of field observations and collection activities should be recorded on the sediment sampling sheet. The following observations should be recorded on the sediment sampling sheet for all sediment sampling activities:

- Weather conditions and other relevant site conditions

- Sample location
- Depth of water to the nearest 0.1 foot. A surveyor rod or weighted line may be used. If the surveyor rod is used, minimize water turbulence and do not disturb any sediment.
- Physical characteristics of the water body such as estimated current speed (stagnant, slow, medium, or fast) and direction, odor, color, presence of any dead vegetation, surface sheens, etc.
- Sediment color
- Sediment grain size

Specific procedures for the collection of sediment core samples using a vibracoring device are presented below.

5.1 Sampling procedures

This section gives the step-by-step procedures for collecting cores using a vibracore. Observations made during sediment core collection should be recorded on core collection log and logbook.

5.2 Decontamination of equipment

Decontamination of the core tubes, stainless steel core cutter, and stainless steel core catcher assemblies will be performed prior to vessel departure in accordance with procedures outlined in POP 105 – Decontamination of Field Equipment). A sufficient amount of decontamination equipment and supplies will be brought on the coring vessel to accommodate the need for miscellaneous, unforeseen decontamination. New core liners/caps will be used for the project and will not require decontamination. The liners will be kept in the manufacturer-supplied packaging (plastic bag) until removed for use. Any liners not kept in closed packaging will be decontaminated prior to use according to POP 012 - Decontamination of Field Equipment.

5.3 Collection of cores

1. Initiate the Core Collection Log.
2. Put on all necessary PPE (including a PFD, if sampling by boat)
3. Attach core catcher
4. Obtain water depth (to nearest 0.1 foot)
5. Slowly lower the vibracore through the water column to the sediment surface using the winch or other deployment equipment.
6. Record the “zero” mark on the winch cable.
7. Slowly lower vibracore into sediment under its own weight until it stops.
8. Turn on the compressor/ actuate the hydraulics. Slowly penetrate the sediment to the target penetration, or until refusal.
9. Lower vibracore approximately 1 foot beyond target to obtain a “plug” at the bottom of the core (i.e., to minimize loss of sediment from core).
10. Upon completion of the required penetration, or upon vibracore refusal, turn the compressor/ hydraulics off. Record the vibracore penetration depth on the Core Collection Log.
11. Record the final core location coordinates.
12. Slowly raise the vibracore, while maintaining the core in a vertical position as field conditions allow.
13. Bring vibracore to sampling vessel deck while maintaining the core in a vertical position. Remove core cutter and core catcher, replace with cap, and secure cap with duct tape.
14. Clean the vibracore barrel and coring assembly by hosing down the equipment with site water as described in POP 105 – Decontamination of Field Equipment.
15. Remove the core tube from the vibracore barrel and place a cap on bottom of the coring tube, keeping the core tube in an upright position, as field conditions allow.
16. Return the vibracore device to its onboard, deck storage location.

17. Clean the core tube by hosing it down with site water. Care should be taken not to direct water into the open end of the core tube.
18. Evaluate whether core penetration and recovery are acceptable using the procedures outlined in Sections 5.4 and 5.5, respectively.
19. Keeping the core tube upright, as field conditions allow, use a core cutter to cut/hole in the core tube approximately 3 to 4 inches above the sediment to allow excess water to seep from the core tube. Continue to make cuts/holes in the core tube, lowering 1 inch each time until reaching the sediment/water interface. When all excess water has been drained from above the sediment/water interface, cut off excess core tube.
20. Cap the cut end of the tube, secure cap with duct tape, and draw an arrow toward the cap. Draw an arrow on the coring tube with permanent marker and label "top" to indicate the top of the core. Label the core with the location ID, date, and time, and record this information on the Core Collection Log.
21. Measure the recovered length of the sediment in the core tube (to the nearest 0.1 foot to the extent possible) and record it on the Log. The distance between the top of the sediment in the coring tube and the bottom of the coring tube corresponds to the recovered length. Apparent gaps should be noted on the Log and the length and location(s) of the gap(s) should be noted. The total gap length will be subtracted from the total recovery length.
22. Store the core vertically in a core storage rack (capable of keeping cores cold) while on the vessel until it can be transported to the sample processing area. Cores greater than 4 feet will be segmented on the vessel to allow for storage and transportation. Cut these cores at the location of a planned sample segmentation using a core cutter and recap the exposed ends. Add appropriate markings to indicate the location and segment of each section.

5.4 Procedures for determining acceptable core penetration

1. Calculate penetration percentage using the following equation:

$$\text{Penetration}\,(\%) = \frac{\text{actual penetration}\,(\text{feet})}{\text{target penetration}\,(\text{feet})} \times 100$$

   Actual penetration is the depth advanced into the sediment not including the depth advanced to form a plug.
2. Record penetration percentage on the Core Collection Log.
3. If penetration is ≥80%, then penetration is acceptable. Proceed to Section 5.5, Procedures for Determining Acceptable Core Recovery.
4. If penetration is <80%, then (a) retain core and (b) record on the Core Collection Log if due to refusal. Reposition vessel and redeploy coring device. Upon three unsuccessful attempts to obtain >80% penetration, contact Project Manager or Field Task Manager to determine if additional cores should be attempted.

5.5 Procedures for determining acceptable core recovery

1. Calculate recovery percentage by the following equation:

$$\text{Recovery}\,(\%) = \frac{\text{recovery}\,(\text{feet}) - \text{gaps}\,(\text{feet})}{\text{actual penetration}\,(\text{feet})} \times 100$$

2. Record recovery percentage on the Core Collection Log.
3. If recovery is ≥80%, then recovery is acceptable. Continue processing core, then move to a new core location.
4. If recovery is <80%, then (a) retain core and (b) move to a new coring position and redeploy coring device. Upon three unsuccessful attempts to obtain >80% recovery, contact Project Manager or Field Task Manager to determine if additional cores should be attempted.

5. Record all attempts on the Core Collection Log. Communications with the Field Task Manager will be documented in the field logbook. Failure to collect a core at a specified location will be recorded in the logbook.

5.6 Management of cores

1. Verify that the lengths of the core tubes, water depth, and positioning data have been recorded on the Core Collection Log.
2. Prior to transit to the next coring location or returning to shore, decontaminate the coring equipment and sampling vessel decking as described in POP 105 – Decontamination of Field Equipment.
3. Proceed to next core location specified for that day and repeat above procedures.
4. Completed Core Collection Logs and a Sample Chain of Custody will be provided when relinquishing cores for processing/analysis.

5.7 Core processing

1. Each core will be logged, photographed, and sub-sampled as per the specified analytes require.
2. The appropriate sediment horizon will be removed from the core tube using a stainless steel spoon/scoop and placed in a decontaminated 1-gallon stainless steel or Pyrex glass mixing bowl.
3. Each sample will be visually examined for physical characteristics such as composition, layering, odor, and discoloration.
4. Samples will be homogenized in the mixing bowl and placed in appropriate sample containers.
5. Sediment sampling equipment such as bowls, spoons, augers, and dredges will be decontaminated prior to and following sample collection as described in POP 105.

6.0 Quality Assurance / Quality Control

All sediment sampling equipment will be thoroughly decontaminated prior to and in between use according to the procedures described in POP 105- Decontamination of Field Equipment

Field accuracy will be assessed through the collection and analysis of equipment blanks. Equipment blanks will be collected for each type of sediment sampling equipment in accordance with the Sampling and Analysis Plan (SAP).

Field precision will be assessed through the collection and analysis of field duplicates. Field duplicates will be collected in accordance with the SAP.

Entries on the forms and in the field logbook will be double-checked by the samplers to verify the information is correct. Completed forms will be reviewed periodically by the Field Task Manager and/or Project Quality Assurance Officer or his/her designees to verify that the requirements are being met.

7.0 Data and Records Management

All data and information (e.g. type of sample equipment used) must be documented on the sediment coring log and/or field logbooks with permanent ink. Deviations to the procedures detailed in this POP should be recorded in the field logbook.

Data recorded will include the following:

- Weather conditions
- Sample location
- Sampling equipment type
- Date and time of sample collection, and the initials of the sampler
- Sediment characteristics (e.g. color and particle size)
- Depth of sediment sampled
- Water depth

- Physical characteristics of the water body such as estimated current speed (stagnant, slow, medium, or fast), odor, color, presence of any dead vegetation, surface sheens, etc.
- Samples and quality assurance/quality control (QA/QC) samples collected

The chain of custody form will be completed following sample collection describing all pertinent sample information, site information, intended analyses, etc. This form must be completed properly and the intended recipients must receive their respective copies.

8.0 Personnel Qualifications and Training

All field samplers are required to take the 40-hour Occupational Health and Safety Administration (OSHA) Hazardous Waste Operations training course and annual 8-hour refresher training prior to engaging in any field collection activities. The individuals executing these procedures will have read, and be familiar with, the requirements of this POP and the corresponding Work plan. Actual vibracoring operations will be conducted only by personnel experienced with the equipment, but subsequent manipulations, measurements, cutting and labeling procedures are relatively simple and can be implemented by personnel without specialized training. It is recommended that initial core manipulations and handling activities be supervised by more experienced personnel

The Project Manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this POP and the project plan. In the absence of a Field Team Leader, the Project Manager is responsible for ensuring that field records are reviewed and approved as described below.

The Field Team Leader is responsible for reviewing and approving the field records for accuracy, completeness, and conformance to the procedures in this POP.

Field personnel are responsible for recording data according to the procedures outlined in this POP.

9.0 References

POP 101-. Field Records

POP 105- Decontamination of Field Equipment

Sealed-Screen Groundwater Profiling – PO 016

1.0 Scope and Applicability

This Project Operating Procedure (POP) defines the procedures for sealed-screen groundwater profiling. Sealed-screen samplers typically consist of a PVC or stainless steel screen nested within a sealed, water-tight sheath. This procedure is used as an efficient means of collecting screening-level groundwater data such as water quality parameters and contaminant concentrations. The data quality should be sufficient enough such that informed decisions can be made when delineating contaminant plumes, inferring source areas, identifying other potential soil sample locations and/or locations for permanent monitoring well installation, and performing contaminant fate and transport evaluations.

2.0 Health and Safety Considerations

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, will be addressed in the site specific Health and Safety Plan (HASP). In the absence of a site-specific HASP, work will be conducted according to the AECOM Health and Safety Policy and Procedures Manual and/or direction from the Regional Health and Safety Manager.

3.0 Interferences

Sealed-screen samplers generally are limited to collecting one sample per advance of the sampler. Because the screen is not exposed to the formation as the sampler is advanced into the subsurface, the screen does not become plugged or damaged. In addition, the potential for cross contamination is greatly reduced and a depth-discrete sample that is representative of the target sampling zone can be collected. However, depending upon the system used, multi-level sampling in a single borehole can be accomplished with sealed-screen samplers by retrieving the sampler and decontaminating it or replacing it with a clean sampler before reentering the hole to collect another sample. The potential for cross contamination may be minimized by purging the screen point prior to collecting a sample. This profiling process may be conducted with an understanding of data quality objectives.

Gas bubbles present in discharge tubing during purging and sampling are a problem: Their presence indicates off-gassing from groundwater or poor purging connections in the airline or groundwater tubing. Sunlight can exacerbate this problem when low pumping rates are used. Check connections at the surface. If bubbles persist, check connections at the pump. During purging and sampling, observe the flow of groundwater in the sample tubing and keep the tubing filled with groundwater, removing all air pockets and bubbles, to the extent possible. Gas bubbles may be reduced by increasing flow, if possible, and keeping tubing shaded.

Pump tubing lengths above the top of the drill rod should be kept as short as possible to minimize heating the groundwater in the tubing by exposure to sun light and ambient air temperatures. Heating may cause the groundwater to de-gas, which is unacceptable for the collection of samples for VOC and dissolved gases analyses.

4.0 Equipment and Materials

4.1 Sealed-Screen Groundwater Sampler

A sealed-screen groundwater sampler (e.g. Geoprobe® Screen Point 22 Groundwater Sampler) is a direct push device consisting of a PVC or stainless steel screen that is driven to depth within a sealed, water-tight sheath and then deployed for the collection of representative groundwater samples. Upon deployment, up to 48 inches of screen can be exposed to the formation.

4.2 Mechanical Bladder Pump

A submersible mechanical bladder pump (e.g. Geoprobe® Model MB470 Mechanical Bladder Pump) will be deployed within the sealed-screen groundwater sampler once it has been installed by direct push advancement. The mechanical bladder pump consists of a corrugated bladder which is mechanically compressed and expanded to push groundwater to the surface through concentric tubing. Teflon or Teflon-lined polyethylene bladder pumps are preferred for sampling VOCs. Check valves above and below the bladder control flow direction. The outer tube of the concentric tubing set holds the pump body in place while the inner tube is used to actuate the bladder and transmit water to the surface. The

bladder pump assembly must accommodate the ID of the probe rods and screen point which typically is 0.5 inch and be long enough to maneuver past rod joints typically occurring every 10 feet. For example, the Geoprobe® Model MB470 Mechanical Bladder Pump has internal components made of stainless steel with an OD of 0.47 inches and an overall length of 26.75 inches with an inlet screen assembly installed

4.3 Inertia Lift Pump

A check-valve affixed to HDPE tubing may be used to withdrawal groundwater from within the screen for purging. The OD of the check-valve should be closely equivalent to the ID of the screen to maximize inertia, as such a surge block may be necessary in conjunction with the check-valve. This method is not preferred for sampling because agitation of groundwater within and around the sample point may result in increased turbidity and sediment load. Samples collected using this method will likely require additional field or laboratory filtration.

4.4 Tubing

Teflon or Teflon-lined polyethylene tubing are preferred for sampling VOCs. Inner tubing diameter should be kept to the smallest size possible to reduce the generation of air pockets during low flow.

5.0 Procedures

5.1 Sealed-Screen Advancement

A direct push rig will advance the sealed-screen sampler to the desired sampling depth. Inner rods will be installed to hold the inner screen in place while the outer sheath is retracted to reveal the screen to the formation. The inner rods can then be removed and the depth to water and total depth of water can be measured using a water level indicator.

5.2 Groundwater Sampling

Samples should be collected in order of decreasing volatility and reactivity so that the most volatile or reactive samples are collected first. The following are general guidelines presented in the order that samples should be collected.

- Volatile Organic Compounds
- Semivolatile Organic Compounds
- Nonvolatile Organic Compounds and Inorganics

During sample collection, allow the water to flow directly into and down the side of the sample container without allowing the tubing to touch the inside of the sample container or lid, in order to minimize aeration and maintain sample integrity.

For metals, collect filtered and unfiltered samples using a 0.45 micron filter for analyses that may be impacted by the elevated turbidity.

5.3 Grouting

Grouting or sealing the borehole with bentonite will be performed during removal of the drill string or following the retrieval of all down-hole equipment.

5.4 Decontamination

All non-dedicated down-well measuring devices (i.e. mechanical bladder pump and water level indicator) will be thoroughly decontaminated before sampling.

6.0 Quality Assurance / Quality Control

Sampling personnel should follow specific quality assurance guidelines as outlined in the QAPP. Proper quality assurance requirements should be provided which will allow for collection of representative samples from representative sampling points. Quality assurance requirements outlined in the QAPP typically suggest the collection of a sufficient quantity of field duplicate, field blank, and other samples.

Quality control requirements are dependent on project-specific sampling objectives. The QAPP will provide requirements for equipment decontamination (frequency and materials), sample preservation and holding times, sample container types, sample packaging and shipment, as well as requirements for the collection of various quality assurance samples such as trip blanks, field blanks, equipment blanks, and field duplicate samples.

7.0 Data and Records Management

Groundwater sampling information specific to each sealed-screen groundwater profiling will be recorded in the field logbook or on a field sample collection sheet. Activities common to more than one sampling location, samples collected, deviations from the POP, QAPP, or Work Plan, and any other unusual occurrences will also be documented in the field logbook in accordance with standard documentation procedures.

Unanticipated changes to the procedures or materials described in this POP (deviations) will be appropriately documented in the project records.

Records associated with the activities described in this POP will be maintained according to the document management policy for the project.

8.0 Personnel Qualifications and Training

8.1 Qualifications and Training

The individual executing these procedures must have read, and be familiar with, the requirements of this POP.

8.2 Responsibilities

The project manager is responsible for providing the project team with the materials, resources and guidance necessary to properly execute the procedures described in this POP.

The individual performing the work is responsible for implementing the procedures as described in this POP and any project-specific work plans.

The entire sampling team should read and be familiar with the site Health and Safety Plan, Work Plan, QAPP (and the most recent amendments), and all relevant POPs before going on site for the sampling event.

9.0 References

United States Environmental Protection Agency. 2001. Guidance for Preparing Standard Operating Procedures (SOPs). EPA QA/G-6. EPA/240/B-01/004. USEPA Office of Environmental Information, Washington, DC. March 2001.

Connecticut Department of Environmental Protection (CTDEP) 2009. Use of Filters in Groundwater Sampling Technical Guidance Document. June 29, 2009.

United States Environmental Protection Agency. 2005. Groundwater Sampling and Monitoring using Direct Push Technologies. OSWER No. 9200.1-51 EPA 540/R-04/005. USEPA Office of Environmental Information, Washington, DC. August 2005.

Niton XL3t 600 XRF – POP 028

1.0 Scope and Applicability

This Project Operating Procedure (POP) provides the proper techniques for safely operating the Niton XL 3t 600 X-Ray fluorescence (XRF) analyzer for field screening of metals, primarily chromium, in soil. The procedure will permit in-situ analysis of soil samples for field decision making and will be used for delineation purposes during the remedial investigation. This procedure is not intended for submission of data to regulatory agencies; confirmatory analysis must be performed by a certified laboratory using EPA total metals methods.

This procedure is to be used in conjunction with the site specific Field Sampling Plan. This procedure is intended to provide the necessary information for setting up and analyzing soil samples with the XRF analyzer and performing associated quality control procedures.

This procedure is to be used in conjunction with the Niton XL 3t 600 XRF User's Guide. This procedure will provide the basic information for set up of the instrument and analysis of soil samples. However, certain custom functions are not covered in this procedure and must be referenced from the instruction manual.

The method sensitivity or lower limit of detection depends on a number of factors including physical and chemical matrix effects and interelement spectral interferences; in-situ analysis and testing of bagged samples are considered field screening procedures. More accurate measurements using XRF are highly dependent on sample homogeneity; samples must be prepared by sieving and potentially grinding to a uniform particle size in order to achieve the most accurate results.

In-situ XRF results alone are not acceptable for determining that a sample is below cleanup levels. In these cases XRF must be performed on a prepared (homogenized) sample and confirmed using a certified laboratory.

2.0 Health and Safety Considerations

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, will be addressed in the site-specific Health and Safety Plan (HASP). In the absence of a site-specific HASP, work will be conducted according to the AECOM Health and Safety Policy and Procedures Manual and/or direction from the Regional Health and Safety Manager.

Field personnel are referred to the HASP for appropriate personal protective equipment (PPE) for this procedure.

The XRF analyzer contains an x-ray tube; when the x-ray tube is turned on by the user and the shutter is open, as during a measurement, the analyzer emits a directed radiation beam. The instrument should never be pointed at anyone or at any body part. Never point the analyzer into the air and perform a test. Never hold a sample in your hand and perform a test.

Each field analyst must undergo training in safe use of the instrumentation by a manufacturer's representative prior to use of the XRF equipment. Protective shielding should never be removed by the analyst or any personnel other than the manufacturer. All maintenance other than that specifically listed in the operating manual must be performed by the manufacturer.

Those operating XRF equipment must be aware of, and comply with, state-specific licensing requirements for the use of XRF analyzers (N.J.A.C 7:28-54.1). A copy of the license should be present with the instrument at all times and available upon request in an audit.

A copy of the United States Department of Transportation (US DOT) compliance statement has been provided with each Niton instrument; this document should be kept in the analyzer case at all times.

The analyst must comply with all safety requirements listed in the instrument specific operating manual.

3.0 Interferences

Physical matrix effects can result from variations in the physical character of the sample. This includes variations in particle size, uniformity, homogeneity and surface condition. As a minimum every effort should be made to thoroughly mix and homogenize samples before analysis. The most accurate data will be obtained if samples are sieved and ground to a uniform particle size prior to testing.

Moisture content of soils and sediments can impact analytical accuracy particularly if the sample is water saturated; moisture levels of 5-20% generally have a minimal impact on accuracy. If field data are to be compared with

laboratory generated results, samples should be dried using a convection or toaster oven; a microwave should not be used due to the potential for arcing if metal fragments are present in the sample. Studies have also shown poor agreement between laboratory confirmatory analysis and field XRF data when microwave drying is used.

Inconsistent positioning of the sample in front of the probe window can produce errors since the x-ray signal decreases as the distance from the radioactive source increases. The best results are obtained when the sample has a flat, smooth surface and the probe window is in direct contact with the surface.

Chemical matrix effects can occur in soils contaminated with metals and result from spectral interferences (peak overlaps) or as x-ray absorption and enhancement phenomena. Peak overlaps occur when certain x-ray lines from different elements are close in energy; the degree to which these peaks can be resolved is dependent upon the instrument detector.

Elevated levels of vanadium have been documented as a potential interference for chromium. Absorption occurs when one element tends to absorb the x-rays of a second element reducing the detector's measurement of the intensity of the second element. Less common are interferences resulting from K/L, K/M, and L/M line overlaps; this interference can cause difficulty in detection of arsenic in the presence of high levels of lead.

Ambient temperature changes can result in instrument drift. The analyst should review the instrument instructions for the optimal operating range of the instrument and assess the accuracy of instrument response through periodic analysis of blanks and QC check samples.

4.0 Equipment and Materials

The following equipment and materials are required for sample analysis using this technique:

- Niton XL 3t 600 XRF
- Niton XL 3t 600 XRF User's Guide, Version 6.5
- U.S. DOT Compliance Statement and any state required licenses
- Battery charger and spare battery
- National Institute of Standards and Testing (NIST) certified standard reference material(s) (SRMs) or similar standards from the U.S. Geological Survey (USGS) or commercial sources.
- Reference standards and samples provided by the instrument manufacturer
- Blank sample of clean quartz, Teflon, or silicon dioxide
- Trowel for smoothing soil surface or collecting sample
- Plastic bags for collection and homogenization of soil samples.
- Field logbook and pen
- Level C PPE
- Camera (optional)

5.0 Procedures

5.1 Initial Setup

Don the PPE as instructed in the site-specific HASP.

- To turn on the analyzer depress the on/off/escape button on the control panel for 10 seconds; the start screen will appear and begin a 10 second countdown. When the log on screen appears, press anywhere on the screen to continue. Acknowledge the radiation warning by pressing "Yes" and enter the security code for the device.
- Confirm that the date/time display is correct. Refer to the Niton XL3t 600 User's Guide for specific instructions on navigation through the menu. If the instrument has been turned off for more than 30 minutes allow a 10 minute warm-up period before calibration. Select Calibrate and Test and press Clear/Enter to begin the self calibration; when the instrument beeps the calibration is complete and the instrument is ready for use.
- For the purposes of in-situ measurements, the instrument will be operated in the Standard Soil Mode. Select Standard Soil Mode from the Bulk Analysis Menu. Calibrate the instrument using the soil

standards supplied by Niton immediately after the instrument completes self-calibration. The standards should be tested every 1- 2 hours during the analysis day and at the conclusion of testing for the day to ensure that no drift has occurred. All calibration procedures and the results of standard check samples must be recorded in the XRF logbook. Until control limits specific to the XRF unit being used are established control limits of ± 20% of the true value should be used.

- The Niton XL3T 600 offers six modes of operation for soil samples. It is expected that the Easy Trigger method will be used for in-situ measurements. Using this technique the measurement window is placed against the sample and the trigger is pulled once to initiate the analysis. The instrument constantly checks the backscatter measurements to determine if a sample is against the measurement window and will shut off any radiation directed through the window if it determines there is no sample present.
- The analyzer will display the results screen throughout the duration of the reading; once the reading is complete, the screen will display the final results of the measurement.

5.2 Sample screening may be performed by holding the probe directly on the soil or on a bagged sample. Clean the measurement window between samples using a cotton swab.

- Remove any obviously non-representative materials such as leaves, vegetation, roots, or concrete from the sample; use caution that COPR related materials are not removed from the sample. Finer and more homogeneous material will yield more accurate results. Increased accuracy can be gained by loosening the soil and letting it dry in the sun prior to testing. The soil sample should not be saturated with water; the XRF technique will generally not produce reliable results if ponded water exists on the surface.
- Use a trowel to level the surface of the soil. Hold the XRF in one hand and place the instrument window flush against the surface of the sample to be tested. The four LED lights on the screen will flash to indicate the initiating preconditions have been met (see page 1-45 of the User's Guide); however as a safety precaution the x-ray tube will not turn on immediately and no reading will begin for approximately 0.5 seconds. Watch the display screen to determine when the test is complete; a typical test will take 30-60 seconds. To end the test simply release the trigger mechanism.
- If direct measurement of the sample is not possible, samples may be placed in plastic bags and analyzed without preparation. However, since the measurement is made through a plastic bag, test results can be 5-10% lower than those obtained by direct measurement. Place 50-100g of soil in a clean zipper locking bag (approximately 1- mil thick polyethylene bag is recommended) removing any obviously non- representative material. Mix the sample thoroughly by kneading the bag and flatten the bag of soil to form uniform layer of approximately 0.5 inch thickness. Place the XRF flat against the bag and take a measurement as described in Section 5.2.2. ***Do not hold the bag in your hand during testing.***

5.3 Download the stored data and spectra to a computer or directly to a database; erase the stored data from the XRF once you have confirmed that all results have been successfully downloaded. ***Do not attempt to take measurements while downloading readings, this will generate an error requiring a system reset and may corrupt stored readings.***

5.4 Routine maintenance procedures include cleaning and replacement of the measurement window.

- Keep the transparent measurement window covering the analysis window clean.
- Clean the measurement window gently with a cotton swab. Clean the body of the analyzer with a soft cloth. The touch screen may be cleaned using a lens cleaning solution with a soft cloth; water should not be used. Never use detergents or solvents on any portion of the analyzer or immerse the analyzer in water.
- 5.4.2 If the measurement window becomes frayed, ripped, or contaminated with metal particulates, replace it with a new window. The User's Guide provides part numbers and instructions for replacement of the windows.
- All other maintenance must be performed by an authorized Niton service center. The instrument must be transported and stored in its padded carrying case when not in use.

6.0 Quality Assurance / Quality Control

An energy calibration check should be run at the start of each day of sampling. This check confirms that the

characteristic x-ray lines are stable and instrument drift is not occurring. This also provides a gain check if the ambient temperature fluctuates significantly. This test must be run at the start of each day, when the batteries are changed, when the instrument is shut down, and at the end of each day. This procedure should also be run any time the operator believes that drift is occurring during analysis.

A blank consisting of silicon dioxide or a Teflon or quartz block must be run at the beginning and end of each day of analysis and after every 20 samples or every hour of operation during the day or at any time the analyst suspects contamination in the analytical system.

An independent standard must be used to verify the accuracy of the instrument and confirm its stability and consistency for the analyte of interest. NIST, USGS or commercial standards may be used. The standard check must be performed at the beginning and end of each analysis day and after every 20 samples or hour of operation during the day. If the measured value falls outside the acceptance range the check sample must be reanalyzed; if it is still outside the acceptance range the instrument must be recalibrated and any samples analyzed since the previous acceptable calibration check must be reanalyzed.

At least one sample in each set of 20 must be analyzed in duplicate to assess measurement precision. Relative percent difference for duplicates should be ≤ 30%.

The field forms and field notes generated from this procedure will be reviewed by the sampling team leader, project manager, or designee. All quality control results must be downloaded to project computer files along with sample data. Any deviations from this POP, problems encountered during the analysis and corrective actions taken must be documented in the field records.

7.0 Data and Records Management

Unanticipated changes to the procedures or materials described in this POP (deviations) will be appropriately documented in the project records.

All data and spectral files must be backed up onto a computer on a regular basis. Any deviations from this POP or problems encountered during the analysis must be documented in a field log book which is dedicated to the XRF analyzer.

Records associated with the activities described in this POP will be maintained according to the specific document management policy for the project.

8.0 Personnel Qualifications and Training

8.1 Qualifications and training

The individual executing these procedures must have read, and be familiar with, the requirements of this POP.

Sampling personnel must be health and safety certified as specified by Occupational Safety and Health Administration (OSHA) 29 CFR 1910.120(e)(3)(i) to work on sites where hazardous materials may be present.

Each person who performs this procedure will undergo training offered by the manufacturer such that the procedure is performed in a consistent manner and all safety procedures are followed.

Individual states and countries have specific regulations and guidelines for the use of X-ray tube devices that produce ionizing radiation. For New Jersey site work, the licensing requirements outlined in N.J.A.C. 7:28-54.1 must be met prior to the start of site work.

8.2 Responsibilities

The project manager is responsible for providing the project team with the materials, resources and guidance necessary to properly execute the procedures described in this POP.

The individual performing the work is responsible for implementing the procedures as described in this POP and any project-specific work plans.

9.0 References

United States Environmental Protection Agency. 2001. Guidance for Preparing Standard Operating Procedures (SOPs). EPA QA/G-6. EPA/240/B-01/004. USEPA Office of Environmental Information, Washington, DC. March 2001.

United States Environmental Protection Agency. 2007. Method 6200, Field Portable X-Ray Fluorescence Spectrometry

for the Determination of Elemental Concentrations in Soil and Sediment, Revision 0. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Washington, D.C. January 2008.

New Jersey Department of Environmental Protection Site Remediation Program. 1994. Field Manual. Trenton, NJ. July 1994.

Thermo Scientific, Niton XL3t 600 Analyzer User's Guide, Version 6.5. Billerica, MA 2009

Field Records – POP 101

1.0 Scope and Method Summary

This Project Operating Procedure (POP) provides guidance for documentation of field activities associated with AECOM Project operations, including, but not limited to; sample collection, field measurements, and groundwater monitoring well installation. Appropriate documentation of field activities provides an accurate and comprehensive record of the work performed, sufficient for a technical peer to reconstruct the day's activities and determine that necessary requirements were met. Field records also provide evidence and support technical interpretations and judgments. The procedures and systems defined in this POP help ensure that the records are identifiable (reference the project task/activity), legible, retrievable, and protected from loss or damage.

Project field data may be recorded electronically or in field logbooks, standardized forms, annotated maps, or photos. This POP provides general guidance on field recordkeeping; additional details for specific procedures (for example, chain of custody, sample collection) are provided in the POPs for the individual task.

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in task-specific work plans and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

2.0 Health and Safety

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, is addressed in the site specific HASP. All work will be conducted in accordance with the HASP.

3.0 Interferences

Not Applicable.

4.0 Equipment and Supplies

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Bound field logbook (preferably waterproof, such as Rite-in-Rain™),
- Standardized field data sheets,
- Black or blue, ballpoint pen with indelible ink,
- Sharpie® (or equivalent permanent marker),
- Site maps,
- Clipboard,
- Three-ring binder or equivalent,
- Camera (optional),
- Time piece,
- Hand-held electronic recording device (such as Trimble Yuma®) (optional), and
- Laptop computer or tablet PC (optional).

5.0 Methods

5.1 General Requirements

- The field records will contain sufficient detail so that the collection effort can be reconstructed without reliance on the collector's memory.
- Pertinent field information will be recorded legibly in a logbook and/or an appropriate standardized form (as described herein). Entries should be made with a ballpoint pen with black or blue indelible ink or a

permanent marker. Pencils should not be used. If a ballpoint pen or permanent marker cannot be used because of adverse weather conditions (rain or freezing temperatures) and only a pencil can be used, an explanation must be included in the logbook and the affected data should be photocopied, signed as verified copy, and maintained in the project files as documentation that the data has not been changed.

- Entries will be signed and dated. No erasures or obliterations will be made. A single line strikeout will be drawn through incorrect entries and the corrected entry written next to the original strikeout. Strikeouts are to be initialed and dated by the originator.
- Entries will be factual and observational (i.e., no speculation or opinion), and will not contain any personal information or non-project-related entries. Abbreviations and acronyms should be defined.
- Field information will be recorded timely – information recorded significantly after the fact will be dated as such.
- Field activities and other events pertinent to the field activities will be documented in chronological order. Times will be recorded using military time or Eastern Standard Time.

5.2 Field Logbooks

The cover and binding of each logbook will be labeled to identify the operation and dates included with the logbook; each page in the logbook will be consecutively numbered. Pages will not be removed or torn out of the logbook.

The title page of each logbook will contain the following:

- AECOM contact, AECOM office location, and phone number;
- Project name and AECOM project number; and
- Start and end dates of work covered by the logbook.

At the front of each logbook will be a page cross-referencing each author's printed name, signature, and initials. A page header will appear on the first page of each day's notes in the logbook, and activities for each day will be recorded on a new page. The page header will include:

- Name of author and other personnel on site (and affiliated organization if applicable);
- Date;
- Time of arrival;
- Proposed activity (task); and
- Current weather and weather forecast for the day.

An abbreviated header, containing at least the date, authors name, and project number, will appear at the top of each additional page for the active date. Field forms require similar header information. The field logbook will provide a chronology of events. At a minimum, documentation in a logbook will include the following (unless documented on a standard form):

- Names of visitor(s), including time of arrival and departure, the visitor's affiliation, and reason for visit;
- Summary of project-related communications, including names of people involved and time;
- Time daily work commences and ceases;
- Start and stop times of new tasks;
- Start and stop times of significant stand-by time (work interruptions);
- Safety or other monitoring data, including units with each measurement;
- Deviations from approved scope of work, including the necessary approvals;
- Progress updates;
- Problems/delays encountered;
- Unusual events; and
- Signature or initials of author on last page of each day's event.

The logbook will cross-reference the field forms if necessary; however, whenever possible, details recorded on the standardized forms will not be replicated in the logbook.

If there are additional lines on the page at the end of the day's activities, a line will be drawn through the empty space, and initialed and dated, leaving no room for additional entries.

5.3 Standardized Forms

Standard forms for field data are provided in the electronic project files.

The information collected on any field form may alternately be collected electronically by a laptop computer or electronic handheld device as appropriate.

The following rules apply to the standardized forms:

- Each form will be signed and dated by the person completing the form.
- There will be no blank spaces on the form – unused spaces will have "not applicable" or "not available" explanations.

5.4 Maps and Drawings

Pre-existing maps and drawings that include notations made in the field (for example, relocating of sample locations) will be referenced in the logbook and, like all field records, include the project/task name and number, site identification, and be signed/dated by the person that prepared them.

Maps and drawings will include compass orientation and scale. Sketches will include points of reference and approximate distances to the reference points.

5.5 Photo Documentation

Photographs or videos may be taken by the field team to help document site conditions, sample locations, or sample characteristics. Photographs and videos will be identified in the logbook or on the standard form by a unique numbering system. If photographs are collected by a digital camera, the photograph number will accompany the description of the photograph in the logbook. At a minimum, the date/time the photograph was taken, the general location, a brief description, and the photographer's name will be recorded. Additional information may include Global Positioning System (GPS) coordinates, direction the photographer was facing, and/or weather conditions. If necessary, an object will be included to indicate the scale of the object in the photograph.

5.6 Electronic Files

Electronically recording devices may include data logging systems, personal digital assistants (PDAs), laptops, tablet PCs, etc.

Sufficient backup systems will be in place to protect against electronic data loss. Information will be saved to a disk or backed up at the end of each day. The backup disk or other media (CD, flash drive) will then be stored in a secure location separate from the laptop, tablet, PDA, etc.

Files will be uniquely identified and will be stored in the project files on the network. An unedited version of the file will be maintained and all subsequent manipulations tracked.

6.0 Data and Records Management

Deviations to the procedures detailed in the POP or approved plans will be noted in the field logbook or other appropriate field form at the time of occurrence. Proposed modifications to the POPs or approved plans will be documented and submitted to the Task Manager.

Logbooks that are taken offsite from the field facility will be photocopied or scanned and filed to mitigate against the loss of historical entries should the logbook be lost in the field.

Field data forms and chain of custody will be filed in the field facility once they have been completed and distributed (if necessary), or at the end of each field day. These documents will be maintained in labeled three-ring binders or contained in some other organized manner that prevents loss. Distribution of daily forms will be performed according to the needs of the project team and at the direction of the Field Task Manager or designee.

7.0 Quality Assurance and Quality Control

Quality Control (QC) samples collected may include field duplicates, equipment and/or field blanks, trip blanks, and matrix spike/matrix spike duplicates (MS/MSD). See the QAPP for collection frequency and methods.

8.0 Personnel Qualifications

It is the responsibility of the field personnel to be familiar with the procedures outlined in this POP. It is also the responsibility of the field personnel to be familiar with the procedures outlined within this *Sampling and Analysis Plan (SAP), the Quality Assurance Project Plan (QAPP), and the Health and Safety Plan (HASP).* Personnel who work on sites where hazardous waste materials may be present will be health and safety certified as specified by the *Occupational Safety and Health Administration (OSHA) (29CFR 1910.120(e)(3)(i)).*

Chain of Custody Procedures – POP Number: 102

1.0 Scope and Method Summary

This POP describes the methods to be used for completing the chain of custody (COC) used in the collection of environmental samples. The National Enforcement Investigations Center of the United States Environmental Protection Agency (U.S. EPA) defines custody of evidence in the following manner:

- It is in your actual possession;
- It is in your view, after being in your physical possession;
- It was in your possession and then you locked or sealed it up to prevent tampering; or
- It is in a secure area.

2.0 Health and Safety Considerations

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, is addressed in the site specific Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

3.0 Equipment and Supplies

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Sample Labels,
- COC Form,
- Field Project Logbook,
- COC Tape or Custody Seals, and
- Pen with indelible ink and/or permanent marker.

4.0 Procedures

4.1 Sample Labeling

Labeling of samples occurs at the time of sample collection. Waterproof, adhesive labels are preferred. Labels should be applied to the container, not the lid whenever possible. Additional interior labels may be required for certain biological samples.

Labels should be completed in indelible ink. Covering the label with clear plastic tape is recommended to protect the legibility of the label and to prevent the label from detaching from the sample container.

The following information should be recorded on the sample label:

- Project Identification (project name and number/client/site),
- Field Sample Identification Number (exactly as it appears on the COC form),
- Sampler's Initials,
- Date and Time of Sample Collection,
- Analyses Requested, and
- Preservation.

4.2 Field Custody

The field personnel are required to complete the following information on the COC form:

- Project Number,

- Client or Project Name,
- Project Location,
- Page number (e.g., 1 of 2, 2 of 2, etc.),
- Laboratory name and address,
- Field Sample Identification Number,
- Date and Time of Sample Collection,
- Sample Matrix,
- Preservative,
- Analysis Requested,
- Sampler's Signature,
- Signature of Person Relinquishing Sample Custody,
- Date and Time Relinquished, and
- Sampler Remarks.

Hand-written COCs must be filled out completely and legibly in indelible ink. Corrections will be made, if necessary, by drawing a single line strikethrough and initialing and dating the error. The correct information is then recorded with indelible ink. If a correction is needed on a computer generated COC form, it must be corrected in the program from which it was created and reprinted. It cannot be corrected with a single line method. All transfers from field personnel to laboratory personnel are recorded on the COC form in the "Relinquished By" and "Received By" sections.

If samples are to be shipped by overnight commercial courier (e.g., Federal Express), the field personnel must complete a COC form for each package (e.g., cooler) of samples and place a copy of each completed form inside the associated package before the package is sealed. Each completed COC form must accurately list the sample identification numbers of the samples with which it is packaged. Alternately, a copy of the original COC form may be placed in each package. The copy of the COC form must at a minimum list the samples that are contained in the respective package. The original COC from must be included in one of the packages. It is not necessary for the shipping company to sign the COC. Sample packaging will be conducted in accordance with POP 103 – Packaging and Shipment of Environmental Samples.

If samples are hand carried to a laboratory, the person hand carrying the samples is the sample custodian. If the carrier is a different person than the one who filled out the COC form and packaged the samples, then that person must transfer custody to the carrier by signing and dating each form in the "Relinquished By" section. The carrier must then sign and date each form in the adjacent "Received By" section. When the carrier transfers the samples to the laboratory, he or she must sign and date each form in the next "Relinquished By" section, and the laboratory sample custodian must sign and date each form in the adjacent "Received By" section.

4.3 Laboratory Sample Receipt and Inspection

Upon sample receipt, the coolers or packages are inspected for general condition and the condition of the COC tape or custody seal. The coolers or boxes are then opened and each sample is inspected for damage.

Sample containers are removed from packing material and sample label field identification numbers are verified against the COC form.

The following information is recorded in the laboratory's records:

- Air Bill number (if appropriate),
- Presence/absence of COC forms,
- Condition of samples,
- Discrepancies noted,
- Holding time and preservatives, and
- Sample storage location.

The COC form is completed by signing and recording the date and time of receipt.

The Task Manager or designee must be notified of any breakage, temperature exceedance, or discrepancies between the COC paperwork and the samples.

5.0 Data and Records Management

The data associated with COC procedures is contained within the following:

- Sample labels,
- Chain of custody records and custody seal(s), and
- Sample collection records.

The following POPs describe the data collection and record management procedures that should be followed as part of the COC procedure:

POP 101 - Field Records, and

POP 103 - Packaging and Shipment of Environmental Samples.

See the referenced POPs for additional details.

6.0 Quality Assurance and Quality Control

The records generated in this procedure are subject to review during data validation, in accordance with the QAPP.

Quality Control (QC) samples collected may include field duplicates, equipment and/or field blanks, trip blanks, and matrix spike/matrix spike duplicates (MS/MSD). See the QAPP for collection frequency and methods.

7.0 Personnel Qualifications and Training

Individuals responsible for completing COC documentation must be personnel working on the specific field program, have read this POP, and have worked under the oversight of experienced personnel. For certain sampling programs, the Project Manager, Task Manager, or designee may assign an individual to serve as sample custodian. This individual is responsible for supervising the implementation of COC procedures in accordance with this POP and any project-specific work plans or Quality Assurance Project Plan (QAPP).

Personnel who will work on sites where hazardous waste materials may be present will be health and safety certified as specified by OSHA (29 CFR 1910.120(e)(3)(i).

Packaging and Shipping – POP 103

1.0 Scope and Method Summary

This Project Operating Procedure (POP) describes the basic techniques and general considerations to be followed for the packaging and shipment of environmental samples consisting of water, soil, sediment and any other matrix sampled and submitted for routine environmental testing.

This POP is designed to provide a high degree of certainty that environmental samples will arrive at their destination intact. While the majority of the samples are delivered via laboratory courier, this POP assumes that samples will often require shipping overnight by a commercial carrier service; therefore, the procedures are more stringent than may be necessary.

Sample packaging and shipment involves the placement of individual sample containers into a cooler or other similar shipping container and placement of packing materials and coolant in such a manner as to isolate the samples, maintain the required temperature, and to limit the potential for damage to sample containers when the cooler is transported

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in task-specific work plans or on Field Modification Forms as appropriate and will be approved in advance by the Task Manager and the Project QA Manager. Deviations from the POP will be documented in the project records and in subsequent reports. The ultimate procedure employed will be documented in the report summarizing the results of the sampling event or field activity.

2.0 Health and Safety

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, are addressed in the site specific HASP. All work will be conducted in accordance with the HASP.

3.0 Interferences

Sample containers with presumed high constituent concentrations should be isolated within their own cooler with each sample container placed into a zipper-lock bag.

4.0 Equipment and Supplies

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Sample coolers,
- Sample containers,
- Shipping labels,
- Chain of custody (COC) form,
- Bubble wrap,
- Vermiculite (granular), or Styrofoam pellets,
- Wet ice,
- Temperature blank,
- Transparent tape,
- Custody seal for the outside of the cooler,

- Fiberglass packaging tape,
- Duct tape,
- Scissors,
- Zipper-lock plastic bags (gallon and quart sizes),
- Trash bags,
- Health and safety supplies (as required by the HASP), and
- Field project logbook/pen with indelible ink.

5.0 Methods

5.1 Preparation

The extent and nature of sample containerization will be governed by the type of sample, and the most reasonable projection of the sample's hazardous nature and constituents. *United States Environmental Protection Agency (U.S. EPA)* regulations (40 CFR Section 261.4(d)) specify that samples of solid waste, water, soil or air, collected for the sole purpose of testing, are exempt from regulation under RCRA when any of the following conditions are applicable:

- Samples are being transported to a laboratory for analysis;
- Samples are being transported to the collector from the laboratory after analysis;
- Samples are being stored (1) by the collector prior to shipment for analyses, (2) by the analytical laboratory prior to analyses, or (3) by the analytical laboratory after testing but prior to return of sample to the collector or pending the conclusion of a court case.

5.2 Sample Information

The following information must accompany each shipment of samples on a chain of custody form where each sample has an individual entry:

- Sample collector's name, mailing address and telephone number,
- Analytical laboratory's name, mailing address and telephone number,
- A unique identification of each sample,
- Sample description (matrix),
- Number and type of sample containers,
- Container size,
- Preservative,
- Type and method of analysis requested,
- Date and time of sample collection, and
- Special handling instructions, including notation of suspected high concentration samples.

5.3 Laboratory Notifications

Prior to sample collection, the Task Manager or designee must notify the laboratory project manager of the number, type, and approximate collection and shipment dates for the samples. If the number, type, or date of sample shipment changes due to program changes that may occur in the field, the Task Manager or alternate should notify the laboratory of the

changes. Additional notification from the field is often necessary when shipments are scheduled for weekend delivery.

5.4 Cooler Inspection and Decontamination

Laboratories will often re-use coolers. Every cooler received at a project location should be inspected for condition and cleanliness. Any coolers that exhibit cracked interiors or exterior linings/panels or hinges should be discarded because the insulating properties of the coolers would be considered compromised. Any coolers missing one or both handles should also be discarded if replacement handles (i.e., knotted rope handles) cannot be fashioned in the field.

The interior and exterior of each cooler should be inspected for cleanliness before using it. Excess strapping tape and old shipping labels should be removed. If the cooler interior exhibits visible contamination or odors it should not be used. Drain plugs should be sealed with duct tape.

5.5 Sample Packaging

Place plastic bubble wrap matting over the base of each cooler or shipping container as needed. A 2- to 3-inch thick layer of vermiculite may be used as a substitute base material. Line the inside of the cooler using a large trash bag with the open end up.

Check that each sample container is sealed, labeled legibly, and is externally clean. Re-label and/or wipe bottles clean if necessary. Place all sample containers in bubble wrap bags and seal the bag using either the adhesive strip on the bag or tape. Place bottles into the cooler (inside the trash bag) in an upright single layer with approximately one inch of space between each bottle. Do not stack bottles or place them in the cooler lying on their side. If plastic and glass sample containers are used, alternate the placement of each type of container within the cooler so that glass bottles are not placed side by side if possible.

Insert the cooler temperature blank supplied by the laboratory into each cooler (if any).

If needed, place additional vermiculite, bubble wrap, and/or Styrofoam pellet packing material throughout the voids between sample containers within each cooler to a level that meets the approximate top of the sample containers. Packing material may require tamping by hand to reduce the potential for settling.

Bag wet ice into gallon-size zipper-lock bags to ensure no leaking occurs during shipment. Insert the bags of ice around, between, and on top of the sample containers. Sufficient ice should be used to maintain the sample temperature at 4° Celsius (C) during shipping. Close and seal the large trash bag that lines the cooler by twisting the open end and taping or knotting the bag closed to prevent the cooler from leaking throughout the shipping process.

Add additional bubble wrap/Styrofoam pellets or other packing materials to fill the balance of the cooler or container.

Complete the COC form per *POP 102 – Chain of Custody Procedures*. If shipping the samples involves use of a third party commercial carrier service, sign the COC record thereby relinquishing custody of the samples. Shippers should not be asked to sign COC records. If a laboratory courier is used, or if samples are transported to the laboratory by field personnel, the receiving party should accept custody and sign the COC records. Remove the last copy from the multi-form COC and retain it with other field notes. If an electronically produced COC is used, make copies of the COC (only after all signatures are in place). Place the original (with remaining copies) in a zipper-lock plastic bag and tape the bag to the inside lid of the cooler or shipping container.

Close the lid of the cooler or the top of the shipping container.

If shipping samples via third party commercial carrier service (e.g., FedEx), obtain COC tape or custody seals and enter the custody tape/seal number(s) in the appropriate place on the COC form. Sign and date the COC tape/seals. If the samples are being transported via laboratory courier, COC tape or custody seals are not required.

When placing COC tape or a signed and dated custody seal on the cooler, place it with half of the seal on the lid and the other half on the body of the cooler.

Packaging tape should be placed entirely around the sample shipment containers. A minimum of two full wraps of packaging tape will be placed at least two places on the cooler/container. The custody seal should be underneath one of the wraps of packaging tape.

Repeat the above steps for each cooler or shipping container.

5.6 Sample Shipping

Transport the cooler/container to the package delivery service office or arrange for package pick-up at the site. Fill out the appropriate shipping form or air bill and affix it to the cooler/container. The shipper should consider an “up arrow” label to direct proper placement of the cooler when set. Some courier services may use multi-package shipping forms where only one form needs to be filled out for all packages going to the same destination. However, separate shipping form should be used for each cooler/container, the multi-package shipping forms should not be used when shipping environmental samples. The receipt for package tracking purposes should be kept in the project files, in the event a package becomes lost.

Each cooler/container also requires a shipping label that indicates point of origin and destination. This will aid in recovery of a lost cooler/container if a shipping form gets misplaced.

Never leave coolers/containers unattended while waiting for package pick-up.

Air bills or way bills will be maintained as part of the custody documentation in the project files.

5.7 Sample Receipt

Upon receipt of the samples, the analytical laboratory will open the cooler or shipping container and will sign "received by laboratory" on each COC form. The laboratory will verify that the COC tape has not been broken previously and that the COC tape/seal number corresponds with the number on the COC record. The laboratory will note the condition of the samples upon receipt and will identify any discrepancies between the contents of the cooler/container and COC. The analytical laboratory will then forward the back copy of the COC record to the project Quality Assurance (QA) Officer to indicate that sample transmittal is complete.

6.0 Data & Records Management

The data associated with packaging and shipment of environmental samples is contained within the following:

- Sample labels,
- Chain of custody records and custody seal(s),
- Field logbook, and
- Sample collection records.

The following POPs describe the data collection and record management procedures that should be followed as part of the packaging and shipment of environmental samples process:

- *POP 101 Field Records, and*
- *POP 102 Chain of Custody Procedures.*

See the referenced POPs for additional details.

7.0 Quality Control and Quality Assurance

Quality Control (QC) samples used in association with packaging and shipment of environmental samples include trip blanks and temperature blanks. See the QAPP for frequency of use and methods.

8.0 Personnel Qualifications

Sample packaging and shipment is a relatively simple procedure requiring minimal training and a minimal amount of equipment. It is recommended that initial attempts be supervised by more experienced personnel.

Personnel who will work on sites where hazardous waste materials may be present will be health and safety certified as specified by the *Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)).*

It is the responsibility of the field personnel to be familiar with the procedures outlined within this POP, quality assurance, and health and safety requirements outlined within this *Sampling and Analysis Plan (SAP)*, the *Quality Assurance Project Plan (QAPP)*, and the *Health and Safety Plan (HASP)*. Field personnel are also responsible for proper documentation in the field logbook.

9.0 References

POP 101 – Field Records

POP 102 – Chain of Custody Procedures

Decontamination of Field Equipment – POP Number: 105

1.0 Scope and Method Summary

This Project Operating Procedure (POP) describes the methods to be used for the decontamination of field equipment used in the collection of environmental samples. Field equipment for decontamination may include a variety of items used in the field for monitoring or for collection of soil, sediment, and/or water samples, such as water level meters, water quality monitoring meters (turbidity meter, multi-parameter meter), split-spoon samplers, trowels, scoops, spoons, and pumps. Heavy equipment such as a drill rig also requires decontamination, usually in a specially constructed temporary decontamination area.

Decontamination is performed as a quality assurance measure and a safety precaution. Improperly decontaminated sampling equipment can lead to misinterpretation of environmental data due to interference caused by cross-contamination between samples or sample locations through use of contaminated equipment. Decontamination also protects field personnel from potential exposure to hazardous materials on equipment.

Decontamination is accomplished by manually scrubbing, washing, or spraying equipment with detergent solutions, tap water, distilled/deionized water, and/or solvents.

Generally, decontamination of equipment is accomplished at each sampling site between collection points. Waste decontamination materials such as spent liquids and solids will be collected and managed as investigation derived waste (IDW) for later management and/or disposal (refer to procedures outlined POP 106 (Investigative Derived Waste Management)).

This POP emphasizes decontamination procedures to be used for decontamination of reusable field equipment. Dedicated or disposable equipment will not be decontaminated.

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in task-specific work plans or on Field Modification Forms as appropriate and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

2.0 Health and Safety Considerations

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, is addressed in the site specific HASP. All work will be conducted in accordance with the HASP.

3.0 Interferences

Equipment decontamination should be performed at a safe distance away from the sampling area so as not to interfere with sampling activities, but close enough to the sampling area to maintain an efficient working environment.

4.0 Equipment and Supplies

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Decontamination agents;
  - ALCONOX®, or other non-phosphate and non-borate biodegradable detergent,
  - Tap water, and
  - Distilled/deionized water.
- Health and safety supplies (as required by the HASP);
- Chemical-free paper towels;
- Waste storage containers: drums, 5-gallon buckets with covers, plastic bags;
- Cleaning containers: plastic buckets or tubs ;

- Cleaning brushes;
- Pressure sprayers;
- Squeeze/spray bottles;
- Plastic sheeting;
- Zipper-lock bags and/or foil wrap; and
- Field project logbook/pen with indelible ink.

5.0 Procedures

5.1 General Preparation

New materials, such as well materials, are generally assumed to be clean and decontamination is not anticipated. However, they should be inspected and if they appear to be dirty, should be decontaminated.

Field equipment should be inspected and decontaminated prior to use if the equipment appears dirty.

Heavy equipment (drill rigs, Geoprobes®, excavators) should be decontaminated prior to beginning any work.

Pre-established IDW containment stations should be used to discard IDW between sampling locations.

5.2 Decontamination for Sampling Equipment

This procedure applies to equipment used in the collection of environmental samples and other field equipment. Examples of relevant items of equipment include split-spoons, trowels, scoops, spoons, and other small items. Submersible pump decontamination procedures are outlined in Section 5.3.

- Decontamination is to be performed before sampling events, between sampling points, and at the end of the day unless otherwise noted in the work plan. After a sample has been collected, remove all gross contamination from the equipment or material by brushing and then rinsing with available tap water. This initial step may be completed using a 5-gallon bucket filled with tap water or by spraying/pouring tap water over the equipment in to a bucket. A water pressure sprayer may also be used to remove solids and/or other contamination.
- Wash the equipment with a non-phosphate and non-borate detergent and tap water solution. This solution should be kept in a 5-gallon bucket with a dedicated brush. Isopropyl alcohol may also be used to remove any contamination that may not be easily removed with detergents. If isopropyl alcohol is used, the equipment must be washed again using a detergent.
- Rinse with tap water or distilled/deionized water until all detergent and other residue is washed away. This step can be performed over an empty bucket using a squeeze bottle, pressure sprayer or by directly pouring the distilled/deionized water over the equipment.
- Place the equipment on a clean surface (foil or plastic) and allow the equipment to air-dry in a clean area or blot with chemical-free paper towels before reuse. All decontaminated equipment should be placed in a clean plastic bag, clean pail, or wrapped in foil once it is dry if it is being stored.
- Dispose of soiled materials and spent solutions in the designated IDW disposal containers.

5.3 Decontamination of Submersible Pumps

This procedure will be used to decontaminate submersible pumps before and between groundwater sample collection points. This procedure applies to both electric submersible and bladder pumps. This procedure also applies to discharge tubing if it will be reused between sampling points.

- Prepare the decontamination area if pump decontamination will be conducted next to the sampling point. If decontamination will occur at another location, the pump and tubing may be removed from the well and placed into a clean trash bag for transport to the decontamination area.
- Once the decontamination station is established, the pump should be removed from the well and the discharge tubing and power cord coiled by hand as the equipment is removed. If any of the equipment needs to be put down temporarily, it should be placed on a plastic sheet (around well) or in a clean trash bag. If a disposable discharge line is used it should be removed and discarded at this time.
- As a first step in the decontamination procedure, use a pressure sprayer with tap water to rinse the exterior of the pump, discharge line, and power cord as necessary. Collect the rinsate and handle as IDW.

- Place the pump into a bucket containing a detergent solution (phosphate-free, borate-free detergent in tap water). Holding the tubing/power cord, pump solution through the pump system. A minimum of one gallon of detergent solution should be pumped through the system. Collect the rinsate and handle as IDW.
- Remove the pump from the bucket and if the pump is reversible, place the pump in the reverse mode to discharge all removable water from the system. If the pump is not reversible the pump and discharge line should be drained by hand as much as possible. Collect the rinsate and handle as IDW.
- Place the pump into a clean bucket containing distilled/deionized water. Holding the tubing/power cord, pump the distilled/deionized water through the pump and tubing to remove any detergent residue that may remain inside the pump and tubing. Using a pressure sprayer with distilled/deionized water, rinse the exterior of the pump, discharge line, and power cord thoroughly, shake off all excess water, and then place the pump system into a clean trash bag for storage. Collect the rinsate and handle as IDW.

5.4 Decontamination of Large Equipment

A temporary decontamination pad may be established for decontamination of heavy equipment. This pad may include a membrane-lined and bermed area large enough to drive heavy equipment (e.g., drill rig, backhoe) onto with enough space to spread equipment and to contain overspray. Usually a small sump is necessary to collect and contain rinsate (a pump is used to remove these wastes from the sump). A water supply and power source is also necessary to run steam cleaning and/or pressure washing equipment.

Upon arrival at the area of investigation, all heavy equipment (such as drill rigs) should be thoroughly cleaned. This can be accomplished by steam cleaning or high pressure water wash and manual scrubbing.

Between each sample location (i.e., between boreholes), heavy equipment that has been in the ground must be cleaned by steam cleaning or high pressure water wash and manual scrubbing. This may be performed at the decontamination pad or in the vicinity of the drilling location.

6.0 Data and Records Management

The data associated with decontamination procedures includes the following:

- Date, time, and location of each decontamination event,
- Equipment decontaminated,
- Method,
- Detergents used,
- Notable circumstances,
- Identification of equipment rinsate blanks,
- Management of decontamination fluids,
- Method, date, and time of equipment blank collection, and
- Disposition of IDW.

Repetitive decontamination of small items of equipment does not need to be logged each time the item is cleaned.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

7.0 Quality Assurance and Quality Control

Quality Control (QC) samples collected in association with decontamination of field equipment may include equipment rinsate blanks. See the QAPP for collection frequency and methods.

8.0 Personnel Qualifications and Training

Decontamination of field equipment is a relatively simple procedure requiring minimal training.

Field personnel must be health and safety certified as specified by Occupational Health and Safety Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

It is the responsibility of field personnel to be familiar with the decontamination procedures outlined within this POP, quality assurance, and health and safety requirements outlined within this Sampling and Analysis Plan (SAP), the Quality Assurance Project Plan (QAPP), and the Health and Safety Plan (HASP). Field personnel are responsible for decontamination of field equipment and for proper documentation in the field logbook or electronic data collector such as the Trimble Yuma® (or equivalent).

9.0 Reference

POP 106 – Investigative Derived Waste Management.

Investigative Derived Waste Management – POP 106

1.0 Scope and Method Summary

This Project Operating Procedure (POP) describes the methods to be used for the collection, containerization, transport, and disposal of waste generated during AECOM field investigations. Types of investigation-derived waste (IDW) may include, but are not limited to, personal protective equipment (PPE); disposable sampling equipment; purge water generated from wells during monitoring events; well development water; extra sample volume not required for analysis in the form of soil, sediment or water; soil cuttings from the installation of wells or soil borings; decontamination fluids, etc.

IDW management is accomplished by appropriately containing, collecting, packaging, characterizing and disposing of the waste. The following guidance documents were used in the development of this POP:

- *REM III Program Guidelines, Field Technical Guidelines 12.02 (United States Environmental Protection Agency (U.S. EPA), 1987)*
- *Management of Investigation-Derived Waste During Site Inspections (U.S. EPA, 1991a)*
- *Standard Operating Procedures and Quality Assurance Manual, Section 4.5 (U.S. EPA, 1991b)*

It is expected that the procedures outlined in this POP will be followed by all personnel during activities that generate and/or manage IDW. Procedural modifications may be warranted depending on field conditions, equipment limitations or limitations imposed by the procedure. Substantive modification to this POP will be noted in task-specific work plans or on Field Modification Forms as appropriate and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

2.0 Health and Safety

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, is addressed in the site specific HASP. All work will be conducted in accordance with the HASP.

3.0 Interferences

Not Applicable.

4.0 Equipment and Supplies

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Sample kit (i.e., bottles, labels, preservatives, custody records and tape, cooler, ice),
- Sample chain of custody forms (as required by *POP 102 – Chain of Custody Procedures*),
- Sample packaging and shipping supplies (as required by *POP 103 – Packaging and Shipment of Environmental Samples*),
- Drum labels,
- Waterproof marker or paint,
- Paper towels,
- Trash bags,
- Health and safety supplies (as required by the HASP),
- Field logbook and pen,
- Drums, tubs, totes, and other receptacles used to contain IDW, and
- Drum bung wrench, drum lid ring's deep well socket and socket wrench.

5.0 Methods

In the process of collecting environmental samples during field investigation activities, many different types of IDW may be

generated. Some of these waste materials may be hazardous wastes which must be properly managed in accordance with U.S. EPA and state regulations. To properly handle IDW in compliance with agency regulations, reasonable efforts should be made to characterize the wastes as non-hazardous or hazardous and to determine if the IDW has been mixed with a listed waste.

Resource Conservation and Recovery Act (RCRA) procedures for determining whether a waste exhibits RCRA hazardous characteristics do not require sampling and analysis if the decision can be made by "applying knowledge of the hazard characteristic in light of the materials or process used" (40 CFR 262.11(c)). The nature of the waste should be assessed by applying best professional judgment and using readily available information about the site (such as manifests, storage records, preliminary assessments, and results of earlier studies that may have been conducted and are available, as well as direct observation of the IDW for discoloration, or other indicators of contamination). The U.S. EPA has specifically indicated that IDW may be assumed to not be a "listed" waste under RCRA unless available information about the site suggests otherwise.

5.1 General

Upon designating IDW as either RCRA hazardous or RCRA non-hazardous using existing information and best professional judgment practices, the Task Manager should assure that appropriate handling procedures have been developed.

5.2 Management of Non-Hazardous IDW

Non-hazardous IDW such as PPE and disposable equipment may be bagged and transported to a local permitted municipal landfill. Non-hazardous IDW such as drill cuttings, purge or development water, decontamination fluids, etc., will be containerized, managed appropriately while on site, and transported to an appropriately licensed off-site disposal facility. Waste hauling services should be obtained and waste storage locations maintained at the project site pending transport.

Purge water from monitoring wells which have already been analyzed and are shown to be below Residential Drinking Water Criteria may be discharged to the ground surface away from the monitoring well unless otherwise prohibited by site protocol.

Purge water from private potable wells which are in use may be discharged directly to the ground surface.

5.3 Management of Hazardous IDW

Hazardous IDW must be managed as specified in applicable U.S. EPA and state regulations. Management of hazardous waste includes both proper handling and disposal within the required time frame in accordance with requirements for small or large quantity generators, as applicable. IDW should be disposed off- site in an appropriately licensed and approved hazardous waste landfill or liquid waste treatment facility. IDW designated for off-site disposal must be properly containerized, characterized, labeled, and stored before transport and disposal.

On-site management of hazardous IDW requires special precautions and planning.

Generation of hazardous IDW should be kept to a minimum. Disposable equipment and PPE can often be cleaned to render it non-hazardous. Decontaminated PPE and disposable equipment should be bagged if sent to an off-site dumpster or a municipal landfill.

5.4 Waste Segregation

If it is determined by the Field Manager that off-site disposal of IDW is required, liquid waste should be contained separately from solid waste for ease of handling. For this POP, liquid wastes include purge and well development water, while solid wastes include soil, drilling mud, and sampling debris. If drums are used for containing the IDW, the Field Sampling Team Leader is responsible for noting in the field logbook, the waste type in each drum and for labeling the drums.

5.5 Solids

Solid waste to be containerized should be placed in Department of Transportation (DOT)-specified, 17H 55-gallon drums (or similar), lined roll off boxes or an appropriately constructed containment building. Under no circumstances should solid residues from a known "hot spot" be combined with other residues containing suspected but unknown contamination, regardless of whether the drum is filled or not. To minimize the number of drums (if used), "hot spot" residues containing similar waste characteristics can be combined. Also, for the collection of solid waste, allow at least 6 to 12 inches of empty

space in each drum if the addition of absorbent is necessary. The following solid matter should be handled as described:

- Soil Cuttings/Excess Soil/Sediment Sample Volume - Soil cuttings or excess soil/sediment volume may be placed in DOT-specified drums, or placed in roll-off boxes or other containers pending transportation. Drums containing soil or sediment should be identified with a particular boring, well, or test pit from which the material was generated. To minimize the number of drums generated during an investigation, soils from several sources in the same general location can be placed in the same drum with proper labeling. Documentation must be maintained to identify the source of the soils (including boring ID and depths) containerized in a particular drum for correlation to laboratory data for future disposal. The description of the waste/soil, boring location, and general observations should also be noted in the field logbook. Soil cuttings from soil borings or well installation activities and sediment associated with sampling efforts will be containerized, labeled, staged for disposal, characterized, and disposed of at an appropriately licensed disposal facility.
- PPE, Sampling Equipment, and Absorbents - Used PPE and disposable sampling equipment can be containerized together but separate from other solid (soil/sediment) and liquid waste. Spent PPE and sampling equipment are typically collected on a daily basis in plastic garbage bags and disposed at the end of daily activities in a drum dedicated for this type of waste or in an on-site dumpster. Non-contaminated PPE and materials that do not come in contact with contaminated media can be disposed along with other general waste generated at the site. Soiled absorbents and PPE will be held in drums or roll-off boxes at the major centers of activity on the site or will be containerized, labeled, staged for disposal, characterized, and disposed of at an appropriately licensed disposal facility.

5.6 Liquids

For this POP, liquid waste refers to well development water, purge water and decontamination fluids. Liquid wastes requiring off-site transport and disposal can be containerized using 55-gallon drums, plastic totes, welded tanks, or liquid tanker trucks. The following liquids should be handled as described:

- Well Purge Water - Well purge water, which includes development and sampling purge water, if drummed, should be containerized separately from solid waste. Proper documentation shall be maintained to ensure that liquid waste containers specify the source of the purge water in order to correlate representative laboratory analyses with waste contained in a particular drum or container. It is acceptable to mix purge water from different wells, provided that proper documentation is maintained. However, the water quality results of the most contaminated well contributing to the mixed water will determine the proper method of disposal.
- Decontamination Water and Sample Preservatives - Decontamination water that includes chemicals used in the decontamination process, such as isopropyl alcohol or hexane, and excess sample preservatives should be containerized separately. Decontamination water is typically collected and disposed of as necessary in a drum(s) dedicated for this type of waste. Steam cleaning rinsate should also be containerized separately from other liquids unless the Field Manager determines that the rinsate is non-hazardous.
- Water generated during well development, well sampling, or decontamination processes will be containerized, labeled, staged, and transported to an appropriately licensed disposal facility.

5.7 On-Site Drum Handling

All filled or partially filled drums must be properly closed, sealed, labeled, and staged before demobilization. If storage is anticipated in excess of two weeks, the drums should be covered with a wind/rain resistant cover such as a plastic or polyethylene tarp.

5.8 Absorbent

Soil cuttings that have been containerized will frequently develop a layer of water after being stored on-site for a period of time. If fluids are present in the drums, an absorbent material may be added prior to removal offsite to prevent accidental spillage. This absorbent material can be added during site operations. The absorbing material should consist of an innocuous material such as vermiculite, sawdust, (or fine wood shavings), or some type of kitty litter. The absorbent should be added on the top of the solid waste and not mixed into the waste since the disposal facility may

wish to separate the generated solids from the absorbed liquid. The depth and volume or weight of absorbent should be noted in the field logbook.

5.9 Staging

All drums shall be staged in a location designated by the Field Manager and approved, in advance, by the Project Manager. Depending upon the accessibility of the site to non-authorized individuals, the staging area may need to be fenced or located inside a larger fenced area. All drums shall be stored on pallets (if possible) in an area where they will stay dry in the case of heavy rain or ponding of water. The drums should be arranged in rows with adequate space between the rows to allow for visual inspection of all drums. The staging area should also be laid out by grouping drums of similar waste together to allow for easier access to waste types during the removal operations, minimizing the need to rearrange drums. Drums should not be stacked on top of each.

Equipment used to move filled drums may include backhoes, forklifts, front-end loaders or drum grapplers operated by qualified and trained personnel. Caution should be exercised to prevent damaging drums. Any drums found to be damaged or leaking must be overpacked in a leak-proof container.

In the event that drums must be stored on-site for longer than 90 days, precautions such as berms, secondary containment, and/or overpacking should be taken to prevent accidental leakage or environmental corrosion.

5.10 Sealing

Proper sealing involves securing and fastening drum rings and bungs. Open-top drums are delivered with the outer ring reversed and fastened with the bolt on the upper side of the drum lid, which is a universal convention indicating an empty drum. When the drums are filled, the drum lid should be secured by placing the ring with the bolt down and tightened over the drum lip. Depending on the access of the site to unauthorized individuals, it may be appropriate to notch or mark the drum and ring to assist in determining whether stored, unsecured drums have been opened. If a drum needs to be opened after sealing, appropriate personal protection shall be required.

5.11 Labeling

Initial labeling of all drums shall be performed through the use of an indelible marker on the top and the side of the drum (i.e., grease pens, Rust-Oleum brand or similar spray paint) or by placing a “Pending Analysis” label on the drum. The markings should be at least one inch in height and consist of a number that will allow the drum to be cross-referenced with the field logbook and include type of contents and generation date.

Upon receipt of the sample characterization analyses, final labeling of the drums will occur in accordance with applicable state and U.S. EPA requirements and AECOM policy. Factory-purchased labels will be utilized that provides space for the following information:

- Site name and drum log number,
- Material description (soil, sludge, etc.) and generation location (i.e., boring SB2),
- Generator’s name and address,
- Generator’s temporary ID number,
- Waste classification (hazardous or non-hazardous)
- DOT shipping name if hazardous
- Date generated, and
- Manifest or Bill of Lading number (if known).

Waste characterized as hazardous will require a Hazardous Waste label, U.S. EPA generator ID number, and proper transportation manifesting prior to transportation to an approved hazardous waste landfill or treatment facility. Drummed waste shown to be non-hazardous should be returned to the site proper and the drum either returned to the manufacturer (if possible) or properly disposed within the federal, state and local regulations.

5.12 Waste Classification

Prior to removal from a site, all waste must be classified to determine appropriate disposal procedures. Analytical data specifically relating to the drum contents can be used to determine the waste classification. Careful separation of wastes and proper documentation of drum contents may prevent the need for drum sampling if prior waste characterization sampling from the site is available. Additionally, analytical results of samples collected from the site and generator knowledge may also be used to classify waste as hazardous or non-hazardous. The official waste profile should be signed by the generator. The waste disposal facility may also perform their sampling, some of which might be performed on-site prior to removal.

5.13 Drum Removal & Disposal

Drummed wastes will be disposed at an appropriate disposal or treatment facility based upon characterization of the waste. Removal of wastes in drums from a site should be performed only by subcontractors holding permits approved by federal and state authorities to transport hazardous materials. In most cases, the various categories of wastes will be transported to one of several destinations. It is the responsibility of the Project Manager to determine that wastes are properly classified and to know their final destination. Furthermore, the Field Manager must inform the Project Manager of the wastes' final destination and secure from the client written concurrence on use of the disposal facility (through signature of the waste profile sheet). Although it is not required, subcontractors may be used to complete the waste profile sheets, classify the waste, perform confirmatory drum sampling, inspect/overpack (if necessary), and complete transportation manifest forms. The manifest forms should be signed by the client or by an authorized representative of the client.

6.0 Data & Records Management

The data associated with waste characterization includes the following:

- Location, date, and time of waste generation,
- Process which generated the waste,
- Assumed contaminants of concern within waste stream based upon current knowledge,
- Sample(s) collected with associated analytical parameter request,
- Sample ID's,
- Date and time of sample collection,
- Name of person collecting sample(s), and
- Chain of custody(s).

Upon receipt of waste classification results, appropriate transportation and disposal events should occur. The following information should be logged when preparing shipments for transport and disposal:

- Number, type, and quantity of containers being shipped,
- Current storage location(s) of containers,
- Waste approval number,
- Transporter (company) name and ID number,
- Manifest number, and
- Disposal facility name and location.

Certificates of Disposal and waste manifests shall be retained in accordance with EPA RCRA regulations and provided to the identified generator. The records generated in this POP will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

7.0 Personnel Qualifications

The management of IDW is a relatively involved procedure requiring specific training. Personnel trained in the containment, characterization, transport and disposal of IDW will oversee IDW management on this project. Additional training and/or certifications may be required if the IDW is characterized as hazardous.

Field personnel must be health and safety certified as specified by the *Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i))* to work on sites where hazardous materials may be present.

It is the responsibility of field personnel to be familiar with the IDW management procedures outlined within this POP as well as quality assurance and health and safety requirements outlined within this *Sampling and Analysis Plan (SAP),* the *Quality Assurance Project Plan (QAPP), and the site-specific Health and Safety Plan (HASP)*.

8.0 Quality Assurance and Quality Control

Quality Control (QC) samples collected may include field duplicates, equipment and/or field blanks, trip blanks, and matrix spike/matrix spike duplicates (MS/MSD). See the QAPP for collection frequency and methods.

9.0 References

Environmental Protection Agency, 1987, REM III Program Guidelines, Field Technical Guidelines 12.02, Region II.

Environmental Protection Agency, 1991a, Management of Investigation-Derived Waste During Site Inspections, Office of Research and Development, Washington, DC.

Environmental Protection Agency, 1991b, Standard Operating Procedures and Quality Assurance Manual (Section 4.5), Environmental Compliance Branch, Region IV, Athens, Georgia.

POP 102 – Chain of Custody

POP 103 – Packaging and Shipment of Environmental Samples

Surface Water Sample Collection – POP Number: 201

1.0 Scope and Method Summary

This POP describes the basic techniques and general considerations to be followed for the collection of surface water samples from streams, rivers, ponds, and lakes.

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in task-specific work plans as appropriate and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

Surface water sample collection generally involves collection of a representative water sample from a water body (e.g., stream, river, pond, or lake) into an appropriate container. Specific field conditions such as water depth, tidal information, and location are recorded. Field parameters (e.g., pH, specific conductivity, water level collection from a stream gage, dissolved oxygen (DO), turbidity, oxidation-reduction potential (ORP), and temperature) will be monitored during surface water sample collection if stated in the work plan.

2.0 Health and Safety Considerations

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, is addressed in the site specific HASP. All work will be conducted in accordance with the HASP.

3.0 Interferences

Potential interferences could result from cross-contamination between sample locations or entrainment of non-target material in the samples. Minimization of cross-contamination will occur through the following:

- Collection of samples from downstream to upstream locations (as appropriate);
- Collection of surface water samples prior to sediment samples at individual locations (when applicable);
- The use of clean, decontaminated sampling equipment at each location; and
- Avoidance of material (e.g., re-suspended solids) that is not representative of the medium to be sampled.

4.0 Equipment and Supplies

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Surface Water Sample Collection Record, field logbook, or electronic data collector,
- Sample chain of custody forms,
- Sample packaging and shipping supplies,
- Equipment decontamination supplies,
- Peristaltic pump,
- Disposable tubing (both for the pump head assembly and for sample collection as appropriate)
- Health and safety supplies (as required by the HASP),
- Waterproof marker pens (Sharpie® or equivalent),
- Rubber boots (waders),

- Individual or multi-parameter meter(s) to measure temperature, pH, specific conductance, DO, ORP, and/or turbidity (if appropriate),
- Instrument calibration solutions and calibration log,
- Water level meter
- Sample kit (i.e., bottles, sample bottle holders, labels, preservatives, custody records, custody seals, cooler, and ice),
- Tide chart, and
- Field notebook/pen.

5.0 Procedures

5.1 Access to Sample Locations

Sample locations are presented in each specific work plan. Where samples are located near bridges or piers, these structures can provide convenient access for sampling. A boat may be needed to sample locations on lakes/impoundments, as well as some locations on the Anacostia River. When boats are used for sampling, health and safety procedures as described in the HASP must be followed. Wading to locations may be considered, but is not the preferred method in the Anacostia River. If it is necessary to wade into the water body to obtain a sample, the sampler shall take care to minimize disturbance of bottom sediments and must enter the water body downstream of the sampling location. If sediment in the sample area is disturbed and water becomes turbid, the sampling technician shall wait for the sediments to settle before taking a surface water sample.

Under ideal and uniform constituent dispersion conditions in a flowing stream, the same concentration of each constituent would occur at all points along the cross section. This situation is most likely near the centroid of flow and away from tributary, eddy, or backwater confluences (USGS, 2006). Careful selection of the sample collection location should assure, as nearly as possible, that samples are taken where uniform flow or dispersion and good mixing conditions exist.

5.2 Surface Water Sampling

Surface water sampling procedures were adapted from USGS (2006) and modified for site-specific conditions. Surface water samples from the Anacostia River will be collected using a peristaltic pump and disposable tubing. A new length of tubing will be used for every location sampled. If necessary the tubing may be attached to an extension pole and lowered into the water column to the target depth. For surface water samples collected on the Anacostia River the general target depth is zero to one foot (ft) below the water surface unless otherwise specified in the work plan. Care should be taken to ensure that the intake end of the sample tubing does not contact the bed of the river, lake, stream, or pond to minimize the turbidity of the sample. The intake end of the tubing should also not contact the boat (if sampling from a boat) or any other potentially contaminated surface to avoid cross contamination. Air will be purged from the tubing prior to sample collection and field parameter readings. Sample containers will be filled in the order of analysis starting with the most volatile compounds with the metals being collected last. To minimize volatilization, the pump will be operated at a low speed for several minutes to slowly fill the tube with water which will then be drained to the volatile organic compound sample containers. The pump's speed may be increased to fill the remaining sample containers, provided the pumping rate does not induce turbidity. Water quality indicator parameter readings (e.g. pH, specific conductance, DO, ORP) will be recorded at the time of sample collection.

During cold weather months a peristaltic pump may become difficult or impossible to use, since the disposable tubing may freeze and portions of the river may be frozen over. A dipping method may be used during these months to help facilitate the sampling and maintain a safe work environment. Using an extension pole with a swing sampler attached, insert a clean one liter glass sample container (no cap is required) into the swing sampler and secure it with zip-ties. A weight attached to a long rope may be needed to break a hole in the ice large enough to fit the swing sampler through. Standing a safe distance from the river bank, extend the pole to the appropriate length and dip the swing sampler to the

targeted sample depth (0-1 ft). Once the sample container is full, lift the pole and swing it back to the river bank. Carefully decant the surface water into the appropriate sample containers starting with most volatile compounds using caution to not displace preservatives if pre-preserved and collect the metals last. A new 1 liter sample container for dipping should be used at every location. The end of the extension pole with the attached swing sampler should be decontaminated in accordance with POP 105 between sample locations.

Samples will be collected farthest downstream first, moving upstream so as to minimize the potential influence on water quality caused by disturbance within the water body.

At each sample location, measurements for pH, specific conductivity, temperature, DO, ORP, and/or turbidity will be collected using either an individual or a multi-parameter meter. The depth of water, depth of sample collection, and visual observations including presence and/or absence of oil or oil sheen of the location will be recorded in the field documentation. At some locations, it will not be possible to measure all field parameters if safe work conditions do not allow – examples include measuring depth of water from a bridge near a dam overflow structure. Tidal information should also be recorded per current tide charts and/or as recorded from gauging a stream gage

A portion of the water sample may be filtered in the field prior to preservation for analysis in the laboratory of dissolved fractions (e.g., selected metals). Filtration procedures and equipment (e.g., vacuum filtration, pressure filtration through cartridge) will be determined by the volume of filtrate desired, presence of fine particulates (e.g., silts, clays) and best professional judgment. Selected filtration methods will be described on the sample collection form, field logbook, and/or electronic data collector.

5.3 Sample Handling and Preservation

Once each sample container is filled, cap and label the container with (at a minimum) the sample identifier, sampler's initials, sampling date and sampling time. Additional information such as preservation information and analytical tests will be added to the sample label as appropriate.

For samples slated for VOC analysis, confirm that no headspace bubbles are present in the sample container following placement of the cap. If bubbles are observed, recollect the sample.

Place the sample containers into a cooler and maintain on ice.

Complete sample chain of custody and other documentation per POP 102 – Chain of Custody Procedures.

Package the samples for shipment to the laboratory per POP 103 – Packaging and Shipment of Environmental Samples.

5.4 Equipment Decontamination

Decontamination is necessary for surface water sampling when using the dipping method described above, for water quality instrumentation, and for any other non-disposable equipment used during the surface water sampling process. When equipment decontamination is required POP 105 - Decontamination of Field Equipment will be followed

6.0 Quality Assurance / Quality Control

An energy calibration check should be run at the start of each day of sampling. This check confirms that the characteristic x-ray lines are stable and instrument drift is not occurring. This also provides a gain check if the ambient temperature fluctuates significantly. This test must be run at the start of each day, when the batteries are changed, when the instrument is shut down, and at the end of each day. This procedure should also be run any time the operator believes that drift is occurring during analysis.

A blank consisting of silicon dioxide or a Teflon or quartz block must be run at the beginning and end of each day of analysis and after every 20 samples or every hour of operation during the day or at any time the analyst suspects contamination in the analytical system.

An independent standard must be used to verify the accuracy of the instrument and confirm its stability and consistency for the analyte of interest. NIST, USGS or commercial standards may be used. The standard check must be performed at the beginning and end of each analysis day and after every 20 samples or hour of operation during the day. If the measured value falls outside the acceptance range the check sample must be reanalyzed; if it is still outside the

acceptance range the instrument must be recalibrated and any samples analyzed since the previous acceptable calibration check must be reanalyzed.

At least one sample in each set of 20 must be analyzed in duplicate to assess measurement precision. Relative percent difference for duplicates should be ≤ 30%.

The field forms and field notes generated from this procedure will be reviewed by the sampling team leader, project manager, or designee. All quality control results must be downloaded to project computer files along with sample data. Any deviations from this POP, problems encountered during the analysis and corrective actions taken must be documented in the field records.

7.0 Data and Records Management

The data associated with surface water sample collection may contain the following:

- Sample labels,
- Chain of custody records and custody seal(s),
- Field logbook,
- Sample collection records,
- Electronic data collection (Trimble Yuma® or equivalent),
- Field Modification Forms (used prior to field work, when required), and
- Nonconformance Records (used after field work, when required).

The following POPs describe the data collection and record management procedures that should be followed as part of the surface water sample collection process:

- *POP 101 Field Records,*
- *POP 102 Chain of Custody Procedures,*
- *POP 103 Packaging and Shipment of Environmental Samples, and*
- *POP 502 Water Quality Instrumentation.*

See the referenced POPs for additional details.

8.0 Personnel Qualifications and Training

Surface water sample collection is a relatively involved procedure requiring formal training and a variety of equipment. It is recommended that initial sampling be supervised by more experienced personnel.

Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

It is the responsibility of field personnel to be familiar with the sampling procedures outlined within this POP, with specific sampling, quality assurance, and health and safety requirements outlined within this Sampling and Analysis Plan (SAP), the Quality Assurance Project Plan (QAPP), and the Health and Safety Plan (HASP). Field personnel are responsible for collecting samples, decontamination of equipment, and proper documentation in the field logbook, field forms, or electronic data collector such as the Trimble Yuma® or equivalent (if appropriate).

9.0 References

POP 102 – Chain of Custody Procedures.

POP 103 – Packaging and Shipment of Environmental Samples.

POP 105 – Decontamination of Field Equipment.

USGS. 2006. Chapter A4. Collection of Water Samples in National field manual for the collection of water-quality data collection of water samples TWRI Book 9.

Sediment Sampling – POP 202

1.0 Scope and Method Summary

This Project Operating Procedure (POP) describes the basic techniques and general considerations to be followed for the collection of surface sediment samples. For the purposes of this POP, sediment is defined as soil, sand, silt, clay, organic matter, or other materials that accumulate on the bottom of a water body (*U.S. EPA* 1998, 2001, and 2005). The specific details of actual sample collection are dependent upon local conditions as well as the purpose of the sampling.

Surface sediment sample collection generally involves collection of a representative sediment sample from, or near, a water body (e.g., stream, wetland, pond, or lake) into an appropriate container(s). Specific field conditions such as water depth, tidal status, and location are recorded. Field observations, such as presence and type of oil sheen and oil will also be recorded.

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in task-specific work plans or on Field Modification Forms as appropriate and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

2.0 Health and Safety

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, is addressed in the site specific HASP. All work will be conducted in accordance with the HASP.

3.0 Interferences

Potential interferences could result from cross-contamination between sample locations or entrainment of non-target material in the samples. Minimization of the cross-contamination will occur through the following:

- Approach of sample locations from downstream (tidal dependant),
- Collection of surface water samples prior to sediment samples at individual locations and as required,
- The use of clean, decontaminated or dedicated sampling tools at each location in the field and during sediment sample processing. Avoidance of material (e.g., re-suspended solids) that is not representative of the medium to be sampled.

4.0 Equipment and Supplies

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions or as specified in a work plan.

- Nautical equipment (anchors, lines, etc.),
- Universal Core® sampler (or similar), Lexan® core tubes (or similar), core tube catchers, core tube caps, aluminum extension rods (water depths less than 20 ft) or a gravity-driven slide hammer (deeper water),
- Petite Ponar® or Ekman dredge sampler,
- Hacksaw, cordless drill, drill bits, and power shears,
- Duct tape,
- Tape measure or survey stadia,

- Equipment decontamination supplies,
- Stainless steel bowls or Pyrex® containers and spoons, or similar disposable containers,
- Health and safety supplies (personal flotation devices, etc., as required by the HASP),
- Waterproof marker pens (Sharpie® or similar),
- Sample kit (i.e., bottles, labels, preservatives, custody records and tape, cooler, ice) or core storage kit (i.e., 5-gallon buckets, garbage bags, paper towels, cooler, ice),
- Sediment Sample Collection Record, field logbook, camera, and electronic data collector,
- Sample chain of custody forms,
- Sample packaging and shipping supplies,
- Field logbook, and
- Access to a boat when required for transportation.

5.0 Methods

5.1 Access to Sample Locations

Sample locations are presented in the project specific work plan. A boat may be needed to access sample locations. When boats are used for sampling, health and safety procedures as described in the HASP must be followed. Wading to locations may be considered, but is not the preferred method in the Anacostia River. If it is necessary to wade into the water body to obtain a sample, the sampler shall take care to minimize disturbance of bottom sediments and must enter the water body downstream of the sampling location.

5.2 Sample Location

Sample location will be identified with a Global Positioning System (GPS) unit. Pre-determined GPS identification numbers and coordinates will be used to determine correct sample placement whenever possible. Consideration must be given to maintain the sample location while sampling from boats; the use of anchors and other stabilizing devices may be required to help maintain a sample location. A measuring tape or measuring rod with a plate on the end will be used to determine water depth at the sample location in shallow water. If the depth of water dictates the use of an alternate measuring method, a sounding disc (secchi or similar) will be used.

5.3 Sediment Retrieval

All necessary sampling equipment and supplies listed in Section 6.0 and required personal protective equipment (PPE) should be loaded on the boat and the float plan communicated to the boat captain. After the sampling location has been reached, field personnel should ready the sampling device. Surface sediment samples will be collected using a Petite Ponar or equivalent sampling device.

5.4 Ponar or Ekman Dredge Sampling

After the sampling location has been reached, field personnel should ready the dredge sampling device by attaching a nylon rope, cable or pole to the top of the sampler. The sampler should then be placed in the “open” position. Slowly lower the sampler to just above the sediment surface and then drop the sampler quickly into the sediment to trigger the release mechanism, which should close the sampler. Raise the sampler to the water surface, inspect sample integrity, and carefully decant off surface water in the sampler through the screens. Open the sampler and transfer the contents to a stainless steel, Pyrex®, or disposable bowl. Samples for VOCs, simultaneously extracted metals (SEM), and acid volatile sulfide (AVS) will be collected prior to homogenization. If additional sample volume is needed, repeat collecting sediment in the manner described above.

5.5 Sample Handling and Preservation

Samples to be analyzed for VOCs, SEM, and AVS will be collected directly from the core or from the grab sample that has been deposited into a stainless steel bowl or similar prior to homogenization. Thoroughly homogenize (until visually uniform) the remaining sample interval after logging the core description. Fill the sample jars provided for the sampling location and appropriate analysis.

Once each sample container is filled, clean the rim and threads of the sample container by wiping with a paper towel.

Cap and label the container with (at a minimum) the sample identifier, sampling date and time, and sampler's initials. Additional information such as preservation information and analytical tests may also be added to the sample label as appropriate. Sample labeling will be conducted per the QAPP.

Place the sample containers into a cooler and maintain on ice. Complete sample chain of custody and other documentation per POP 102 Chain of Custody Procedures. Package the samples for shipment to the laboratory per POP 103 Packaging and Shipment of Environmental Samples.

5.6 Equipment Decontamination

All reusable equipment shall be decontaminated in accordance with *POP 105 Decontamination of Field Equipment.* All investigation derived waste generated from the sampling effort (gloves, disposable sampling equipment, decontamination water, etc.) shall be appropriately containerized and transported to the onsite collection area for appropriate disposal per *POP 106 Investigation Derived Waste Management*.

6.0 Data and Records Management

The data associated with sediment sample collection may be contained in the following:

- Sample labels,
- Chain of custody records and custody seal(s),
- Field logbook,
- Sample collection records,
- Electronic data collection (Trimble Yuma® or equivalent),
- Field Modification Forms (used prior to field work, when required), and
- Nonconformance Records (used after field work, when required).

The following POPs describe the data collection and record management procedures that should be followed as part of the sediment sample collection process:

- *POP 101 Field Records,*
- *POP 102 Chain of Custody Procedures,*
- *POP 103 Packaging and Shipment of Environmental Samples,*
- *POP 105 Decontamination of Field Equipment, and*
- *POP 106 Investigative Derived Waste Management.*

See the referenced POPs for additional details.

7.0 Quality Assurance and Quality Control

Quality Control (QC) samples collected during sediment sample collection may include field duplicates, equipment and/or

field blanks, trip blanks, and matrix spike/matrix spike duplicates (MS/MSD). See the QAPP for collection frequency and methods.

8.0 Personnel Qualifications

Sediment sample collection is a relatively involved procedure requiring formal training and a variety of equipment. It is recommended that initial sampling be supervised by more experienced personnel.

Field personnel must be health and safety certified as specified by the *Occupational Safety and Health Administration* (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

It is the responsibility of the field personnel to be familiar with the sampling procedures outlined within this POP, with specific analytical sampling procedures, quality assurance, and health and safety requirements outlined within this *Sampling and Analysis Plan* (SAP), the *Quality Assurance Project Plan* (QAPP), the Health and Safety Plan (HASP) and work plans under which the sampling will be conducted. Field personnel are responsible for sample collection, decontamination of equipment, and proper documentation in the field logbook, field forms, or electronic data collector such as the Trimble Yuma® or equivalent (as appropriate).

9.0 References

ASTM-2488-09a Standard Practice for Description and Identification of Soils (Visual-Manual Procedure).

Code of Federal Regulations, Chapter 40 (Section 261.4(d)).

POP 101 – Field Records.

POP 102 – Chain of Custody Procedures.

POP 103 – Packaging and Shipment of Environmental Samples.

POP 105 – Decontamination of Field Equipment.

POP 106 – Investigation Derived Waste Management.

U.S. EPA. 1998. EPA's Contaminated Sediment Management Strategy. U.S. Environmental Protection Agency, Office of Water, Washington, DC. EPA 823/R-98/001.

U.S. EPA. 2001. Methods for Collection, Storage, and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual. Office of Water EPA-823-B-01-002 October 2001.

U.S. EPA. 2005. Contaminated Sediment Remediation Guidance for Hazardous Waste Sites USEPA, Office of Solid Waste and Emergency Response, EPA-540/R-05/012, 236 pp, 2005.

Subsurface Soil Sampling by Direct Push Methods – POP Number: 301

1.0 Scope and Method Summary

1.1 Purpose and Applicability

This POP describes the basic techniques and general considerations to be followed for the collection of subsurface soil samples using commercially available direct-push (Geoprobe Systems® for example) soil probing equipment. Subsurface soil samples may be obtained using this system for purposes of determining subsurface soil conditions and for obtaining soil samples for physical and/or chemical evaluation.

The purpose of this POP is to provide a description of a specific method or procedure to be used in the collection of subsurface soil samples using the direct push methods. Subsurface soil is defined as unconsolidated material which may consist of one or a mixture of the following materials: sand, gravel, silt, clay, peat (or other organic soils), and fill material. Subsurface soil sampling, conducted in accordance with this POP will promote consistency in sampling and provide a basis for sample representativeness.

This POP covers subsurface soil sampling using Geoprobe Systems® equipment (or equivalent); specifically, the Dual Tube Sampling Systems, the Macro-Core® Soil Sampler, and the Large Bore Sampler. Use of this sampling equipment requires use of a hydraulically-powered direct push percussion/probing machine or equivalent (Geoprobe Systems®).This technique is usually performed by subcontractors, although rental equipment is available for use by trained operators. For this project it is preferred that any direct-push sampling equipment be operated by a qualified and trained subcontractor.

Direct push sampling methods covered in this POP are applicable to unconsolidated soil/fill materials. Sampling depths are greatly dependent upon soil density as the hydraulically-powered probing unit has power limitations. Sample recovery is also somewhat dependent on grain size as very coarse gravel, cobbles, and boulders will occasionally cause premature refusal of the sample tooling. It is generally preferable to have some prior knowledge of site soil conditions if sampling activities are proposed where equipment limitations may become a factor.

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in task-specific work plans as appropriate and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

1.2 General Principles

Soil sampling using the Geoprobe System® requires use of the hydraulically-powered percussion/probing machine and one of the Dual Tube Sampling Systems (DT22 or DT 325), the Macro-Core® Soil Sampler or the Large Bore Sampler soil sampling devices. The percussion/probing machine is typically mounted on a tracked or truck chassis. The percussion/probing machine, through its hydraulic operation, pushes and hammers the soil sampling equipment vertically into the ground. The soil sampler is then extracted from the ground to recover the sample.

The Dual Tube Sampling Systems (Figure 1) use two sets of probe rods to collect a continuous soil core; an outer rod and an inner rod containing a polyvinyl chloride (PVC) liner. The outer set of probe rods are directly driven by the percussion/probing machine and act as an outer casing preventing borehole collapse and providing a sealed borehole from which continuous soil samples can be collected. The smaller inner probe rods hold the sampler liner in place as the outer probe rods are driven into the ground. The inner rods are then removed from within the outer rods to retrieve the filled sample liner. Once the inner rods and attached sample liner are removed from the outer casing, the plastic liner containing the soil sample is removed from the tool. The liner is then cut, exposing the soil to be evaluated. This sampling tool is most often used for soil profiling and collection of larger volume soil samples.

Macro-Core® Sampler (Figure 2) consists of a 1.5-inch diameter open-ended steel sampling tool with liners made of clear plastic (Polyethylene Terephthalate Glycol (PETG) or PVC), stainless steel, or Teflon®. This sampler is designed for discrete interval sampling and is not affected significantly by borehole wall collapse. This sampler is similar to a piston sampler where a retractable drive (piston) point is withdrawn when the targeted sampling interval is achieved and

the soil sample enters the sampler. Once the sampling tool is removed from the ground, the plastic liner containing the soil sample is removed from the tool. The liner is then cut, exposing the soil to be evaluated. This sampling tool is most often used for soil profiling and collection of larger volume soil samples.

The Large Bore Sampler (Figure 3) consists of a 22-inch long by a slightly over 1-inch diameter steel sampling tool and may be used for sampling to depths up to approximately 30 feet. Various liner types are available for use with this sampler, and include: plastic, brass, stainless steel, and Teflon®. The metal liners are available in segmented 6-inch lengths. This sampler is designed for discrete interval sampling and is not affected significantly by borehole wall collapse. This sampler is similar to a piston sampler where a retractable drive (piston) point is withdrawn when the targeted sampling interval is achieved and the soil sample enters the sampler. Once the sampler is removed from the ground, the inserted liner containing the soil sample is extracted from the sampler and the soil sample is then cut from or extracted from the liner. The segmented liner materials and discrete interval sampling capability gives this device greater suitability for collection of smaller volume soil samples.

2.0 Health and Safety Considerations

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, is addressed in the site specific Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

Boring completion may involve physical and/or chemical hazards associated with exposure to soil, water, sediment, or materials in contact with soil, water, or sediment. When Geoprobe® sampling is performed, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project HASP

3.0 Interferences

Potential interferences could result from cross-contamination between borehole locations. Minimization of the cross-contamination will occur through the use of clean sampling tools at each location, which will require decontamination of sampling equipment as per POP 105 – Decontamination of Field Equipment

4.0 Equipment and Supplies

In addition to those materials provided by the subcontractor, the following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Boring logs or electronic data collection (such as Trimble Yuma® or equivalent),
- Teaspoon, spatula, or equivalent,
- Analytical Sample kit (bottles, labels, preservatives, custody records, tape, cooler, and ice),
- Sample collection bowl or pan (if collecting a composite sample),
- Folding rule or tape measure,
- Munsell Soil Color Chart
- Equipment decontamination materials (as required by POP 105),
- Health and safety equipment (as required by the HASP), and
- Field project notebook and pen.

Sampling equipment which comes in direct contact with environmental samples during the sample collection process should be constructed of stainless-steel, Teflon®, or glass, unless specified otherwise in a work plan or Quality Assurance Project Plan (QAPP).

- Other materials that may be required:
- Liner cutter,
- Camera,
- Color chart,
- Gloves,
- Potable water supply,

- Plastic sheeting,
- Trash bags, and
- Paper towels
- Appropriate containers and materials to manage investigation derived waste (as specified in the Work Plan and as required by POP 106 – Investigative Derived Waste Management

5.0 Procedures

5.1 General Method Description

Direct Push soil sampling methods generally involve collection of soil samples by driving the sampling tool directly into the ground using the percussion/probing machine and without the aid of hollow-stem augers or other casing-installed drilling methods. The Dual Tube Sampling Systems, Macro-Core®, and Large Bore soil samplers consist of metal tubes of seamless construction which cannot be split apart like split-spoons. Liner/sleeve inserts are used to extract an intact soil core/sample from the sampling device.

These sampling devices operate by being directly pushed and/or hammered into the ground by the percussion/probing machine. The borehole is created as the sampling device is advanced downward. The Dual Tube Sampling Systems collect a continuous soil core utilizing an outer rod and an inner rod with a PVC (or other) liner. The outer set of probe rods are directly driven by the percussion/probing machine and act as an outer casing preventing bore hole collapse and providing a sealed borehole from which continuous soil samples can be collected. The smaller inner probe rods hold the sampler liner in place as the outer probe rods are driven into the ground. The inner rods are then removed from within the outer rods to retrieve the filled sample liner. Once the inner rods and attached sample liner are removed from the outer casing, the plastic liner containing the soil sample is removed from the tool. The liner is then cut, exposing the soil to be evaluated by the field staff.

The Macro-Core® Sampler can collect samples either continuously requiring an open borehole be maintained for efficient sample recovery or as a discrete sampler. The Large Bore Sampler contains a piston tip/drive point which allows for advancing the sampler to a designated depth for discrete interval sampling. The piston tip is retracted when the desired sampling interval is reached. When the soil sampling device is retrieved from the borehole, the drive head, cutting shoe and/or piston assembly is removed, and the liner insert with sample is removed from the sampling device. Field staff is then given access to the sample for whatever purpose is required.

Table 1 summarizes the construction characteristics and sampling attributes of each type of sampler. The appropriate type of sampler should be selected based on project-specific sampling requirements.

5.2 Equipment Decontamination

Non-dedicated sampling devices must be decontaminated prior to its initial use and following collection of each soil sample, especially if sampling for analytical testing purposes is conducted. If sampling for soil logging only is conducted, thorough sampler decontamination between samples may not be necessary although sufficient cleansing is necessary for the sampler to operate properly. Site-specific requirements for equipment decontamination are outlined in the POP 105 - Decontamination of Field Equipment.

5.3 Sampling Procedure – Dual Tube Sampling System

Sample Tooling

- Decontaminate the sampler parts (cutting shoe, inner and outer probe rods, and drive tips) before assembly.
- Assemble the outer probe rod with a cutting shoe. Tighten the cutting shoe with the shoe wrench or pipe wrench.
- Assemble the inner sampler by first placing a catch basket on one end of the PVC liner. Then place the drive head on the opposing end of the PVC liner. Insert the liner/drive head assembly into the outer probe rod such that the core catcher contacts the cutting shoe.
- Install the threadless drive cap onto the outer probe rod.
- Place entire assembly under the percussion/probing machine for driving.

Sampling

- Using the percussion/probing machine, drive the sampler completely into the ground until the drive head reaches the ground surface.
- Use the machine hydraulics to pull the inner rod(s) and sample liner from the outer probe rod.
- Repeat, adding another liner/drive head assembly and additional inner and outer probe rods to the drill string and proceed to collect continuous soil core until the targeted end-of-boring is reached.
- Once end-of-boring is attained, use the machine hydraulics to pull the outer probe rods before or during borehole abandonment.

Sample Recovery

- Use the machine hydraulics to pull the inner rod(s) and sample liner from the outer probe rod.
- Once the inner probe rods and liner/drive head assembly has been removed from the outer probe rods, the liner must be removed from the drive head.
- Disconnect the drive head from the liner which contains the soil sample. The recovered soil sample may now be viewed, logged, and extracted from the liner for analysis.

5.4 Sampling Procedure - Macro-Core® Sampler

Sample Tooling

- Decontaminate the sampler parts (cutting shoe, sample tube, liners (plastic liners are disposable and do not require decontamination)) before assembly.
- Assemble the sampler by first placing the catch basket in the end of the liner. Then place the basket and liner over the inside end of the cutting shoe, then inserting the liner/shoe assembly into the sample tube, and then finally threading the cutting shoe into the sample tube. Tighten the cutting shoe with the shoe wrench or pipe wrench.
- Thread the sampler onto the drive head.

Sampling

- Using the percussion/probing machine, drive the sampler completely into the ground until the drive head reaches the ground surface.
- Use the machine hydraulics to pull the sampler from the borehole.
- Repeat, advancing the sampler to the prior depth, adding a length of drilling rod.
- For sampling where subsurface conditions result in borehole collapse or sampling starts below ground surface, the sampler can be assembled as a discrete sampler with the addition of a piston rod, piston tip, and stop pin. Drive the sampler into the ground until the upper portion of the targeted sampling interval is achieved. Unthread and remove the stop-pin from the drive head using extension rods. This will activate the piston tip/rod.
- Drive the sampler through the targeted sampling interval to collect the sample. The piston tip/rod will retract as the sample enters the sample tube.
- Use the machine hydraulics to pull the sampler from the borehole.

Sample Recovery

- Once the sampler has been removed from the borehole, the sampler must be unthreaded from the drive head, the cutting shoe unthreaded from the sampler, and the liner/shoe assembly removed from the sample tube.
- Disconnect the cutting shoe from the liner which contains the soil sample. The recovered soil sample may now be viewed, logged, and extracted from the liner for analysis.

5.5 Sampling Procedure – Large Bore Sampler

Sampler Preparation

- Decontaminate the sampler parts (cutting shoe, piston rod/tip, sample tube, liners) before assembly.
- Assemble the sampler by first placing the catch basket and liner on the cutting shoe, then threading the liner/shoe assembly into the sample tube, then connecting the piston tip to the piston rod, and then finally

inserting the piston tip/rod assembly into the sample tube. Tighten the cutting shoe with the shoe wrench.
- Thread the sampler onto the drive head. Thread the stop-pin onto the drive head (stop-pin holds the piston tip/rod in place while driving the sampler to the desired sample interval).

Sampling

- Using the percussion/probing machine, drive the sampler into the ground until the upper portion of the targeted sampling interval is achieved.
- Unthread and remove the stop-pin from the drive head using extension rods. This will activate the piston tip/rod.
- Drive the sampler through the targeted sampling interval to collect the sample. The piston tip/rod will retract as the sample enters the sample tube.
- Use the machine hydraulics to pull the sampler from the ground.

Sample Recovery

- Once the sampler has been removed from the ground, the sampler must be unthreaded from the drive head, then the cutting shoe unthreaded from the sample tube, and the liner/shoe assembly removed from the sample tube.
- Disconnect the cutting shoe from the liner which contains the soil sample. The recovered soil sample may now be viewed, logged, and extracted from the liner for analysis.

5.6 Sample Containment

- The soil sample can be removed from the liner following viewing and/or logging. Non-segmented plastic or Teflon® liners should be cut in half with a retractable blade or other safe utensil to facilitate sample extraction or to isolate specific sample zones targeted for analysis. Segmented metal liners can be manually separated.
- The individual halves of the liners can then be screened with UV light if desired and fluorescence is noted on the boring log.
- Once the soil has been screened with UV light if conducted, the soil sample is inspected and a soil boring log can then be completed describing the soil type, color, visible oil, cohesiveness, moisture, plasticity, drive and recovery depths.
- The soil sample may then be extracted from the individual liner segments with a spoon or spatula. Then the sample should be placed directly into the required sample container.
- Once filled, the sample container should be properly capped, cleaned and labeled and recorded in the field book. Sample chain of custody and preservation procedures should then be initiated.
- If using disposable equipment, perform equipment decontamination following collection of the sample.

6.0 Data and Records Management

The data associated with subsurface soil sampling by Geoprobe® methods will be contained in the following:

- Boring logs (example shown as Figure 4 or equivalent),
  - Field screen results/observations and sample collection locations/intervals will be included on the Boring Log.
  - Driven depth and recovered depth will also be recorded.
- Sample collection records,
- Field logbook,
- Chain of custody records,
- Shipping labels,
- Electronic data collection (Trimble Yuma® or equivalent),
- Field Modification Forms (used prior to field work, when required), and
- Nonconformance Records (used after field work, when required).

The following POPs describe the data collection and record management procedures that should be followed as part of the sample collection process:

- *POP 101 Field Records,*

- *POP 102 Chain of Custody Procedures,*
- *POP 103 Packaging and Shipment of Environmental Samples, and*
- *POP 501 Photoionization Detector Measurement.*

See the referenced POPs for additional details.

7.0 Quality Assurance and Quality Control

Quality Control (QC) samples collected via subsurface soil sampling may include field duplicates, equipment and/or field blanks, trip blanks, and matrix spike/matrix spike duplicates (MS/MSD). See the QAPP for collection frequency and methods.

8.0 Personnel Qualifications and Training

8.1 Field Staff

It is the responsibility of the field staff to conduct subsurface soil sampling in a manner which is consistent with this POP. Field staff will observe all activities pertaining to subsurface soil sampling to ensure that the POP is followed, and to record all pertinent data into a digital capture device, onto a boring log or into field logbook. It is also the responsibility of field staff to indicate the specific targeted sampling depth or sampling interval to the drilling subcontractor. Field staff will also collect representative environmental or stratigraphic characterization samples once the sampling device has been retrieved and opened. Additional sample collection responsibilities include labeling, handling, and storage of samples until further chain of custody procedures are implemented. Field personnel must be health and safety certified as specified by the Occupational Health and Safety Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous waste materials may be present.

8.2 Drilling Subcontractor

It is the responsibility of the drilling subcontractor to provide the necessary equipment for obtaining subsurface soil samples. This generally includes the truck- or all terrain vehicle-mounted percussion/probing machine and the Dual Tube System or one or more Macro-Core® and Large Bore samplers in good operating condition, appropriate liners, and other necessary equipment for borehole preparation and sampling. Equipment decontamination materials should also be provided by the subcontractor and decontamination should follow POP 105 – Decontamination of Field Equipment. Drilling personnel must be health and safety certified as specified by OSHA to work on sites where hazardous waste materials may be present.

9.0 References

Geoprobe Systems®, January 2011. Geoprobe® DT325 Dual Tube Sampling System, Standard Operating Procedure. Technical Bulletin No. MK3138.

Geoprobe Systems®, January 2011. Geoprobe® Macro-Core® MC5 1.25-inch Light-Weight Center Rod Soil Sampling System, Standard Operating Procedure. Technical Bulletin No. MK3139.

Geoprobe Systems®, January 2011. Geoprobe® DT22 Dual Tube Sampling System, Standard Operating Procedure. Technical Bulletin No. MK3140.

POP 101 – Field Records

POP 102 – Chain of Custody Procedures

POP 103 – Packaging and Shipment of Environmental Samples

POP 105 – Decontamination of Field Equipment

POP 106 – Investigative Derived Waste Management.

POP 503 – Photoionization Detector Measurement

Subsurface Soil Sampling by Hollow Stem Auger and Split-Spoon Sampler Methods– POP 302

1.0 Scope and Applicability

This Project Operating Procedure (POP) describes the basic techniques/procedures and general considerations to be followed for collecting subsurface soil samples using Hollow Stem Auger (HSA) and split-spoon sampler equipment. Subsurface soil samples may be obtained using this system for purposes of determining subsurface soil conditions and for obtaining soil samples for physical and/or chemical evaluation.

The sampling methods covered in this POP are applicable to unconsolidated soil/fill materials. Sample recovery is somewhat dependent on grain size as very coarse gravel, cobbles, and boulders will occasionally cause premature refusal of the sample tooling. It is generally preferable to have some prior knowledge of site soil conditions if sampling activities are proposed where equipment limitations may become a factor.

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in task-specific work plans or on Field Modification Forms as appropriate and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

1.2 General Principles

Soil sampling using the split spoon sampler requires use of a 140 pound weight dropped 30 inches (ASTM Method D1586) if blow counts are required for geotechnical purposes or a hydraulically-powered percussion hammer to drive the sampler. The manual or hydraulic hammer drives the split spoon sampler vertically into the undisturbed soil ahead of the HSA. The soil sampler is then extracted from the ground to recover the sample.

The split-spoon sampler (Figure 1) consists of a 2-inch diameter by 2-foot long open-ended steel sampling tool that can be split in half by unscrewing the drive shoe. The sampler is attached to drilling rods and lowered through the HSAs where it is then driven ahead of the lead auger. Once the sampler is removed from the ground, the drive shoe is removed and the spoon is split in half, exposing the soil to be evaluated. This sampling tool is most often used for soil profiling and collection of soil samples.

2.0 Health and Safety Considerations

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, is addressed in the site specific Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

Boring completion may involve physical and/or chemical hazards associated with exposure to water, sediment, or materials in contact with either water or sediment. When sediment sampling is performed, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project HASP.

3.0 Interferences

Potential interferences could result from cross-contamination between borehole locations. Minimization of the cross-contamination will occur through the use of clean sampling tools at each location, which will require decontamination of sampling equipment as per POP 105 – Decontamination of Field Equipment.

4.0 Equipment and Materials

In addition to those materials provided by the subcontractor, the following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Boring Logs or electronic data collected (such as Trimble Yuma® or equivalent),
- Teaspoon, spatula, or equivalent,
- Sample kit (bottles, labels, custody records, tape, cooler, and ice),
- Sample collection pan (if collecting a composite sample),
- Folding rule or tape measure,
- Munsell Soil Color Charts

- Equipment decontamination materials (as required by the Quality Assurance Project Plan (QAPP),
- Health and safety equipment (as required by the HASP),
- Field project notebook, camera and pen,
- Work plan including site map and boring locations, and
- Ziploc® - style bags.

Sampling equipment which comes in direct contact with environmental samples during the sample collection process should be constructed of stainless steel, Teflon®, or glass, unless specified otherwise in the work plan or QAPP.

5.0 Procedures

5.1 General Method Descriptions

Split-spoon soil sampling methods generally involve collection of soil samples by driving the split-spoon sampler through the HSAs directly into the undisturbed soil ahead of the lead auger using the weight drop or percussion hammer.

When the split-spoon sampler is retrieved from the borehole, the drive shoe is removed, and the barrel is split in half to access the retrieved material. Field staff is then given access to the sample for visual examination/viewing and for whatever purpose is required.

5.2 Equipment Decontamination

Each split-spoon sampling device must be decontaminated prior to its initial use and following collection of each soil sample, especially if sampling for analytical testing purposes is conducted. If sampling for soil logging only is conducted, thorough sampler decontamination between samples may not be necessary although sufficient cleansing is necessary for the sampler to operate properly. Site-specific requirements for equipment decontamination are outlined in this Sampling and Analysis Plan (SAP). Equipment decontamination procedures are also outlined within POP 105 - Decontamination of Field Equipment.

5.3 Sampling Procedure – Split-Spoon Sampler

Sample Tooling

- Decontaminate the sampler parts (drive head, cutting shoe, and sample barrel) before assembly.
- Assemble the sampler by first placing the catch basket in the cutting shoe. Then assemble the two halves of the sample barrel and thread the cutting shoe and drive head onto the sample barrel. Tighten the drive head and cutting shoe with a pipe wrench.
- Thread the assembled sampler onto the drilling rod.

Sampling

- Lower the sampler to the bottom of the borehole by adding the appropriate amount of drilling rods.
- Drive the split-spoon sampler 24 inches (if a 24-inch sampler is used) and record the number of blow counts per 6 inches as appropriate.
- Use the drilling rig to pull the sampler from the borehole.

Sample Recovery

- Once the sampler has been removed from the borehole, the sampler must be unthreaded from the drilling rods and the drive head and cutting shoe unthreaded from the sample barrel.
- The sample barrel is split which contains the soil sample. The recovered soil sample may now be viewed, logged, and removed from the barrel for analysis.

5.4 Sample Containment

General

- Once the barrel has been split, the soil sample may be extracted from the sample barrel with a spoon or spatula. Then, the sample should be placed directly into the required sample container.
- Once filled, the sample container should be properly capped, cleaned, labeled and recorded in the field book. Sample chain of custody and preservation procedures should then be initiated.
- Perform equipment decontamination following collection of the sample.

6.0 Quality Assurance / Quality Control

Quality Control (QC) samples collected via hollow stem auger methods may include field duplicates, equipment

and/or field blanks, trip blanks, and matrix spike/matrix spike duplicates (MS/MSD). See the QAPP for collection frequency and methods.

7.0 Data and Records Management

The data associated with hollow stem auger split spoon sampling may be contained on the following:

- Sample labels,
- Chain of custody records and custody seal(s),
- Boring logs (example shown as Figure 2 or equivalent),
    - Field Screen results/observations and sample collection locations/intervals will be included on the Boring Log.
- Field logbook,
- Sample collection records, or
- Electronic data collection (Trimble Yuma® or equivalent),
- Field Modification Forms (used prior to field work, when required), and
- Nonconformance Records (used after field work, when required)

The following POPs describe the data collection and record management procedures that should be followed as part of the sample collection process:

- POP 101 – Field Records,
- POP 102 – Chain of Custody Procedures, and
- POP 103 – Packaging and Shipment of Environmental Samples.

See the referenced POPs for additional details.

8.0 Personnel Qualifications and Training

8.1 Field Staff

It is the responsibility of the field staff to conduct subsurface soil sampling in a manner which is consistent with this POP. Field staff will observe all activities pertaining to subsurface soil sampling to ensure that the POP is followed, and to record all pertinent data into a digital capture device, onto a boring log or into field logbook. It is also the responsibility of field staff to indicate the specific targeted sampling depth or sampling interval to the drilling subcontractor. Field staff will also collect representative environmental or lithologic characterization samples once the sampling device has been retrieved and opened. Additional sample collection responsibilities include labeling, handling, and storage of samples until further chain of custody procedures are implemented.

Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous waste materials may be present.

8.2 Drilling Subcontractor

It is the responsibility of the drilling subcontractor to provide the necessary tooling for obtaining subsurface soil samples. This generally includes the truck or All Terrain Vehicle-mounted HSA drilling rig and one or more split-spoon samplers in good operating condition, and other necessary equipment for borehole preparation and sampling. Equipment decontamination materials should also be provided by the subcontractor and should meet project specifications.

Drilling personnel must be health and safety certified as specified by OSHA to work on sites where hazardous waste materials may be present.

9.0 References

- ASTM Method D 1586-08a, Standard Test Method for Standard Penetration Test (STP0 and Split-Barrel Sampling of Soil, ASTM Committee on Standards, Philadelphia, PA.
- POP 101 – Field Records
- POP 102 – Chain of Custody Procedures
- POP 103 – Packaging and Shipment of Environmental Samples
- POP 105 – Decontamination of Field Equipment

Figure 1 – Split-Spoon Sampler

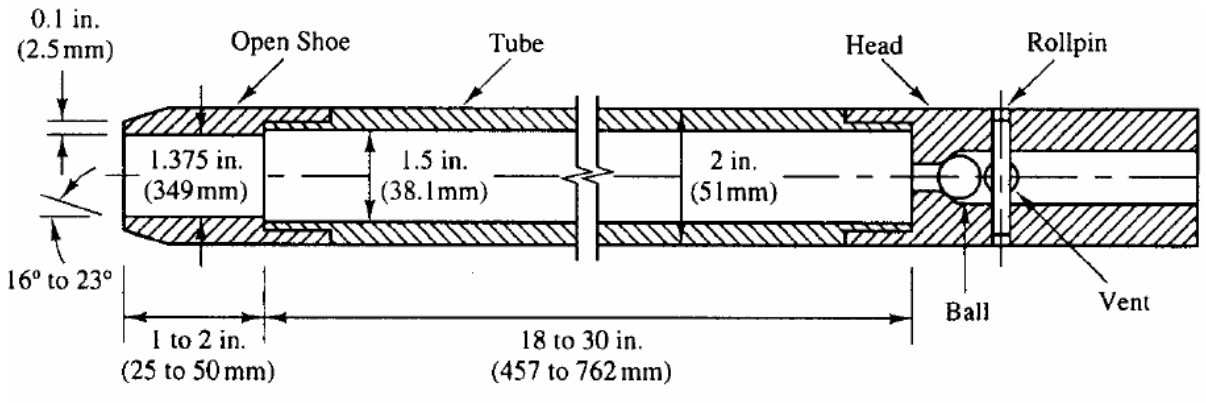

Figure 2 Typical Boring Log

Client:	***LOCATION ID:***
Site Location:	
Task:	
Date/Time Core Collected:	*Sheet: _____ of _____*
Date/Time Core Logged:	
Logged By:	*Settled Recovery:*
Top of Casing Observations:	
	Sample Time:

BORING COMPLETION DETAIL

Depth (ft)	Depth to Groundwater	U.S.C.S.	**MATERIALS: Color, CLASSIFICATION (USCS - ASTM D2488), moisture, plasticity, cohesiveness, sedimentary structure, secondary grain size, other.**	Sample ID	UV Light Observations		Depth (ft)
					Core	Pan	

NOTES:

Surface Soil Sampling – POP Number: 304

1.0 Scope and Method Summary

1.1 Purpose and Applicability

This POP describes the basic techniques and general considerations to be followed for obtaining surface soil samples for physical and/or chemical analysis. For purposes of this POP, surface soil (including shallow subsurface soil) is loosely defined as soil that is present within one foot of the ground surface and can be sampled with the use of readily available and easy-to-operate sampling equipment.

The purpose of this POP is to provide a specific method and/or procedure to be used in the collection of surface soil samples which, if followed properly, will promote consistency in sampling and provide a basis for sample representativeness.

This POP is generally applicable to surface soils which are unconsolidated and are of low to moderate density. Higher density or compacted soils may require use of drill rigs or other powered equipment to effectively obtain representative samples.

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in work plans or on Field Modification Forms as appropriate and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

1.2 General Principles

Surface soil sampling generally involves use of hand-operated equipment to obtain representative soil samples from the ground surface and to shallow depths below the ground surface. If soil conditions are appropriate, surface soil sampling, following the procedures described in this POP, can provide representative soil samples in an efficient manner.

2.0 Health and Safety Considerations

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, is addressed in the site specific Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

Surface soil sampling may involve physical and/or chemical hazards associated with exposure to water, sediment, or materials in contact with either water or sediment. When sediment sampling is performed, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project HASP.

3.0 Interferences

Potential interferences could result from cross-contamination between samples or sample locations. Additional interference could result from using contaminated equipment, disturbance of the matrix in compaction of the sample or inadequate homogenization of the sample. Minimization of the cross-contamination will occur through the use of clean sampling tools at each location, which will require decontamination of sampling equipment as per POP 105 – Decontamination of Field Equipment. Improper sample collection will be minimized by careful adherence to this POP.

4.0 Equipment and Supplies

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Survey equipment or global positioning system (GPS) to locate sampling points,
- Work Plan including site map and sample parameters,
- Spoons or scoops, trowel, spatula, shovel, or hand or bucket auger,

- Field forms or electronic data collected (such as Trimble Yuma® or equivalent),
- Sample kit (bottles, preservatives, labels, custody records, tape, cooler, and ice),
- Ziploc®-style bags,
- Plastic sheeting or tarp,
- Stainless steel, plastic, or other appropriate homogenization bucket, bowl or pan,
- Camera, logbook, and pen,
- Folding rule or tape measure,
- Munsell Soil Color Charts
- Equipment decontamination materials (as required by Quality Assurance Project Plan (QAPP), and
- Health and safety equipment (as required by the HASP).

Sampling equipment which comes in direct contact with environmental samples during the sample collection process should be disposable or constructed of stainless steel, Teflon®, or glass, unless specified otherwise in the work plan or QAPP. Chrome plated equipment typically found in hardware stores should not be used for sampling equipment.

5.0 Procedures

5.1 General Method Description

Site-specific soil characteristics such as soil density and moisture will generally dictate the preferred type of sampling equipment for use at a particular site. Similarly, other project-specific requirements such as sampling depth and requested type of analysis such as physical testing (e.g., grain-size distribution) and/or chemical analysis will dictate the use of a preferred type of sampling equipment. Analytical testing requirements will indicate sample volume requirements that also will influence the selection of the appropriate type of sampling tool.

Sample volume and sampling depth requirements are defined in the Work Plan. For samples requiring a large volume of soil, multiple holes and soil compositing may be necessary.

5.2 Equipment Decontamination

Unless disposable or one time use sampling equipment is used, each piece of equipment needs to be decontaminated prior to its initial use and following collection of each individual soil sample. Site-specific requirements for equipment decontamination are outlined within POP 105 - Decontamination of Field Equipment.

5.3 Collection of Samples for Volatile Organic Compound Analysis

Collection of surface soil samples for VOC analysis is different than collection of soil samples for other routine physical or chemical testing primarily because of the concern for potential loss of volatiles during the normal sample collection procedure. To limit the potential for loss of volatiles, the soil sample must be obtained as quickly and as directly as possible. This generally means that if a VOC sample is to be collected as part of a multiple analyte sample, the VOC sample portion should be obtained first. The VOC sample should also be obtained from a discrete portion of the entire collected sample and not from a sample which has been composited or homogenized from the entire sample interval. In general, it is best to collect the VOC sample by transferring the sample directly from the sampling tool into the sample bottles. Intermediate sample containers such as collection pans should not be used during collection of VOC samples.

5.4 Standard Procedures

Surface Preparation

At some sampling locations, the ground surface may require preparation in advance of sampling. Surface preparation can include the following: removal of concrete or asphalt; removal of surface debris which blocks access to the actual soil surface; and loosening of dense surface soils such as those encountered in heavy traffic areas, or frozen soils. If sampling equipment is used for both removal of surface debris and for collection of the soil sample, the equipment should be decontaminated prior to sample collection to reduce the potential for sample interferences between the surface debris and the underlying soil.

Spoon, Scoop, and Trowel Sampling Procedure

Shovels, spoons, scoops, and trowels are of similarly designed construction and can therefore be operated in accordance with the following procedure.

- Select the sampling location and prepare the surface by removal of surface debris if present. Surface preparation should be completed using other appropriately decontaminated sampling equipment.

- Decontaminate the shovel, spoon, scoop, or trowel in accordance with POP 105 - Decontamination of Field Equipment prior to use.
- The soil sample should be obtained by inserting the sampling tool into the ground and rotating the tool so that a representative "column" of soil is removed from the ground.
- The immediate objective is to collect the VOC sample fraction first if this is required. If a specific depth below the ground surface has been targeted for the VOC sample, the overlying soils should be removed and discarded or placed into a soil collection pan as part of the remaining composite sample.
- Regardless of whether or not a VOC sample is required, one or more cores or scoops of soil may be needed until the desired sampling depth is achieved. Removal of a representative column of soil in cohesionless soils may be difficult to achieve. If more soil is needed to meet sample volume requirements, additional columns of soil may be collected from an immediately adjacent location.
- Except for VOC samples, as each portion of the sample is removed from the ground, it should be placed into an intermediate sample container (collection pan or bowl) until the entire sample interval of soil is removed and all vertical intervals are adequately represented.
- Once the sample interval has been collected, the soil sample should be thoroughly homogenized within the collection pan prior to bottling. Sample homogenizing is accomplished by manually mixing the entire soil sample in the collection pan until a uniform mixture is achieved.
- The appropriate sample containers should be filled with soil from the collection pan.
- Once each sample container is filled, the rim and threads of the sample container will be cleaned of soil, then capped and labeled. Do not submerge the sample containers in water to clean them. Once labeled the sample containers should be placed into a cooler for protection. Sample chain of custody and other documentation requirements should be completed at this time or in the field office.
- The sampling tool and other sampling equipment (if not disposable) should be decontaminated prior to reuse. All investigation derived waste should be properly contained before leaving the area.
- The sample hole should be backfilled to eliminate any surface hazard.

6.0 Data and Records Management

The data associated with subsurface soil sampling by Geoprobe® methods will be contained in the following:

- Sample collection records,
- Field logbook,
- Chain of custody records,
- Shipping labels,
- Electronic data collection (Trimble Yuma® or equivalent),
- Field Modification Forms (used prior to field work, when required), and
- Nonconformance Records (used after field work, when required).

The following POPs describe the data collection and record management procedures that should be followed as part of the sample collection process:

- *POP 101 Field Records,*
- *POP 102 Chain of Custody Procedures,*
- *POP 103 Packaging and Shipment of Environmental Samples, and*

See the referenced POPs for additional details.

7.0 Quality Assurance and Quality Control

Quality Control (QC) samples collected via subsurface soil sampling may include field duplicates, equipment and/or field blanks, trip blanks, and matrix spike/matrix spike duplicates (MS/MSD). See the QAPP for collection frequency and methods.

8.0 Personnel Qualifications and Training

It is the responsibility of the field staff to conduct surface soil sampling in a manner which is consistent with this POP. Field staff will observe all activities pertaining to surface soil sampling to ensure that the POP is followed, and to record all pertinent data into a digital capture device, onto a boring log or into a field logbook. Additional sample collection responsibilities include labeling, handling, and storage of samples until further chain of custody procedures are implemented.

9.0 References

POP 101 – Field Records

POP 102 – Chain of Custody Procedures

POP 103 – Packaging and Shipment of Environmental Samples

POP 105 – Decontamination of Field Equipment

Soil Sampling via Hand Auger – POP 305

1.0 Scope and Applicability

This Project Operating Procedure (POP) describes the basic techniques and general considerations to be followed for the collection of subsurface soil samples for physical and/or chemical analysis. For purposes of this POP, subsurface soil is loosely defined as soil that is located greater than one foot from the ground surface and can be sampled with the use of readily available and easy-to-operate sampling equipment. This POP is generally applicable to subsurface soils which are unconsolidated and are of low to moderate density. Higher density or compacted soils may require use of drill rigs or other powered equipment to effectively obtain representative samples.

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in task-specific work plans or on Field Modification Forms as appropriate and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

1.2 General Principles

Subsurface soil sampling generally involves the use of hand-operated equipment to obtain representative soil samples from shallow depths below the ground surface. If soil conditions are appropriate, subsurface soil sampling, following the procedures described in this POP, can provide representative soil samples in an efficient manner.

2.0 Health and Safety Considerations

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, are addressed in the site specific Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

3.0 Interferences

Potential interferences could result from cross-contamination between samples or sample locations. Additional interference could result from using contaminated equipment, disturbance of the matrix in compaction of the sample or inadequate homogenization of the sample. Minimization of the cross-contamination will occur through the use of clean sampling tools at each location, which will require decontamination of sampling equipment as per POP 105 – Decontamination of Field Equipment. Improper sample collection will be minimized by careful adherence to this POP.

4.0 Equipment and Materials

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Survey equipment or global positioning system to locate sampling points;
- Work plan including site map and sample parameters;
- Spoons or scoops, trowel, spatula, shovel, and hand or bucket auger;
- Field forms or electronic data collected (such as Trimble Yuma® or equivalent);
- Sample kit (bottles, labels, custody records, tape, cooler, and ice);
- Ziploc®-style bags;
- Plastic sheeting or tarp;
- Stainless steel, plastic, or other appropriate homogenization bucket, bowl or pan;
- Camera, logbook, and pen;
- Folding rule or tape measure;
- Munsell Soil Color Charts
- Equipment decontamination materials (as required by the Quality Assurance Project Plan (QAPP); and

- Health and safety equipment as required by the HASP.

Sampling equipment which comes in direct contact with environmental samples during the sample collection process should be disposable or constructed of stainless steel, Teflon®, or glass, unless specified otherwise in a work plan or the QAPP. Chrome plated equipment typically found in hardware stores should not be used for sampling equipment.

5.0 Procedures

5.1 General Method Descriptions

Site-specific soil characteristics such as soil density and moisture will generally dictate the preferred type of sampling equipment for use at a particular site. Similarly, other project-specific requirements such as sampling depth and requested type of analysis such as physical testing (e.g., grain-size distribution) and/or chemical analysis will dictate the use of a preferred type of sampling equipment. Analytical testing requirements will indicate sample volume requirements that also will influence the selection of the appropriate type of sampling tool.

Sample volume and sampling depth requirements are defined in the work plan. For samples requiring a large volume of soil, multiple holes and soil compositing may be necessary. Collection of the requisite volume of soil to meet sample volume requirements without underestimating the sample volume is the overall objective and is a technique which improves with experience.

5.2 Equipment Decontamination

Unless disposable or one time use sampling equipment is used, each piece of equipment needs to be decontaminated prior to its initial use and following collection of each individual soil sample. Site-specific requirements for equipment decontamination are outlined within POP 105 - Decontamination of Field Equipment.

5.3 Collection of Samples for Volatile Organic Compound (VOC) Analysis

Collection of subsurface soil samples for VOC analysis is different than collection of soil samples for other routine physical or chemical testing primarily because of the concern for potential loss of volatiles during the normal sample collection procedure. To limit the potential for loss of volatiles, the soil sample must be obtained as quickly and as directly as possible. This generally means that if a VOC sample is to be collected as part of a multiple analyte sample, the VOC sample portion should be obtained first. The VOC sample should also be obtained from a discrete portion of the entire collected sample and not from a sample which has been composited or homogenized from the entire sample interval. In general, it is best to collect the VOC sample by transferring the sample directly from the sampling tool into the sample bottles. Intermediate sample containers such as collection pans should not be used during collection of VOC samples.

5.4 Standard Procedures

<u>Surface Preparation</u>

- At some sampling locations, the ground surface may require preparation in advance of sampling. Surface preparation can include removal of surface debris which blocks access to the actual soil surface or loosening of dense surface soils such as those encountered in heavy traffic areas, or frozen soils. If sampling equipment is used for both removal of surface debris and for collection of the soil sample, the equipment should be decontaminated prior to sample collection to reduce the potential for sample interferences between the surface debris and the underlying soil.

<u>Auger Sampling</u>

- A bucket auger may be used to collect soil samples from depths ranging from one to approximately five feet. In some instances, soil samples may be collected from greater depths, but often with considerable difficulty. Bucket augers allow for discrete depth interval sampling as the soil is retained within the hollow tube of the auger when it is extracted from the ground. It should be noted that if depth-discrete sampling is the objective, more

than one auger may be necessary, with one auger used to provide access to the required sampling depth and the other (clean) auger used for sample collection.

- Select the sampling location and prepare the surface by removal of surface debris, if present.
- Decontaminate re-usable equipment in accordance with POP 105 - Decontamination of Equipment.
- When using the bucket auger, the auger should be pushed downward and rotated until the bucket becomes filled with soil. Usually a 6 - to 12-inch core of soil is obtained each time the auger is inserted. Once filled, the auger should be removed from the ground and emptied on a sterile surface (plastic sheeting) and transfer to a plastic bag if sampling is required. If a VOC sample is required, the sample should be taken directly from the auger using a teaspoon or spatula and/or directly filling the sample container from the auger. The augering process should be repeated until the desired sample interval has been augered.
- If the desired sample interval is located at a specific depth below the ground surface, the unwanted interval can be removed with one auger and the soil discarded. Sample collection can then proceed in normal fashion using a clean auger or following decontamination of the original auger.
- Except for VOC sample fractions, the remainder of the soil sample should be thoroughly homogenized in the soil collection pan prior to the collection of the sample.
- The appropriate sample containers should be filled with soil from the collection pan. Once each sample container is filled, the rim and threads of the sample container will be cleaned of gross soil, then capped and labeled. Do not submerge the sample containers in water to clean them. Once labeled the sample containers should be placed into a cooler for protection. Sample chain of custody and other documentation requirements should be completed at this time.
- All used sampling equipment should be decontaminated prior to reuse and investigation-derived waste should be properly contained before leaving the area.
- The sample hole should be backfilled with clean soil and/or a combination of clean soil and bentonite chips to eliminate any surface hazard.

6.0 Quality Assurance / Quality Control

Quality Control (QC) samples collected via hand auger may include field duplicates, equipment and/or field blanks, trip blanks, and matrix spike/matrix spike duplicates (MS/MSD). See the QAPP for collection frequency and methods.

7.0 Data and Records Management

The data associated with soil sampling via hang auger will be contained in the following:

- Sample labels,
- Chain of custody records and custody seal(s),
- Boring logs,
- Field logbook,
- Sample collection records,
- Electronic data collection (Trimble Yuma® or equivalent),
- Field Modification Forms (used prior to field work, when required), and
- Nonconformance Records (used after field work, when required).

The following POPs describe the data collection and record management procedures that should be followed as part of the sample collection process:

- POP 101 Field Records,
- POP 102 Chain of Custody Procedures, and
- POP 103 Packaging and Shipment of Environmental Samples.

See the referenced POPs for additional details.

8.0 Personnel Qualifications and Training

It is the responsibility of the field staff to conduct subsurface soil sampling in a manner which is consistent with this POP.

Field staff will observe all activities pertaining to subsurface soil sampling to ensure that the POP is followed, and to record all pertinent data into a digital capture device, onto a boring log or into field logbook. Additional sample collection responsibilities include labeling, handling, and storage of samples until chain of custody procedures are implemented.

9.0 References

- POP EN 101 – Field Records
- POP 102 – Chain of Custody Procedures
- POP 103 – Packaging and Shipment of Environmental Samples
- POP 105 – Decontamination of Field Equipment

Monitoring Well Construction and Installation, POP Number: 401

1.0 Scope and Method Summary

This Project Operating Procedure (POP) describes the basic techniques and general considerations to be followed when installing groundwater monitoring wells. Monitoring wells may be installed to monitor the depth to groundwater, to measure aquifer properties, and to obtain samples of groundwater for chemical analysis.

Monitoring well construction and installation generally involves drilling a borehole using conventional drilling equipment, installing commercially available well construction and filter/sealing materials, and development of the well prior to sampling. This POP covers well construction and installation methods only. Well development methods are covered under POP No. 402 - Monitoring Well Development.

This POP is applicable to installation of single monitoring wells within a borehole.

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in work plans or on Field Modification Forms as appropriate and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

2.0 Health and Safety Considerations

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, is addressed in the site specific HASP. All work will be conducted in accordance with the HASP.

3.0 Interferences

Potential interferences could result from cross-contamination between borehole locations. Minimization of the cross-contamination will occur through the use of clean sampling tools at each location, which will require decontamination of sampling equipment as per POP 105 – Decontamination of Field Equipment.

Other potential interferences may be due to well materials or interactions between well materials and the formation. The process of installing a well necessarily disturbs the geologic formation. Wells will be developed appropriately as described in POP 402 – Monitoring Well Development. The wells will be allowed to stabilize a minimum of twenty-four hours after development before a well is sampled to allow stabilization of both well construction and geological material.

Cross-contamination may also result when surface water runoff or other materials enter the well from the ground surface. To minimize this, wells will be installed with stick-up casings where possible. Where such wells may be at risk of damage from traffic (i.e., near roadways), bumpers may be placed around the well to prevent them from being hit. Where flush-mount well completions are necessary, such as at locations preferred by property owners, appropriate steps will be taken to reduce the potential for infiltration into the well as described in the following sections.

4.0 Equipment and Supplies

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

4.1 Well Construction Materials

Well construction materials are usually provided by the drilling subcontractor. The wells will consist of commercially available flush-threaded, wire wrap (if requested) well screen and riser pipe constructed of poly vinyl chloride (PVC), or stainless steel. Typically these will be with a minimum 2 or 4-inch inside diameter, however, alternate diameter wells may be used.

4.2 Well Completion Materials

Well completion materials include silica sand, bentonite, cement, protective casings, J-plugs, and locks. Completion materials are generally provided by the drilling subcontractor.

4.3 Other Required Materials

- Monitoring Well Construction Diagrams and field logbook and pen,
- Potable water supply,
- Plastic sheeting,
- Trash bags,
- Paper towels,
- Water level meter,
- Self-adhesive well labels,
- Waterproof marker or paint (to label wells),
- Equipment decontamination supplies,
- Health and safety supplies (as required by the HASP),
- Appropriate containers and materials to manage investigation derived waste (IDW) (as specified in POP 106 Investigative Derived Waste), including non-hazardous waste labels.

5.0 Procedures

5.1 General Preparation

Borehole Preparation

Standard drilling methods including, but not limited to, direct push, hollow stem auger and sonic drilling, should be used by the drilling subcontractor under the supervision of field personnel to achieve the desired drilling/well installation target depths. A hand auger may be used at shallow well locations not accessible by a drilling rig.

The typical diameter of the borehole (inside the auger) will be a minimum of 2-inches greater than the outside diameter of the well screen/ riser pipe used to construct the well. This is necessary so that sufficient annular space is available to install filter packs, bentonite seals, and grout seals. However, in limited situations, due to the potential need for direct drive monitoring wells, a smaller diameter annulus may limit the diameter of the filter pack. In some situations, for example pre-pack or “stab” wells, little to no filter pack may be used.

If the borehole is installed using hand auger techniques, a bucket auger will be used to install the boring to the proposed depth. If the soil conditions do not allow the boring to remain open, a 4- to 6-inch diameter casing may be driven to depth to keep soil from collapsing into the boring.

Well Material Decontamination

New well materials (well screen and riser pipe) generally arrive at the site boxed and sealed within plastic bags, so decontamination prior to use is not anticipated. Well materials should be inspected by the field personnel upon delivery to check cleanliness. If the well materials appear dirty, then they should not be used and new materials should be requested.

5.2 Well Construction Procedure

Depth Measurement

Once the target drilling depth has been reached, the drilling subcontractor will measure the total open depth of the borehole with a weighted tape measure or equivalent. Adjustments of borehole depth can be made at this time by drilling further or installing a small amount of sand filter material to achieve the desired depth. The water table depth may also be checked with a water level indicator.

Well Construction

The well screen and riser pipe generally are assembled by hand as they are lowered into the borehole through the

hollow-stem augers. Before the well screen is inserted into the borehole, an end cap will be placed on the screen and the full length of the slotted portion of the well screen as well as the un-slotted portion of the bottom of the screen and end cap should be measured with a measuring tape. These measurements should be recorded on the well construction diagram.

After the above measurements have been taken, the drilling subcontractor may begin assembling the well. As the assembled well is lowered, care should be taken to ensure that it is centered in the hole. The well should be temporarily capped or covered before filter sand and other annular materials are installed. The well should be set at the base of the borehole or set on a sand pack if the borehole is back filled to the target screen depth, and this should be confirmed by observation or measurement at the time of installation.

Filter Sand Installation

A natural collapse sand pack around the well screen may be used at select locations to aid in the migration of free phase oil through pre-wetted soil. Filter sand will be added to the annular space that does not collapse as described below. The drilling subcontractor should fill the annular space surrounding the screened section of the monitoring well to at least one foot above the top of the slotted portion of the screen, or as dictated by field conditions, with appropriately graded, clean sand or fine gravel. In general, the filter pack should not extend more than three feet above the top of the slotted portion of the screen to limit the thickness of the monitoring zone. If coarse filter materials are used, an additional 1-foot thick layer of fine sand should be placed immediately above the filter pack to prevent the infiltration of sealing components (bentonite or grout) into the filter pack. As the filter pack is placed, a weighted tape should be lowered into the annular space to verify the depth to the top of the layer. Depending upon depth, some time may be required for these materials to settle. If necessary, to eliminate possible bridging or creation of voids, placement of the sand pack may require the use of a tremie pipe. Tremie pipe sand pack installations are generally suggested for deep water table wells and for wells that are screened some distance beneath the water table. The augers/casing should be gradually removed from around the well as the sand pack is being installed.

Bentonite Seal Installation

A minimum 2-foot thick layer of bentonite pellets or slurry seal will be installed by the drilling subcontractor immediately above the well screen filter pack in all monitoring wells. The purpose of the seal is to provide a barrier to vertical flow of water in the annular space between the borehole and the well casing. Bentonite is used because it swells significantly upon contact with water. Pellets or chips generally can be installed in shallow boreholes by pouring them very slowly from the surface. If they are poured too quickly, they may bridge at some shallow, undesired depth. As an option, powdered bentonite may be mixed with water into a thick slurry and a tremie pipe can be used to inject the material at the desired depth. The bentonite materials will be hydrated by adding water to them after they have been placed in the borehole.

Under normal circumstances, extreme care will be undertaken to avoid advancement of boreholes through confining layers. If it becomes necessary to do so, however, an outer casing will be set in the confining layer and grouted in place. The integrity of the casing seal will be verified by evacuating the casing of all accumulated water and monitoring the casing interior for 24 hours to ensure no formation water enters the casing before proceeding with borehole advancement. If the confining layer is present above the well screen, an attempt will be made to set the bentonite seal at the same depth as the confining layer if possible to isolate the permeable zone from other portions of the borehole.

Annular Grout Seal Installation

The remainder of the annular space between the bentonite seal and the bottom of the concrete pad (typically 0 to 3 ft below grade), will be filled with grout or continued to be filled with bentonite chips or pellets. The grout seal should consist of a bentonite/cement mix with a ratio of bentonite to cement of between 1:5 and 1:20. The grout ratio should be chosen by the drilling subcontractor based on site conditions with a higher percentage of bentonite generally used for formations with higher porosity. The grout material will be mixed with water and placed into the borehole using a tremie pipe.

Bentonite chips or pellets utilized to backfill the annular space should be placed in the borehole and hydrated utilizing potable water taking care not to allow bridging of the material. Drill cuttings will not be used as backfill material.

Protective Casing/Concrete Pad Installation

The drilling subcontractor will cut the top of the well to the desired height and install a locking cap. Well casings are

usually cut to be a certain height above ground surface (typically 2.5 to 3 feet) or are cut to be slightly below the ground surface, depending on the well location.

The drilling subcontractor will install a protective casing for wells finished above grade. A cement apron, flush to grade, will be installed to hold the protective casing (i.e., road boxes or stand up casing) in place. The surface of the concrete pad will be sloped so that drainage occurs away from the well. Flush-mount protective casings should be completed such that they are slightly mounded above the surrounding surface to prevent surface water from running over or ponding on top of the casing.

In areas subject to snowfall, flush-mount casings may have to be installed so that they are entirely flush with the ground surface as they may be damaged by snow plows.

Above-ground protective casings should also be vented or should have non-air tight caps. Road box installations should not be vented. Installation of additional guard pipes or bollard posts may be necessary around above-ground well completions in traffic areas. All new monitoring wells will include a locking well cap with locks that are keyed alike.

Well Numbering

The field personnel will number each well casing with an indelible marker or paint to identify the well. This is particularly important with nested or paired wells to distinguish between shallow and deep wells. The well should be labeled on both the outside of the protective casing and inside beneath the protective casing lid. Well identification numbers will be as specified in the work plan and this SAP.

Measuring Point Identification

Field personnel will mark the measuring point (normally on the north side of the well casing) from which water level measurements will be made at the upper edge of the well casing. PVC wells can be notched with a pocket knife or saw, or can be marked with a waterproof marker on the outside of the well casing with an arrow pointing to the measuring point location or a mark on the rim of the casing. The measuring point is the point that will require surveying during the well elevation survey task.

Well Measurements

Upon completion, the following well measurements should be taken by field personnel and recorded on the Monitoring Well Construction Diagram (form or digital capture):

- Depth to static water level if water level has stabilized (refer to POP 403 – Water Level Measurement in a Monitoring Well),
- Total length of well measured from top-of-well casing (refer to POP 403 – Water Level Measurement in a Monitoring Well),
- Height of well casing above/below ground surface,
- Height of protective casing above/below ground surface,
- Depth of bottom of protective casing below ground surface (may be estimated).

Well screen filter pack, bentonite seal, and annular seal thicknesses and depths should also be recorded on the Monitoring Well Construction Diagram.

Disposal of Drilling Wastes

Drill cuttings and other disposable materials must be properly contained, labeled, and disposed of. Site-specific requirements for collection and removal of these waste materials are outlined in the POP or work plan. Containment of these materials should be performed by the drilling subcontractor.

Well Development

At some point after installation of a well and prior to use of the well for water level measurements or collection of water quality samples, development of the well shall be undertaken in accordance with POP 402 - Monitoring Well Development.

Well Elevation Survey

At the completion of the well installation program, all monitoring wells will be surveyed to provide, at a minimum, the location (x and y coordinates), top-of-casing measuring point elevation for water level monitoring purposes, and ground

surface elevation. All top-of-casing measurements will be made to within 0.01-feet and horizontal measurements to within 0.1 foot.

6.0 Data and Records Management

All field information will be recorded in the field logbook or on a field collection form or in an electronic data collector (such as a Trimble Yuma® or equivalent) by field personnel. In addition, a field project logbook will be maintained detailing any problems or unusual conditions that may have occurred during the well drilling and installation process. The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

7.0 Quality Assurance and Quality Control

Field personnel should follow specific quality assurance guidelines as outlined in the QAPP and/or this SAP. Certain quality control measures, as noted below, should be taken to ensure proper well completion.

- The borehole will be checked for total open depth, and extended by further drilling or shortened by backfilling, if necessary, before any well construction materials are placed.
- The water level will be checked during well installation to ensure that the positions of well screen, sand pack, and seal relative to water level conform to project requirements.
- The depth to the top of each layer of packing (i.e., sand, bentonite, and grout) will be verified and adjusted if necessary to conform to project requirements before the next layer is placed.
- If water or other drilling fluids (for example, to control heaving sands) have been introduced into the boring during drilling or well installation, samples of these fluids may be required for analysis of chemical constituents of interest.
- The volume of water or other drilling fluids introduced into the boring will be accurately measured by using a flow gauge or documenting the volume of water in the storage tank before and after the introduction of the fluids. These measurements will be recorded in the field log for future reference.

8.0 Personnel Qualifications and Training

Well construction and installation requires a moderate degree of training and experience as numerous drilling situations may occur that will require field decisions to be made. It is recommended that inexperienced personnel be supervised for several well installations before working on their own. Geologists or personnel with applicable experience should supervise well installation.

It is the responsibility of the field personnel to be familiar with the procedures outlined in this POP and to directly oversee the construction and installation of the monitoring well by the drilling subcontractor to ensure that well installation specifications are completed in accordance with this POP. It is also the responsibility of the field personnel to be familiar with the procedures outlined within this SAP, the Quality Assurance Project Plan (QAPP), and the Health and Safety Plan (HASP). Field personnel are also responsible to make sure that proper decontamination procedures are followed, as well as proper documentation in the field logbook or field forms or field computer is completed.

It will be the responsibility of the drilling subcontractor to provide a trained operator and the necessary equipment for well construction and installation. Well construction materials should be consistent with project requirements. Monitoring well construction personnel who work on sites where hazardous waste materials may be present will be health and safety certified as specified by OSHA (29 CFR 1910.120(e)(3)(i)).

9.0 Reference

POP 105 – Decontamination of Field Equipment.

POP 106 –Investigative Derived Waste Management.

POP 402 – Monitoring Well Development.

POP 403 – Water Level Measurement in a Monitoring Well.

Monitoring Well Development – POP Number: 402

1.0 Scope and Method Summary

This Project Operating Procedure (POP) describes the basic techniques and general considerations to be followed for the development of newly installed monitoring wells and/or existing wells that may require redevelopment/rehabilitation.

Monitoring well development and/or redevelopment is necessary for several reasons:

- To restore hydraulic conductivity of the surrounding formations as they have likely been disturbed during the drilling process, or may have become partially plugged with silt,
- To remove drilling fluids (such as water and mud), when used, from the borehole and surrounding formations, and
- To remove residual fines from well filter materials and reduce turbidity of groundwater, thereby, reducing the chance of chemical alteration of groundwater samples caused by suspended sediments and providing representative groundwater samples.

Well development generally involves withdrawing water from a well using a pump, surge block or other suitable method such that, when completed effectively, the well is in good or restored hydraulic connection with the surrounding water bearing unit, produces minimal sediment, and is suitable for obtaining representative groundwater samples or for other testing purposes. Well development should be continued until the well produces water which is relatively free of sediments considering natural groundwater conditions and not be based solely on a specified volume of water removal.

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in task-specific work plans or on Field Modification Forms as appropriate and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

2.0 Health and Safety Considerations

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, are addressed in the site specific Health and Safety Plan HASP. All work will be conducted in accordance with the HASP.

3.0 Interferences

Potential interferences could result from cross-contamination between monitoring wells. Minimization of cross-contamination will occur through the use of clean tools at each location, which will require decontamination of sampling equipment as per POP 105 – Decontamination of Field Equipment.

The process of installing a well necessarily disturbs the geologic formation. Wells will be developed appropriately as described in this POP. The wells will be allowed to stabilize a minimum of twenty-four hours, depending on grout type, after development before a well is sampled.

4.0 Equipment and Supplies

Well development can be performed using a variety of methods and equipment. The specific method chosen for development of any given well is governed by the purpose of the well, well diameter and materials, depth, accessibility, geologic conditions, static water level in the well, and type of constituents present, if any.

4.1 Pump Development

A pump is often necessary to remove large quantities of sediment-laden groundwater from a well after using the surge block. In some situations, the pump alone can be used to develop the well and remove the fines by over-pumping

(pumping at a high rate). Because the purpose of well development is to remove suspended solids from a well and the surrounding filter pack, the pump must be capable of moving some solids without damage. The preferred pump is a submersible pump, which can be used in both shallow and deep groundwater situations. A centrifugal pump may be used in shallow wells, but will work only where the depth to static groundwater is less than approximately 25 feet. Pumping may not be successful in low-yielding aquifer materials or in wells with insufficient hydraulic head.

4.2 Bailer Purging

A bailer is used to purge sediment-laden water from wells after using other devices such as a surge block. In some situations, the bailer can be used to develop a well by bailing and surging, often accompanied with pumping when appropriate. A bailer can be used for purging in situations where the depth to static water is greater than 25 feet and/or where insufficient hydraulic head is available for use of other development methods.

4.3 Surge Block Development

Surge blocks are commercially available for use with Waterra-type (or equivalent) pumping systems or may be manufactured using a "plunger" attached to a rod or pipe of sufficient length to reach the bottom of the well.

4.4 Other Materials

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Well Development Records, and/or field logbook and pen, and/or electronic data collector,
- Boring and well construction logs (if available),
- Plastic sheeting,
- Buckets,
- Paper towels,
- Trash bags,
- Power source (generator or 12-volt marine battery),
- Water level meter and/or well depth measurement device,
- Equipment decontamination supplies (as required by POP 105 – Decontamination of Field Equipment.),
- Health and safety supplies (as required by the HASP), and
- Appropriate containers, labels and materials to manage investigation-derived waste (IDW) (as specified in this SAP and as required by POP 106 – Investigative Derived Waste Management).

5.0 Procedures

5.1 General Preparation

Develop wells as soon as possible after construction, but no sooner than 12 hours after placing the annular seal. If bentonite chips are used as an annular seal, development should occur after 24 hours. If grout or neat cement is used, the time before well development should increase to 48 hours. The main concern is that the method being used for development does not interfere with allowing the grout to set. Develop the entire vertical screened interval using surge blocks, bailers, pumps, or other equipment which frequently reverses the flow of water through the well screen and prevents bridging of formation or filter particles.

Well construction logs should be reviewed to determine well construction characteristics. Formation characteristics should also be determined from review of available boring logs.

Provisions should be in place for collection and management of IDW relating to well development such as l development water and miscellaneous expendable materials generated during the development process. The collection of IDW in drums or tanks may be required depending on project-specific requirements.

The water level and well depth should be measured in accordance with POP 403 – Water Level Measurement in a

Monitoring Well and written on the field documentation (field log book, well development record, and/or electronic data collector). This information is used to calculate the volume of standing water (i.e., the well volume) within the well.

The quantity of drilling fluids such as mud or water, if used during the drilling and well installation process, should be recorded and a minimum of 3 times the volume of fluid introduced during drilling should be removed during the well development procedure.

5.2 Development Procedure

Development Method Selection

The construction details of each well shall be used to define the most suitable method of well development. Some consideration should be given to the potential concentrations of constituents in each well as this will impact IDW containment requirements.

The criteria for selecting a well development method include well diameter, total well depth, static water depth, screen length, the likelihood and potential concentrations of constituents, and characteristics of the geologic formation adjacent to the screened interval.

The limitations, if any, of a specific procedure are discussed within each of the following procedures.

Turbidity

Turbidity of development water will be observed during well development to monitor the progress of development. Visual observations of turbidity, such as silty or cloudy water, should be noted in the field documentation.

Bailer Procedure

Bailers shall preferably not be used for well development but may be used in combination with a surge block to remove sediment-laden water from the well.

- When using a bailer to purge well water; select the appropriate bailer, then tie a length of bailer cord onto the end of the bailer.
- Lower the bailer into the screened interval of the monitoring well. Sediment , if present, will generally accumulate within the lower portions of the well screen.
- The bailer may be raised and lowered repeatedly in the screened interval to further simulate the action of a surge block and pull silt through the well screen.
- Remove the bailer from the well and empty it into the appropriate storage container.
- Continue surging/bailing the well until relatively sediment-free water is obtained considering background aquifer conditions. If moderate to heavy sedimentation is still present, the surge block procedure should be repeated and followed again with bailing. If it is not possible to further reduce the turbidity, the well will be purged a minimum of 10 minutes after this determination.
- Visually check turbidity periodically.

Surge Block Procedure

A surge block effectively develops most monitoring wells.

- Insert the surge block into the well and lower it slowly to the level of static water. Start the surge action slowly and gently above the well screen using the water column to transmit the surge action to the screened interval. A slow initial surging, using plunger strokes of approximately 3 feet, will allow material that is blocking the screen to separate and become suspended.
- After 5 to 10 plunger strokes, sediment-laden water will be removed from the well using a pump integrated with the surge block, or removing the surge block to purge the well using a pump or bailer. Discharge the purged water into the appropriate storage container.
- Repeat the process. As development continues, slowly increase the depth of surging to the bottom of the well screen. For monitoring wells with long screens (greater than 10 feet) surging should be undertaken along the entire screen length in short intervals (3 feet) at a time. Continue this cycle of surging and purging until the water yielded by the well is free of visible suspended material. If it is not possible to further reduce the turbidity the well will be purged a minimum of 10 minutes after this determination.

- Visually check turbidity periodically.

Pump Procedure

Well development using only a pump is most effective in monitoring wells that will yield water continuously. Effective development cannot be accomplished if the pump has to be shut off to allow the well to recharge.

- When using a submersible pump or surface pump, set the intake of the pump or intake line in the center of the screened interval of the monitoring well.
- Pump a minimum of three well volumes of water from the well and raise and lower the pump line through the screened interval to remove any silt/laden water.
- Continue pumping water from the well until sediment-free water is obtained. This method may be combined with the manual surge block method if well yield is not rapid enough to extract silt from the surrounding formations. If it is not possible to further reduce the turbidity, the well will be purged a minimum of 10 minutes after this determination
- Visually check turbidity periodically.

5.3 Equipment Decontamination

All equipment that comes into contact with groundwater (e.g., surge block) will be decontaminated in accordance with POP 105 – Decontamination of Field Equipment before moving to the next location. If a disposable bailer is used, it should be properly discarded and disposed of in accordance with procedures for managing IDW outlined in this SAP.

6.0 Data and Records Management

All field information will be recorded in the field logbook, on a field collection form, or with an electronic data collector by field personnel. This information will include, at a minimum, well and sample designation, pre-sampling water level elevation, volume of purge water removed from each well, pre and post purge sampling parameters. In addition, the field project logbook will include notes regarding any problems or unusual conditions that may have occurred during the development process.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

7.0 Quality Assurance and Quality Control

Field personnel should follow specific quality assurance guidelines as outlined in the QAPP and/or this SAP.

A well will have been successfully developed when one or more of the following criteria are met:

- The sediment load in the well has been eliminated or greatly reduced based upon visual observation of turbidity or field measurement of turbidity.
- If it is not possible to further reduce the visible turbidity, the well will be purged a minimum of 10 minutes after this determination.

8.0 Personnel Qualifications and Training

Well development procedures vary in complexity and are commonly conducted by a subcontractor. It is recommended that initial development attempts be supervised by more experienced personnel.

Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous waste materials may be present.

It is the responsibility of the field personnel to be familiar with the procedures outlined within this POP, quality assurance, and health and safety requirements outlined within this Sampling and Analysis Plan (SAP), the Quality Assurance Project Plan (QAPP), and the Health and Safety Plan (HASP). Field personnel are responsible for completing proper well development, decontamination of equipment, as well as proper documentation in the field logbook, field forms, or electronic data collector such as the Trimble Yuma® or equivalent (if appropriate).

9.0 Reference

POP 105 – Decontamination of Field Equipment.

POP 106 –Investigative Derived Waste Management.

POP 403 – Water Level Measurement in a Monitoring Well.

Water Level Measurement in a Monitoring Well – POP 403

1.0 Scope & Method Summary

This Project Operation Procedure (POP) describes the methods to be used for measuring depth to groundwater, non-aqueous phase liquid (NAPL) levels, and total depth of groundwater monitoring wells and piezometers. Similar procedures will also be used to measure the depth to water in surface water bodies from a stream gage.

Water and NAPL level and well depth measurements collected from monitoring wells, stream gages or piezometers are used to assess:

- The horizontal hydraulic gradient and the direction of groundwater flow,
- The vertical hydraulic gradient, if well nests are used (i.e., the direction of groundwater flow in the vertical plane),
- The calibration of a numerical groundwater flow model,
- The thickness of NAPL in a monitoring well, and
- Surface Water Elevation.

This information, when combined with other location-specific information, such as hydraulic conductivity or transmissivity, may be used to estimate the rate of constituent movement, etc. Total well depth measurements are also collected as an indicator of siltation within the well column and to calculate well volumes if necessary.

Measurements will involve measuring the depth to NAPL, depth to water or total well depth to the nearest 0.01 foot using an electronic probe (water level or product level meter). The depths within wells will be measured from the top of the inner casing at the surveyed elevation point as marked on the top of the inner casing.

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in task-specific work plans or on Field Modification Forms as appropriate and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

2.0 Health and Safety

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, is addressed in the site specific HASP. All work will be conducted in accordance with the HASP.

3.0 Interferences

Potential interferences could result in inaccurate readings if the sensor on the water or product level meter is dirty, or if the cable cannot be kept vertically upright (for example, from a bridge in the wind). Care shall be taken to keep the probe clean. If wells are not installed plumb, the probe may rest against the side of the well, which may be wet. Care shall be taken in measuring water or NAPL levels to reduce these interferences. If there is any concern that a particular reading may not be accurate, this shall be noted in the field documentation.

Pressure build up in a sealed flush mounted well may also cause initial water levels to be different than actual static water levels. In areas with low permeability and where sealed well caps (not vented) have been installed, wells should be left uncapped for a period ranging from a minute to ten minutes prior to measuring the water levels. However, one to ten minutes may not be sufficient for water levels to stabilize to atmospheric pressure in some wells and may require a number of readings over time to establish that equilibration and stabilization have been achieved. If any indication of gas build up in the well is observed upon removing the cap, such as a sound of air rushing into or out of the well, then a resting period should be allowed for the water level in the well to equilibrate with atmospheric pressure.

4.0 Equipment & Supplies

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, depending on field conditions.

4.1 Electronic Water Level Meter

Electronic water and product level meters consist of a spool of small-diameter cable (or tape) with a weighted probe attached to the end. When the probe comes in contact with the NAPL and/or water, an electrical circuit is closed, and a light and/or buzzer within the spool will signal the contact. A different tone or light is used to indicate NAPL and water. The probe shall be tested at the start of the field program to ensure proper operation.

4.2 Other Materials that may be required

- Health and safety supplies (as required by the HASP),
- Equipment decontamination materials (as required by *POP 105, Decontamination of Field Equipment*),
- Water and NAPL level field form or electronic data collector such as the Trimble Yuma® or equivalent (if applicable),
- Well construction records and previous monitoring data, and
- Field project logbook and pen.

5.0 Methods

5.1. Water and LNAPL Level/Well Depth Measurement

The water and NAPL level should be measured with a water or product level meter and written in the field logbook, field form, and/or electronic data collector. If the well depth is not known it should be measured with a water or product level meter and recorded in the field logbook, field form, and/or electronic data collector. This information is used to calculate groundwater elevations. All data will be maintained in the project files.

5.2 Equipment Decontamination

All equipment should be decontaminated prior to use and between well locations in accordance with *POP 105.*

5.3 Measurement Procedures

At each location (well, piezometer, etc.), determine the location of the surveyed elevation mark. For wells, general markings include either a notch in the riser pipe or a permanent ink mark on the riser pipe. For monitoring surface water levels, there may be a painted mark on an existing structure or the reference point must be known if not painted. All groundwater and NAPL level measurements should be collected prior to any ground water sampling.

To obtain a water and/or NAPL level measurement, lower the probe of a water or product level meter down into the water or NAPL until the audible sound of the unit is detected or the light on an electronic sounder illuminates. The light and/or sound will change as the NAPL probe passes through the NAPL and enters the water. In wells and piezometers, the probe shall be lowered slowly into the well to avoid disruption of formation water and creation of turbulent surface water within the well. At this time, the precise measurement should be determined (to nearest 0.01 feet) by repeatedly raising and lowering the tape to converge on the exact measurement. Obtain the reading from the surveyed elevation mark. When measuring water levels in wells installed in low permeability material, additional readings should be collected over 10 to 30 minutes to establish that equilibration has been achieved. This will be site or well dependent.

Record the water and NAPL level measurements as well as the location identification number, date, time, and weather conditions in the field logbook, field form and/or electronic data collector.

To measure the total depth of a well, lower the probe (turn down signal as appropriate) slowly to the bottom of the well. The depth may be difficult to determine for wells with “soft” or silty bottoms. It may be helpful to lower the probe until there is slack in the tape, and gently pull up until it feels as if there is a weight at the end of the tape. Observe the measurement (to the nearest 0.01 foot) of the tape against the surveyed elevation mark.

Record the total well depth in the field logbook, field form, and/or electronic data collector.

The meter will be decontaminated in accordance with POP 105. Generally, only that portion of the tape that enters the NAPL and water needs to be decontaminated. It is important that the measuring tape is never allowed to become kinked.

6.0 Data & Records Management

All field information will be recorded in the field logbook, on a field collection form, or in an electronic data collector such as the Trimble Yuma® or equivalent, by field personnel. Any problems or unusual conditions that may have occurred during the measurement process will be noted.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

7.0 Quality Assurance & Quality Control

Field personnel will follow specific quality assurance guidelines as outlined in the QAPP and/or this SAP. Where measured depths are not consistent with well records or previously measurements, the depths should be re-measured and verified.

8.0 Personnel Qualifications

Collecting water and NAPL level measurements is a relatively simple procedure requiring minimal training and a relatively small amount of equipment.

Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous waste materials may be present.

It is the responsibility of the field sampling personnel to be familiar with the sampling procedures outlined within this POP, and with specific sampling, quality assurance, and health and safety requirements outlined in this *Sampling and Analysis Plan (SAP)*, the *Quality Assurance Project Plan (QAPP)*, and the *Health and Safety Plan (HASP).* Field personnel are responsible for the proper use, maintenance, and decontamination of all equipment used for obtaining water and NAPL level measurements, as well as proper documentation in the field logbook, field forms, or electronic documentation (if appropriate).

9.0 References

POP 105 – Decontamination of Field Equipment.

Low Flow Groundwater Sampling – POP 404

1.0 Scope and Method Summary

This Project Operation Procedure (POP) describes the method for collecting valid and representative samples of groundwater from monitoring wells. This POP is written such that consideration of different sampling equipment may be used in different instances for collecting representative groundwater samples. The procedures presented in this POP are taken from the United States Environmental Protection Agency's documents; *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures* (U.S. EPA, 1996) and *Low Stress (low flow) Purging and Sampling Procedure for the Collection of Groundwater Samples from Monitoring Wells* (U.S. EPA, 2010).

Groundwater sample collection generally involves purging the water that is non-representative of the formation water from a well prior to sample collection. Water quality indicator parameters are monitored until all parameters have stabilized for three successive readings. After the indicator parameters have stabilized, groundwater samples are then collected into the appropriate bottle or containers.

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in task-specific work plans or on Field Modification Forms as appropriate and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

2.0 Health and Safety

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, is addressed in the site specific HASP. All work will be conducted in accordance with the HASP.

3.0 Interferences

Potential interferences could result from cross-contamination between samples and sample locations. Minimization of cross-contamination will occur through the use of clean or new sampling tools at each location, which will require decontamination of sampling equipment following *POP 105 – Decontamination of Field Equipment.*

Potential interferences could result from the power source (e.g. generator). Minimization of contamination will occur through locating the power source a sufficient distance away from the well and sampling equipment and handling the power source with dedicated or disposable gloves.

4.0 Equipment and Supplies

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Well keys for secured wells;
- Road box (flush mount) keys;
- Purging and Sampling Pumps;
    - Peristaltic pump,
    - Submersible pump, and
    - Bladder pumps & extra bladders.
- Field Instruments;
    - Individual or multi-parameter meter(s) to measure temperature, pH, specific conductance, dissolved oxygen (DO), oxidation reduction potential (ORP), and turbidity, and
    - Water level meter.
- Tubing (Silicone and polyethylene (or as required for sampling, air supply, etc.));

- Previous Sample Collection Records or Electronic Data Collector such as Trimble Yuma® or equivalent;
- Disposable nitrile gloves
- Sample kit (i.e., bottles, labels, preservatives, cooler, ice);
- Filtration equipment (if necessary);
- Sample Chain of Custody forms (as required by POP 102 – Chain of Custody Procedures);
- Sample packaging and shipping supplies (as required by POP 103 – Packaging and Shipment of Environmental Samples);
- Waterproof marker or paint;
- Distilled or deionized water and dispenser bottles;
- Flow measurement cup or bucket;
- Buckets with lids;
- Instrument calibration solutions;
- Power source (generator or 12-volt marine battery) and extension cords with ground fault interrupt (GFI) protection;
- Air compressor or compressed gas for bladder pump;
- Paper towels;
- Plastic sheeting;
- Trash bags;
- Ziploc®-style bags;
- Equipment decontamination supplies (as required by POP 105 – Decontamination of Field Equipment);
- Health and safety supplies (as required by the HASP); and
- Field project logbook and pen.

5.0 Methods

5.1 Instrument Calibration

Field instruments will be calibrated according to the requirements of the QAPP and manufacturer's specifications for each piece of equipment (e.g., *POP 502 – Water Quality Instrumentation*). Calibration records shall be recorded in the field logbook, appropriate field form, or electronic data collector.

5.2 Well Security and Condition

At each monitoring well location, observe the conditions of the well and surrounding area. Any issues with the following information should be noted on the groundwater sample collection record, field logbook, or electronic data collector.

- Condition of the well's identification marker;
- Condition of the well lock and associated locking cap;
- Integrity of the well - protective outer casing, obstructions or kinks in the well casing, presence of water in the annular space, and the top of the interior casing; and
- Condition of the general area surrounding the well.

5.3 Measuring Point Determination

Identify an existing measuring point in accordance with *POP 403 – Water Level Measurement in a Monitoring Well.* Generally, the measuring point is referenced from the top of the well casing (TOC), not the protective casing. If no

measuring point exists, a measuring point should be established on the north side of the well casing, clearly marked, and identified on field documentation (i.e., groundwater sample collection record, field logbook, or electronic data collector). The same measuring point should be used for subsequent sampling events.

5.4 Water Level Measurement

Water level measurements should be collected in accordance with *POP 403 – Water Level Measurements*. DO NOT collect total well depth until sample has been collected. Taking a total depth measurement will disturb sediments that have settled to the bottom of the well. This most likely will create high turbidity readings. The water level measurement should be entered on appropriate field documentation.

5.5 Well Purging Methods and Procedures

Objectives

Prior to sample collection, purging must be performed for all groundwater monitoring wells to remove water from within the casing and filter pack to ensure that a representative groundwater sample is obtained.

All groundwater samples will be collected using low flow (low-stress) purging and sampling procedures. The low-flow method emphasizes the need to minimize water level drawdown and low groundwater pumping rates to collect samples with minimal alterations to groundwater chemistry.

During well purging, the water level will be measured with a water level meter in accordance with *POP 403 – Water Level Measurement*. Water level drawdown and flow rate will be recorded on field documentation. A final purging rate will be selected that does not exceed 0.5 liters per minute (L/min) (typically between 0.1 L/min and 0.3 L/min), and results in little to no drawdown, ideally less than 0.3 feet.

The general types of non-dedicated equipment used for well purging include surface pumps and down-well pumps. Peristaltic pumps will generally be used unless the depth to water is too great, in which case submersible pumps will be used.

Purge water will be pumped through a flow-through cell and the following parameters will be measured: pH, specific conductivity, temperature, DO, ORP, and turbidity. These parameters will be measured with a water quality meter, calibrated according to the manufacturer's specifications (see *POP 502 - Water Quality Instrumentation*). A round of parameter measurements will be recorded approximately 10 minutes after the flow-through cell is full, and then every 3 to 5 minutes thereafter, until parameter values have stabilized.

Purging is considered complete and sampling may begin when all parameter values have stabilized and turbidity is below 10 Nephelometric Turbidity Units (NTU). Stabilization is considered to be achieved when three consecutive readings, taken at 3- to 5-minute intervals, are within the following limits:

- Turbidity : less than 10 NTU or ± 10%
- DO : ± 10%
- Specific Conductance : ± 3%
- Temperature : ± 3% or less than 0.5 degrees C
- pH : ± 0.1 standard units
- ORP : ± 10 millivolts

Every effort will be made to lower the turbidity to less than 10 NTU before sampling. If the turbidity cannot be reduced to below 10 NTU, the pumping rate will be reduced for 10 minutes. If turbidity still cannot be reduced below 10 NTU, samples may be collected if all other parameters are stable and the turbidity is stable (i.e. not improving). The condition will be noted on the field documentation. During hot and cold weather sampling, short tubing lengths should be utilized to avoid temperature changes and freezing of the tubing – if the sample temperature does not stabilize as the water flows through tubing exposed to ambient temperatures, this should be noted in the field notes.

If after one hour of purging, stabilization of parameters is not achieved, a sample will be collected and recorded in the field notes.

All purge water will be containerized and disposed per the project plan.

If a well purges dry, a groundwater sample will be collected when sufficient water has recharged the well. The condition will be noted on the field documentation.

5.6 Surface Pumps

General

Well purging using pumps located at the ground surface can be performed with a peristaltic pump if the water level in the well is within approximately 20 feet of the top of the well.

Peristaltic pumps provide a low rate of flow typically in the range of 0.075-0.750 L/min and a minimal disturbance of the water column.

Peristaltic Pump Procedure

Attach a new sample tube set-up to the peristaltic pump. Silicone tubing must be used through the pump head and must meet the pump head specifications. A second type of tubing (e.g., polyethylene) will be attached to the silicone tubing for use as the suction and discharge lines.

Measure the length of the suction line and lower it down the monitoring well until the end is located at the midpoint of the saturated screen and at least 2 feet above the bottom of the well to preclude excess turbidity from the bottom of the well. Start the pump and direct the discharge into a graduated bucket. Adjust the pumping rate with the speed control knob so that a smooth flowing discharge is attained.

Measure the pumping rate by recording the time required to fill a flow measurement cup or bucket. The pumping shall be monitored to assure continuous discharge. If drawdown causes the discharge to stop, the suction line will be lowered very slowly further down into the well until pumping restarts. The pumping rate will be adjusted so that drawdown is stabilized, ideally at a level less than 0.3 feet.

5.7 Down-Well Pumps

General

Groundwater withdrawal using non-dedicated down-well pumps may be performed with a submersible pump or a bladder pump.

Electric submersible pumps provide an effective means for well purging and in some cases sample collection. Submersible pumps are particularly useful for situations where the depth to water table is greater than 20 feet and where the depth or diameter of the well requires that a large purge volume be removed before sample collection.

A commonly available submersible pump, the Grundfos Redi-Flo2TM pump (or equivalent), is suited for operation in 2-inch or larger internal diameter wells. Pumping rates are adjusted to low-flow levels by adjusting the current to the pump motor rather than using a flow valve.

Bladder pumps may also be used. Bladder pumps usually consist of a stainless steel pump housing with an internal Teflon® or polyethylene bladder. Discharge and air line tubing is connected to the bladder pump to the air compressor and control unit. The pump is operated by lowering it into the water column to the midpoint of the well screen, then pulsing air into the bladder from the air compressor and pump controller unit. Pumps and controllers are often not interchangeable between manufacturers; therefore, it is usually necessary to have both items provided by the same manufacturer. Pump bladders are generally field-serviceable and replaceable.

A check of well condition shall be completed prior to inserting any down-well pump if the well has not been sampled for some time or if groundwater quality conditions are not known. The well condition check should include a check of the casing to determine if there are any obstructions.

Electric Submersible Pump Procedure

Slowly lower the submersible pump with attached discharge line into the monitoring well taking notice of any roughness or restriction within the well riser pipe. The inlet of the pump should be placed at the midpoint of the saturated monitoring well screen. The power cord should be attached to the discharge line with an inert material (i.e., zip-ties) to prevent the power cord from getting stuck between the pump, discharge line, and the well casing. Secure the discharge line and power cord to the well casing, using tape or a clamp, taking care not to crimp or cut either the discharge line or power cord.

Connect the power cord to the power source (i.e., rechargeable battery pack, auto battery, or generator) and turn the pump on. Voltage and amperage meter readings on the pump controller (if provided) should be monitored closely during purging. The operations manual for the specific pump used should be reviewed regarding changes in voltage/amperage and the potential impacts on pump integrity. The pumping rate will be adjusted so that drawdown is stabilized, ideally at a level less than 0.3 feet.

Bladder Pump Procedure

To operate the bladder pump system, the pump and discharge line should be lowered into the well until the inlet of the pump is at the midpoint of the saturated monitoring well screen. Secure the discharge and power lines to the well casing with a clamp. The air compressor should then be turned on to activate pumping. The pump controller is used to vary the discharge rate to the required flow. The pumping rate will be adjusted so that drawdown is stabilized, ideally at a level less than 0.3 feet.

5.8 Sample Collection Methods and Procedures

Objectives

Groundwater samples can be collected using similar methods employed for purging. In most cases during sampling, groundwater will be transferred to the appropriate containers directly from the discharge source. It is important that the tubing from the pump to the flow-through cell be disconnected prior to sample collection. During transfer, discharge tubing and other equipment shall not contact the inside of the sample containers.

Groundwater samples that may require filtration (if specified in the work plan), will be filtered in the field at the wellhead using a 0.45-micron (or other as specified), in-line filter.

Surface Pumps

Using the methods and procedures described in Section 6.5, groundwater samples will be collected from the peristaltic pump. Sample bottles shall be filled directly from the pump's discharge line (after tubing has been disconnected from the flow-through cell) and care shall be taken to keep the discharge tube from contacting the sample container.

Down-Well Pumps

Using the pump methods described in Section 6.6, groundwater samples should be collected from either the electric submersible or bladder pump directly from the discharge line (after tubing has been disconnected from the flow-through cell). Sample bottles will be filled directly from the discharge line of the pump.

Sample Handling and Preservation

- Cap and label the container. .
- Place the sample containers into a cooler and maintain on ice.
- Complete sample chain of custody and other documentation per *POP 102 – Chain of Custody Procedures.*
- Package the samples for shipment to the laboratory per *POP 103 – Packaging and Shipment of Environmental Samples.*

5.8 Equipment Decontamination

All equipment that comes into contact with groundwater (e.g., submersible pumps) will be decontaminated in accordance with *POP 105 – Decontamination of Equipment* protocol before moving to the next location. Dedicated or disposable equipment will not be decontaminated.]

6.0 Data & Records Management

Specific information regarding sample collection should be documented in several areas: the sample Chain of Custody Record; sample collection record, field logbook, or electronic data collector; and sample labels or tags. Additional information regarding each form of documentation is presented in the following paragraphs.

6.1 Sample Chain of Custody Record

This standard form requires input of specific information regarding each collected sample for laboratory analytical purposes, as specified in POP 102.

6.2 Sample Collection Record or Electronic Data Collector

The sample collection record requires input of specific information regarding the collection of each individual sample including sample identification, water quality parameters, collection method, and containers/preservation

requirements. An electronic data collector such as a Trimble Yuma® may be used in place of or in addition to the sample collection record.

6.3 Field Logbook

The logbook should be dedicated to the project and should be used by field personnel to maintain a general log of activities throughout the sampling program. The logbook should be used in support of, and/or in combination with, the sample collection record or electronic data collector. Documentation within the logbook should be thorough and sufficiently detailed to present a concise, descriptive history of the sample collection process.

6.4 Sample Labels

Sample labels shall be completed at the time each sample is collected and attached to each sample container. Sample labeling will be conducted per this SAP and the QAPP. Labels will include the information listed below.

- Client or project name/project number,
- Sample number or designation,
- Analysis type,
- Preservative,
- Sample collection date,
- Sample collection time, and
- Sampler's name.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

7.0 Personnel Qualifications

Groundwater sample collection is a relatively involved procedure requiring formal training and a variety of equipment. It is recommended that initial sampling of groundwater wells be supervised by more experienced personnel.

Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

It is the responsibility of the field sampling personnel to be familiar with the sampling procedures outlined within this POP, and with specific sampling, quality assurance, and health and safety requirements outlined in this *Sampling and Analysis Plan (SAP)*, the *Quality Assurance Project Plan (QAPP)*, and the *Health and Safety Plan (HASP)*. Field personnel are responsible for the proper use, maintenance, and decontamination of all equipment used for obtaining water level measurements, as well as proper documentation in the field logbook, field forms, or electronic documentation (as appropriate).

8.0 Quality Assurance & Quality Control

Field personnel should follow specific quality assurance guidelines as outlined in the QAPP and/or this SAP.

Quality assurance requirements typically suggest the collection of a sufficient quantity of quality control (QC) samples such as field duplicate, equipment and/or field blanks and matrix spike/matrix spike duplicate (MS/MSD) samples. These requirements are outlined in the QAPP.

9.0 References

POP 102 – Chain of Custody Procedures.

POP 103 – Packaging and Shipment of Environmental Samples.

POP 105 – Decontamination of Field Equipment.

POP 403 – Water Level Measurement in a Monitoring Well

POP 502 – Water Quality Instrumentation

United States Environmental Protection Agency, Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures (U.S. EPA April 1996.

United States Environmental Protection Agency, Region 1, Low Stress (low flow) Purging and Sampling Procedure for the Collection of Groundwater Samples from Monitoring Wells, Revision No. 3 (U.S. EPA January 2010.

Headspace Analysis of VOCs in Unsaturated Soil Samples – POP 501

1.0 Scope and Method Summary

This Project Operating Procedure (POP) provides guidance for the headspace analysis to screen for volatile organic compounds (VOCs) in unsaturated soil samples using a Photoionization Detector (PID) (OVM®, MiniRAE®, or equivalent).

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in task-specific work plans or on Field Modification Forms and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

2.0 Health and Safety

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, are addressed in the site specific Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

3.0 Interferences

Regardless of which gas is used for calibration, the instrument will respond to all analytes present in the sample that can be detected by the type of lamp used in the PID.

Moisture will generate a positive interference in the concentration measured for a PID and is characterized by a slow increase in the reading as the measurement is made. Care must be taken to minimize uptake of moisture to the extent possible. Refer to the manufacturers' instructions for care, cleaning, and maintenance.

Uptake of soil into the PID must be avoided as it will compromise instrument performance by blocking the probe, causing a positive interference, or dirtying the PID lamp. Refer to the manufacturers' instructions for care, cleaning, and maintenance.

The user should listen to the pitch of the sampling pump. Any changes in pitch may indicate a blockage and corrective action should be initiated.

Make sure readings are not collected near a vehicle exhaust or downwind of the drill rig exhaust.

Potential interferences could result from cross-contamination between sample locations. Change gloves between samples to avoid cross contamination. Also, minimize cross-contamination through the use of clean sampling equipment at each location. Decontamination of sampling equipment is acceptable; therefore non-disposable sampling equipment will be decontaminated according to *POP 105 – Decontamination of Field Equipment.*

4.0 Equipment & Supplies

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- PID (with correct sized lamp as determined by the Task Manager and communicated in the work plan),
- Ziploc® Bags or equivalent (either quart or gallon size) or glass jars (8 oz or 16 oz) with aluminum foil,
- Field Notebook or Soil Boring/Monitoring Well Log Sheet or digital capture device (such as Trimble® Yuma®),
- Pen with indelible ink (blue or black ink),
- Permanent marker,
- Personal protective equipment (PPE) and health and safety equipment as specified in the HASP.

5.0 Methods

5.1 Preparation

Review available project information to determine the types of organic vapors that will likely be encountered to select the right instrument. The correct ultraviolet (UV) light bulb must be selected according to the types of organic vapors that will likely be encountered. The energy of the UV light must equal or exceed the ionization potential of the organic molecules that the PID will measure. The *National Institute for Occupational Safety and Health (NIOSH) Pocket Guide to Chemical Hazards* is one source for determining ionization potentials for different chemicals. Bulbs available for PIDs include 9.4 electron volts (eV), 10.6 (or 10.2) eV, and 11.7 eV bulbs. The 10.6 eV bulb is most commonly used as it detects a fairly large range of organic molecules and does not burn out as easily as the 11.7 eV bulb. The 9.4 eV bulb is the most rugged, but detects only a limited range of compounds. Under very humid or very cold ambient conditions, the window covering the UV light may fog up, causing inaccurate readings.

After selecting the correct instrument, calibrate the PID according to manufacture directions. Record background/ambient levels of organic vapors measured on the PID after calibration and make sure to subtract the background concentration (if any) from your readings. Check the PID readings against the calibration standard every 20 readings or at any time when readings are suspected to be inaccurate, and recalibrate, if necessary. Be aware that, after measuring highly contaminated soil samples, the PID may give artificially high readings for a time due to saturation.

5.2 Equipment Decontamination

If new Ziploc® bags or new glass jars will be used with each new sample, equipment decontamination will not be required. If previously used glass jars are used, all soil should be removed from the used jars and the jars should be rinsed out with tap water. The jars should be allowed to dry. Once dry, the jars should be checked with a PID. The previously used jars should only be re-used if the PID reading is 0.0 parts per million (ppm). Removed soil and rinse water should be managed according to *POP 106 – Investigative Derived Waste Management.*

5.3 Sampling Procedure - Ziploc® Bags

Place a quantity of soil in a top-sealing plastic bag and seal the bag immediately. The volume of soil to be used should be determined by the Task Manager or Field Task Manager. Ideally, the bag should be at least 1/10th-filled with soil and no more than half-filled with soil. Once the bag is sealed, shake the bag to distribute the soil evenly. If the soil is hard or clumpy, use your fingers to gently work the soil (through the bag) to break up the clumps. Do not use a sampling instrument or a rock hammer since this may create small holes in the plastic bag and allow organic vapors to escape. Alternatively, the sample may be broken up before it is placed in the bag. Use a permanent marker to record the following information on the outside of the bag:

- Site identification information (i.e., borehole number),
- Depth interval, and
- Time the sample was collected.

Headspace should be allowed to develop before organic vapors are measured with a PID. Allow the headspace to develop inside the bag for a minimum of five minutes. Equilibration time should be the same for all samples to allow an accurate comparison of organic vapor levels between samples. However, adjustments to equilibration times may be necessary when there are large variations in ambient temperature from day to day. When ambient temperatures are below 32 degrees Fahrenheit (°F) (0 degrees Celsius [°C]), headspace development should be within a heated building or vehicle. When heating samples, be sure there is adequate ventilation to prevent the build-up or organic vapors above action levels.

Following headspace development, open a small opening in the seal of the plastic bag. Insert the probe of the PID and seal the bag back up around the probe as tightly as possible, minimizing the air loss from the bag. Alternatively, the probe can be inserted through the bag to avoid loss of volatiles. If this alternative method is used, make sure the PID probe does not get clogged with plastic when puncturing the bag. Since PIDs are sensitive to moisture, avoid touching the probe to the soil or any condensation that has accumulated inside of the bag. Since the PID consumes organic vapors, gently agitate the soil sample during the reading to release fresh organic vapors from the sample. Analyze the sample with the PID for at least one minute, making note of the average and peak readings. Record the PID results (in ppm) in the field notebook, soil boring/monitoring well log, or digital capture device. Dispose of the soil with the rest of the investigation derived waste (IDW) in accordance with *POP 106 – Investigative Derived Waste Management.*

5.4 Sampling Procedure - Jars with Aluminum Foil

Half-fill a clean glass jar with the soil sample to be screened. Quickly cover the jar's opening with one or two sheets of clean aluminum foil and apply the screw cap to tightly seal the jar. Use a permanent marker to record the following information on the top of the foil seal or jar cap:

- Site identification information (i.e., borehole number),
- Depth interval, and
- Time the sample was collected.

Allow headspace development for at least five minutes. Equilibration time should be the same for all samples to allow an accurate comparison of organic vapor levels between samples. However, adjustments to equilibration times may be necessary when there are large variations in ambient temperature from day to day. Vigorously shake the jar for approximately15 seconds, both at the beginning and at the end of the headspace development period. When ambient temperatures are below 32°F (0 °C), headspace development should be within a heated area. When heating samples, be sure there is adequate ventilation to prevent the build-up of organic vapors above action levels.

Subsequent to headspace development, remove the jar lid and expose the foil seal. Quickly puncture the foil seal with the PID probe, to a point about one-half of the headspace depth. Exercise care to avoid uptake of water droplets or soil particulates. Analyze the sample with the PID for at least one minute, making note of the average and peak readings. Record the PID results (in ppm) in the field notebook, soil boring/monitoring well log, or digital capture device. Dispose of the soil with the rest of the IDW in accordance with *POP 106 – Investigative Derived Waste Management.*

6.0 Data & Records Management

All data generated (results and duplicate comparisons) will be recorded in the field notebook, electronic data collector, and/or on the field form. Any deviation from the outlined procedure will also be noted. Data to be recorded includes:

- Field conditions,
- Field personnel performing task,
- When the PID was calibrated (date/time) and calibration standard used,
- Background/ambient concentrations measured after PID calibration,
- Location of sample (i.e., bore-hole number),
- Depth interval of sample measured,
- Lithology of material measured, and
- PID readings (average and peak) and units of measure.

Note that if PID measurements are recorded on a boring log, it is not necessary to duplicate information in the column where the PID readings are recorded (e.g., borehole number, depth interval, lithology type).

All documentation will be stored in the project files and retained following completion of the project.

7.0 Personnel Qualifications

The Project Manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this POP and any associated work plan(s).

The field operator is responsible for verifying that the PID is in proper operating condition prior to use and for implementing the calibration and measurement procedures in accordance with this POP and any associated work plan(s).

It is the responsibility of the field staff to conduct headspace analysis in a manner which is consistent with this POP. Field staff will also record all pertinent data into a digital capture device, onto a boring log or into a field logbook.

8.0 References

POP 105 – Decontamination of Field Equipment

POP 106 – Investigative Derived Waste Management

Water Quality Instrumentation – POP 502

1.0 Scope and Method Summary

The purpose of this Project Operating Procedure (POP) is provide a framework for calibrating instruments used to measure water quality parameters for ground water and surface water. Water quality parameters include temperature, pH, dissolved oxygen (DO), conductivity/specific conductance, and oxidation reduction potential (ORP). Manufactures instructions will be used in place of this POP, where available.

This POP is written specifically for the YSI Model 6-Series Sondes (which include the 600R, 600XL, 600XLM, 6820, 6920 and 6600 models), and the YSI 650 MDS (Multi parameter Display System) display/logger. However, the general calibration processes discussed herein are applicable to the YSI Professional Plus and other manufactures sondes and displays/loggers (e.g., Horiba U-22, InSitu Troll 9500). Consult the manufacturer's instruction manuals for specific procedures.

It is expected that the procedures outlined in this POP will be followed. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this POP will be noted in task-specific work plans or on Field Modification Forms as appropriate and will be approved in advance by the Task Manager. Deviations from the POP will be documented in the project records and in subsequent reports.

2.0 Health & Safety

The health and safety considerations for the work associated with this POP, including both potential physical and chemical hazards, are addressed in the site specific Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

Site investigation activities may involve physical and/or chemical hazards associated with exposure to water, sediment, or materials in contact with either water or sediment. When sediment sampling is performed, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project HASP.

3.0 Interferences

Each of the parameters measured with this procedure is subject to various interferences including cross-contamination, turbidity, aeration, and temperature fluctuations. Care must be taken to ensure that the instrument remains in a stable, controlled environment throughout the calibration and monitoring process and that the conditions under which the samples are analyzed are the same as those under which calibration is conducted.

4.0 Equipment and Supplies

The following equipment list contains materials which may be needed in carrying out the procedures contained in this POP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Thermometer (with National Institute of Standards and Technology [NIST] trace),
- pH Buffers of 4, 7, and 10 standard units,
- Conductivity standards (concentration dependent upon expected field conditions),
- Eureka ORP calibration standard (or similar)
- Zero Dissolved Oxygen Solution,
- Standard Deionized) Water provided by the laboratory,
- YSI Sonde with attached Turbidity, pH, Conductivity, DO, and ORP probes with clear flow-through cell or probe guard,
- YSI 650 MDS Multiparameter Display System (display logger),

- Sonde communications cable,
- Ring stand or similar capable of holding the sonde and flow-through cell upright during low-flow groundwater sampling,
- Gallon-size plastic freezer bags (e.g. Ziploc) to protect the MDS and the top of the Sonde from rain,
- Field data sheets, logbook, and/or electronic data capture device,
- Pen with indelible ink, and
- Personal protective equipment (PPE) and health and safety equipment as specified in the HASP.

5.0 Methods

All instrument probes must be calibrated before they are used to measure environmental samples, and the calibration should be checked daily, if possible, and whenever any anomalous readings are obtained.

5.1 Set-up

Before performing any calibration procedure the sonde and display/logger must warm-up for at least 15 minutes.

During the warm-up period, set the sonde up on a ring stand.

Prior to calibration, all instrument probes on the sonde must be cleaned according to the manufacturer's instructions. Failure to perform this step can lead to erratic measurements. The probes must also be cleaned by rinsing with deionized (DI) water before and after immersing the probe in a calibration solution.

For each of the calibration solutions, provide enough volume so that the probe and the temperature sensor are sufficiently covered. Additional detail on volume is provided under each section and in the manufacturer's instructions.

Check the battery level in the display/logger to see if recharging or new batteries are necessary.

Set up instrument display so that the following items are displayed:

- DO %,
- ORP (mV),
- DO (milligrams per liter (mg/L)),
- Specific Conductivity (milli per centimeters (mS/cm)),
- Turbidity ,
- Temperature (°C), and
- pH (standard units).

5.2 Temperature

For instrument probes that rely on the temperature sensor (pH, dissolved oxygen/specific conductance, and ORP), the sonde temperature sensor needs to be checked for accuracy against a thermometer that is traceable to the NIST. This accuracy check should be performed at least once a year, and the date and results of the check kept with the instrument. Temperature checks will be performed by the rental company for rented units, and by the AECOM Equipment Manager for AECOM-owned units. Prior to mobilizing, obtain the date and results of the check from the equipment room manager or check the outside of the case for rental units. If the check has not been performed within the past year, do not use the instrument. Document the date, results, and company that performed the check on the calibration log sheet or in the field logbook. Below is the verification procedure:

- Allow a container filled with water and the sonde to equilibrate to room temperature, and
- Place a thermometer that is traceable to the NIST into the water and wait for both temperature readings to stabilize.

Compare the two measurements. The instrument's temperature sensor must agree with the reference thermometer within the accuracy of the sensor (+/- 0.15 degrees Celsius [°C]). If the measurements do not agree, the instrument may not be working correctly and the manufacturer should be contacted.

5.3 Dissolved Oxygen

The DO content in water is measured using a membrane electrode. The DO probe's membrane and electrolyte solution

should be inspected for any damage or air bubbles prior to calibration. If air bubbles or damage are present, replace the membrane according to manufacturer's suggestions. After changing the membrane, it is preferable to wait 12 hours before use to allow the membrane to equilibrate if time allows. If this is not possible, note this in the calibration log. The YSI 6-Series DO probe must be calibrated using the calibration cup provided with the sonde. Calibration of the DO probe requires inputting the current barometric pressure. The YSI 650 display/logger has a barometer within the unit and automatically provides this during the calibration procedure. The barometric pressure for all units onsite should be checked for agreement between units, or checking using the onsite barometer. Other display/loggers do not supply the barometric pressure, and this must be obtained from other sources. Do not use barometric pressure obtained from meteorology reports as these are usually corrected to sea level.

Calibration is performed using 100% saturated air, and checked immediately after with a solution of zero dissolved oxygen. The calibration check at the end of the day also uses 100% saturated air.

5.3.1 DO Calibration

- Place a small amount of water (<1/8 inch) in the bottom of the calibration cup. Engage only one thread of the calibration cap onto the sonde so that the DO probe is readily vented to the atmosphere. Take care to avoid touching the oxygen membrane with the calibration cups and flow-cell. The DO probe and thermistor must not be in contact with the water. Keep the instrument in run mode and wait approximately 15 minutes for the air in the calibration cup to become water-saturated (100% humidity at atmospheric pressure) and the temperature to equilibrate. Set up the remaining instruments and solutions in the meantime.
- When the temperature has stabilized, go to Calibrate mode - Calibrate DO%
- Record the temperature on the calibration log. Check the barometric pressure reading on the YSI versus the barometer and other YSIs present. Record the barometric pressure on the calibration log. (Note: barometric pressures presented in meteorological reports are generally corrected to sea level. These are not useful for calibrating the sonde, which requires uncorrected barometric pressure).
- When the DO% and temperature readings have stabilized for at least one minute, press "enter". Record the number that appears on the screen. Record also the DO mg/L value.
- Check the oxygen solubility at that pressure and temperature on the attached Table 1 and record under "Std temperature/pressure correction." The instrument DO reading should be comparable with the value on the table (within +0.2 mg/L). If not, recalibrate, or replace DO membrane.
- Make up the zero DO solution by filling the calibration cap with DI water, adding approximately 1 gram of sodium sulfite to supersaturate the solution. Add a few crystals of the cobalt chloride (purple salt) and stir. There should be solids on the bottom of the cap. Screw the cap tightly onto the YSI. Water should leak out to indicate that there is no air around the probes.
- Immediately after calibration, if the DO is at or below 0.50 mg/L, record the value on the calibration log. If the number stabilizes at a value > 0.50 mg/L, change the DO membrane. At the end of the day, if the DO is at or above 1.0 mg/L, note the failed criteria and the readings that are impacted, and repeat the analyses at the discretion of the field team leader.
- Remove the cap, and rinse the probes well with DI water. Blot the probes dry, carefully avoiding the DO membrane.

5.3.2 DO End-of-Day Check

- Follow the first step of the DO calibration in Section 5.3.1 above.
- Allow the DO % and temperature readings to stabilized for at least one minute. Record the number that appears on the screen. Record also the DO mg/L value.
- Check the oxygen solubility at that pressure and temperature on the attached Table 1 and record under "Std temp/pressure correction." The instrument DO reading should be comparable with the value on the table (within ±0.5 mg/L).

5.4 pH

The pH of a sample is determined electrometrically using a glass electrode. Choose the appropriate standards that will bracket the expected values at the sampling locations. A two or three-point calibration can be performed. Typically, a three-point calibration using standards pH 4, pH 7, and pH 10 will be required. A calibration check is performed immediately after calibration using the pH 7 standard and a criterion of ±0.05 pH units. A calibration check is also performed at the end of the day using the pH 7 standard and a criteria of 0.3 pH units.

5.4.1 pH Calibration

- Allow the buffered samples to equilibrate to the ambient temperature.
- Remove the calibration cap and clean all of the probes on the sonde with deionized water. Begin with pH 7.00. Wipe with Kimwipe and immerse all the probes in the 7.00 pH solution. Place enough pH 7.00 solution in the calibration cup to immerse the pH probe, reference junction, and thermistor. Return to calibration mode.
- Scroll to pH on the calibration menu. Select 3-pt calibration.
- Enter pH 7.00 when prompted for the first value, and press “enter”.
- When value is stable for approximately 30 seconds, press enter, and record the number that appears on the screen. The display will indicate that the calibration has been accepted and will prompt the analyst to enter a second pH value.
- Remove probes from solution. Rinse with DI water, wipe carefully, and put all probes in solution pH 4.00. Make sure that there is enough pH 4.00 buffer to immerse the pH probe, reference junction, and thermistor.
- Enter pH 4.00 when prompted for the second pH solution, press “enter”.
- Allow at least one minute for temperature equilibration. When value is stable for at least 30 seconds, press “enter”, and record the number that appears on the screen.
- Repeat steps 5, 6, and 7 for the pH 10.00 solution.
- Press “enter” or “esc” to go to calibration menu.
- Go to the run mode to perform a calibration check of the pH 7.00 solution. Rinse the probe and immerse in pH 7.00 solution. The reading should be within ± 0.05 standard units of 7.00. If not, recalibrate. Record the reading.

5.4.2 pH End-of-Day Check

- Go to the run mode to perform a calibration check of the pH 7.00 solution.
- Rinse the probe and immerse in pH 7.00 solution. Record the reading. The reading should be within ± 0.3 standard units of 7.00.
- If not, record on the impacted measurements that the pH calibration check criterion was not met.

5.5 Conductivity

Conductivity is used to measure the ability of an aqueous solution to carry an electrical current. Specific conductance is the conductivity value corrected to 25°C. Note that the pH buffers are highly conductive and will adversely impact calibration of conductivity. Thoroughly rinse the probes after performing pH calibration, and then pre-rinse the probe with the conductivity solution to be used.

U.S. EPA recommends that conductivity be calibrated using standards that bracket the range of concentrations expected. Conductivities in groundwater frequently range below 1,000 µS/cm; however YSI does not recommend calibration with standards below 1,000 µS/cm because interference with the instrument from outside electrical noise (RF) may be a factor. Since the calibration for conductivity is a 1-point calibration, and expected conductivities will generally be less than 1,000 µS/cm, calibrate with the 1,000 µS/cm standard.

Conductivity Calibration

- Carefully rinse the probes in deionized water provided by the laboratory then in the first conductivity solution to be used.
- Immerse all probes completely in the conductivity calibration solution. Make sure that the thermistor is immersed, and the conductivity cell is immersed past the vent hole. Gently tap the side of the calibration cup to dislodge any air bubbles trapped inside the cell.
- Scroll to conductivity on the screen. Select calibrate to ms/cm. Check the standard solution on the temperature correction table (Table 1, below), or the table supplied with the bottle, and enter the corrected conductivity value. (Both should be in µs/cm.)
- Press “enter” and wait for the readings to stabilize. Press “enter”. Record the readings for conductivity and specific conductivity in the calibration log. Do not exit conductivity.
- Do not indicate “accept” when the calibration indicates “Out of Range.” Attempt to recalibrate. If the problem persists, use another instrument. Return the instrument to the vendor or equipment room.

- Perform a check of the calibration. Remove the probes from the solution. Rinse with the next conductivity solution. Immerse all probes in the conductivity calibration solution. Allow the number to stabilize and record the values for conductivity and specific conductivity in the calibration log. If the specific conductivity result is not within 5% of the value on the bottle, recalibrate. Remove probes from solution and rinse with DI water. Wipe dry.

Conductivity End-of-Day Check

- Rinse the probes with the conductivity solution then immerse all probes in the conductivity calibration solution.
- Allow the read out number to stabilize and record the values for conductivity and specific conductivity in the calibration log. If the specific conductivity result is not within 20% of the value on the bottle, note on the measurements obtained that the conductivity calibration check criteria were not met.
- Remove the probes from solution and rinse with DI water. Wipe dry.

5.6 Oxidation Reduction Potential

ORP will be checked for accuracy, and will only be field calibrated if the calibration check fails criteria.

ORP Calibration

- Switch to run mode. If not already pre-mixed, gently mix the ORP solution and open the packet. Put all but the DO probe in the ORP solution. Allow to stabilize and record reading. If reading is within ±10 millivolts (mV) of the actual value corrected for temperature (see table below), calibration is not required. If reading is not within ±10 mV of the actual value corrected for temperature (see table below), proceed to the next step below.
- Go to Calibration mode. Scroll to ORP and press “enter”. Enter ORP value (corrected for temperature - see above) and press “enter”. When the number is stable for 20 seconds, press “enter” and record the number. If instrument says “Out of Range,” do not accept the value: Use a different instrument. If a different instrument is not available, record the number and note that it is not within limits.

ORP End-of-Day Check

- Switch to run mode.
- Gently mix the ORP solution and open the packet. Put all but the DO probe in the ORP solution.
- Allow to stabilize and record reading. If reading is not within ±10 mV of the actual value corrected for temperature (see table below), note on the measurements affected that the criterion for ORP check was not met.

Instrument Shutdown

- Replace the storage cup with a wet sponge in the bottom over probes.
- Select run mode. Reset the parameters to the following:
  - pH,
  - specific conductivity,
  - ORP,
  - Temperature,
  - DO mg/L,
  - Shut off hand held display and return to case.

7.0 Data & Records Management

Calibration log sheets shall be used to document the details of instrument calibration and calibration checks.

The site logbook should be used to note when instrument calibration and instrument calibration checks were conducted, and should reference the calibration log sheets for details.

Readings measured by instruments that are subsequently found to be outside of criteria during the calibration check shall

be documented on the sampling worksheet used to document the sample collection.

All field records will be maintained in the project files.

8.0 Personnel Qualifications

The Project Manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this POP and the project plans.

The field operator is responsible for verifying that the YSI is in proper operating condition prior to use and for implementing the calibration and measurement procedures in accordance with this POP and the project plan.

9.0 Quality Assurance and Quality Control

9.1 Quality Control

Criteria are summarized in Table 3, which is attached..

9.2 Pollution Prevention

Containers used to calibrate the probes shall be sized to use the smallest amount of standard possible but still accommodate all probes which need to be in the calibration solution such that they are adequately covered.

Conductivity and pH calibration solutions may be reused at the end of the day with caution if properly stored. However, a calibration check that reuses standard but does not meet criteria should be re-checked with fresh standard, and calibration should be conducted with fresh standards.

9.3 Waste Management

Unused calibration standards should be returned to the equipment room manager or equipment rental vendor for proper disposal and/or storage. Do not combine ORP standards with other standards since cyanide could be released. Used calibration standards should be disposed of in accordance with *POP 106 – Investigative Derived Waste Management.*

10.0 References

POP 106 – Investigative Derived Waste Management

YSI, Inc. (YSI). 2002. YSI Calibration Procedures: Profiling and Logging, www.water-monitor.com.

Part II
Quality Assurance Project Plan

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1 Project Description

1.1 Introduction

This Quality Assurance Project Plan (QAPP) is prepared to supplement the Remedial Investigation and Feasibility Study (RI/FS) Work Plan for the RI/FS at Pepco's Benning Road facility (the Site), located at 3400 Benning Road NE, Washington, D.C., and a segment of the Anacostia River adjacent to the Site. The general site location is shown on **Figure 1** of the Field Sampling Plan (FSP). Together, the Site and the adjacent segment of the River are referred to herein as the "Study Area". The RI/FS Study Area consists of a "landside" component which will focus on the Site itself, and a "waterside" component that will focus on the shoreline and sediments in the segment of the river adjacent to and immediately downstream of the Site. The landside and waterside areas of investigation are depicted in **Figure 2** of FSP.

The purpose of this QAPP is to present the organization, objectives, planned activities, and specific quality assurance/quality control (QA/QC) procedures associated with the RI activities to be conducted at the Site. Specific protocols for sampling, sample handling and storage, COC, and laboratory and field analyses are described herein. This QAPP has been prepared in accordance with the United States Environmental Protection Agency (USEPA) QAPP policy as presented in USEPA Requirements for Quality Assurance Project Plans (USEPA QA/R-5, March 2001). This QAPP (Part II of the Sampling and Analysis Plan) is also prepared in accordance with the outline provided in the Final RI/FS Scope of Work (SOW).

1.2 Project Background

The Site is one of several properties along the Anacostia River that are suspected sources of contamination. There have been five instances since 1985 in which materials containing polychlorinated biphenyls (PCBs) were released at the Site. In each case, Pepco promptly cleaned up the releases in accordance with applicable legal requirements. Nonetheless, it is suspected that these releases, and possibly other historical operations or activities at the Site, may have contributed to contamination in the river. In particular, a site inspection conducted for the USEPA in 2009 linked polycyclic aromatic hydrocarbons (PAH), PCBs, and inorganic constituents detected in Anacostia River sediments to potential historical discharges from the Site. The site inspection contractor also stated that currently the Site is properly managed and that any spills or leaks of hazardous substances are quickly addressed and, if necessary, properly remediated. The RI will evaluate all spills at the Site as necessary.

Pepco has agreed to perform the RI/FS pursuant to a consent decree that was entered by the U.S. District Court for the District of Columbia on December 1, 2011 (the Consent Decree). The Consent Decree documents an agreement between Pepco and the District of Columbia (District) which is part of the District's larger effort to address contamination in and along the lower Anacostia River. The purpose of the RI/FS is to (a) characterize environmental conditions within the Study Area, (b) investigate whether and to what extent past or current conditions at the Site have caused or contributed to contamination of the river, (c) assess current and potential risk to human health and environment posed by conditions within the Study Area, and (d) develop and evaluate potential remedial actions.

The 77-acre Site is bordered by a DC Solid Waste Transfer Station to the north, Kenilworth Maintenance Yard (owned by the National Park Service, NPS) to the northwest, the Anacostia River to the west, Benning Road to the south and residential areas to the east and south (across Benning Rd.). Most of the Site is comprised of the Benning Service Center, which involves activities related to construction, operation and maintenance of Pepco's electric power transmission and distribution system serving the Washington, D.C., area. The Service Center accommodates more than 700 Pepco employees responsible for maintenance and construction of Pepco's electric transmission and distribution system; system engineering; vehicle fleet maintenance and refueling; and central warehousing for materials, supplies and equipment. The Site is also the location of the Benning Road Power Plant, which is scheduled to be shut down in 2012.

Pepco conducted several investigations and removal actions at the Site since 1985 (**Table 1** and **Figure 3** in the FSP). The USEPA conducted two studies, a Multi-media Inspection and a Comprehensive Environmental Liability and Compensation Act (CERCLA) Site Inspection, within the Study Area. In addition, the National Park Service (NPS) completed a remedial investigation at the adjacent Kenilworth Landfill and a Preliminary Assessment/Site Investigation (PA/SI) at Langston Golf Course. AECOM reviewed available information from these studies and other studies conducted in the River by various governmental and non-governmental organizations, and incorporated the findings into the Conceptual Site Model (CSM) and Work Plan development. Detailed information on previous investigations, geology, hydrogeology, hydrology, and site and area descriptions can be found in the RI/FS Work Plan.

The RI/FS will be overseen by the District Department of the Environment (DDOE) and will be performed in accordance with the USEPA *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA, Office of Solid Waste and Emergency Response (OWSER)* Directive 9355.3-01, dated October 1988, and other applicable USEPA and DDOE guidance documents.

1.3 Analytical Task Description

To accomplish the RI/FS objectives, the following field sampling tasks will be implemented:

- Landside surface and subsurface soil sampling and analysis from areas within the Site;
- Landside collection and analysis of groundwater from monitoring wells ;
- Waterside collection and analysis of surface water from the Anacostia River; and
- Waterside collection and analysis of sediments from the Anacostia River.

Tables 4 and **5** of the FSP summarize the analyses that will be performed on the samples collected at the Site as part of the RI/FS on the Landside and Waterside, respectively. In general, analyses to be performed by matrix are:

- Target Compound List (TCL) Volatile Organic Compounds (VOCs), TCL Semi-volatile Organic Compounds (SVOCs), Priority Pollutant Polycyclic Aromatic Hydrocarbons (PP PAHs or PAH16), TCL Organo-chlorine Pesticides (OCPs), TCL PCB-Aroclors, Target Analyte List (TAL) metals (total and dissolved for groundwater), Gasoline Range Organics (GRO), Diesel Range Organics/Oil Range Organics (DRO/ORO), and Polychlorinated Dibenzodioxins and Dibenzofurans (PCDDs/PCDFs) in soil and groundwater.
- TCL VOCs, TCL SVOCS, PP PAHs, TCL OCPs, TCL PCB-Aroclors or PCB-Homologs, TAL metals (total and dissolved), GRO, DRO/ORO, and PCDDs/PCDFs in surface water.
- TCL VOCs, TCL SVOCs, PP PAHs, TCL OCPs, TCL PCB-Aroclors or PCB-Homologs, TAL metals (total and dissolved), GRO, DRO/ORO, PCDDs/PCDFs, Acid Volatile Sulfide/Simultaneously Extracted Metals (AVS/SEM), and Grain Size in sediments.
- PCB-congeners (all 209) and an extended list of parent and alkyl PAHs may be performed on selected soil and sediment samples for forensic purposes.

2 Project Organization and Responsibilities

2.1 Project Schedule

A tentative project schedule is provided in the RI/FS Work Plan. According to the Consent Decree deadlines, field work must begin within 30 days of the approval of the Final RI/FS Work Plan, Health and Safety Plan (HASP), FSP and QAPP.

2.2 Project Organization

The responsibilities of key personnel are described below.

2.2.1 Management Responsibilities

Pepco Project Manager

As Pepco Project Manager, Ms. Mahvi's responsibilities include:

- Representing Pepco management,
- Primary interface with DDOE,
- Securing project funding,
- Working with Pepco Community Involvement Coordinator (Donna Cooper) to implement the Community Involvement Plan (CIP), and
- Reviewing all project documents before submission to DDOE.

AECOM Project Manager

The AECOM Project Manager, Mr. Ravi Damera, has responsibility for day-to-day management of technical and scheduling matters related to the project. Other duties, as necessary, of the AECOM Project Manager include:

- Subcontractor procurement,
- Assignment of duties to project staff and orientation of the staff to the specific needs and requirements of the project,
- Ensuring that data assessment activities are conducted in accordance with the QAPP,

- Approval of project-specific procedures and internally prepared plans, drawings, and reports,
- Serving as the focus for coordination of all field and laboratory task activities, communications, reports, and technical reviews, and other support functions, and facilitating site activities with the technical requirements of the project, and
- Maintenance of the project files.

2.2.2 Quality Assurance Responsibilities

AECOM Project Quality Assurance (QA) Officer

The AECOM Project QA Officer, Mr. Gary Grinstead, has overall responsibility for quality assurance oversight. The AECOM Project QA Officer communicates directly to the AECOM Project Manager. Specific responsibilities include:

- Preparing the QAPP,
- Reviewing and approving QA procedures, including any modifications to existing approved procedures,
- Ensuring that QA audits of the various phases of the project are conducted as required,
- Providing QA technical assistance to project staff,
- Ensuring that data validation/data assessment is conducted in accordance with the QAPP, and
- Reporting on the adequacy, status, and effectiveness of the QA program to the AECOM Project Manager.

AECOM Analytical Task Manager

The AECOM Project Chemist/Laboratory Coordinator, Mr. Robert Kennedy, will be responsible for managing the subcontractor laboratories, serving as the liaison between field, laboratory personnel, data validation and database teams and assessing the quality of the analytical data.

2.2.3 Laboratory Responsibilities

Pending final procurement, TestAmerica is proposed to perform the chemical analyses of all samples as detailed in **Section 7.0**.

Laboratory Manager

The Laboratory Manager is ultimately responsible for the data produced by the laboratory. Specific responsibilities include:

- Implementing and adhering to the laboratory QA manual and all corporate policies and procedures within the laboratory,
- Approving the standard operating procedures (SOPs),
- Maintaining adequate staffing, and
- Implementing internal/external audit findings corrective actions.

Laboratory QA Coordinator

The Laboratory QA Coordinator reports to the Laboratory Manager. Specific responsibilities include:

- Approving SOPs,
- Assessing and maintaining the laboratory QA manual implementation within the facility operations,
- Recommending resolutions for ongoing or recurrent nonconformances within the laboratory,
- Performing QA assessments, and
- Reviewing and approving corrective action plans for nonconformances, tracking trends of nonconformances to detect systematic problems, and initiating additional corrective actions as needed.

Laboratory Project Manager

The TestAmerica Laboratory Project Manager is anticipated to be Ms. Carrie Gamber at TestAmerica-Pittsburgh. She will be the primary point of contact between the TestAmerica network laboratories and AECOM. The ECCS on-site mobile lab Project Manager will be Nick Nigro. Specific responsibilities of the Laboratory Project Manager include:

- Monitoring analytical and QA project requirements for a specified project,
- Acting as a liaison between the client and the laboratory staff,
- Reviewing project data packages for completeness and compliance to client needs, and
- Monitoring, reviewing, and evaluating the progress and performance of projects.

2.2.4 Field Responsibilities

AECOM Field Team Leader

The AECOM Field Team Leader, Mr. Scott Beatson, has overall responsibility for completion of all field activities in accordance with the QAPP and is the communication link between AECOM project management and the field team. Specific responsibilities of the AECOM Field Team Leader include:

- Coordinating activities at the site,
- Assigning specific duties to field team members,
- Mobilizing and demobilizing of the field team and subcontractors to and from the site,
- Directing the activities of subcontractors on site,
- Resolving any logistical problems that could potentially hinder field activities, such as equipment malfunctions or availability, personnel conflicts, or weather dependent working conditions,
- Implementing field quality control (QC) including issuance and tracking of measurement and test equipment; the proper labeling, handling, storage, shipping, and chain-of-custody (COC) procedures used at the time of sampling; and control and collection of all field documentation, and
- Communicating any non-conformances or potential data quality issues to AECOM project management.

AECOM Field Staff

The field staff reports directly to the AECOM Field Team Leader, although the Field Team Leader in some cases will be conducting the duties of the field staff listed below. The responsibilities of the field team include:

- Collecting samples, conducting field measurements, and decontaminating equipment according to documented procedures stated in the QAPP,
- Ensuring that field instruments are properly operated, calibrated, and maintained, and that adequate documentation is kept for all instruments,
- Collecting the required QC samples and thoroughly documenting QC sample collection,
- Ensuring that field documentation and data are complete and accurate, and
- Documenting and communicating any nonconformance or potential data quality issues to the AECOM Field Team Leader.

3 Quality Assurance Objectives for Measurement

3.1 Data Quality Objectives

The field investigation activities are designed to characterize conditions in soil, groundwater, surface water and sediment, further refine the CSM, and collect data to support risk assessment and Natural Resource Damage Assessment (NRDA). Data gaps identified during the review of existing data were used to guide the scope of this investigation. Field investigation activities are divided into Landside and Waterside activities and are noted in **Section 1**. All field investigation activities will be conducted in accordance with the RI/FS Work Plan, the FSP, and the HASP, submitted under separate covers.

The data quality objectives (DQOs) for this investigation are:

- To characterize environmental conditions within the Study Area and refine the CSM
- To collect data to update existing Landside and Waterside datasets so the nature and extent of impacts can be better defined
- To collect data to determine whether and to what extent past or current conditions at the Site have caused or contributed to contamination of the Anacostia River
- To collect data within the Anacostia River to identify potential Site-related, near-Site and far-Site sources of contaminants of potential concern (COPCs) in sediment and surface water
- To collect hydraulic data to better understand the site-specific hydrogeology and evaluate the volumetric flux of groundwater to the Anacostia River
- To collect data to better understand sedimentation in the portion of the Anacostia River in Study Area
- To collect data to support performance of Human Health and Ecological Risk Assessments
- To collect data to support development and evaluation of remedial alternatives
- To collect data for NRDA evaluation

The Landside and Waterside DQO development process is presented in **Tables 2** and **3** of the FSP, respectively.

3.2 Data Quality Objectives for Measurement Data

3.2.1 Precision

Precision is a measure of the degree to which two or more measurements are in agreement. Field precision is assessed through the collection and measurement of field duplicates at a rate of one duplicate per twenty analytical samples, per matrix, per sampling technique.

Precision will be measured through the calculation of relative percent difference (RPD). The objective for field precision RPDs is < 30% RPD for aqueous samples, and < 50% RPD for solid samples, where results reported at greater than five times the reporting limit.

Precision in the laboratory is assessed through the calculation of RPD for duplicate samples, either as matrix spike/matrix spike duplicates (MS/MSDs) or as laboratory duplicates. The control limits provided in **Table 1** for each parameter will be utilized.

3.2.2 Accuracy

Accuracy is the degree of agreement between the observed value and an accepted reference or true value. Accuracy in the field is assessed through the use of trip blanks and equipment blanks and through the adherence to all sample handling, preservation, and holding time requirements. The objective for trip blanks and equipment blanks is that no target compounds are present above the reporting limit. Sampling preservation and holding time requirements are provided in **Table 4**.

Laboratory accuracy is assessed through the analysis of laboratory method blanks, and spiked samples such as MS/MSDs, laboratory control samples (LCSs), and surrogate compounds. Method blanks should not contain any target compounds above the reporting limits (RLs) which are quantitation limits based on the low point of calibration, or Estimated Minimum Level (EML) for all isotope dilution analytes. For spiked samples, the accuracy objectives, as measured by percent recoveries (%Rs), will be the control limits provided in **Table 1**.

3.2.3 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. "Normal conditions" are defined as the conditions expected if the sampling plan was implemented as planned.

Field completeness is a measure of the amount of valid samples obtained during all sampling for the project. The field completeness objective is greater than 90 percent.

Laboratory completeness is a measure of the amount of valid measurements obtained from all the measurements taken in the project. The laboratory completeness objective is greater than 95 percent.

3.2.4 Sensitivity

Sensitivity of analytical data is demonstrated by laboratory RLs and Method Detection Limits (MDLs). The target RLs for the analytes to be analyzed are presented in **Tables 2** and **3**. The RLs for the actual samples may differ due to analytical dilutions, sample volume, or sample matrix.

Reporting limits were selected in part by consideration of the applicable screening levels which are risk based and used as Project Screening Limits (PSLs), and in part by consideration of the actual ability of the laboratory to attain reporting limits at the screening levels. Selected Ion Monitoring (SIM) will be performed for selected gas chromatography/mass spectrometry (GC/MS) analysis targets to obtain lower reporting and detection limits. Not all risk based target analyte PSLs are obtainable using the RLs of conventional USEPA methods.

To maximize the usability of the data, any analytes detected below the RLs and above the MDL will be reported by the laboratory as estimated ("J") values for the following parameters: VOCs, SVOCs, OCPs, PCBs as Aroclors, GRO, DRO, ORO, and metals. For PCB congener and PCDD/PCDF analyses by high resolution mass spectrometry (HRMS), detected concentrations below the EML and above the Estimated Detection Limit (EDL) will be reported by the laboratory as estimated ("J") values. EDLs are sample specific limits based on signal-noise ratio and will be used as the reporting detection limit for nondetect results.

3.2.5 Comparability

Comparability expresses the confidence with which one data set can be compared to another. Comparability is dependent upon the proper design of the sampling program and will be satisfied by ensuring that the protocols described in this QAPP are followed and that proper sampling techniques are used. Planned analytical data will be comparable when similar sampling and analytical methods are used as documented in the QAPP.

3.2.6 Representativeness

Representativeness expresses the degree to which data accurately and precisely represents a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition within a defined spatial and/or temporal boundary.

Representativeness is ensured through the design of the sampling program and will be satisfied by ensuring that the Work Plan and QAPP are followed and that proper sampling techniques are used. Within the laboratory, representativeness will be ensured by the use of appropriate methods, conformance to the approved analytical procedures, and adherence to sample holding times.

3.3 Special Training/ Certifications

3.3.1 Training

This investigation includes routine field sampling techniques, field measurements, and laboratory analyses. No specialized training is therefore necessary. Prior to starting work, personnel will be given instruction specific to the project, covering the following areas:

- Organization and lines of communication and authority,
- Overview of the scope of work,
- QA/QC requirements,
- Documentation requirements, and
- Health and safety requirements.

Instructions will be provided by the AECOM Project Manager, AECOM Field Team Leader, and AECOM Project QA Officer.

3.3.2 Certifications

The chemical analysis laboratories hold National Environmental Laboratory Accreditation Program (NELAP) accreditation.

3.4 Documents and Records

3.4.1 Project Files

The project files will be the central repository for all documents which constitute evidence relevant to sampling and analysis activities as described in this QAPP. AECOM is the custodian of the project files and will maintain the contents of the project files for the investigation, including all relevant records, reports, logs, field notebooks, pictures, subcontractor reports, and data reviews in a secured, limited access area and under custody of the AECOM Project Manager.

The project files will include at a minimum:

- Field logbooks,
- Field data and data deliverables,
- Photographs,
- Drawings,
- Sample collection logs,
- Laboratory data deliverables,
- Data validation reports,
- Data assessment reports,
- Access/Legal agreements with property owners,
- A copy of final plans and other documents,
- Progress reports, QA reports, interim project reports, etc.,
- All custody documentation (tags, forms, airbills, etc.)

Records will be retained for a minimum of 6 years or the duration requested by USEPA.

3.4.2 Field Records

Field logbooks will provide the means of recording the data collection activities and will be maintained in accordance with Project Operating Procedure (POP) 101 – Field Records located in **Appendix A** of the FSP. As such, entries will be described in as much detail as possible so that persons going to the facility could reconstruct a particular situation without reliance on memory.

Field logbooks will be bound field survey books or notebooks. Logbooks will be assigned to field personnel, but will be stored in the project files when not in use. Each logbook will be identified by the project-specific document number.

The title page of each logbook will contain the following:

- Person to whom the logbook is assigned,
- The logbook number,
- Project name and number,
- Project start date, and
- End date.

Entries into the logbook will contain a variety of information. At the beginning of each entry, the date, start time, weather, names of all sampling team members present, and the signature of the person making the entry will be entered. The names of visitors to the site, field sampling or investigation team personnel, and the purpose of their visit, will also be recorded in the field logbook.

Field logbooks will be supplemented by standardized field measurement and sample collection forms. All measurements made and samples collected will be recorded. All entries will be made in permanent ink, signed, and dated and no erasures or obliterations will be made. If conditions are such that only a pencil can be used (e.g., extreme cold), the procedures for using a pencil in **Section 6.1** of POP 101 – Field Records must be followed. If an incorrect entry is made, the information will be crossed out with a single strike mark, which is initialed and dated by the sampler. Whenever a sample is collected, or a measurement is made, a detailed description of the sampling location, which includes compass and distance measurements, or, latitude and longitude information (e.g., obtained by using a global positioning system) will be recorded. The number of photographs taken of the sampling location, if any, will be noted. Equipment used to make measurements will be identified, along with the date of calibration.

3.4.3 Laboratory Records and Deliverables

Laboratory data reduction procedures will be performed according to the following protocol.

- All information related to analysis will be documented in controlled laboratory logbooks, instrument printouts, or other approved forms.
- All entries that are not generated by an automated data system will be made neatly and legibly in permanent, waterproof ink.
- Information will not be erased or obliterated. Corrections will be made by drawing a single line through the error and entering the correct information adjacent to the cross-out. All changes will be initialed, dated, and, if appropriate, accompanied by a brief explanation.
- Unused pages or portions of pages will be crossed out to prevent future data entry.
- Analytical laboratory records will be reviewed by the supervisory personnel on a regular basis and by the Laboratory QA Coordinator periodically, to verify adherence to documentation requirements.

On-site mobile laboratory turnaround time will be 24 hours. The standard fixed laboratory turnaround time will be 15 business days for all parameters except PCB congeners and PCDD/PCDFs. The turnaround time for PCB congener and PCDD/PCDF analysis is four weeks. The laboratory will provide a complete report in portable document format (PDF) format, and an electronic data deliverables (EDDs). The EDD will be provided as text files in AECOM-specific EQuIS® 4-file format. The PDF format data packages will be contract laboratory program (CLP)-

like reports containing QC summary forms and all raw data and will be completely paginated and bookmarked. All text in the reports should be electronically searchable.

4 Sampling Procedures

4.1 Sampling Design

A summary of the sample locations, types of samples collected, analyses to be performed, monitoring wells to be installed, and rationale for sample collection is presented in **Tables 4** and **5** of the FSP.

4.2 Sampling Methods

The reader is referred to FSP Section 5 and FSP Appendix A for details on field sampling methods and AECOM POPs, respectively.

4.3 QC sample collection

QC samples for laboratory analyses will include field duplicates, MS/MSDs, equipment blanks, trip blanks, and temperature blanks. These samples will be collected as described below:

Field duplicates

Field duplicates will be collected at a frequency of one field duplicate per 20 field samples, per matrix, per sampling technique. Field duplicates for solid samples will be collected by alternately filling two sets of identical sample containers from the interim container used to homogenize the sample. For soil VOC samples, the field duplicate will be collected using the collection device (e.g., sample coring device) from the same areas as the parent sample (i.e., soil VOC samples are not homogenized). For aqueous samples, the parent sample and field duplicate sample containers will be filled in an alternating fashion (i.e., one parent sample container filled, one field duplicate container filled. All field duplicates will be analyzed for the same parameters as their associated samples.

MS/MSDs

MS/MSD samples will be collected at a frequency of one for every 20 field samples, per matrix for all parameters except PCB congeners and PCDD/PCDFs. The HRMS isotope dilution methods for PCB congeners and PCDD/PCDFs include labeled analog spikes in every sample. For those samples designated as MS/MSDs, sufficient additional volume or mass (based on the laboratory's requirements) will be collected.

Equipment blanks

Equipment blanks will be collected at a rate of one for every 20 field samples, per matrix, per sampling technique. Equipment blanks will be collected by pouring laboratory volatile organic analysis (VOA)-free water over the decontaminated sampling equipment, and collecting the rinsate into the appropriate sample containers. Equipment blanks will not be collected when dedicated sampling equipment is used (e.g., peristaltic pump with dedicated tubing).

Trip blanks

Trip blanks will be included with each shipment of groundwater and soil samples collected for VOC and GRO analyses. Trip blanks associated with groundwater samples will originate in the laboratory and will be prepared by filling two 40-mL VOA vials with laboratory VOA-free water and the chemical preservative, and sealing the vials with septum-lined caps (allowing no headspace). Trip blanks associated with soil VOC samples will consist of one set of the soil VOA vials (i.e., two low level VOA vials and one high level VOA vial). Trip blanks associated with soil GRO samples will consist of one soil GRO vial (i.e., one VOA vial containing methanol). Trip blanks will accompany the sample bottles to the site and will remain (unopened) in the shipping container until the sample bottles are received back at the laboratory.

Temperature blanks

Temperature blanks will be included in each cooler, allowing the laboratory to determine the temperature of the shipment without disturbing the field samples. Temperature blanks will be prepared by filling a plastic or glass vial with water.

5 Sample Custody

5.1 Sample Containers, Preservation, and Holding Times

Sample bottles and chemical preservatives will be provided by the laboratories. The containers will be cleaned by the manufacturer to meet or exceed all analyte specifications established in the latest USEPA's Specifications and Guidance for Contaminant-Free Sample Containers. Certificates of analysis will be provided with each lot of containers and maintained on file to document conformance to USEPA specifications. A summary of sample container, preservation, and holding time requirements is presented in **Table 4**.

5.2 Sample Labeling

Immediately upon collection, each sample will be labeled with an adhesive label. Samples will be assigned unique sample identifications. Each sample label will include the sample number, location, date/time of collection, and analysis. Each sample number will consist of a four part identification system that describes the sampling method, location ID, depth, and sample type, as described below:

- Sampling Method: This part is represented by a three letter code as follows:

Monitoring Well Soil	MWS
Monitoring Well Water	MWW
Soil Boring Soil	SBS
Soil Boring Water	SBW
Direct Push Soil	DPS

Direct Push Water	DPW
Surface Soil Sample	SUS
Sediment	SED
Surface Water	SUW

- Location: This will be a two digit code consisting of numbers, letters or a combination (e.g., 01, 15, C2).
- Sample Depth: Sample depth will be identified using a two digit number (e.g., 05 representing 5 feet below grade). Where sample depth involves an interval, this identifier identifies the starting depth of the interval only. The number "00" will represent surface samples.
- Sample Type: The last character of the sample ID will represent the sample type:
  - N – Field sample
  - R – Field duplicate
  - Q – Quality control (QC) sample (e.g., equipment blank, trip blank)

- Equipment Blank – "EB" followed by date (e.g., EB-070110). If multiple EBs are collected on the same day for differing types of sampling equipment, numerical designations will be used to differentiate the type of equipment blank (e.g., EB01-070110, EB02-070110), with the type of sampling equipment associated with each type of equipment blank documented in the field log book (e.g., EB01-070110 collected from split spoon sampler, EB02-070110 collected from Geoprobe® cutting shoe)
- Trip Blank – "TB" followed by date (e.g., TB-070110). If multiple TBs are collected on the same day for multiple coolers of VOC samples, numerical designations will be used to differentiate the different trip blanks (e.g., TB01-070110, TB02-070110). The cooler specific chain-of-custody forms will document which VOC samples are associated with the trip blanks.

An example of a complete sample ID would be MWW0515N for the groundwater sample collected from monitoring well MW-5 at15 feet below grade. Another example would be SEDC200R representing duplicate of a surface sediment sample collected at grid node C2.

Samples being designated for matrix spike and matrix spike duplicate (MS/MSD) analysis will *not* include an identifier as part of the sample code, but will be identified as such on the chain-of-custody in the comments section on the same row as the parent sample.

5.3 Custody Procedures

Custody is one of several factors that are necessary for the admissibility of environmental data as evidence in a court of law. Custody procedures help to satisfy the two major requirements for admissibility: relevance and authenticity. Sample custody is addressed in two parts: field sample collection and laboratory analysis.
A sample is considered to be under a person's custody if

- the item is in the actual possession of a person;
- the item is in the view of the person after being in actual possession of the person;
- the item was in the actual physical possession of the person but is locked up to prevent tampering; and
- the item is in a designated and identified secure area.

5.3.1 Field Custody Procedures

The field sampler is personally responsible for the care and custody of the samples until they are transferred or dispatched properly. Field procedures have been designed such that as few people as possible will handle the samples. Field custody procedures will be performed according to POP 102 - Chain of Custody Procedures located in **Appendix A** of the FSP.

All sample containers will be identified by the use of sample labels with sample numbers, sampling locations, date/time of collection, and type of analysis. Sample labels will be completed for each sample using waterproof ink unless prohibited by weather conditions. For example, a logbook notation would explain that a pencil was used to fill out the sample tag because the pen would not function in freezing weather.

Samples will be accompanied by a properly completed COC form. The sample numbers and locations will be listed on the COC form. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents the transfer of custody of samples from the sampler to another person, to the permanent laboratory, or to/from a secure storage location. An example COC form is presented as **Figure 1**. All sample shipments will be accompanied by the COC record identifying the contents. The original record will accompany the shipment, and the back copy will be retained by the sampler and placed in the project files.

Field samples will be packed and shipped to the laboratory according to POP 103 – Packaging and Shipment of Samples, located in **Appendix A** of the FSP. Samples will be properly packaged on ice at 4°C for shipment and dispatched to the laboratory for analysis, with a separate signed custody record enclosed in and secured to the inside top of each sample box or cooler. Shipping containers will be sealed and secured with strapping tape and custody seals for shipment to the laboratory. The custody seals will be attached to the front right and back left of the cooler and covered with clear plastic tape after being signed by field personnel. The cooler will be strapped shut with strapping tape in at least two locations.

If the samples are sent by common carrier, the waybill will be used. Waybills will be retained as part of the permanent documentation. Commercial carriers are not required to sign off on the custody forms since the custody forms will be sealed inside the sample cooler and the custody seals will remain intact.

5.3.2 Laboratory Custody Procedures

Samples will be received and logged in at the laboratory by a designated sample custodian or his/her designee. Upon sample receipt, the sample custodian will

- Examine the shipping containers to verify that the custody tape is intact,
- Examine all sample containers for damage,
- Determine if the temperature required for the requested testing program has been maintained during shipment and document the temperature on the COC form or in sample log-in records,
- Compare samples received against those listed on the COC,

- Verify that sample holding times have not been exceeded,
- Examine all shipping records for accuracy and completeness,
- Determine if sample pH is adequate and whether any adjustments were required (if applicable) and record sample receipt form,
- Sign and date the COC immediately (if shipment is accepted) and attach the waybill,
- Note any problems associated with the coolers and/or samples on the cooler receipt form and notify the Laboratory Project Manager, who will be responsible for contacting the client,
- Attach laboratory sample container labels with unique laboratory identification and analyses required, and
- Place the samples in the proper laboratory storage.

Following receipt, samples will be logged in according to the following procedure:

- The samples will be entered into the laboratory information management system (LIMS). At a minimum, the following information will be entered: project name or identification, unique sample identification numbers (both client and internal laboratory), type of sample, required analyses, and date and time of laboratory receipt of samples.
- The appropriate laboratory personnel will be notified of sample arrival.
- The completed COC, waybills, and any additional documentation will be placed in the project file.

Specific details of laboratory custody procedures for sample receiving, sample identification, sample control, and record retention are described in the Laboratory QA Manual and laboratory SOPs.

6 Calibration Procedures

6.1 Instrument/Equipment Testing, Inspection, and Maintenance

The field equipment for this project will include a photoionization detector (PID), an electronic water level indicator, and water quality instrumentation. AECOM field personnel will be responsible for ensuring that the instruments are properly functioning. At a minimum, this will entail checking the instrument prior to shipment to the field and performing daily operational checks and calibration as described in **Section 6.2**. Routine maintenance and trouble-shooting procedures will be performed as described in the manufacturer's instructions. Spare parts will be readily available on site or from the vendor.

Routine testing and preventive maintenance is performed by the laboratory as part of their QA program. Details on the type of checks, frequencies, and corrective actions are included in the Laboratory QA Manual.

6.2 Instrument/Equipment Calibration and Frequency

The field instrumentation requiring field calibration will include a PID, YSI water quality meter, and LaMotte turbidity meter. Calibration will be performed daily or anytime that the operator suspects that the instrument is not reading accurately according to POP 502 – Water Quality Instrumentation located in **Appendix A** of the FSP:

All calibrations and calibration checks will be documented in the field records. Calibration records will include the date/time of calibration/calibration check, name of the person performing the calibration, reference standard used, and the results of the calibration or check.

Calibration procedures for laboratory instruments will consist of initial calibrations, initial calibration verifications, and continuing calibration verification. The SOP for each analysis performed in the laboratory describes the calibration procedures, their frequency, acceptance criteria, and the conditions that will require recalibration. This information is summarized in **Table 7**.

The laboratory maintains documentation for each instrument, which includes the following information: instrument identification, serial number, date of calibration, analyst, calibration solutions, and the samples associated with these calibrations.

6.3 Inspection/ Acceptance of Supplies and Consumables

For this project, critical supplies for field activities will be tracked through AECOM's system in the following manner.

Critical Supplies and Consumables	Inspection Requirements and Acceptance Criteria	Responsible Individual
Sample bottles	Visually inspected upon receipt for cracks, breakage, and cleanliness. Must be accompanied by certificate of analysis.	Field Team
Chemicals and reagents	Visually inspected for proper labeling, expiration dates, appropriate grade	Field Team
Field measurement equipment	Functional checks to ensure proper calibration and operating capacity	Field Team
Sampling equipment	Visually inspected for obvious defects, damage, and contamination	Field Team

Supplies and consumables not meeting acceptance criteria will initiate the appropriate corrective action. Corrective measures may include repair or replacement of measurement equipment, and/or notification of vendor and subsequent replacement of defective or inappropriate materials. All actions will be documented in the project files.

The laboratory system of inspection and acceptance of supplies and consumable is documented in the Laboratory QA Manual.

7 Analytical Procedures

Soil, sediment, groundwater, and surface water samples will be analyzed by the NELAP-certified fixed and mobile laboratories listed below.

Groundwater, surface water, soil, and sediment samples collected for VOCs, SVOCs, OCPs, and metals will be analyzed by:

TestAmerica
301 Alpha Drive
Pittsburgh, PA 15238
412-963-7058

Groundwater and surface water samples collected for GRO, DRO/ORO will be analyzed by:

TestAmerica
3355 McLemore Drive
Pensacola, FL
850-474-1001

Soil and sediment samples collected for PCB-Aroclors and DRO/ORO will be analyzed at the on-site mobile laboratory by:

ECCS
2525 Advanced Road
Madison, WI 534718
608-221-8700

All PCB congener, alkylated PAH, and PCDD/PCDF analyses will be performed by:

TestAmerica
5815 Middlebrook Pike
Knoxville, TN 37921
865-291-3000

A summary of the sample locations, types of samples collected, and analyses to be performed is presented in **Tables 4** and **5** of the FSP. Details for conditional sample analyses are provided in the Work Plan.
EPA Method 1668A and EPA Method 8290A are ultratrace isotope dilution based HRMS analytical techniques. When concentrations exceed the calibration range in soil or sediment then results may be flagged E if they exceed

the upper confidence limit (UCL) but are within linear range of instrument response. If the labeled internal standard spike is diluted out during reanalysis then quantitation of target congeners may be performed by the internal standard method rather than true isotope dilution. These results will be appropriately qualified in the laboratory narrative and data validation reports.

Samples will be analyzed for the analytes listed in **Tables 2** and **3**. The laboratory analytical methods to be used are summarized in **Table 5**. Laboratory SOPs that will be utilized for the analyses are listed in **Table 6** and are included in **Appendix A** on CD-ROM. Note the laboratory SOPs are proprietary business information to be shared only with Pepco, AECOM, and DDOE.

8 Data Reduction, Validation and Reporting

8.1 Data Review, Verification, and Validation

All data generated through field activities, or through the analytical program, will be reduced, verified and/or validated prior to reporting. No data will be disseminated by AECOM or its subcontractors until it has been subjected to the procedures summarized below.

8.1.1 Field Data

Field data will be reviewed daily by the AECOM Field Team Leader to ensure that the records are complete, accurate, and legible and to verify that the sampling procedures are in accordance with the protocols specified in the Work Plan and QAPP.

8.1.2 Internal Laboratory Review

Prior to the release of any data from the laboratory, the data will be reviewed and approved by laboratory personnel. The review will consist of a tiered approach that will include reviews by the person performing the work, by a qualified peer, and by supervisory and/or QA personnel.

8.1.3 Validation of Analytical Data

AECOM's validation staff will perform validation on the data for all parameters as described in **Section 8.2.3** of this QAPP. The validation will primarily be based on information provided by the laboratory on QC summary forms, and will include minimal or no raw data review. At a minimum, the validation will include the following data elements:

- Agreement of analyses conducted with COC requests
- Holding times and sample preservation
- Initial and continuing calibrations and analytical sequence
- Mass spectrometer tuning (GC/MS only)
- Internal standard performance (GC/MS only)
- Laboratory blanks/equipment blanks/trip blanks
- Surrogate recoveries
- Laboratory control sample/laboratory control sample (LCS/LCSD) results
- Matrix spike/matrix spike duplicate (MS/MSD) results

- Laboratory duplicate results
- Field duplicate results
- Interference check sample results
- Inductively Coupled Plasma (ICP) serial dilution results
- Endrin/dichlorodiphenyltrichloroethane (DDT) breakdown check standard results (pesticides only)
- Labeled toxics/level of chlorination/window defining/labeled clean-up recoveries (PCB congeners only)
- Percent solids
- Quantitation limits and sample results (limited to evaluating dilutions and reanalyses)

8.1.4 Data Management

Data management operations include data recording, validation, transformation, transmittal, reduction, analysis, tracking, storage and retrieval.

Upon receipt from the laboratory, PDF format reports and EDDs will be checked for completeness. During the data analysis process, a variety of quality checks are performed to ensure data integrity. These checks include:

- Audits to ensure that laboratories reported all requested analyses;
- Checks that all analytes are consistently and correctly identified;
- Reviews to ensure that units of measurement are provided and are consistent;
- Reports to review sample definitions (depths, dates, locations); and
- Proofing manually entered data against the PDF format original.

Records of the checks are maintained on file.

Once all data quality checks are performed, the data will be exported to a variety of formats to meet project needs. Cross-tab tables showing concentrations by sample location will be prepared.

The project data will be maintained on a secure network drive, which is backed up regularly. Access to the data will be limited to authorized users and will be controlled by password access. Data will be retained in accordance with the requirements stated in **Section 3.4.1** of this QAPP.

8.2 Verification and Validation methods

8.2.1 Field Data Verification

Field records will be reviewed by the AECOM Field Team Leader to ensure that:

- Logbooks and standardized forms have been filled out completely and that the information recorded accurately reflects the activities that were performed.
- Records are legible and in accordance with good recordkeeping practices, i.e., entries are signed and dated, data are not obliterated, changes are initialed, dated, and explained.
- Sample collection, handling, preservation, and storage procedures were conducted in accordance with the protocols described in the QAPP, and that any deviations were documented and approved by the appropriate personnel.
- Field calibration, replicate and duplicate sample results are within acceptable ranges and any deviations were properly documented and approved by the appropriate personnel.

8.2.2 Laboratory Data Verification

Prior to being released as final, laboratory data will proceed through a tiered review process. Data verification starts with the analyst who performs a 100 percent review of the data to ensure the work was done correctly the first time. The data reduction and initial verification process must ensure that:

- Sample preparation and analysis information is correct and complete,
- Analytical results are correct and complete,
- The appropriate SOPs have been followed and are identified in the project records,
- Proper documentation procedures have been followed, and
- All nonconformances have been documented.

Following the completion of the initial verification by the analyst performing the data reduction, a systematic check of the data will be performed by an experienced peer or supervisor. This check will be performed to ensure that initial review has been completed correctly and thoroughly and will include a review of

- Adherence to the requested analytical method SOP,
- Correct interpretation of chromatograms, mass spectra, etc.,
- Correctness of numerical input when computer programs are used (checked randomly),
- Correct identification and quantification of constituents with appropriate qualifiers,
- Numerical correctness of calculations and formulas (checked randomly),

- Acceptability of QC data,
- Documentation that instruments were operating according to method specifications (calibrations, performance checks, etc.),
- Documentation of dilution factors, standard concentrations, etc.,
- Sample holding time assessment.

A third-level review will be performed by the Laboratory Project Manager before results are submitted to clients. This review serves to verify the completeness of the data report and to ensure that project requirements are met for the analyses performed. A narrative to accompany the final report will be prepared by the Laboratory Project Manager.

8.2.3 Validation of Analytical Deliverables

Validation of the data described in **Section 8.1.3** of this QAPP will be performed using EPA National Functional Guidelines for Inorganic Superfund Data Review (USEPA, 2010) and EPA National Functional Guidelines for Superfund Organic Methods Data Review (USEPA, 2008), modified as appropriate for non-CLP methods.

Upon completion of the validation, a report will be prepared. This report will summarize the samples reviewed, elements reviewed, any non-conformances with the established criteria, and validation actions (including application of data qualifiers). Data qualifiers will be consistent with the USEPA guidelines.

8.2.4 Verification during Data Management

All manually entered data (e.g., field data) will be proofed 100 percent against the original. Electronic data will be checked after loading against laboratory data sheets for completeness and spot checked for accuracy.

8.3 Reconciliation with User Requirements

8.3.1 Comparison to Measurement Objectives

The field and laboratory data collected during this investigation will be used to achieve the objectives identified in **Section 3.3** of this QAPP. The QC results associated with each analytical parameter for each matrix will be compared to the measurement objectives presented in **Section 3.3.2** of this QAPP. Only data generated in association with QC results meeting the stated acceptance criteria (i.e., data determined to be valid) will be considered usable for decision making purposes. Rejected data will be clearly indicated during validation and made unavailable for use.

Accuracy Assessment

One measure of accuracy will be %Rs, which is calculated for matrix spikes, surrogates, and LCSs. Percent recoveries for MS/MSD results will be determined according to the following equation:

$$\%R = \frac{(Amount\ in\ Spiked\ Sample - Amount\ in\ Sample)}{Known\ Amount\ Added} x\,100$$

Percent recoveries for surrogates and LCS results will be determined according to the following equation:

$$\%R = \frac{Experimental\ Concentration}{Known\ Amount\ Added} x\,100$$

An additional measure of accuracy is blank contamination. The blanks associated with this project include laboratory method blanks and field blanks (e.g., trip blanks). The results of the laboratory and field blanks will be compared to the objectives in stated **Table 1** of the QAPP. Failure to meet these objectives may indicate a systematic laboratory or field problem that should be investigated and resolved immediately. Associated data may be qualified and limitations placed on its use, depending on the magnitude of the problem.

Precision Assessment

The RPD between the matrix spike and matrix spike duplicate and field duplicate pair is calculated to compare to precision objectives (**Table 1** of this QAPP). The RPD will be calculated according to the following formula.

$$RPD = \frac{(Amount\ in\ Sample\,1 - Amount\ in\ Sample\ 2)}{0.5\,(Amount\ in\ Sample\,1 + Amount\ in\ Sample\ 2)} x\,100$$

Failure to achieve precision objectives may result in the associated data being qualified (**Section 8.2.3**) and limitations placed upon its use.

Completeness Assessment

Completeness is the ratio of the number of valid sample results to the total number of samples analyzed with a specific matrix and/or analysis. Following completion of the analytical testing, the percent completeness will be calculated by the following equation:

$$Completeness = \frac{(number\ of\ valid\ measurements)}{(number\ of\ measurements\ planned)} x\,100$$

Failure to meet the completeness objective will require an assessment to determine if the missing or invalid data are critical to achieving the project objectives. Corrective actions may include resampling or re-analysis, depending on the type of problem, logistical constraints, etc.

8.3.2 Comparison to Project Objectives

In addition to the comparison described in **Section 8.3.1**, the data obtained will be both qualitatively and quantitatively assessed on a project-wide, matrix-specific, and parameter-specific basis. Factors to be considered in this assessment of field and laboratory data will include, but not necessarily be limited to, the following.

- Conformance to the field methodologies and SOPs proposed in the Work Plan and QAPP,
- Conformance to the analytical methodologies provided in the QAPP,
- Adherence to proposed sampling strategy,
- Presence of elevated detection limits due to matrix interferences or contaminants present at high concentrations,
- Unusable data sets (qualified as "R") based on data validation,
- Data sets identified as usable for limited purposes (qualified as "J") based on data validation,
- Effect of qualifiers applied as a result of data review on the ability to implement the project decision rules, and
- Status of all issues requiring corrective action, as presented in the QA reports to management.

The effect of nonconformance (procedures or requirements) or noncompliant data on project objectives will be evaluated. Minor deviations from approved field and laboratory procedures and sampling approach will likely not affect the adequacy of the data as a whole in meeting the project objectives. The assessment will also entail the identification of any remaining data gaps and need to reevaluate project decision rules.

This assessment will be performed by the AECOM technical team, in conjunction with the AECOM Project QA Officer, and the results presented and discussed in detail in the final report.

9 Laboratory Quality Control

9.1 Laboratory QC samples

The analytical laboratories have a QC program in place to ensure the reliability and validity of the analysis performed at the laboratory. All analytical procedures are documented in writing as SOPs and each SOP includes the minimum requirements for the procedure. The internal QC checks differ slightly for each individual procedure and are outlined in the SOPs included in **Appendix A**. In general they include:

- Blanks (method, reagent/preparation, instrument)
- MS/MSDs
- Surrogate spikes (organic analyses)
- Laboratory duplicates
- LCSs
- Internal standard area counts (GC/MS analyses and ICP/mass spectrometry analysis)
- Endrin/DDT breakdown check standard results (OCP only)
- Calibration check compounds
- Interference checks (ICP analysis)
- Serial dilutions (ICP analysis)
- Labeled analog spike recovery (PCB congeners, PAHs by ID0016, and PCDD/PCDFs only)

The control limits for precision and accuracy will be those listed in **Table 1**.

9.2 Assessment/oversight

9.2.1 Assessment

The types of planned assessments pertinent to this program include technical surveillance audits (TSAs) of field and laboratory activities, data package audits, and data validation audits.

Field Activity TSA

If requested by the AECOM Project Manager, a TSA of field activities may be conducted by the AECOM Project QA Officer or his/her designate. The TSA includes an examination of field sampling records, field measurement results, field instrument operating and calibration records, sample collection, handling, and packaging procedures, QA

procedures, COC, sample documentation, etc. If significant deficiencies are noted, follow-up audits will be conducted.

During the audit, the auditor will keep detailed notes of audit findings. Preliminary results of the audit will be reviewed with the AECOM Field Team Leader while on site to ensure that deficiencies adversely affecting data quality are immediately identified and corrective measures initiated. Upon completion of the audit, the AECOM Project QA Officer will prepare a written audit report, which summarizes the audit findings, identifies deficiencies and recommends corrective actions. This report will be submitted to the AECOM Project Manager, who will be responsible for ensuring that corrective measures are implemented and documented. The results of the audit process will be included in the QA reports to management.

Laboratory TSA

Laboratory TSAs are conducted periodically by AECOM's QA staff as part of their analytical subcontractor monitoring program. The laboratory TSA includes a review of the following areas:

- QA organization and procedures,
- Personnel training and qualifications,
- Sample log-in procedures,
- Sample storage facilities,
- Analyst technique,
- Adherence to laboratory SOPs and project QAPP,
- Compliance with QA/QC objectives,
- Instrument calibration and maintenance,
- Data recording, reduction, review, and reporting, and
- Cleanliness and housekeeping.

Preliminary results of the systems audit will be discussed with the Laboratory Manager, Laboratory Project Manager, and Laboratory QA Coordinator. A written report that summarizes audit findings and recommends corrective actions will be prepared and submitted to the Laboratory Manager for response, and to the AECOM Project Manager. The results of the audit, including resolution of any deficiencies, will be included in the QA reports to management.

9.2.2 Response Actions

Corrective action is the process of identifying, recommending, approving, and implementing measures to counter unacceptable procedures or out-of-limit QC performance that can affect data quality. Corrective action can occur

during field activities, laboratory analyses, and data assessment. All corrective action proposed and implemented should be documented in the QA reports to management. Corrective action should only be implemented after approval by the AECOM Project Manager, or his designate.

The DDOE Project Manager will be notified of significant issues that potentially impact the achievement of the project objectives.

Field Corrective Action

Corrective action in the field may be needed when the sample network is changed (i.e., more/less samples, sampling locations other than those specified in the QAPP, etc.), or when sampling procedures and/or field analytical procedures require modification, etc. due to unexpected conditions. The field team may identify the need for corrective action. The AECOM Field Team Leader will approve the corrective action and notify the AECOM Project Manager. The AECOM Project Manager, in consultation with the AECOM Project QA Officer, will approve the corrective measure. The AECOM Field Team Leader will ensure that the corrective measure is implemented by the field team.

Corrective action resulting from internal field audits will be implemented immediately if data may be adversely affected due to unapproved or improper use of approved methods. The AECOM Project QA Officer will identify deficiencies and recommend corrective action to the AECOM Project Manager. Implementation of corrective actions will be performed by the AECOM Field Team Leader and field team. Corrective action will be documented in QA reports to the project management team.

Corrective actions will be implemented and documented in the field record book. Documentation will include:

- A description of the circumstances that initiated the corrective action,
- The action taken in response,
- The final resolution, and
- Any necessary approvals.

No staff member will initiate corrective action without prior communication of findings through the proper channels.

Laboratory Corrective Action

Corrective action in the laboratory may occur prior to, during, and after initial analyses. A number of conditions such as broken sample containers, multiple phases, low/high pH readings, and potentially high concentration samples

may be identified during sample log-in or analysis. Following consultation with laboratory analysts and supervisory personnel, it may be necessary for the Laboratory QA Coordinator to approve the implementation of corrective action. If the nonconformance causes project objectives not to be achieved, the AECOM Project Manager will be notified.

These corrective actions are performed prior to release of the data from the laboratory. The corrective action will be documented in both the laboratory's corrective action files, and in the narrative data report sent from the laboratory to the AECOM Project Manager. If the corrective action does not rectify the situation, the laboratory will contact the AECOM Project Manager, who will determine the action to be taken and inform the appropriate personnel.

Corrective Action during Data Review and Data Assessment

The need for corrective action may be identified during either data review or data assessment. Potential types of corrective action may include resampling by the field team or reinjection/reanalysis of samples by the laboratory. These actions are dependent upon the ability to mobilize the field team and whether the data to be collected is necessary to meet the required QA objectives. If the AECOM data reviewer or data assessor identifies a corrective action situation, the AECOM Project Manager will be responsible for informing the appropriate personnel.

9.2.3 Reports to Management

QA reports will be submitted to the AECOM Project Manager to ensure that any problems identified during the sampling and analysis programs are investigated and the proper corrective measures taken in response. The QA reports will include (where applicable):

- All results of field and laboratory audits,
- A summary of revisions to the QAPP,
- Results of any performance evaluation (PE) or split samples,
- Problems noted during data validation and assessment, and
- Significant QA/QC problems, recommended corrective actions, and the outcome of corrective actions.

QA reports will be prepared by the AECOM Project QA Officer and submitted on an as-needed basis.

10 References

United States Environmental Protection Agency, 2010. *National Functional Guidelines for Inorganic Superfund Data Review*. Contract Laboratory Program. January.

United States Environmental Protection Agency, 2008. *National Functional Guidelines for Superfund Organic Methods Data Review*. Contract Laboratory Program. June.

United States Environmental Protection Agency, 2001. *Quality Staff. EPA Requirements for Quality Assurance Project Plans*, EPA QA/R-5. EPA/240/B-01/003. March.

United States Environmental Protection Agency, 2006. *Quality Staff. Guidance on Systematic Planning Using the Data Quality Objectives Process*, EPA QA/G-4. EPA/240/B-06/001. February.

United States Environmental Protection Agency, 2002. *Quality Staff. EPA Guidance for Quality Assurance Project Plans*, EPA QA/G-5. EPA/240/R-02/009. December.

United States Environmental Protection Agency, 1988. *Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA*, Interim Final, EPA-540-G-89-004. October.

Figures

pepco

A PHI Company

Figure 1. Example of AECOM Chain of Custody Form

AECOM

CHAIN OF CUSTODY RECORD

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Client/Project Name:	Project Location:		Analysis Requested
Project Number:	Field Logbook No.:		
Sampler (Print Name)/(Affiliation):	Chain of Custody Tape Nos.:		
Signature:	Send Results/Report to:	TAT:	

Container Type
P – Plastic
A – Amber Glass
G – Clear Glass
V – VOA Vial
O – Other
E – Encore

Preservation
1 – HCl, 4°
2 – H_2SO_4, 4°
3 – HNO_3, 4°
4 – NaOH, 4°
5 – NaOH/ZnAc, 4°
6 – $Na_2S_2O_3$, 4°
7 – 4°

Matrix Codes:
DW – Drinking Water
WW – Wastewater
GW – Groundwater
SW – Surface Water
ST – Storm Water
W – Water
S – Soil
SL – Sludge
SD – Sediment
SO – Solid
A – Air
L – Liquid
P – Product

Field Sample No./Identification	Date	Time	COMP	GRAB	Sample Container (Size/Mat'l)	Matrix	Preserv.	Field Filtered											Lab I.D.	Remarks

Relinquished by: (Print Name)/(Affiliation) Signature:	Date: Time:	Received by: (Print Name)/(Affiliation) Signature:	Date: Time:	Analytical Laboratory (Destination):
Relinquished by: (Print Name)/(Affiliation) Signature:	Date: Time:	Received by: (Print Name)/(Affiliation) Signature:	Date: Time:	
Relinquished by: (Print Name)/(Affiliation) Signature:	Date: Time:	Received by: (Print Name)/(Affiliation) Signature:	Date: Time:	Sample Shipped Via: UPS FedEx Courier Other — Temp blank: Yes No

Serial No. ____________

Tables

Table 1. Field and Laboratory QC

QC Sample→	Field Duplicate	MS/MSD	LCS/LCSD	MS/MSD	LCS/LCSD	Surrogate Spikes	Laboratory Method Blanks	Equipment Rinsate Blanks and/or Trip Blanks	Cooler Temperature Blanks
DQI	Precision			Accuracy - Bias			Accuracy-Bias/ Contamination		Accuracy-Bias/Preservation
VOCs	Soil RPD ≤ 50%; Aqueous RPD ≤ 30%	See laboratory % recovery limits in Appendix B					Target analytes < RL*	Target analytes < RL	4°C ± 2°C
SVOCs							Target analytes < RL*	Target analytes < RL	
OCPs							Target analytes < RL	Target analytes < RL	
PCBs - Aroclors							Target analytes < RL	Target analytes < RL	
PCBs - Congeners							Target analytes < EML	Target analytes < EML	
PCDD/PCDFs							Target analytes < EML	Target analytes < EML	
Metals		Matrix Duplicate Soil RPD ≤ 35%;aqueous RPD ≤ 20%	NA	75-125%	Soil- vendor control limits; aqueous 80-120%	NA	Target analytes < RL	Target analytes < RL	
GRO		RPD ≤ 50%	RPD ≤ 25%	40 – 140%; nonane 30 – 140%	40 – 140%; nonane 30 – 140%	40 -140%	Target analytes < RL	Target analytes and ranges < RL	
DRO/ORO		RPD ≤ 50%	RPD ≤ 25%	60 – 140%	70 – 130%	60-140%	Target analytes < RL	Target analytes and ranges < RL	

*VOCs and SVOCs: Common laboratory contaminants should be <5x RL
DQI – Data Quality Indicator
NA Not applicable
MS/MSDs not applicable PCB – congener analyses
Note all limits are subject to change based on final laboratory selection and required annual laboratory QC limit updates.

Table 2. Analyte lists and reporting limits for soil and groundwater (all parameters except PCB – congeners and PCDDs/PCDFs).

Parameter	Project Screening Limits[1]				Laboratory Limits[2]			
	Water (ug/L)		Solids (mg/Kg)		Water (ug/L)		Solids (mg/Kg)	
	GW	SW	SO	SE	RL	MDL	RL	MDL
VOCs by SW-846 8260B								
1,1,1-Trichloroethane	NV	1.10E+01	3.80E+03	7.00E-02	1.00E+00	2.86E-01	5.00E-03	4.86E-04
1,1,2,2-Tetrachloroethane	4.00E+01	4.00E+00	2.80E+00	1.36E+00	1.00E+00	2.00E-01	5.00E-03	7.18E-04
1,1,2-Trichloro-1,2,2-trifluoroethane	NV	NV	1.80E+04	NA	1.00E+00	3.20E-01	5.00E-03	1.07E-03
1,1,2-Trichloroethane	1.60E+02	1.60E+01	6.80E-01	4.00E-01	1.00E+00	2.01E-01	5.00E-03	8.31E-04
1,1-Dichloroethane	nv	4.70E+01	1.70E+01	2.00E-02	1.00E+00	1.16E-01	5.00E-03	5.75E-04
1,1-Dichloroethene	7.10E+04	2.50E+01	1.10E+02	1.00E-01	1.00E+00	2.96E-01	5.00E-03	8.48E-04
1,2,3-Trichlorobenzene	7.00E+02	8.00E+00	4.90E+01	1.10E-02	1.00E+00	1.54E-01	5.00E-03	8.45E-04
1,2,4-Trichlorobenzene	7.00E+02	7.00E+01	2.70E+01	1.10E-02	1.00E+00	2.71E-01	5.00E-03	8.82E-04
1,2-Dibromo-3-chloropropane	NV	NV	6.90E-02	NA	1.00E+00	1.41E-01	5.00E-03	7.49E-04
1,2-Dibromoethane	NV	NV	1.70E-01	NA	1.00E+00	1.80E-01	5.00E-03	8.63E-04
1,2-Dichlorobenzene	1.30E+04	2.00E+02	9.80E+02	3.00E-02	1.00E+00	1.52E-01	5.00E-03	7.98E-04
1,2-Dichloroethane	3.70E+02	3.70E+01	2.20E+00	2.00E-02	1.00E+00	2.12E-01	5.00E-03	6.13E-04
1,2-Dichloropropane	1.50E+02	1.50E+01	4.70E+00	2.00E-03	1.00E+00	9.48E-02	5.00E-03	5.43E-04
1,3-Dichlorobenzene	1.90E+03	2.00E+02	1.20E+01	3.00E-02	1.00E+00	1.05E-01	5.00E-03	6.56E-04
1,4-Dichlorobenzene	1.90E+03	1.90E+02	1.20E+01	3.00E-02	1.00E+00	2.06E-01	5.00E-03	6.37E-04
1,4-Dioxane	NV	NV	1.70E+01	1.19E-01	2.00E+02	3.43E+01	1.00E+00	2.76E+02
2-Butanone	NV	1.40E+04	2.00E+04	3.50E+01	5.00E+00	5.48E-01	5.00E-03	8.82E-04
2-Hexanone	NV	9.90E+01	1.40E+02	5.82E-02	5.00E+00	1.59E-01	5.00E-03	6.90E-04
4-Methyl-2-pentanone	NV	1.70E+02	5.30E+03	2.51E-02	5.00E+00	5.28E-01	5.00E-03	6.53E-04
Acetone	NV	1.50E+03	6.30E+04	9.90E-03	5.00E+00	2.50E+00	2.00E-02	5.00E-03
Benzene	5.10E+02	5.10E+01	5.40E+00	1.00E-02	1.00E+00	1.05E-01	5.00E-03	6.75E-04
Bromochloromethane	NV	NV	6.80E+01	NA	1.00E+00	1.80E-01	5.00E-03	6.88E-04
Bromodichloromethane	1.70E+02	1.70E+01	1.40E+00	NA	1.00E+00	1.30E-01	5.00E-03	5.61E-04
Bromoform	1.40E+03	1.40E+02	2.20E+02	7.50E+01	1.00E+00	1.91E-01	5.00E-03	4.42E-04
Bromomethane	1.50E+04	1.50E+03	3.20E+00	1.37E-03	1.00E+00	3.13E-01	5.00E-03	7.39E-04
Carbon disulfide	NV	9.20E-01	3.70E+02	8.51E-04	1.00E+00	2.12E-01	5.00E-03	5.12E-04
Carbon tetrachloride	1.60E+01	1.60E+00	3.00E+00	1.70E-01	1.00E+00	1.37E-01	5.00E-03	4.46E-04
Chlorobenzene	1.60E+04	1.60E+03	1.40E+02	3.00E-02	1.00E+00	1.35E-01	5.00E-03	7.57E-04
Chloroethane	NV	NV	6.10E+03	NA	1.00E+00	2.15E-01	5.00E-03	1.55E-03
Chloroform	4.70E+03	4.70E+02	1.50E+00	2.00E-02	1.00E+00	1.71E-01	5.00E-03	5.85E-04
Chloromethane	NV	NV	5.00E+01	NA	1.00E+00	2.83E-01	5.00E-03	8.52E-04
cis-1,2-Dichloroethene	NV	NV	2.00E+02	2.00E-01	1.00E+00	2.37E-01	5.00E-03	7.03E-04
cis-1,3-Dichloropropene	NV	NV	8.30E+00	NA	1.00E+00	1.87E-01	5.00E-03	6.78E-04
Cyclohexane	NV	NV	2.90E+03	NA	1.00E+00	2.54E-01	5.00E-03	3.71E-04
Dibromochloromethane	1.30E+02	1.30E+01	3.30E+00	NA	1.00E+00	1.37E-01	5.00E-03	7.10E-04
Dichlorodifluoromethane	NV	NV	4.00E+01	NA	1.00E+00	1.93E-01	5.00E-03	6.66E-04

Table 2. Analyte lists and reporting limits for soil and groundwater (all parameters except PCB – congeners and PCDDs/PCDFs).

	Project Screening Limits[1]				Laboratory Limits[2]			
	Water (ug/L)		Solids (mg/Kg)		Water (ug/L)		Solids (mg/Kg)	
Parameter	GW	SW	SO	SE	RL	MDL	RL	MDL
Ethylbenzene	2.10E+04	4.00E+01	2.70E+01	3.00E-02	1.00E+00	2.27E-01	5.00E-03	6.43E-04
Isopropylbenzene	NV	2.60E+00	1.10E+03	8.60E-02	1.00E+00	1.64E-01	5.00E-03	6.79E-04
Methyl acetate	NV	NV	1.00E+05	NA	1.00E+00	1.38E-01	5.00E-03	9.01E-04
Methylcyclohexane	NV	NV	2.90E+03	NA	1.00E+00	2.61E-01	5.00E-03	7.25E-04
Methylene chloride	NV	5.90E+02	3.10E+02	1.80E-02	1.00E+00	1.49E-01	5.00E-03	6.72E-04
Methyl-tert-butyl ether	NV	1.11E+04	2.20E+02	1.00E+02	1.00E+00	1.83E-01	5.00E-03	7.48E-04
o-Xylene	NV	3.50E+02	3.00E+02	8.90E-02	1.00E+00	1.09E-01	5.00E-03	7.79E-04
p+m-Xylene	NV	NV	2.60E+02	NA	2.00E+00	4.06E-01	1.00E-02	1.47E-03
Styrene	NV	7.20E+01	3.60E+03	2.00E-01	1.00E+00	9.66E-02	5.00E-03	7.05E-04
Tetrachloroethene	3.30E+01	3.30E+00	4.10E+01	2.00E-03	1.00E+00	1.49E-01	5.00E-03	6.80E-04
Toluene	1.50E+05	6.00E+02	4.50E+03	1.00E-02	1.00E+00	1.50E-01	5.00E-03	7.30E-04
trans-1,2-Dichloroethene	1.00E+05	1.00E+04	6.90E+01	2.00E-01	1.00E+00	1.70E-01	5.00E-03	5.96E-04
trans-1,3-Dichloropropene	NV	5.50E-02	8.30E+00	NA	1.00E+00	1.48E-01	5.00E-03	5.98E-04
Trichloroethene	3.00E+02	NV	2.00E+00	NA	1.00E+00	1.43E-01	5.00E-03	6.58E-04
Trichlorofluoromethane	NV	1.10E+04	3.40E+02	NA	1.00E+00	1.99E-01	5.00E-03	9.19E-04
Vinyl chloride	2.40E+01	2.40E+00	1.70E+00	1.00E-02	1.00E+00	2.27E-01	5.00E-03	4.69E-04
SVOCs by SW-846 8270C (with low level PAHs)								
1,1-Biphenyl	NV	1.40E+01	2.10E+01	1.22E+00	1.00E+00	4.15E-02	3.30E-02	2.98E-03
1,2,4,5-Tetrachlorobenzene	NV	1.10E+00	1.80E+01	1.00E-02	1.00E+00	6.51E-02	3.30E-02	2.53E-02
2,2'-Oxybis(1-chloropropane)	6.50E+06	6.50E+04	2.20E+01	NA	2.00E-01	1.97E-02	6.70E-03	7.20E-04
2,3,4,6-Tetrachlorophenol	NV	1.20E+00	1.80E+03	1.00E-02	1.00E+00	1.35E-01	3.30E-02	2.14E-02
2,4,5-Trichlorophenol	NV	3.60E+03	6.20E+03	1.00E-02	1.00E+00	1.53E-01	3.30E-02	3.56E-03
2,4,6-Trichlorophenol	2.40E+01	2.40E+00	6.20E+01	1.00E-02	1.00E+00	1.75E-01	3.30E-02	4.99E-03
2,4-Dichlorophenol	2.90E+03	1.10E+01	1.80E+02	1.00E-02	2.00E-01	3.34E-02	6.70E-03	6.69E-04
2,4-Dimethylphenol	8.50E+03	2.00E+02	1.20E+03	2.90E-02	1.00E+00	8.52E-02	3.30E-02	5.22E-03
2,4-Dinitrophenol	5.30E+04	5.30E+03	1.20E+02	6.21E-03	5.00E+00	6.13E-01	1.70E-01	3.97E-02
2,4-Dinitrotoluene	3.40E+01	3.40E+00	5.50E+00	4.16E-02	1.00E+00	5.36E-02	3.30E-02	2.69E-03
2,6-Dinitrotoluene	5.30E+04	3.40E+00	6.20E+01	4.16E-02	1.00E+00	7.97E-02	3.30E-02	3.44E-03
2-Chloronaphthalene	1.60E+04	2.00E+02	8.20E+03	2.50E-01	2.00E-01	1.51E-02	6.70E-03	6.96E-04
2-Chlorophenol	1.50E+03	1.00E+02	5.10E+02	5.50E-02	1.00E+00	1.65E-01	3.30E-02	2.73E-03
2-Methylnaphthalene	NV	4.70E+00	2.20E+02	2.02E-02	2.00E-01	1.22E-02	6.70E-03	6.00E-04
2-Methylphenol	NV	1.30E+01	3.10E+03	5.10E-03	1.00E+00	8.62E-02	3.30E-02	2.33E-03
2-Nitroaniline	NV	NV	6.00E+02	NV	5.00E+00	3.52E-01	1.70E-01	1.49E-02
2-Nitrophenol	8.60E+06	1.92E+03	1.80E+04	1.33E-02	1.00E+00	1.71E-01	3.30E-02	3.68E-03
3& 4-Methylphenol	NV	2.80E-02	3.80E+00	1.27E-01	1.00E+00	9.02E-02	3.30E-02	3.27E-03
3,3'-Dichlorobenzidine	2.80E-01	NV	8.60E+01	NV	1.00E+00	1.12E-01	3.30E-02	3.53E-03
3-Nitroaniline	NV	2.80E+02	4.90E+00	1.04E-01	5.00E+00	3.21E-01	1.70E-01	1.37E-02
4,6-Dinitro-2-methylphenol	2.80E+03	1.50E+00	NV	1.23E+00	5.00E+00	2.20E-01	1.70E-01	1.34E-02

Table 2. Analyte lists and reporting limits for soil and groundwater (all parameters except PCB – congeners and PCDDs/PCDFs).

	Project Screening Limits[1]				Laboratory Limits[2]			
	Water (ug/L)		Solids (mg/Kg)		Water (ug/L)		Solids (mg/Kg)	
Parameter	GW	SW	SO	SE	RL	MDL	RL	MDL
4-Bromophenyl phenyl ether	NV	NV	6.20E+03	1.50E+01	1.00E+00	6.35E-02	3.30E-02	2.90E-03
4-Chloro-3-methyl phenol	1.50E+03	2.32E+02	8.60E+00	1.46E-01	1.00E+00	7.54E-02	3.30E-02	3.07E-03
4-Chloroaniline	NV	NV	NV	NV	1.00E+00	8.85E-02	3.30E-02	2.67E-03
4-Chlorophenyl phenyl ether	NV	5.43E+02	6.20E+03	5.10E-03	1.00E+00	5.03E-02	3.30E-02	3.71E-03
4-Nitroaniline	NV	NV	8.60E+01	NV	5.00E+00	1.72E-01	1.70E-01	1.35E-02
4-Nitrophenol	8.60E+06	6.00E+01	1.80E+04	1.33E-02	5.00E+00	6.47E-01	1.70E-01	1.22E-02
Acenaphthene	9.90E+03	5.00E+01	3.30E+03	6.71E-03	2.00E-01	1.44E-02	6.70E-03	6.41E-04
Acenaphthylene	9.90E+03	4.84E+03	3.30E+03	5.87E-03	2.00E-01	1.52E-02	6.70E-03	7.64E-04
Acetophenone	NV	NV	1.00E+04	NV	1.00E+00	8.00E-02	3.30E-02	2.74E-03
Anthracene	4.00E+05	4.00E+04	1.70E+04	1.00E-02	2.00E-01	1.51E-01	6.70E-03	6.53E-04
Atrazine	NV	1.80E+00	7.50E+00	2.00E-04	1.00E+00	8.92E-02	3.30E-02	3.25E-03
Benzaldehyde	NV	NV	1.00E+04	NV	1.00E+00	1.50E-01	3.30E-02	5.00E-03
Benzo(a)anthracene	1.80E-01	1.80E-02	2.10E-01	3.19E-02	2.00E-01	1.47E-02	6.70E-03	8.36E-04
Benzo(a)pyrene	1.80E-01	1.80E-02	2.10E+00	1.57E-02	2.00E-01	1.34E-02	6.70E-03	6.68E-04
Benzo(b)fluoranthene	1.80E-01	1.80E-02	2.10E+00	1.04E+01	2.00E-01	1.57E-02	6.70E-03	1.05E-03
Benzo(g,h,i)perylene	4.00E+04	7.64E+00	1.70E+03	1.70E-01	2.00E-01	1.51E-02	6.70E-03	6.64E-04
Benzo(k)fluoranthene	1.80E-01	NV	2.10E+01	2.72E-02	2.00E-01	5.47E-02	6.70E-03	1.35E-03
bis(2-Chloroethoxy)methane	NV	1.10E+04	1.80E+02	NV	1.00E+00	5.81E-02	3.30E-02	2.20E-03
bis(2-Chloroethyl)ether	5.30E+00	NV	1.00E+00	3.52E+00	2.00E-01	2.51E-02	6.70E-03	8.95E-04
bis(2-Ethylhexyl)phthalate	2.20E+01	1.60E+01	1.20E+02	1.00E-01	2.00E+00	1.25E+00	6.67E-02	5.39E-03
Butyl benzyl phthalate	1.90E+04	1.90E+01	9.10E+02	1.00E-01	1.00E+00	1.42E-01	3.30E-02	4.56E-03
Caprolactam	NV	NV	3.10E+04	NV	5.00E+00	1.19E+00	1.70E-01	2.52E-02
Carbazole	NV	NV	2.20E+03	NV	2.00E-01	1.58E-02	6.70E-03	6.15E-04
Chrysene	1.80E-01	1.80E-02	2.10E+02	2.68E-02	2.00E-01	1.40E-02	6.70E-03	7.94E-04
Dibenzo(a,h)anthracene	1.80E-01	1.80E-02	2.10E-01	6.22E-03	2.00E-01	1.55E-02	6.70E-03	7.42E-04
Dibenzofuran	NV	3.70E+00	1.00E+02	5.10E+00	1.00E+00	6.17E-02	3.30E-02	3.28E-03
Diethyl phthalate	4.40E+05	2.10E+02	4.90E+04	5.30E-01	1.00E+00	1.46E-01	3.30E-02	3.64E-03
Dimethyl phthalate	1.10E+07	3.00E+00	4.90E+04	1.00E+00	1.00E+00	7.65E-02	3.30E-02	3.63E-03
Di-n-butyl phthalate	4.50E+04	1.90E+01	6.20E+03	1.10E-01	1.00E+00	1.25E-01	3.30E-02	4.18E-03
Di-n-octyl phthalate	NV	2.20E+01	6.20E+03	1.00E-01	1.00E+00	2.07E-01	3.30E-02	3.52E-03
Fluoranthene	1.40E+03	1.40E+02	2.20E+03	3.15E-02	2.00E-01	1.62E-02	6.70E-03	7.13E-04
Fluorene	5.30E+04	5.30E+03	2.20E+03	1.00E-02	2.00E-01	2.16E-02	6.70E-03	8.79E-04
Hexachlorobenzene	2.90E-03	2.90E-04	1.10E+00	1.40E-03	2.00E-01	1.83E-02	6.70E-03	7.11E-04
Hexachlorobutadiene	1.80E+02	1.00E+01	2.20E+01	2.65E-02	2.00E-01	1.66E-02	6.70E-03	7.47E-04
Hexachlorocyclopentadiene	1.10E+04	5.00E-01	3.70E+02	9.01E-01	1.00E+00	5.18E-02	3.30E-02	3.60E-03
Hexachloroethane	3.30E+01	3.30E+00	4.30E+01	1.03E+00	1.00E+00	6.28E-02	3.30E-02	2.40E-03
Indeno(1,2,3-cd)pyrene	1.80E-01	4.31E+00	2.10E+00	1.73E-02	2.00E-01	1.99E-02	6.70E-03	6.87E-04
Isophorone	9.60E+03	9.60E+02	1.80E+03	4.32E-01	1.00E+00	6.44E-02	3.30E-02	2.51E-03

Table 2. Analyte lists and reporting limits for soil and groundwater (all parameters except PCB – congeners and PCDDs/PCDFs).

	Project Screening Limits[1]				Laboratory Limits[2]			
	Water (ug/L)		Solids (mg/Kg)		Water (ug/L)		Solids (mg/Kg)	
Parameter	**GW**	**SW**	**SO**	**SE**	**RL**	**MDL**	**RL**	**MDL**
Naphthalene	NV	6.00E+02	1.80E+01	1.47E-02	2.00E-01	1.40E-02	6.70E-03	5.75E-04
Nitrobenzene	6.90E+03	6.90E+02	2.40E+01	1.45E-01	2.00E+00	8.43E-02	6.67E-02	2.78E-03
N-Nitroso-di-n-propylamine	5.10E+00	NV	2.50E-01	NV	2.00E-01	3.08E-02	6.70E-03	7.82E-04
N-Nitrosodiphenylamine	6.00E+01	2.10E+02	3.50E+02	2.68E+00	1.00E+00	8.53E-02	3.30E-02	3.09E-03
Pentachlorophenol	3.00E+01	3.00E+00	2.70E+00	1.00E-02	1.00E+00	6.63E-02	3.30E-02	2.98E-03
Phenanthrene	4.00E+05	4.00E-01	1.70E+04	1.87E-02	2.00E-01	4.27E-02	6.70E-03	1.06E-03
Phenol	8.60E+06	4.00E+00	1.80E+04	4.80E-02	2.00E-01	5.81E-02	6.70E-03	7.88E-04
Pyrene	4.00E+04	2.50E-02	1.70E+03	4.43E-02	2.00E-01	1.57E-02	6.70E-03	6.75E-04
Pesticides by SW-846 8081B (low level)								
4,4'-DDD	3.10E-03	3.10E-04	7.20E+00	3.54E-03	1.30E-03	6.70E-04	8.33E-05	1.09E-05
4,4'-DDE	2.20E-03	2.20E-04	5.10E+00	3.16E-03	1.30E-03	7.90E-04	8.33E-05	1.26E-05
4,4'-DDT	2.20E-03	2.20E-04	7.00E+00	1.19E-03	1.30E-03	7.40E-04	8.33E-05	1.25E-05
Aldrin	5.00E-04	3.00E+00	1.00E-01	2.00E-03	1.30E-03	8.30E-04	8.33E-05	1.49E-05
alpha-BHC	4.90E-02	1.00E-02	2.70E-01	6.00E-03	1.30E-03	6.60E-04	8.33E-05	1.36E-05
alpha-Chlordane	8.10E-04	2.20E-03	6.50E+00	<0.00003	1.30E-03	9.80E-04	8.33E-05	1.65E-05
beta-BHC	1.70E-01	1.00E-02	9.60E-01	5.00E-03	1.30E-03	1.00E-03	8.33E-05	2.16E-05
delta-BHC	4.90E-02	1.41E+02	2.70E-01	1.00E-02	1.30E-03	3.80E-04	8.33E-05	1.28E-05
Dieldrin	5.40E-04	5.60E-02	1.10E-01	1.90E-03	1.30E-03	8.20E-04	8.33E-05	1.39E-05
Endosulfan I	8.90E+02	5.60E-02	3.70E+02	2.90E-03	1.30E-03	9.40E-04	8.33E-05	1.57E-05
Endosulfan II	8.90E+02	5.60E-02	3.70E+02	1.40E-02	1.30E-03	9.80E-04	8.33E-05	1.47E-05
Endosulfan Sulfate	8.90E+02	5.60E-02	3.70E+02	5.40E-03	1.30E-03	5.70E-04	8.33E-05	8.70E-06
Endrin	6.00E-01	3.60E-02	1.80E+01	2.22E-03	1.30E-03	9.60E-04	8.33E-05	1.62E-05
Endrin Aldehyde	3.00E+00	3.00E-01	1.80E+01	2.22E-03	1.30E-03	9.00E-04	8.33E-05	1.62E-05
Endrin Ketone	6.00E-01	3.60E-02	1.80E+01	2.22E-03	1.30E-03	9.20E-04	8.33E-05	1.30E-05
gamma-BHC (Lindane)	1.80E+01	1.00E-02	2.10E+00	2.37E-03	1.30E-03	8.00E-04	8.33E-05	1.46E-05
gamma-Chlordane	8.10E-03	2.20E-03	6.50E+00	<0.00003	1.30E-03	9.60E-04	8.33E-05	1.64E-05
Heptachlor	7.90E-04	7.90E-05	3.80E-01	1.00E-02	1.30E-03	9.90E-04	8.33E-05	1.85E-05
Heptachlor Epoxide	3.90E-04	3.90E-05	1.90E-01	6.00E-04	1.30E-03	9.70E-04	8.33E-05	1.62E-05
Methoxychlor	NV	3.00E-02	3.10E+02	1.87E-02	2.50E-03	9.10E-04	1.67E-04	1.74E-05
Toxaphene	2.80E-03	2.80E-04	1.60E+00	1.00E-04	1.00E-01	1.86E-02	3.33E-03	5.56E-04
PCB – Aroclors by SW-846 8082A								
Aroclor -1016	6.40E-04	6.40E-05	3.70E+00	2.60E-02	1.00E-02	2.52E-03	8.33E-01	1.24E-01
Aroclor -1221	6.40E-04	6.40E-05	5.40E-01	2.60E-02	1.00E-02	2.49E-03	8.33E-01	1.59E-01
Aroclor -1232	6.40E-04	6.40E-05	5.40E-01	2.60E-02	1.00E-02	2.93E-03	8.33E-01	1.43E-01
Aroclor -1242	6.40E-04	6.40E-05	7.40E-01	2.60E-02	1.00E-02	1.86E-03	8.33E-01	1.36E-01
Aroclor -1248	6.40E-04	6.40E-05	7.40E-01	2.60E-02	1.00E-02	2.27E-03	8.33E-01	7.88E-02
Aroclor -1254	6.40E-04	6.40E-05	7.40E-01	6.00E-02	1.00E-02	2.29E-03	8.33E-01	1.19E-01
Aroclor -1260	6.40E-04	6.40E-05	7.40E-01	2.60E-02	1.00E-02	1.36E-03	8.33E-01	1.18E-01

Table 2. Analyte lists and reporting limits for soil and groundwater (all parameters except PCB – congeners and PCDDs/PCDFs).

	Project Screening Limits[1]				Laboratory Limits[2]			
	Water (ug/L)		Solids (mg/Kg)		Water (ug/L)		Solids (mg/Kg)	
Parameter	**GW**	**SW**	**SO**	**SE**	**RL**	**MDL**	**RL**	**MDL**
Aroclor -1262	6.40E-04	6.40E-05	7.40E-01	2.60E-02	1.00E-02	1.36E-03	8.33E-01	1.18E-01
Aroclor -1268	6.40E-04	6.40E-05	7.40E-01	2.60E-02	1.00E-02	1.36E-03	8.33E-01	1.18E-01
GRO by SW-846 8015B								
Gasoline Range Organics (C6-C10)	NV	NV	NV	NV	100	TBD	0.05	TBD
DRO and ORO by SW-846 8015B								
Diesel Range Organics (C10-C28)	NV	NV	NV	NV	100	TBD	40	TBD
Oil Range Organics (C28-C36)	NV	NV	NV	NV	100	TBD	40	TBD
Metals by SW-846 6020A, 6010C, 7471B , and 7470A								
Aluminum	NV	8.70E+01	9.90E+04	NV	2.00E+02	9.68E+00	2.00E+01	1.08E+00
Antimony	6.40E+03	6.40E+02	4.10E+01	2.00E+00	2.00E+00	1.87E-02	2.00E-01	2.60E-03
Arsenic	1.40E+00	1.40E-01	1.60E+00	5.90E+00	1.00E+00	2.91E-01	1.00E-01	1.81E-02
Barium	NV	4.00E+00	1.90E+04	7.00E-01	1.00E+01	9.80E-02	1.00E+00	1.07E-02
Beryllium	NV	6.60E-01	2.00E+02	NV	1.00E+00	3.67E-02	1.00E-01	7.50E-03
Cadmium	NV	8.35E-01	8.00E+01	5.83E-01	1.00E+00	1.14E-01	1.00E-01	7.00E-03
Calcium	NV	1.16E+05	NV	NV	5.00E+03	9.68E+00	5.00E+02	9.82E-01
Chromium	NV	8.50E+01	5.60E+00	2.60E+01	2.00E+00	5.43E-01	2.00E-01	6.10E-03
Cobalt	NV	2.30E+01	3.00E+01	5.00E+01	5.00E-01	2.63E-02	5.00E-02	1.50E-03
Copper	NV	2.03E+01	4.10E+03	3.16E+01	2.50E+01	2.71E+00	2.50E+00	3.42E-01
Iron	NV	1.00E+03	7.20E+04	2.00E+04	1.00E+02	1.19E+01	1.00E+01	2.98E+00
Lead	NV	3.60E+00	8.00E+01	3.10E+01	1.00E+00	1.92E-02	1.00E-01	3.80E-03
Magnesium	NV	8.20E+04	NV	NV	5.00E+03	2.07E+01	5.00E+02	2.21E+00
Manganese	1.00E+03	1.20E+02	2.30E+03	4.60E+02	1.50E+01	6.80E-01	1.50E+00	4.80E-02
Mercury	NV	7.70E-01	4.30E+00	1.74E-01	2.00E-01	3.84E-02	3.30E-02	1.09E-02
Nickel	4.60E+04	7.28E+01	2.00E+03	1.60E+01	1.00E+00	1.75E-01	1.00E-01	1.13E-02
Potassium	NV	5.30E+04	NV	NV	5.00E+03	7.50E+02	5.00E+02	7.50E+01
Selenium	4.20E+04	5.00E+00	5.10E+02	NV	5.00E+00	4.22E-01	5.00E-01	5.02E-02
Silver	NV	3.20E+00	5.10E+02	5.00E-01	1.00E+00	3.62E-02	1.00E-01	3.90E-03
Sodium	NV	6.80E+05	NV	NV	5.00E+03	2.15E+02	5.00E+02	8.21E+00
Thallium	4.70E+00	4.70E-01	1.00E+00	NV	1.00E+00	1.52E-02	1.00E-01	2.00E-03
Vanadium	NV	2.00E+01	5.20E+02	NV	1.00E+00	8.24E-02	1.00E-01	7.90E-03
Zinc	2.60E+05	1.67E+02	3.10E+04	9.80E+01	2.00E+01	2.46E+00	2.00E+00	2.23E-01

Notes:

1. Project Screening Limits derived the following sources by matrix:

Groundwater (GW) = USEPA National Recommended Water Quality Criteria 2009 for human health (organisms only), default DAF of 10 applied.
Surface Water (SW) = lowest of DDOE WQS Criteria, USEPA Region 3 Surface Water Criteria, and literature based benchmarks (Suter & Tsao 1996 and Buchman 2008)
Soils (SO) = USEPA Regional Screening Levels (RSLs). Industrial Soil. May 2010
Sediment (SE) = lowest of the NOAA SQuiRTS, USEPA Region 3 BTAG Freshwater Sediment Screening Benchmarks, USEPA Region 5 Ecological Screening Levels, or Ontario Ministry of the Environment Provincial Sediment Quality Guidelines

NOTE: Project Screening Limits are risk based and may not be achievable using EPA method laboratory techniques.

2 Adjustments for sample moisture and dilutions may elevate sample specific limits. Note all limits are subject to change based on final laboratory selection and required annual laboratory detection limit updates

NV No value available NA Not applicable

Table 3. Analyte lists and detection limits for HRMS and isotope dilution methods.

Parameter		Project Screening Limit[1]				Estimated Minimum Level/ Estimated Detection Limit*			
		Water (pg/L)		Solids (pg/g)		Water (pg/L)		Solids (pg/g)	
		GW	SW	SO	SE	EML	EDL	EML	EDL
CB Name	IUPAC Number								
PCB – Congeners by EPA Method 1668C									
2-MoCB	1	640	NV	740000	2.5	40	0.6	5	0.2
3-MoCB	2	640	NV	740000	2.5	40	0.64	5	0.23
4-MoCB	3	640	NV	740000	2.5	40	0.7	5	0.27
2,2'-DiCB	4	640	NV	740000	2.5	40	3.8	5	1.54
2,3-DiCB	5	640	NV	740000	2.5	40	2.9	5	1.26
2,3'-DiCB	6	640	NV	740000	2.5	40	2.68	5	1.19
2,4-DiCB	7	640	NV	740000	2.5	40	2.76	5	1.22
2,4'-DiCB3	8	640	NV	740000	2.5	40	2.6	5	1.16
2,5-DiCB	9	640	NV	740000	2.5	40	2.76	5	1.23
2,6-DiCB	10	640	NV	740000	2.5	40	2.98	5	1.32
3,3'-DiCB	11	640	NV	740000	2.5	40	2.64	5	1.17
3,4-DiCB	12	640	NV	740000	2.5	40	2.7	5	1.2
3,4'-DiCB	13	640	NV	740000	2.5	40	2.7	5	1.2
3,5-DiCB	14	640	NV	740000	2.5	40	2.34	5	1.03
4,4'-DiCB	15	640	NV	740000	2.5	40	2.76	5	1.31
2,2',3-TrCB	16	640	NV	740000	2.5	40	2.58	5	1.03
2,2',4-TrCB	17	640	NV	740000	2.5	40	2.16	5	0.86
2,2',5-TrCB3	18	640	NV	740000	2.5	40	1.88	5	0.75
2,2',6-TrCB	19	640	NV	740000	2.5	40	2.64	5	1.06
2,3,3'-TrCB	20	640	NV	740000	2.5	40	0.9	5	0.47
2,3,4-TrCB	21	640	NV	740000	2.5	40	0.9	5	0.47
2,3,4'-TrCB	22	640	NV	740000	2.5	40	0.92	5	0.48
2,3,5-TrCB	23	640	NV	740000	2.5	40	0.94	5	TBD
2,3,6-TrCB	24	640	NV	740000	2.5	40	1.8	5	0.72
2,3',4-TrCB	25	640	NV	740000	2.5	40	0.84	10	0.43
2,3',5-TrCB	26	640	NV	740000	2.5	40	0.88	10	0.46
2,3',6-TrCB	27	640	NV	740000	2.5	40	1.56	10	0.62
2,4,4'-TrCB3	28	640	NV	740000	2.5	40	0.9	10	0.47
2,4,5-TrCB	29	640	NV	740000	2.5	40	0.88	10	0.46
2,4,6-TrCB	30	640	NV	740000	2.5	40	1.92	10	0.76
2,4',5-TrCB	31	640	NV	740000	2.5	40	0.88	10	0.46
2,4',6-TrCB	32	640	NV	740000	2.5	40	1.52	10	0.61
2',3,4-TrCB	33	640	NV	740000	2.5	40	0.9	10	0.47
2',3,5-TrCB	34	640	NV	740000	2.5	40	0.92	10	0.48
3,3',4-TrCB	35	640	NV	740000	2.5	40	0.94	10	0.49

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Table 3. Analyte lists and detection limits for HRMS and isotope dilution methods.

Parameter		Project Screening Limit[1]				Estimated Minimum Level/ Estimated Detection Limit*			
		Water (pg/L)		Solids (pg/g)		Water (pg/L)		Solids (pg/g)	
		GW	SW	SO	SE	EML	EDL	EML	EDL
3,3',5-TrCB	36	640	NV	740000	2.5	40	0.92	10	0.48
3,4,4'-TrCB	37	640	NV	740000	2.5	40	0.94	10	0.49
3,4,5-TrCB	38	640	NV	740000	2.5	40	0.96	10	0.5
3,4',5-TrCB	39	640	NV	740000	2.5	40	0.86	10	0.45
2,2',3,3'-TeCB	40	640	NV	740000	2.5	40	1.42	10	0.73
2,2',3,4-TeCB	41	640	NV	740000	2.5	40	1.42	10	0.73
2,2',3,4'-TeCB	42	640	NV	740000	2.5	40	1.44	10	0.74
2,2',3,5-TeCB	43	640	NV	740000	2.5	40	1.32	10	0.68
2,2',3,5'-TeCB3	44	640	NV	740000	2.5	40	1.26	10	0.64
2,2',3,6-TeCB	45	640	NV	740000	2.5	40	1.48	10	0.75
2,2',3,6'-TeCB	46	640	NV	740000	2.5	40	1.74	10	0.89
2,2',4,4'-TeCB	47	640	NV	740000	2.5	40	1.28	10	0.65
2,2',4,5-TeCB	48	640	NV	740000	2.5	40	1.4	10	0.72
2,2',4,5'-TeCB	49	640	NV	740000	2.5	40	1.18	10	0.6
2,2',4,6-TeCB	50	640	NV	740000	2.5	40	1.36	10	0.7
2,2',4,6'-TeCB	51	640	NV	740000	2.5	40	1.48	10	0.75
2,2',5,5'-TeCB3	52	640	NV	740000	2.5	40	1.36	10	0.69
2,2',5,6'-TeCB	53	640	NV	740000	2.5	40	1.36	10	0.7
2,2',6,6'-TeCB	54	640	NV	740000	2.5	40	2.06	10	0.85
2,3,3',4-TeCB	55	640	NV	740000	2.5	40	1.1	10	0.56
2,3,3',4'-TeCB	56	640	NV	740000	2.5	40	1.04	10	0.53
2,3,3',5-TeCB	57	640	NV	740000	2.5	40	1.04	10	0.54
2,3,3',5'-TeCB	58	640	NV	740000	2.5	40	1.04	10	0.53
2,3,3',6-TeCB	59	640	NV	740000	2.5	40	1.02	10	0.52
2,3,4,4'-TeCB	60	640	NV	740000	2.5	40	1.06	10	0.55
2,3,4,5-TeCB	61	640	NV	740000	2.5	40	1.02	10	0.52
2,3,4,6-TeCB	62	640	NV	740000	2.5	40	1.02	10	0.52
2,3,4',5-TeCB	63	640	NV	740000	2.5	10	0.98	10	0.5
2,3,4',6-TeCB	64	640	NV	740000	2.5	40	0.96	10	0.49
2,3,5,6-TeCB	65	640	NV	740000	2.5	40	1.28	10	0.65
2,3',4,4'-TeCB3	66	640	NV	740000	2.5	40	1.0	10	0.51
2,3',4,5-TeCB	67	640	NV	740000	2.5	40	0.94	10	0.48
2,3',4,5'-TeCB	68	640	NV	740000	2.5	40	0.94	10	0.49
2,3',4,6-TeCB	69	640	NV	740000	2.5	40	1.18	10	0.6
2,3',4',5-TeCB	70	640	NV	740000	2.5	40	1.02	10	0.52
2,3',4',6-TeCB	71	640	NV	740000	2.5	40	1.42	10	0.73
2,3',5,5'-TeCB	72	640	NV	740000	2.5	40	1.02	10	0.52
2,3',5',6-TeCB	73	640	NV	740000	2.5	40	1.32	10	0.68

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Table 3. Analyte lists and detection limits for HRMS and isotope dilution methods.

Parameter		Project Screening Limit[1]				Estimated Minimum Level/ Estimated Detection Limit*			
		Water (pg/L)		Solids (pg/g)		Water (pg/L)		Solids (pg/g)	
		GW	SW	SO	SE	EML	EDL	EML	EDL
2,4,4',5-TeCB	74	640	NV	740000	2.5	40	1.02	10	0.52
2,4,4',6-TeCB	75	640	NV	740000	2.5	40	1.02	10	0.52
2',3,4,5-TeCB	76	640	NV	740000	2.5	40	1.02	10	0.52
3,3',4,4'-TeCB3,6 DL	77	640	NV	110000	2.5	40	0.96	10	0.5
3,3',4,5-TeCB	78	640	NV	740000	2.5	40	1.08	10	0.55
3,3',4,5'-TeCB	79	640	NV	740000	2.5	40	0.96	10	0.49
3,3',5,5'-TeCB	80	640	NV	740000	2.5	40	0.92	10	0.47
3,4,4',5-TeCB6 DL	81	640	NV	38000	2.5	40	0.98	10	0.49
2,2',3,3',4-PeCB	82	640	NV	740000	2.5	40	2.12	10	0.89
2,2',3,3',5-PeCB	83	640	NV	740000	2.5	40	1.78	10	0.75
2,2',3,3',6-PeCB	84	640	NV	740000	2.5	40	2.04	10	0.85
2,2',3,4,4'-PeCB	85	640	NV	740000	2.5	40	1.48	10	0.61
2,2',3,4,5-PeCB	86	640	NV	740000	2.5	40	1.5	10	0.63
2,2',3,4,5'-PeCB	87	640	NV	740000	2.5	40	1.5	10	0.63
2,2',3,4,6-PeCB	88	640	NV	740000	2.5	40	1.82	10	0.76
2,2',3,4,6'-PeCB	89	640	NV	740000	2.5	40	1.96	10	0.82
2,2',3,4',5-PeCB	90	640	NV	740000	2.5	40	1.54	10	0.63
2,2',3,4',6-PeCB	91	640	NV	740000	2.5	40	1.82	10	0.76
2,2',3,5,5'-PeCB	92	640	NV	740000	2.5	40	1.74	10	0.73
2,2',3,5,6-PeCB	93	640	NV	740000	2.5	40	1.74	10	0.73
2,2',3,5,6'-PeCB	94	640	NV	740000	2.5	40	1.96	10	0.82
2,2',3,5',6-PeCB	95	640	NV	740000	2.5	40	1.86	10	0.77
2,2',3,6,6'-PeCB	96	640	NV	740000	2.5	40	1.48	10	0.61
2,2',3',4,5-PeCB	97	640	NV	740000	2.5	40	1.5	10	0.63
2,2',3',4,6-PeCB	98	640	NV	740000	2.5	40	1.7	10	0.71
2,2',4,4',5-PeCB	99	640	NV	740000	2.5	40	1.78	10	0.75
2,2',4,4',6-PeCB	100	640	NV	740000	2.5	40	1.74	10	0.73
2,2',4,5,5'-PeCB3	101	640	NV	740000	2.5	40	1.52	10	0.63
2,2',4,5,6'-PeCB	102	640	NV	740000	2.5	10	1.7	10	0.71
2,2',4,5,'6-PeCB	103	640	NV	740000	2.5	40	1.72	10	0.72
2,2',4,6,6'-PeCB	104	640	NV	740000	2.5	40	1.32	10	0.55
2,3,3',4,4'-PeCB3,6 DL	105	640	NV	380000	1500	40	0.88	10	0.42
2,3,3',4,5-PeCB	106	640	NV	740000	2.5	40	0.94	10	0.46
2,3,3',4',5-PeCB	107	640	NV	740000	2.5	40	0.92	10	0.45
2,3,3',4,5'-PeCB	108	640	NV	740000	2.5	40	0.96	10	0.47
5/2,3,3',4,6-PeCB	109	640	NV	740000	2.5	40	1.5	10	0.63
2,3,3',4',6-PeCB	110	640	NV	740000	2.5	40	1.3	10	0.54
2,3,3',5,5'-PeCB	111	640	NV	740000	2.5	40	1.24	10	0.51

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Table 3. Analyte lists and detection limits for HRMS and isotope dilution methods.

Parameter		Project Screening Limit[1]				Estimated Minimum Level/ Estimated Detection Limit*			
		Water (pg/L)		Solids (pg/g)		Water (pg/L)		Solids (pg/g)	
		GW	SW	SO	SE	EML	EDL	EML	EDL
2,3,3',5,6-PeCB	112	640	NV	740000	2.5	40	1.34	10	0.56
2,3,3',5',6-PeCB	113	640	NV	740000	2.5	40	1.54	10	0.63
2,3,4,4',5-PeCB6 DL	114	640	NV	380000	2.5	40	0.88	10	0.41
2,3,4,4',6-PeCB	115	640	NV	740000	2.5	40	1.3	10	0.54
2,3,4,5,6-PeCB	116	640	NV	740000	2.5	40	1.48	10	0.61
2,3,4',5,6-PeCB	117	640	NV	740000	2.5	40	1.48	10	0.61
2,3',4,4',5-PeCB3,6 DL	118	640	NV	380000	2.5	40	0.88	10	0.42
2,3',4,4',6-PeCB	119	640	NV	740000	2.5	40	1.5	10	0.63
2,3',4,5,5'-PeCB	120	640	NV	740000	2.5	40	1.26	10	0.53
2,3',4,5,'6-PeCB	121	640	NV	740000	2.5	40	1.28	10	0.53
2',3,3',4,5-PeCB	122	640	NV	740000	2.5	40	1.04	10	0.5
2',3,4,4',5-PeCB6 DL	123	640	NV	380000	2.5	40	1.02	10	0.45
2',3,4,5,5'-PeCB	124	640	NV	740000	2.5	40	0.96	10	0.47
2',3,4,5,6'-PeCB	125	640	NV	740000	2.5	40	1.5	10	0.63
3,3',4,4',5-PeCB3,6 DL	126	640	NV	110	2.5	40	0.92	10	/0.47
3,3',4,5,5'-PeCB	127	640	NV	740000	2.5	40	0.94	10	0.45
2,2',3,3',4,4'-HxCB3	128	640	NV	740000	2.5	40	1.4	10	0.69
2,2',3,3',4,5-HxCB	129	640	NV	740000	2.5	40	1.46	10	0.72
2,2',3,3',4,5'-HxCB	130	640	NV	740000	2.5	40	1.88	10	0.93
2,2',3,3',4,6-HxCB	131	640	NV	740000	2.5	40	1.92	10	0.96
2,2',3,3',4,6'-HxCB	132	640	NV	740000	2.5	40	1.38	10	0.91
2,2',3,3',5,5'-HxCB	133	640	NV	740000	2.5	40	1.76	10	0.88
2,2',3,3',5,6-HxCB	134	640	NV	740000	2.5	40	1.88	10	0.94
2,2',3,3',5,6'-HxCB	135	640	NV	740000	2.5	40	2.44	10	1.02
2,2',3,3',6,6'-HxCB	136	640	NV	740000	2.5	40	1.8	10	0.75
2,2',3,4,4',5-HxCB	137	640	NV	740000	2.5	40	1.62	10	0.81
2,2',3,4,4',5'-HxCB3	138	640	NV	740000	2.5	40	1.44	10	0.71
2,2',3,4,4',6-HxCB	139	640	NV	740000	2.5	40	1.6	10	0.8
2,2',3,4,4',6'-HxCB	140	640	NV	740000	2.5	40	1.6	10	0.8
2,2',3,4,5,5'-HxCB	141	640	NV	740000	2.5	40	1.68	10	0.83
2,2',3,4,5,6-HxCB	142	640	NV	740000	2.5	40	1.84	10	0.92
2,2',3,4,5,6'-HxCB	143	640	NV	740000	2.5	40	1.88	10	0.94
2,2',3,4,5',6-HxCB	144	640	NV	740000	2.5	40	2.26	10	0.95
2,2',3,4,6,6'-HxCB	145	640	NV	740000	2.5	40	1.72	10	0.72
2,2',3,4',5,5'-HxCB	146	640	NV	740000	2.5	40	1.52	10	0.76
2,2',3,4',5,6-HxCB	147	640	NV	740000	2.5	40	1.56	10	0.78
2,2',3,4',5,6'-HxCB	148	640	NV	740000	2.5	40	2.4	10	1.01
2,2',3,4',5',6-HxCB	149	640	NV	740000	2.5	40	1.56	10	0.78

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Table 3. Analyte lists and detection limits for HRMS and isotope dilution methods.

Parameter		Project Screening Limit[1]				Estimated Minimum Level/ Estimated Detection Limit*			
		Water (pg/L)		Solids (pg/g)		Water (pg/L)		Solids (pg/g)	
		GW	SW	SO	SE	EML	EDL	EML	EDL
2,2',3,4',6,6'-HxCB	150	640	NV	740000	2.5	40	1.68	10	0.7
2,2',3,5,5',6-HxCB	151	640	NV	740000	2.5	40	2.44	10	1.02
2,2',3,5,6,6'-HxCB	152	640	NV	740000	2.5	40	1.7	10	0.71
2,2',4,4',5,5'-HxCB3	153	640	NV	740000	2.5	40	1.24	10	0.62
2,2',4,4',5',6-HxCB	154	640	NV	740000	2.5	40	1.98	10	0.83
2,2',4,4',6,6'-HxCB	155	640	NV	740000	2.5	40	1.62	10	0.68
2,3,3',4,4',5-HxCB6 DL	156	640	NV	380000	2.5	40	1.38	10	0.69
2,3,3',4,4',5'-HxCB6 DL	157	640	NV	380000	2.5	40	1.38	10	0.69
2,3,3',4,4',6-HxCB	158	640	NV	740000	2.5	40	1.14	10	0.57
2,3,3',4,5,5'-HxCB	159	640	NV	740000	2.5	40	1.22	10	0.61
2,3,3',4,5,6-HxCB	160	640	NV	740000	2.5	40	1.46	10	0.72
2,3,3',4,5',6-HxCB	161	640	NV	740000	2.5	40	1.22	10	0.61
2,3,3',4',5,5'-HxCB	162	640	NV	740000	2.5	40	1.22	10	0.6
2,3,3',4',5,6-HxCB	163	640	NV	740000	2.5	40	1.46	10	0.72
2,3,3',4',5',6-HxCB	164	640	NV	740000	2.5	40	1.28	10	0.64
2,3,3',5,5',6-HxCB	165	640	NV	740000	2.5	40	1.34	10	0.67
2,3,4,4',5,6-HxCB	166	640	NV	740000	2.5	40	1.4	10	0.7
2,3',4,4',5,5'-HxCB6 DL	167	640	NV	380000	2.5	40	0.92	10	0.45
2,3',4,4',5',6-HxCB	168	640	NV	740000	2.5	40	1.26	10	0.62
3,3',4,4',5,5'-HxCB3,6 DL	169	640	NV	380	2.5	40	1.1	10	0.55
2,2',3,3',4,4',5-HpCB3	170	640	NV	740000	2.5	40	1.54	10	0.77
2,2'3,3',4,4',6-HpCB	171	640	NV	740000	2.5	40	1.68	10	0.78
2,2',3,3',4,5,5'-HpCB	172	640	NV	740000	2.5	40	1.66	10	0.77
2,2',3,3',4,5,6-HpCB	173	640	NV	740000	2.5	40	1.68	10	0.78
2,2',3,3',4,5,6'-HpCB	174	640	NV	740000	2.5	40	1.56	10	0.72
2,2',3,3',4,5',6-HpCB	175	640	NV	740000	2.5	40	1.5	10	0.69
2,2',3,3',4,6,6'-HpCB	176	640	NV	740000	2.5	40	1.14	10	0.69
2,2',3,3',4',5,6-HpCB	177	640	NV	740000	2.5	40	1.6	10	0.74
2,2',3,3',5,5',6-HpCB	178	640	NV	740000	2.5	40	1.62	10	0.75
2,2',3,3',5,6,6'-HpCB	179	640	NV	740000	2.5	40	1.2	10	0.56
2,2',3,4,4',5,5'-HpCB3	180	640	NV	740000	2.5	40	1.62	10	0.57
2,2',3,4,4',5,6-HpCB	181	640	NV	740000	2.5	40	1.5	10	0.69
2,2',3,4,4',5,6'-HpCB	182	640	NV	740000	2.5	40	1.46	10	0.67
2,2',3,4,4',5',6-HpCB	183	640	NV	740000	2.5	40	1.48	10	0.69
2,2',3,4,4',6,6'-HpCB	184	640	NV	740000	2.5	40	1.24	10	0.57
2,2',3,4,5,5',6-HpCB	185	640	NV	740000	2.5	40	1.48	10	0.69
2,2',3,4,5,6,6'-HpCB	186	640	NV	740000	2.5	40	1.2	10	0.55
2,2',3,4',5,5',6-HpCB3	187	640	NV	740000	2.5	40	1.38	10	0.63

Table 3. Analyte lists and detection limits for HRMS and isotope dilution methods.

Parameter		Project Screening Limit[1]				Estimated Minimum Level/ Estimated Detection Limit*			
		Water (pg/L)		Solids (pg/g)		Water (pg/L)		Solids (pg/g)	
		GW	SW	SO	SE	EML	EDL	EML	EDL
2,2',3,4',5,6,6'-HpCB	188	640	NV	740000	2.5	40	1.16	10	0.51
2,3,3',4,4',5,5'-HpCB6 DL	189	640	NV	380000	2.5	40	0.84	10	0.43
2,3,3',4,4',5,6-HpCB	190	640	NV	740000	2.5	40	1.16	10	0.54
2,3,3',4,4',5',6-HpCB	191	640	NV	740000	2.5	40	1.14	10	0.53
2,3,3',4,5,5',6-HpCB	192	640	NV	740000	2.5	40	1.28	10	0.59
2,3,3',4',5,5',6-HpCB	193	640	NV	740000	2.5	40	1.26	10	0.58
2,2',3,3',4,4',5,5'-OcCB	194	640	NV	740000	2.5	40	1.14	10	0.62
2,2',3,3',4,4',5,6-OcCB3	195	640	NV	740000	2.5	40	1.22	10	0.66
2,2',3,3',4,4',5,6'-OcCB	196	640	NV	740000	2.5	40	1.22	10	0.82
2,2',3,3',4,4',6,6'-OcCB	197	640	NV	740000	2.5	40	1.24	10	0.61
2,2',3,3',4,5,5',6-OcCB	198	640	NV	740000	2.5	40	1.72	10	0.85
2,2',3,3',4,5,5',6'-OcCB	199	640	NV	740000	2.5	40	1.22	10	0.6
2,2',3,3',4,5,6,6'-OcCB	200	640	NV	740000	2.5	40	1.18	10	0.58
2,2',3,3',4,5',6,6'-OcCB	201	640	NV	740000	2.5	40	1.72	10	0.85
2,2',3,3',5,5',6,6'-OcCB	202	640	NV	740000	2.5	40	1.32	10	0.66
2,2',3,4,4',5,5',6-OcCB	203	640	NV	740000	2.5	40	1.54	10	0.76
2,2',3,4,4',5,6,6'-OcCB	204	640	NV	740000	2.5	40	1.3	10	0.64
2,3,3',4,4',5,5',6-OcCB	205	640	NV	740000	2.5	40	0.96	10	0.53
2,2',3,3',4,4',5,5',6-NoCB3	206	640	NV	740000	2.5	40	1.7	10	0.91
2,2',3,3',4,4',5,6,6'-NoCB	207	640	NV	740000	2.5	40	1.2	10	0.64
2,2',3,3',4,5,5',6,6'-NoCB	208	640	NV	740000	2.5	40	1.24	10	0.66
DeCB3	209	640	NV	740000	2.5	40	1.64	10	0.66

Table 4. Analyte lists and detection limits for HRMS and isotope dilution methods.

Parameter	CAS Number	Project Screening Limit[1]				Lower Calibration Level/ Estimated Detection Limit*			
		Water (pg/L)		Solids (pg/g)		Water (pg/L)		Solids (pg/g)	
		GW	SW	SO	SE	EML	EDL	EML	EDL
PCDD/PCDFs –by EPA Method 8290A									
1,2,3,4,6,7,8-HPCDD	35822-46-9	NV	NV	NV	NA	50	1.6	5	0.18
1,2,3,4,6,7,8-HPCDF	67562-39-4	NV	NV	NV	NA	50	1.1	5	0.11
1,2,3,4,7,8-HxCDD	39227-28-6	NV	NV	NV	NA	50	1.6	5	0.17
1,2,3,4,7,8-HXCDF	70648-26-9	NV	NV	NV	NA	50	1.4	5	0.13
1,2,3,4,7,8,9-HPCDF	55673-89-7	NV	NV	NV	NA	50	0.82	5	0.078
1,2,3,6,7,8-HxCDD	57653-85-7	NV	NV	NV	NA	50	1.5	5	0.16
1,2,3,6,7,8-HXCDF	57117-44-9	NV	NV	NV	NA	50	0.83	5	0.077
1,2,3,7,8,9-HxCDD	19408-74-3	NV	NV	NV	NA	50	1.3	5	0.12
1,2,3,7,8,9-HXCDF	72918-21-9	NV	NV	NV	NA	50	1.1	5	0.12
1,2,3,7,8-PeCDD	40321-76-4	NV	NV	NV	NA	50	1.8	5	0.17
1,2,3,7,8-PECDF	57117-41-6	NV	NV	NV	NA	50	1.4	5	0.12
2,3,4,6,7,8-HXCDF	60851-34-5	NV	NV	NV	NA	50	0.86	5	0.084
2,3,4,7,8-PECDF	57117-31-4	NV	NV	NV	NA	50	1.2	5	0.11
2,3,7,8-TCDD	1746-01-6	5.10E-08	0.00001	18	0.85	10	3.5	1	0.31
2,3,7,8-TCDF	51207-31-9	NV	NV	NV	NA	10	2.3	1	0.20
OCDD	3268-87-9	NV	NV	NV	NA	100	1.7	10	0.20
OCDF	39001-02-0	NV	NV	NV	NA	100	1.9	10	0.21
Total HpCDF	3898-75-3	NV	NV	NV	NA	NA	NA	NA	NA
Total HpCDD	37871-00-4	NV	NV	NV	NA	NA	NA	NA	NA
Total HxCDF	55684-94-1	NV	NV	NV	NA	NA	NA	NA	NA
Total HxCDD	34465-46-8	NV	NV	NV	NA	NA	NA	NA	NA
Total PeCDF	60402-15-4	NV	NV	NV	NA	NA	NA	NA	NA
Total PeCDD	36088-22-9	NV	NV	NV	NA	NA	NA	NA	NA
Total TCDF	55722-27-5	NV	NV	NV	NA	NA	NA	NA	NA

Table 5. Analyte lists and detection limits for HRMS and isotope dilution methods.

Parameter	CAS Number	Project Screening Limit[1]				Lower Calibration Level/ Method Detection Limit*			
		Water (ug/L)		Solids (mg/kg)		Water (ng/L)		Solids (ng/g)	
		GW	SW	SO	SE	QL	MDL	QL	MDL
PAHs and alkylated PAH homologs –by Method ID0016									
Acenaphthene	83-32-9	9.90E+03	5.00E+01	3.30E+03	6.71E-03	10	2.4	1	0.21
Acenaphthylene	208-96-8	9.90E+03	4.84E+03	3.30E+03	5.87E-03	10	0.15	1	0.063
Anthracene	120-12-7	4.00E+05	4.00E+04	1.70E+04	1.00E-02	10	0.71	1	0.19
Benzo(a)anthracene	56-55-3	1.80E-01	1.80E-02	2.10E-01	3.19E-02	10	1.5	1	0.29
Benzo(b)fluoranthene	205-99-2	1.80E-01	1.80E-02	2.10E+00	1.04E+01	10	1.5	1	0.25
Benzo(k)fluoranthene	207-08-9	1.80E-01	NV	2.10E+01	2.72E-02	10	1	1	0.22
Benzo(ghi)perylene	191-24-2	4.00E+04	7.64E+00	1.70E+03	1.70E-01	10	0.51	1	0.15
Benzo(a)pyrene	50-32-8	1.80E-01	2.10E+00	1.57E-02	2.00E-01	10	0.4	1	0.19
Benzo(e)pyrene	192-97-2	NV	NV	NV	NV	10	1.4	1	0.17
Chrysene	218-01-9	1.80E-01	1.80E-02	2.10E+02	2.68E-02	10	0.22	1	0.2
C1-Chrysenes/benz(a)anthracenes	NV	NV	NV	NV	NV	10	10	1	1
C2-Chrysenes/benz(a)anthracenes	NV	NV	NV	NV	NV	10	10	1	1
C3-Chrysenes/benz(a)anthracenes	NV	NV	NV	NV	NV	10	10	1	1
C4-Chrysenes/benz(a)anthracenes	NV	NV	NV	NV	NV	10	10	1	1
Dibenz(a,h)anthracene	53-70-3	1.80E-01	1.80E-02	2.10E-01	6.22E-03	10	0.78	1	0.07
Dibenzothiophene	132-65-0	NV	NV	NV	NV	10	0.69	1	0.14
C1-Dibenzothiophenes	NA	NV	NV	NV	NV	10	10	1	1
C2-Dibenzothiophenes	NA	NV	NV	NV	NV	10	10	1	1
C3-Dibenzothiophenes	NA	NV	NV	NV	NV	10	10	1	1
C4-Dibenzothiophenes	NA	NV	NV	NV	NV	10	10	1	1
2,6-Dimethylnaphthalene	581-42-0	NV	NV	NV	NV	10	2.2	2	0.44
Fluoranthene	206-44-0	1.40E+03	1.40E+02	2.20E+03	3.15E-02	10	2.4	1	0.36
C1-Fluoranthenes/pyrenes	NA	NV	NV	NV	NV	10	10	1	1
Fluorene	86-73-7	5.30E+04	5.30E+03	2.20E+03	1.00E-02	10	1.5	1	0.47
C1-Fluorenes	NA	NV	NV	NV	NV	10	10	1	1
C2-Fluorenes	NA	NV	NV	NV	NV	10	10	1	1
C3-Fluorenes	NA	NV	NV	NV	NV	10	10	1	1
Indeno(1,2,3-cd)pyrene	193-39-5	1.80E-01	4.31E+00	2.10E+00	1.73E-02	10	1	1	0.17
2-Methylnaphthalene	91-57-6	NA	4.70E+00	2.20E+02	2.02E-02	20	8.3	10	2.9
1-Methylnaphthalene	90-12-0	NA	NV	NV	NV	10	4.1	5	1.3
Naphthalene	91-20-3	NV	6.00E+02	1.80E+01	1.47E-02	50	16	20	5.3
C2-Naphthalenes	NA	NV	NV	NV	NV	10	10	2	2
C3-Naphthalenes	NA	NV	NV	NV	NV	10	10	2	2
C4-Naphthalenes	NA	NV	NV	NV	NV	10	10	1	1
Perylene	198-55-0	NV	NV	NV	NV	10	0.81	1	0.12
Phenanthrene	85-01-8	4.00E+05	4.00E-01	1.70E+04	1.87E-02	20	11	2	1.6

Table 5. Analyte lists and detection limits for HRMS and isotope dilution methods.

Parameter	CAS Number	Project Screening Limit[1]				Lower Calibration Level/ Method Detection Limit*			
		Water (ug/L)		Solids (mg/kg)		Water (ng/L)		Solids (ng/g)	
		GW	SW	SO	SE	QL	MDL	QL	MDL
C1-Phenanthrenes/anthracenes	NA	NV	NV	NV	NV		10	1	1
C2-Phenanthrenes/anthracenes	NA	NV	NV	NV	NV	10	10	1	1
C3-Phenanthrenes/anthracenes	NA	NV	NV	NV	NV	10	10	1	1
C4-Phenanthrenes/anthracenes	NA	NV	NV	NV	NV	10	10	1	1
Pyrene	129-00-0	4.00E+04	2.50E-02	1.70E+03	4.43E-02	10	1.7	2	1.1
2,3,5-Trimethylnaphthalene	2245-38-7	NV	NV	NV	NV	10	1.6	2	0.46

Notes:

1. Project Screening Limits derived the following sources by matrix:
   Groundwater (GW) = USEPA National Recommended Water Quality Criteria 2009 for human health (organisms only), default DAF of 10 applied.
   Surface Water (SW) = lowest of DDOE WQS Criteria, USEPA Region 3 Surface Water Criteria, and literature based benchmarks (Suter & Tsao 1996 and Buchman 2008)
   Soils (SO) = USEPA Regional Screening Levels (RSLs). Industrial Soil. May 2010
   Sediment (SE) = lowest of the NOAA SQuiRTS, USEPA Region 3 BTAG Freshwater Sediment Screening Benchmarks, USEPA Region 5 Ecological Screening Levels, or Ontario Ministry of the Environment Provincial Sediment Quality Guidelines
   NOTE: Project Screening Limits are risk based and may not be achievable using EPA method laboratory techniques.

*Average estimated detection limits for soil and water method blanks. Note all PCDD/PCDF and PCB congener results above the sample specific EDL will be reported and reporting detection limits will be based on the EDL, not the EML or QL. Adjustments for sample moisture and dilutions may elevate sample specific limits. Note all limits are subject to change based on final laboratory selection and required annual laboratory detection limit updates

NR Not reported

NV No Value

DL Dioxin-like

Table 6. Sample container, preservation, and holding time requirement.

Parameter	Container [1]	Preservation	Holding Time [2]
Solid Samples			
VOCs	High level analysis: 1- 40 mL vial filled with 5 mL methanol (5 g soil to 5 mL methanol) Low level analysis: 2-40 mL vials with teflon stir bar and filled with 5 mL deionized water (5 g soil to 5 mL deionized water) % solids: 1 - 60 mL plastic	Ice, 4°C, in field	48 hours to freezing for water preserved samples; 14 days from collection to analysis for methanol and water preserved samples
SVOCs	1-8 oz amber glass with Teflon-lined cap	Ice, 4°C.	14 days to extraction; 40 days from extraction to analysis
PAHs	1-8 oz amber glass with Teflon-lined cap	Ice, 4°C. Maintain in dark; lab storage at <-10°C.	100 days to extraction; 40 days from extraction to analysis
Metals	1-8 oz amber glass with Teflon-lined cap	Ice, 4°C.	28 days to analysis (mercury); 180 days to analysis (other metals).
AVS/SEM	1-4 oz. amber glass with Teflon-lined cap	Ice, 4°C, no headspace	14 days to analysis
DRO/ORO	1-8 oz amber glass with Teflon-lined cap	Ice, 4°C.	14 days to extraction; 40 days from extraction to analysis
GRO	1-40 mL vial filled with 5 mL methanol (5 g soil in 5 mL methanol)	Ice, 4°C.	28 days
OCPs	1-8 oz amber glass with Teflon-lined cap	Ice, 4°C.	14 days to extraction; 40 days from extraction to analysis
PCBs as Aroclors	1-8 oz amber glass with Teflon-lined cap	Ice, 4°C.	14 days to extraction; 40 days from extraction to analysis
PCBs as Congeners	1-8 oz amber glass with Teflon-lined cap	Ice, 4°C. Maintain in dark; lab storage at <-10°C.	365 calendar days for preparation and analysis
PCDDs/PCDFs	1-8 oz amber glass with Teflon-lined cap	Ice, 4°C. Maintain in dark; ; lab storage at <-10°C.	365 calendar days for preparation and analysis

Table 6. Sample container, preservation, and holding time requirement.

Parameter	Container [1]	Preservation	Holding Time [2]
Aqueous Samples			
VOCs	3 x 40 mL vials	HCl to pH <2; Ice, 4°C.	14 days
SVOCs (incl. PAHs only)	2 x 1 L, amber glass	Ice, 4°C	7 days to extraction; 40 days from extraction to analysis
Metals, total	500 mL, plastic	HNO_3 to pH <2 Ice, 4°C.	28 days to analysis (mercury); 180 days to analysis (other metals).
DRO	1 x 2 L, amber glass	HCl to pH <2; Ice, 4°C	14 days to extraction; 40 days from extraction to analysis
GRO	2 x 40 mL vials	HCl to pH <2; Ice, 4°C.	14 days
PCBs -Aroclors	2 x 1 L, amber glass	Ice, 4°C	7 days to extraction; 40 days from extraction to analysis
OCP	2 x 1 L, amber glass	Ice, 4°C	7 days to extraction; 40 days from extraction to analysis
PCB - congeners	2 x 1 L, amber glass	Ice, 4°C	365 calendar days for preparation and analysis
PCDDs/PCDFs	1-8 oz amber glass with Teflon-lined cap	Ice, 4°C. Maintain in dark	365 calendar days for preparation and analysis

[1] Laboratory may provide alternate containers as long as the containers meet the requirements of the method and allow the collection of sufficient volume to perform the analyses and any reanalyses required by the method.

[2] Holding time begins from date of sample collection.

Table 7. Preparation and Analytical methodologies

Parameter	Methodology
TCL VOCs	SW-846 5030B/5035A/8260B
TCL SVOCs	SW-846 8270C
TAL Metals	SW-846 6010C/6020A/7470A/7471B
TCL Pesticides (low level for aqueous samples)	SW-846 8081B
TCL PCBs - Aroclors	SW-846 8082A
PCB – Homologs (optional)	EPA 680 modified
DRO and ORO	SW-846 8015B
GRO	SW-846 8015B
AVS/SEM	EPA-821-R-91-100
PCB - congeners	EPA 1668
PCDD/PCDFs	SW-846 8290

Table 8. Laboratory Preparation and Analytical SOPs

Reference Number	Fixed or Mobile Laboratory Performing Analysis	Title	Analytical Parameter
PT-MS-002, Rev.17	TestAmerica - Pittsburgh	Volatile Compounds by GC/MS	VOCs
PT-MS-001, Rev.11	TestAmerica - Pittsburgh	Semivolatile Organic Analysis by GC/MS	SVOCs
PT-GC-006, Rev.3	TestAmerica - Pittsburgh	Chlorinated Pesticides	OCPs
LAM-005, Rev 3	ECCS Mobile Lab	Polychlorinated Biphenyl (PCB) as Arolcors by Gas Chromatography	PCB Aroclors
KNOX-ID-0013, Rev 11	TestAmerica – Knoxville	Analysis of Polychlorinated Biphenyl (PCB) Isomers by Isotope Dilution HRGC/HRMS	PCB Congeners
PT-MT-002, Rev. 8	TestAmerica - Pittsburgh	Analysis of Metals by Inductively Coupled Plasma/Mass Spectrometry (ICPMS)	Metals (aqueous, excl. mercury)
PT-MT-001, Rev.11	TestAmerica - Pittsburgh	Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP)	Metals (soils, excl. mercury)
PT-MT-007, Rev.9	TestAmerica - Pittsburgh	Preparation and Analysis of Mercury in Solid Samples by Cold Vapor Atomic Absorption	Mercury (soil)
PT-MT-005, Rev. 9	TestAmerica - Pittsburgh	Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption	Mercury (aqueous)
PT-WC-008 R4_AVS_SEM_F, Rev. 4	TestAmerica - Pittsburgh	Acid Volatile Sulfides (AVS) and Simultaneously Extracted Metals (SEM) in Sediment	AVS/SEM
LAM-023, Rev 2.0	ECCS Mobile Lab	Diesel Range Organics	DRO/ORO
KNOX-ID-0016, Rev 8	TestAmerica – Knoxville	Isotope Dilution Analysis of Selected Semivolatile Organic Compounds and Alkylated PAHs by Gas Chromatography/Mass Spectrometry - Selected Ion Monitoring	Parent and alkylated PAHs by isotope dilution and selected ion monitoring
PS-GCV-001, Rev.6	TestAmerica - Pensacola	Gasoline Range Organics (GRO)	GRO

Table 9. Fixed and Mobile Laboratory Instrument Maintenance and Calibration.

Instrument	Maintenance Activity	Testing/ Inspection Activities	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)
GC/MS (VOC soil)	Clean sources and quadrupole rods; maintain vacuum pumps	Tuning/ instrument performance and sensitivity	IC: Initial setup; after major maintenance; or after CCV failure. ICV: after each IC CCV: Every 12 hours	IC: Minimum of 5 point curve with %RSD ≤30 for CCCs; if %RSD >15%, use curve fit r^2>0.990;no single analyte %RSD >45% ICV: <20% RSD; no single analyte >60% RSD CCV : <20% difference for CCCs; non-CCC and non-SPCC average %D <20% and no single analyte %D >60% See SOP for details	Perform maintenance and recalibrate See SOP for details
GC/MS (VOC water)	Clean sources and quadrupole rods; maintain vacuum pumps	Tuning/ instrument performance and sensitivity	IC: Initial setup; after major maintenance; or after CCV failure. ICV: after each IC CCV: Every 12 hours	IC: Minimum of 5 point curve with %RSD ≤30 for CCCs; if mean %RSD <15% and each analyte <30% use avg RRF all, if any analyte >30% use curve fit r^2>0.990 ICV: <20% RSD for CCCs; no single analyte >30% RSD with 6 exceptions per SOP. ICV: <20% RSD for CCCs; no single analyte >30% RSD with 6 exceptions per SOP. See SOP for details	Perform maintenance and recalibrate See SOP for details
GC/MS (SVOC,PAHs)	Clean sources and quadrupole rods; maintain vacuum pumps	Tuning/ instrument performance and sensitivity	IC: Initial setup; after major maintenance; or after CCV failure. ICV: after each IC. CCV: Every 12 hours	IC: Minimum of 5 point curve with %RSD ≤30% for CCCs; if %RSD >15%, use curve fit r^2>0.990; no single analyte %RSD >60% ICV: <20% difference; no single analyte >60% difference CCV : <20% difference for CCCs; no single analyte %D >60% See SOP for details	Perform maintenance and recalibrate See SOP for details

Table 9. Fixed and Mobile Laboratory Instrument Maintenance and Calibration.

Instrument	Maintenance Activity	Testing/ Inspection Activities	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)
HRGC/HRMS (PCB – Congeners)	Clean sources; maintain vacuum pumps	Tuning/ instrument performance and sensitivity	IC: Initial setup; after major maintenance; or after CCV failure. CCV: Every 12 hours	IC: %RSD ≤20% for target analytes calculated by isotope dilution; %RSD ≤35% for target analytes calculated by internal standard CCV: ≤30% drift for Toxics and LOC congeners; 40-160% for non-toxic congeners See SOP for details	Perform maintenance and recalibrate See SOP for details
HRGC/HRMS (PCDD/PCDFs)	Clean sources; maintain vacuum pumps	Tuning/ instrument performance and sensitivity	IC: Initial setup; after major maintenance; or after CCV failure. CCV: Every 12 hours	IC: %RSD ≤20% for target analytes calculated by isotope dilution; %RSD ≤30% for target analytes calculated by internal standard CCV: ≤20% drift for native congeners; ≤30% for lableled congeners See SOP for details	Perform maintenance and recalibrate See SOP for details
GC/ECD (Pesticides)	Change septa, clean injectors, change or trim columns, install new liners	Detector signals and chromatogram review/instrument performance and sensitivity	IC: Initial setup; after major maintenance; or after CCV failure. ICV: prior to samples CCV:Every 12 hours or 20 samples (whichever is more frequent), beginning and end of run	IC: Five point curve;RSD <20%; r^2>0.990 ICV: <20% difference CCV: <20%D; no single analyte >60% See SOPs for details	Perform maintenance and recalibrate See SOP for details
GC/ECD (PCB – Aroclors)	Change septa, clean injectors, change or trim columns, install new liners	Detector signals and chromatogram review/instrument performance and sensitivity	IC: Initial setup; after major maintenance; or after CCV failure. ICV: prior to samples CCV: Every 12 hours or 20 samples (whichever is more frequent), beginning and end of run	IC: Five point curve;RSD <20%; r^2>0.990 ICV: <20% difference CCV: <15%D; no single analyte >60% See SOP for details	Perform maintenance and recalibrate See SOP for details
GC/PID/FID (GRO)	Change septa, clean injectors, change or trim columns, install new liners	Detector signals and chromatogram review/instrument performance and sensitivity	IC: Initial setup; after major maintenance; or after ICV or CCV failure. ICV: after each IC CCV: Prior to samples, every 24 hours or every 20 samples, whichever is more frequent and at end of run	IC: Minimum of five standards, %RSD ≤25, r ≥0.99 ICV: 80-120% recovery CCV: %D or %drift ≤25, except nonane (≤30). See SOP for details	Perform maintenance and recalibrate See SOP for details

Table 9. Fixed and Mobile Laboratory Instrument Maintenance and Calibration.

Instrument	Maintenance Activity	Testing/ Inspection Activities	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)
GC/FID (DRO)	Change septa, clean injectors, change or trim columns, install new liners	Detector signals and chromatogram review/instrument performance and sensitivity	IC: Initial setup; after major maintenance; or after ICV or CCV failure ICV: after each IC CCV: Every 12 hours and at end of run	IC: Minimum of five standards, %RSD ≤20 ICV: 70-130% recovery CCV: %D or %drift ≤20 See SOP for details	Perform maintenance and recalibrate See SOP for details
ICP/MS (Metals Analysis [excl. mercury])	Replace disposables, flush lines	Tuning/ instrument performance and sensitivity	IC: Daily, prior to analysis of samples ICV: Immediately following calibration CCV: After every 10 samples; beginning and end of run	IC: Minimum of one standard and one blank with correlation coefficient ≥0.998 for multi-point curves ICV: 90-110% recovery CCV: 90-110% recovery See SOP for details	Perform maintenance and recalibrate See SOP for details
ICP/AES (Metals Analysis [excl. mercury])	Replace disposables, flush lines	Verify intensity counts/ instrument performance and sensitivity	IC: Daily, prior to analysis of samples ICV: Immediately following calibration CCV: After every 10 samples; beginning and end of run	IC: Minimum of one standard and one blank with correlation coefficient ≥0.998 for multi-point curves ICV: 90-110% recovery CCV: 90-110% recovery See SOP for details	Perform maintenance and recalibrate See SOP for details
CVAA (Mercury Analysis)	Replace disposables, flush lines	Sensitivity check/ check connections	IC: Daily, prior to analysis of samples ICV: Immediately following calibration CCV: After every 10 samples; beginning and end of run	IC: Five standards and one blank with correlation coefficient ≥0.995. ICV: 90-110% recovery CCV: 80-120% recovery	Perform maintenance and recalibrate See SOP for details

ICV – Initial calibration verification
CCV – Continuing calibration verification
RSD – Relative standard deviation
SPCC – System performance check compounds
RF – Response factor
CCC – Calibration check compound
LCS – Laboratory control sample
LOC – Level of chlorination
D – Difference

Appendix A

Laboratory Standard Operating Procedures

****** Laboratory SOPs are proprietary business information to be shared for review among Pepco, AECOM, and DDOE only ******

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Pittsburgh

SOP No. PT-MS-002, Rev. 17
Effective Date: 08/16/2011

Title: DETERMINATION OF VOLATILE ORGANICS BY GC/MS

Methods: SW-846 8260B AND EPA 624

Approvals (Signature/Date):

Kathy L Gordon	
7/20/2011	7/26/2011
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Nasreen DeRubeis, Date	Debbie Lowe, Date
Quality Assurance Manager	Laboratory Director

Distributed To: QA Web Page:

Company Confidential & Proprietary

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Volatile Organic Compounds in waters, wastewater, soils, sludges and other solid matrices. Standard analytes are listed in Tables 1, 2, and A-1. For DoD current version refer to SOP PT-QA-029.

1.2. This SOP is applicable to method 8260B and 624. Appendix A present modifications to the procedures in the main SOP that are necessary for analysis of water samples by method 624. For DoD QSM 3.0 requirements refer to SOP PT-QA-025, Implementation of DoD QSM Version 3, January 2006. For DoD QSM current version requirements refer to SOP PT-QA-029.

1.3. This method can be used to quantify most volatile organic compounds that have boiling points below 200℃ and are insoluble or sli ghtly soluble in water. Volatile water soluble compounds can be included in this analytical technique; however, for more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency.

1.4. The method is based upon a purge and trap, gas chromatograph/mass spectrometric (GC/MS) procedure. The approximate working range is 5 to 250 µg/L for 5 mL standard level waters, 1 to 40 µg/L for low level waters, 5 to 250 µg/kg for low-level soils, and 250 to 25,000 µg/kg for medium-level soils. Reporting limits are listed in Tables 1, 2, and A-1.

1.5. Method performance is monitored through the use of surrogate compounds, matrix spike/matrix spike duplicates, and laboratory control spike samples.

2. SUMMARY OF METHOD

2.1. Volatile compounds are introduced into the gas chromatograph by the purge and trap method. The components are separated via the chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.2. Aqueous samples are purged directly. Generally, soils are preserved by extracting the volatile analytes into methanol. If especially low detection limits are required, soil samples may be frozen and purged directly.

2.3. In the purge and trap process, an inert gas is bubbled through the solution at ambient temperature or at 40°C (40°C required for low level soils) and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbant column where the volatile components are

trapped. After purging is completed, the sorbant column (trap) is heated and back flushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is then heated to elute the components, which are detected with a mass spectrometer.

2.4. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples, and comparing the resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

3. DEFINITIONS

3.1. Batch: The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. Using this method, each BFB analysis will normally start a new batch. Batches for medium level soils are defined at the sample preparation stage and may be analyzed on multiple instruments over multiple days, although reasonable effort should be made to keep the samples together.

6.8.1 The Quality Control batch must contain a matrix spike/spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. If insufficient sample is received, an LCS/LCSD will be used in the place of an MS/MSD. Refer to the TestAmerica Pittsburgh QC Program document (PT-QA-021) for further details of the batch definition.

3.2. Method Blank

A method blank consisting of all reagents added to the samples must be analyzed with each batch of samples. The method blank is used to identify any background interference or contamination of the analytical system, which may lead to the reporting of elevated concentration levels or false positive data.

3.3. Laboratory Control Sample (LCS)

Laboratory Control Samples are well characterized, laboratory generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the

laboratory is performing the method within accepted QC guidelines for accuracy and precision.

3.4. Surrogates

Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples. Each sample, blank, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

3.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second aliquot of the same sample, which is prepared and analyzed along with the sample and matrix spike. Matrix spikes and duplicates are used to evaluate accuracy and precision in the actual sample matrix.

3.6. Calibration Check Compound (CCC)

CCCs are a representative group of compounds, which are used to evaluate initial calibrations and continuing calibrations. Relative standard deviation (%RSD) for the initial calibration and % drift or % deviation (%D) for the continuing calibration response factors are calculated and compared to the specified method criteria.

3.7. System Performance Check Compounds (SPCC)

SPCCs are compounds, which are sensitive to system performance problems and are used to evaluate system performance and sensitivity. Response factors from the initial and continuing calibrations are calculated for the SPCC compounds and compared to the specified method criteria.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. The use of ultra high purity gases, pre-purged purified reagent water, and approved lots of purge and trap grade methanol will greatly reduce introduction of contaminants. In extreme cases the purging vessels may be pre-purged

to isolate the instrument from laboratory air contaminated by solvents used in other parts of the laboratory.

4.2. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) into the sample through the septum seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.3. Matrix interferences may be caused by non-target contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.4. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.

4.5. Some samples may foam when purged due to surfactants present in the sample. When this kind of sample is encountered an antifoaming agent (Dow Corning Antifoam C) can be used. A blank spiked with this agent must be analyzed with the sample to show there is no target interferences induced by this agent. The antifoaming agent is not used routinely. If it needs to be used, approval from Project Manager is obtained, unless prior client approval has been obtained.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2. The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.3. There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.4. The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.5. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.6. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately.

5.7. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.8. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.9. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor or EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Microsyringes: 10 uL and larger, 0.006 inch ID needle.

6.2 Syringe: 5 or 25 mL glass with luerlok tip, if applicable to the purging device.

6.2. Balance: Top-loading balance capable of weighing 0.01 g

6.3. Glassware:

6.8.1 Vials: 40 mL with screw caps and Teflon liners.

6.8.2 Volumetric flasks: 10 mL, 50 mL and 100 mL, class A with ground-glass stoppers.

6.4. Spatula: Stainless steel.

6.5. Disposable pipettes: Pasteur.

6.6. pH paper: Narrow range.

6.7. Gases: Helium: Ultra high purity, gr. 99.999%.

6.8. Purge and Trap Device: The purge and trap device consists of the sample purger, the trap, and the desorber.

6.8.1 Sample Purger: The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. Alternative sample purge devices may be used provided equivalent performance is demonstrated. Low level soils are purged directly from a VOA vial.

6.8.2 Trap: OI # 10

6.8.3 Desorber: The desorber should be capable of rapidly heating the trap to at least 180°C. Many such devices are commercially available.

6.8.4 Sample Heater: A heater capable of maintaining the purge device at 40°C is necessary for low level soil analysis.

6.9 Gas Chromatograph/Mass Spectrometer System:

6.9.1 Gas Chromatograph: The gas chromatograph (GC) system must be capable of temperature programming.

6.9.2 Gas Chromatographic Columns: Capillary columns are used. Some typical columns are listed below:

6.9.2.1 Column 1: 20m x 0.18 ID J&W DB-624 or Restek 502.2 with 1 µm film thickness.

6.9.3 Mass Spectrometer: The mass spectrometer must be capable of scanning 35-300 AMU every two seconds or less, using 70 volts electron energy in the electron impact mode and capable of producing a mass spectrum that meets the required criteria when 50 ng or 25 ng of 4-Bromofluorobenzene (BFB) are injected onto the gas chromatograph column inlet.

6.9.4 Data System: A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between the specified time or scan-number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The most recent release of the NIST/EPA mass spectral library should be used as the reference library. The computer system must also be capable of backing up data for long-term off-line storage.

7. REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Methanol: Purge and Trap Grade, High Purity

7.1.2 Reagent Water: High purity water that meets the requirements for a method blank when analyzed. (See section 9.5) Reagent water is obtained from Millipore system. Other methods of preparing reagent water are acceptable.

7.1.3 1:1 HCl

7.2 Standards

7.2.1 Calibration Standard

7.2.1.1 Stock Solutions: Stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon-sealed screw-cap bottles with minimal headspace at -10□ to -20□C.

7.2.1.2 Working standards: A working solution containing the compounds of interest is prepared from the stock solution(s) in methanol. The working standard solutions will be prepared monthly with the exceptions of the gases and 2-chloroethylvinyl ether solutions, which will be prepared on a weekly basis. These standards are stored in the freezer or as recommended by the manufacturer. Working standards are monitored by comparison to the initial calibration curve. If any of the calibration check compounds drift in response from the initial calibration by more than 20% then corrective action is necessary. This may include steps such as instrument maintenance, preparing a new calibration verification standard or tuning the instrument. If the corrective actions do not correct the problem then a new initial calibration must be performed.

7.2.1.3 Aqueous Calibration Standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily.

7.2.1.4 If stock or secondary dilution standards are purchased in sealed ampoules they may be used up to the manufacturers expiration date.

7.2.2 Internal Standards: Internal standards are added to all samples, standards, and blank analyses. Refer to Table 6 for internal standard components.

7.2.3 Surrogate Standards: Refer to Table 7 for surrogate standard components and spiking levels.

7.2.4 Laboratory Control Sample Spiking Solutions: Refer to Table 8 for the normal control LCS components and spiking levels.

7.2.5 Matrix Spiking Solutions: The matrix spike contains the same control components as the LCS. Refer to Table 8.

7.2.6 Tuning Standard: A standard is made up that will deliver up to 50 ng on column upon injection. A recommended concentration of 25 ng/mL of 4-Bromofluoro-benzene in methanol is prepared as described in Sections 7.2.1.1 and 7.2.1.2.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Holding time for preserved volatile samples is 14 days from sample collection. Holding times for unpreserved waters is 7 days. Holding time for unpreserved soils requires that they are analyzed or preserved within 48 hours of sampling.

8.2 Water samples are normally preserved at pH < 2 with 1:1 hydrochloric acid.

8.3 Several different approaches to sample preservation and storage are presented below. The appropriate procedure selection is subject to project or program specific requirements.

8.4 Solid samples are prepped in a VOA vial with volatile free water and frozen within 48 hours of sampling for low level analysis, or with methanol for medium level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted. Terra Core™ kits (from C &G Scientific) can also be used. The kits are shipped to the field. Each kit includes two low level vials, one medium level vial and one bottle for percent moisture. One kit is used per each sample.

8.5 There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore or Terra CoreTM sample. Following shipment back to the lab the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 µg/kg for most analytes) then it will be necessary to use two additional 5 g EnCore samplers or Terra CoreTM kits or field preservation. The water preservation with freezing method is referenced in Method 5035A, Sec 8.2.1.2 and Appendix A table A-1.

8.6 Sample collection for medium level analysis using EnCore or Terra Core™ samplers.

8.6.1 Ship one 5 g EnCore or Terra Core™ sampler per field sample position.

8.6.2 An additional bottle must be shipped for percent moisture determination.

8.7 When the EnCore samples are returned to the lab, extrude the (nominal) 5g sample into a tared VOA vial containing 5 mL methanol. Obtain the weight of the soil added to the vial and note on the label. The surrogate and the matrix spike solution is added at the time of analysis. Terra Core™ samples are already prepared when received at the laboratory.

8.7.1 Prepare an LCS for each batch. Spike the LCS at the time of analysis.

8.7.2 Shake the samples for two minutes to distribute the methanol throughout the soil.

8.7.3 Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4 + 2 ℃ until analysis.

8.8 Sample collection for medium level analysis using field methanol preservation

8.8.1 A 5 g sample is to be used, add 5 mL methanol to a 40 ml VOA vial. The surrogate and matrix spike solution is added at the time of analysis).

8.8.2 Seal the bottle and attach a label.

8.8.3 Weigh the bottle to the nearest 0.01g and note the weight on the label.

8.8.4 Ship with appropriate sampling instructions.

8.8.5 Each sample will require an additional bottle with no preservative for percent moisture determination.

8.8.6 At client request, the methanol addition and weighing may also be performed in the field.

8.8.7 When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.

8.9 Low level procedure

8.9.1 If low detection limits are required (typically < 50 µg/kg) freezing the EnCore or Terra Core™ may be used. However, it is also necessary to take a sample for the medium level (field methanol preserved or using the EnCore or Terra Core™ sampler) procedure, in case the concentration of analytes in the soil is above the calibration range of the low level procedure.

8.9.2 A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method. (Varian Archon or O.I. 4552).

8.9.3 The soil sample is taken using a 5g EnCore sampling device or Terra CoreTM and returned to the lab. It is recommended that two EnCore or Terra CoreTM samplers be used for each field sample position, to allow for any reruns than may be necessary. A separate sample for % moisture determination is also necessary.

8.9.4 Prepare VOA vials by adding 5 mL of reagent water only.

8.9.5 Seal and label the vial. It is strongly recommended that the vial is labeled with an indelible marker rather than a paper label, since paper labels may cause the autosampler to bind and malfunction. The label absolutely must not cover the neck of the vial or the autosampler will malfunction.

8.9.6 Weigh the vial to the nearest 0.01g and note the weight on the label.

8.9.7 Extrude the soil sample from the EnCore sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil and note. Terra CoreTM samples are already prepared when received at the laboratory. Water preserved vials must be frozen.

8.9.8 Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional bottle with no preservative for percent moisture determination, and an additional bottle preserved with methanol for the medium level procedure. Depending on the type of soil it may also be necessary to ship vials with no or extra preservative.

8.10 Unpreserved soils

8.10.1 At specific client request unpreserved soils packed into glass jars or brass tubes may be accepted and subsampled in the lab. This is the old procedure based on SW-846 Method 5030A. It is no longer included in SW-846 and is likely to generate results that are biased low, possibly by more than an order of magnitude.

8.11 Aqueous samples are stored in glass containers with Teflon lined septa at 4ºC ± 2ºC, with minimum headspace.

8.12 Medium level solid extracts are aliquoted into 4 mL glass vials with Teflon lined caps and stored at 4ºC ± 2ºC. The extracts are stored with minimum headspace.

8.13 The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time for the EnCore sampler (before the sample is added to methanol or frozen) is 48 hours.

8.14 A holding blank is stored with the samples. This is analyzed and replaced if any of the trip blanks show any contamination. Otherwise it is replaced every 7 days.

8.15 Regulatory requirements for Acrolein, Acrylonitrile and 2-Chloroethyl vinyl ether

8.15.1 **Acrolein**: Both 40 CFR 136 and SW 846 (chapter 4) have special preservation requirements to adjust pH to between 4-5. For properly preserved samples (pH 4-5) the holding time is 14 days. There are currently no regulatory options for HCL preservation to < 2, however there are options for an unpreserved water sample.

- **40 CFR 136 (Method 624)**

  Unpreserved sample: If Acrolein is a target analyte the holding time is 3 days.
- **SW 846 (Method 8260) Chapter 4**

  SW 846 does not provide guidance on processing of unpreserved samples. However, EPA MICE has interpreted the holding time on an unpreserved sample as 7 days.

8.15.2 Acrylonitrile: Both 40 CFR 136 and SW 846 (chapter 4) have special preservation requirements to adjust pH to between 4-5. For properly preserved samples (pH 4-5) the holding time is 14 days. However, according to 40 CFR 136, the pH adjustment is not necessary for Acrylonitrile therefore the holding time for unpreserved samples is also 14 days.

- **40 CFR 136 (Method 624)**

  Unpreserved sample: If only Acrylonitrile (no acrolein) is a target analyte the holding time is 14 days.

- **SW 846 (Method 8260) Chapter 4**
  SW 846 does not provide guidance on processing of unpreserved samples. However, EPA MICE has interpreted the holding time on an unpreserved sample as 7 days.

8.15.3 2-Chloroethyl-vinyl ether (2-CEVE): According to 40 CFR 136 purgeable halocarbons (2-CEVE's category) do not require acid preservation and the holding time is 14 days. When Aromatics are included as compounds of interest, samples require acid preservation due to rapid breakdown through bio degradation. The method (624) is designed to use unpreserved containers but includes a caveat that refrigeration alone won't suffice for aromatics stored past 7 days. When aromatics are included the method recommends collection of a separate acidified sample aliquot followed by refrigeration up to 14 days. SW846 includes specific information on the handling of this analyte.

8.15.4 Technical Guidance

Acid preservation or pH adjustment

The stability of 2-Chloroethylvinyl ether and Acrolein is reduced when subjected to low pH. It is therefore not recommended that these compounds be analyzed from routinely preserved VOA vials and since there is no reasonable way to achieve a pH between 4 and 5, it is recommended that unpreserved vials be used for analysis of these compounds.

Holding Time

Where Method 624 data are being used for compliance monitoring, the regulatory holding times take precedence (see above discussion and table).

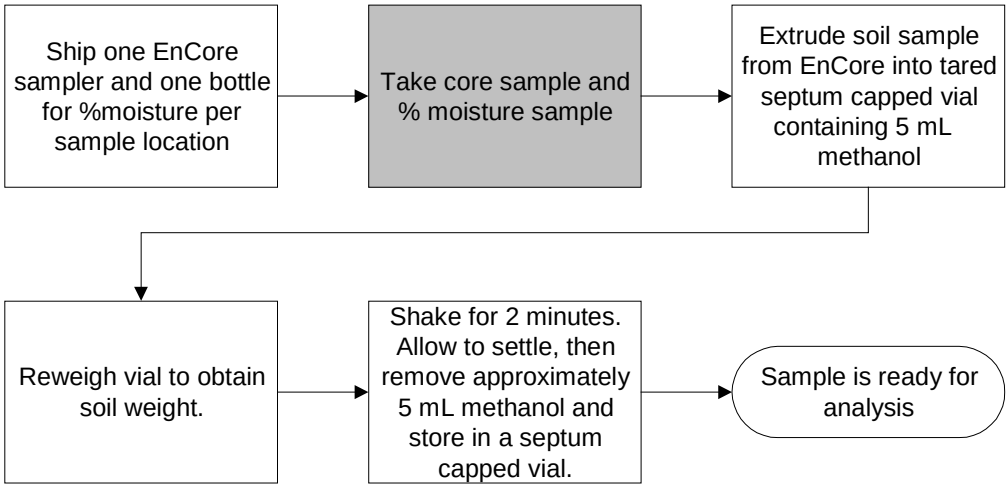
Where Method 624 data are not being generated for compliance purposes, the technical stability of the compounds may be considered. Where the base method stems from SW846, it is allowable to qualify the results. However, the laboratory should make every attempt to analyze samples within the most liberal holding time. To deviate from the regulatory holding times, the following documentation must be maintained:

A. Written confirmation must be obtained from the client that samples are non-compliant.
B. Written approval must be obtained from the client that regulatory holding times may be exceeded (e-mail is acceptable).
C. A method non-conformance statement must be included in the data report.

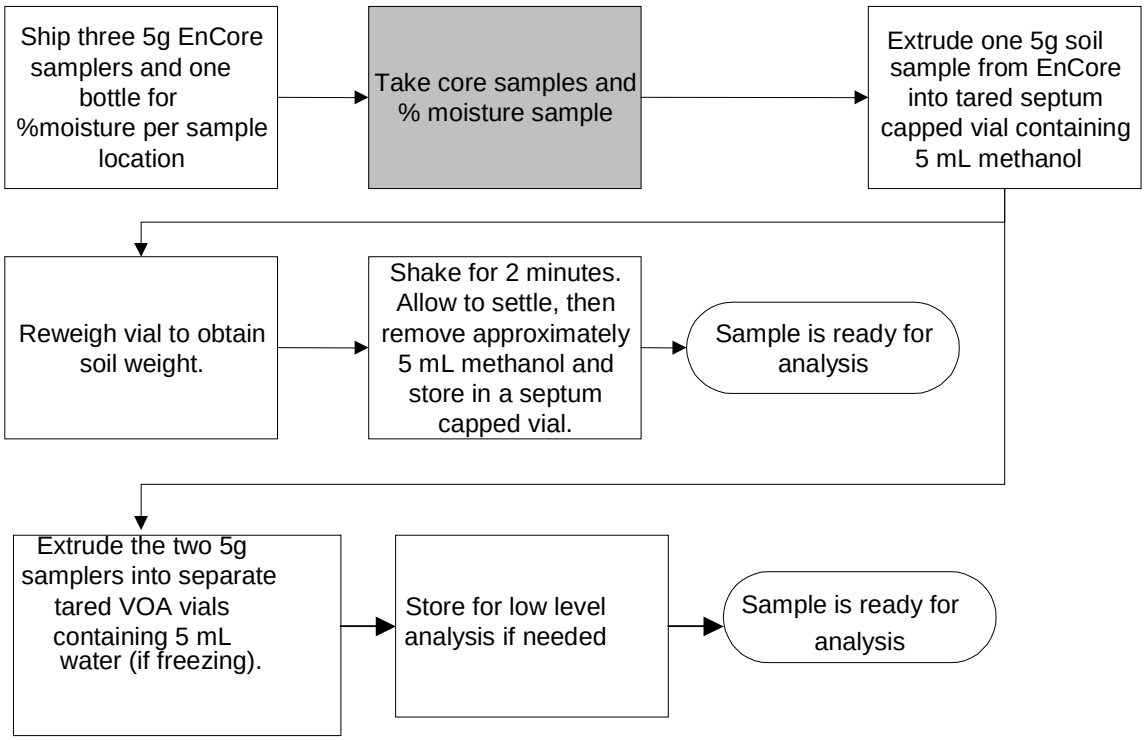
Preservation and Holding Time Table for Volatiles (Dechlorination as needed per Methods)			
Analyte	**Method**	**Preservation**	**Holding Time**
Acrolein	8260	< 6ºC (No HCl)	7 days
	8260	pH 4-5, < 6ºC	14 days
	624	< 6ºC (No HCl)	3 days
	624	pH 4-5, < 6ºC	14 days
Acrylonitrile	8260	< 6ºC (No HCl)	7 days
	8260	pH 4-5, < 6ºC	14 days
	624	< 6ºC (No HCl)	14 days
	624	pH 4-5, < 6ºC	14 days
2-CEVE	8260	< 6ºC (No HCl)	7 days
	624	< 6ºC (No HCl)	14 days

NOTE: If Aromatics are compounds of interest and biological activity is known or suspected to be present, preserved aliquots must be collected.

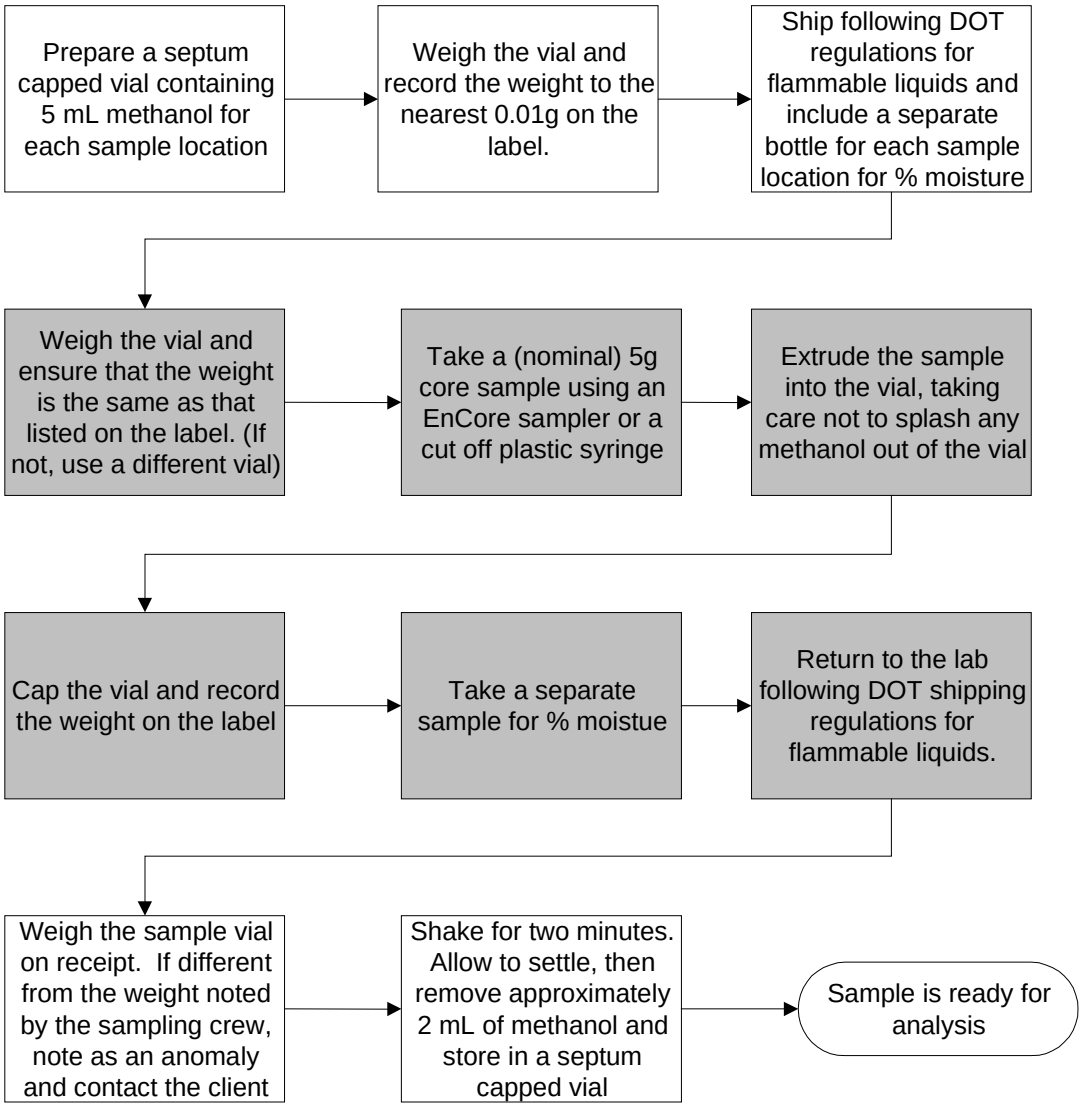
EnCore procedure when low level is not required (field steps in gray)



EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



9 QUALITY CONTROL

9.1 See Document PT-QA-021 "TestAmerica Quality Control Program" for additional detail. For DoD requirements refer to SOP # PT-QA-025, Implementation of DoD QSM Version 3 January 2006, current version and DoD Tables B-1 and B-3. For DoD current version refer to SOP PT-QA-029.

9.2 In-house historical control limits have been determined for surrogates, matrix spikes, and laboratory control samples (LCS). The LCS limits for method 624 are defined in the method and are listed on Table A-2. These limits must be re-checked at least annually. The recovery limits are mean recovery ± 3 standard deviations for surrogates, matrix spikes and LCS. Precision limits for matrix spikes / matrix spike duplicates are 0 to mean relative percent difference ± 3 standard deviations.

9.2.1 All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.2.2 Refer to the QC Program document (PT-QA-021) for further details of control limits.

9.3 Surrogates

Every sample, blank and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. The compounds included in the surrogate spiking solutions are listed in Table 8. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions)

9.3.1 Check all calculations for error.

9.3.2 Ensure that instrument performance is acceptable.

9.3.3 Recalculate the data and/or reanalyze if either of the above checks reveal a problem

9.3.4 Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem

9.3.5 Samples that have major matrix interference, which is obvious from the chromatogram, will not be rerun for confirmation of matrix interference.

9.3.6 The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare/reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.3.7 If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then reanalysis or flagging of the data is required.

9.3.8 Refer to the TestAmerica Pittsburgh QC Program document (PT-QA-021) for further details of the corrective actions.

NOTE: When Calgon samples are analyzed for GC/MS Volatiles, as per the client and PM, no re-extraction or reanalysis will take place when surrogates recover outside of control limits. These samples are carbon in nature and surrogate recoveries are known to be poor when analyzing this matrix.

9.4 Method Blank

For DoD method blank criteria, see SOP # PT-QA-025 and PT-QA-029. For each batch of samples, analyze a method blank. The method blank is analyzed after the calibration standards, normally before any samples. If the first method blank does not meet criteria, a second blank may be analyzed. The method blank must meet criteria before proceeding with sample analyses. For low-level volatiles, the method blank consists of reagent water or 5 grams of Ottawa sand (soil blanks). For medium-level volatiles, the method blank consists of 100 ul of methanol extract into 4.9 mls of reagent water. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

9.4.1 If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone) the data may be reported with qualifiers if the concentration of the analyte is not more than five times the reporting limit. Such action must be taken in consultation with the client.

9.4.2 Reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

9.4.3 If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be done in consultation with the client.

9.4.4 The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the sample analysis is free of contamination. All non-conforming blanks will be documented in a non-conformance memo and if reported the reasons for reporting the data will be summarized. For example, if surrogate recoveries are low, re-extraction and/or reanalysis of the blank and affected samples will normally be required. Consultation with the client should take place. If the surrogate recoveries are high and there are target compounds found in the associated sample the samples will require re-extraction and/or reanalysis.

9.4.5 If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all compounds detected in the blank are flagged with a "B" in the associated samples, and appropriate comments are made in a narrative to provide further documentation.

9.4.6 Refer to the TestAmerica Pittsburgh QC Program document (PT-QA-021) for further details of the corrective actions.

9.5 Laboratory Control Samples (LCS)

For DoD LCS criteria, see SOP # PT-QA-025 and PT-QA-029. For each batch of samples, analyze a LCS. The LCS is analyzed after the calibration standard. The LCS contains a representative subset of the analytes of interest (See Table 8), and must contain the same analytes as the matrix spike. If any control analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch. Please refer to Appendix A and Table A-2 for LCS criteria for method 624.

9.5.1 If the batch cannot be re-prepped and/or reanalyzed due to insufficient sample, a discussion should be provided of the data quality indicators and must be clearly presented in the project records and the report.

9.5.2 If re-extraction and/or reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.5.3 Refer to the TestAmerica Pittsburgh QC Program document (PT-QA-021) for further details of the corrective action.

9.5.4 If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be expected statistically. These requirements should be negotiated with the client. Unless otherwise agreed only the control analytes (Table 8) are used to evaluate analytical performance control.

9.5.5 Use of marginal exceedances are not permitted for South Carolina work.

NOTE: Due to the nature of Safety Kleen samples an LCS/LCSD will be analyzed for QC purposes, as per client/PM instruction.

9.6 Matrix Spikes

For DoD MS/MSD criteria, see SOP # PT-QA-025 and PT-QA-029. For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in Table 8. Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits. Refer to Table A-2 for method 624 spike limits.

9.6.1 If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

9.6.2 If the recovery for any control component is outside QC limits for both the matrix spike/ spike duplicate and the LCS, the laboratory operation is out of control and corrective action must be taken. Corrective action will normally include reanalysis of the batch.

9.6.3 If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

9.6.4 The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

NOTE: If a Calgon sample is selected to be analyzed as an MS/MSD and the parent sample requires a 5X dilution or greater, as per instruction from the client/PM, an LCS/LCSD will be analyzed instead.

9.7 Nonconformance and Corrective Action

Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

9.8 Quality Assurance Summaries

Certain clients may require specific project or program QC, which may supersede these method requirements. Quality Assurance Summaries should be developed by the Project Manager to address these requirements.

9.9 TestAmerica Pittsburgh QC Program

Further details of QC and corrective action guidelines are presented in the TestAmerica Pittsburgh QC Program document (PT-QA-021). Refer to this document if in doubt regarding corrective actions.

10 PROCEDURE

CALIBRATION AND STANDARDIZATION:

10.1 Summary

Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked through the analysis of 4-Bromofluorobenzene (BFB) to establish that a given GC/MS system meets the standard mass spectral abundance criteria. The GC/MS system must be calibrated initially at a minimum of seven concentrations (analyzed under the same BFB tune), to determine the linearity of the response utilizing target calibration standards. Once the system has been calibrated, the calibration must be verified each twelve hour time period for each GC/MS system. The use of separate calibrations is required for water and low soil matrices.

10.2 Recommended Instrument Conditions

10.2.1 General

Electron Energy:	70 volts (nominal)
Mass Range:	35–300 AMU
Scan Time:	to give at least 5 scans/peak, but not to exceed 2 second/scan
Injector Temperature:	200–250℃
Source Temperature:	According to manufacturer's specifications
Transfer Line	Temperature: 250–300℃

Purge Flow:	40 mL/minute
Carrier Gas	Flow: 15 mL/minute
Make-up Gas Flow:	25–30 mL/minute

10.2.2 Gas chromatograph suggested temperature program

Parameter	Sample Analysis	BFB Analysis
Initial Temperature:	35℃	35℃
Initial Hold Time:	4 minutes	2 min
Temperature Program:	15℃/minute	20℃/minute
Final Temperature:	200℃	200℃
Final Hold Time:	1.1 minutes	1.0 min.

10.3 Instrument Tuning

Each GC/MS system must be hardware-tuned to meet the abundance criteria listed in Table 9 for a maximum of a 50 ng injection or purging of BFB. Analysis must not begin until these criteria are met. These criteria must be met for each twelve-hour time period. The twelve-hour time period begins at the moment of injection of BFB.

10.3.1 Acceptable procedures for BFB tuning are as follows:

10.3.1.1 Tune evaluations usually utilize the “Autofind” function and are set up to look at the apex + or - 1 scan and average the three scans. Background correction is required prior to the start of the peak but no more than 20 scans before. Background correction cannot include any part of the target peak.

10.3.1.2 Adjustments such as adjustments to the repeller and the ion focus lenses, adjusting the EM Voltage, etc. may be made prior to tune verification as long as **ALL** of the subsequent injections in the 12 hour tune cycle are analyzed under the same MS tune settings and it is documented in the run sequence log and/or maintenance log that an adjustment was made. Excessive adjusting (more than 2 tries) without clear documentation is not allowed. Necessary maintenance is performed and documented in the instrument maintenance log.A single scan at the apex (only) may also be used for the evaluation of the tune. For SW-846 and EPA 600 series methods, background correction is still required.

10.3.1.3 Tune evaluation printouts must include the chromatogram and spectra as well as the tune evaluation information. In addition, the verifications

must be sent directly to the printer of pdf file (NO screen prints for BFB tunes). This ability should be built in to the instrument software.

10.3.1.4 If the instrument has a built in macro that checks the BFB, use of this macro with no manual manipulation is also acceptable. (Assuming, of course that the correct ion ratios are being checked.)

10.3.1.5 NOTE: If the background scan selected includes significant ions at 95 or 174 or 176, then the scan is almost certainly part of the BFB peak and is not acceptable.

10.4 Initial Calibration

10.4.1 A series of seven initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. Typical calibration levels for a standard 5 mL purge are: 5, 10, 25, 40, 50, 125 and 250 □g/L. Certain analytes are prepared at higher concentrations due to poor purge performance. Typical calibration levels for a Low Level purge are 1, 5, 10, 15, 20, 35 and 40 µg/L. Again, some analytes are prepared at higher levels. Tables 3 and 4 list the calibration levels for each analyte. Other calibration levels and purge volumes may be used depending on the capabilities of the specific instrument. However, the same purge volume must be used for calibration and sample analysis, and the low level standard must be at or below the reporting limit. See Table 3 and 4 for medium level soil standard concentration. **Note: South Carolina can only be analyzed using linear calibration, quadratic is not allowed.**

10.4.2 It may be necessary to analyze more than one set of calibration standards to encompass all of the analytes required for same tests. For example, the Appendix IX list requires the Primary standard (Table 3) and the Appendix IX standard (Table 4). If acceptable analytical performance can be obtained the primary and appendix IX standards may be analyzed together.

10.4.3 Internal standard calibration is used. The internal standards are listed in Table 6. Target compounds should reference the nearest internal standard (see Table 6A). Each calibration standard is analyzed and the response factor (RF) for each compound is calculated using the area response of the characteristic ions against the concentration for each compound and internal standard. See equation 1, Section 12, for calculation of response factor.

10.4.4 The % RSD of the calibration check compounds (CCC) must be less than 30%. Refer to Table 11 for the CCCs. Acceptable CCC compounds will use average RF curve.

10.4.4.1 If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.4.5 The average RF must be calculated for each compound. A system performance check is made prior to using the calibration curve. The five system performance check compounds (SPCC) are checked for a minimum average response factor. Refer to Table 10 for the SPCC compounds and required minimum response factors.

10.4.6 Note: the laboratory may not use the "grand mean" rule. The following are guidelines that are used for routine SW-846 analysis within the laboratory, however these guidelines are subject to program and project specific requirements.

10.4.6.1 Where a target compound is ≤15% RSD an average response factor curve may be used. If the 15% RSD criteria are exceeded the analyst must assess the curve and attempt to apply a "best-fit" curve function and a graphical representation of the curve will be provided as documentation of this review. The first step of the assessment is to find out if the quadratic curve will have a correlation coefficient of ≤ .995. If it does not, then use the average response factor. If it does, then review where the quadratic curve intercepts the y-axis in comparison to the MDL and origin. Also review the shape of the curve. Does it overlap itself or have other potential problems? These steps should all be used in deciding when a quadratic curve or average response factor curve would be best.

10.4.6.2 Where a quadratic or polynomial curve is used R must be ≥.995 for a curve to be considered to be an acceptable fit.

10.4.6.3 All linear curves for non-CCC compounds that exceed 15% RSD or best-fit curve functions that have R < .995 are in exceedance of guidance criteria and must be evaluated for corrective action. The following exceptions may be reportable with narration depending on the project DQO's and data usability requirements:

10.4.6.4 Where a target compound is ≥15% but ≤30% an average response factor curve may still be used if the analyst shows that the average response factor is an acceptable fit over the range of use. A graphical representation of the curve should be presented for documentation. However, if the quadratic curve is clearly a better fit it should be used.

10.4.6.5 Compound list will be divided into two lists: List 1 (reliable performers) and List 2 (poor performers). List 1 compounds should always have a %RSD less than 30% or correlation coefficient of .995 with an allowance of up to two sporadic marginal failures for volatiles. Sporadic marginal failures for these compounds should be </= 40% or >0.990. Sporadic marginal failures require a print out of the curve and narration.

NOTE: Sporadic marginal failures will not be used for South Carolina regulatory compliance samples.

10.4.6.6 List 2 compounds are comprised of the list of known poor performers. For List 2 analytes, where the %RSD is ≤15% an average response factor will be used. For %RSDs >15% and ≤60% the best fit curve will be selected. For these compounds a print out of the curve will be provided as a graphical documentation of curve performance.

10.4.6.7 Documentation: Raw target curve summary with all compounds set to average response factor will be provided. If quadratic or polynomial equations are used a reprint of the curve table will be provided to show the correlation coefficient for the "best fit" equation. And as noted above, compounds that need additional documentation to demonstrate the curve fit will have a graphical presentation of the curve provided for reference.

10.4.6.8 Any analyte **not** on List 1 or List 2 would be held to specific criteria based on project specific requirements.

10.4.6.9 Any non-CCC compound being reported from a curve that does not meet either the 15% RSD criteria or the R = .995 for a "best-fit" curve will be narrated as a non-conformance.

10.4.6.10 All %RSDs that are >30% must be narrated and when using an average response factor curve for a %RSD >30% this should also be narrated.

10.4.6.11 **Note:** Project Specific DQOs or program specific requirements supercede routine lab reporting practices listed in this section.

10.4.7 Weighting of data points

In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.4.8 If time remains in the 12-hour period initiated by the BFB injection after the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.9 A separate seven-point calibration must be prepared for analysis of low level soils. Low level soil analyses require the use of a closed vial autosampler, such as the Varian Archon, O.I. 4552 or Tekmar Precept. Each standard is prepared by spiking the methanolic standard solution through the septum of a VOA vial containing 5 mL of water. The standards are heated to 40□C for purging. All low-level soil samples, standards, and blanks must also be heated to 40□C for purging. Medium soil extracts should be analyzed using the water (unheated) calibration curve.

10.4.10 Non-standard analytes are sometimes requested. Where it is acceptable to the client, it may be is possible to analyze a single standard at the reporting limit (to screen for the compounds) with each continuing calibration rather than a six point initial calibration. If the analyte is detected in any of the samples, a six point initial calibration must be generated and the sample(s) reanalyzed for quantitation. However, if the analyte is not detected, the non-detect may be reported and no further action is necessary. This is not an acceptable procedure for compliance work. When doing non-standard analytes an MDL will be run before analysis.

10.4.11 All ICALs will be verified by a Second Source Standard. The acceptance criteria are 75-125% for most compounds and 50-150% for poor method performers. The poor performers are footnoted in Tables 3 and 4. Any compound not listed will fall into the 50-150% criteria until knowledge of the compound can be developed. **For DoD QSM 3.0 the second source must be ± 25% for all compounds, refer to SOP PT-QA-025. For DoD QSM 4.1 the second source must be ± 20% for all compounds, refer to SOP PT-QA-029.**

10.4.12 Outliers will be evaluated on a project by project basis and narrated in the case narrative if necessary.

10.5 Continuing Calibration: The initial calibration must be verified every twelve hours.

10.5.1 Continuing calibration begins with analysis of BFB as described in Section 10.3. If the system tune is acceptable, the continuing calibration standard(s) are analyzed. The level 3 calibration standard is used as the continuing calibration for low level waters. The level 4 calibration standard is used as the continuing calibration for low level soils and 5 ml waters.

10.5.2 The RF data from the continuing calibration standards are compared with the average RF from the initial seven-point calibration to determine the percent drift or percent deviation of the CCC compounds. The calculations are given in equations 4 (Section 12.3.4) and equation 5 (Section 12.3.5).

10.5.3 Continuing Calibration Verification

10.5.3.1 Calculation Type

10.5.3.1.1 Average Response Factor curves should be verified using a %Difference equation. The %Difference equation compares the RRF factor calculated for the Calibration Verification Standard to the Average RRF of the curve.

10.5.3.1.2 The Quadratic Curves should be verified using a %Drift equation. The %Drift equation compares the measured value of the Calibration Verification Standard to the theoretical value of the standard.

10.5.3.2 %Difference and %Drift Criteria

10.5.3.2.1 CCCs must be ≤20 %Diff

10.5.3.2.2 List One compounds that are non-CCCs must be ≤25 %Diff or Drift

10.5.3.2.3 Up to two Volatile and four Semivolatile compounds that are List One analytes may exceed the 25% criteria, but must be ≤40%.

10.5.3.2.4 List Two Target Analytes including Appendix IX compounds will be accepted where the % Difference or % Drift ≤50%. Please see Table 4-1.

NOTE: See Table 4-2 for South Carolina 8260 ICAL Control List.

10.5.3.2.5 Where a CCV is out high by >50% and the compound is ND in the samples, the samples may be reported with narration.

10.5.3.3 RRF Criteria

10.5.3.3.1 SPCCs must be as per method requirements. Please see Table 10.

10.5.3.3.2 All other compounds must be ≤0.01 (footnote exceptions).

10.5.4 If the CCCs and/or the SPCCs do not meet the criteria in Sections 10.5.3 after the continuing calibration has been attempted twice, the system must be evaluated and corrective action must be taken. The BFB tune and continuing calibration must be acceptable before analysis begins. Extensive corrective action such as a different type of column will require a new initial calibration.

10.5.5 Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the BFB have passed. (A sample desorbed less than or equal to 12 hours after the BFB is acceptable.).

10.6 Sample Analysis:

10.6.1 Procedural Variations: One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation shall be completely documented using a Nonconformance Memo and approved by a Supervisor or group leader and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

10.6.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.6.3 See Appendix A for method 624 criteria.

10.6.4 Preliminary Evaluation

10.6.4.1 Where possible, samples are screened by headspace or GC/MS off-tune analysis to determine the correct aliquot for analysis. Alternatively, an appropriate aliquot can be determined from sample histories.

10.6.4.2 Samples are screened on a headspace analyzer. The instrument is calibrated for select compounds at three levels. There are 200ppb, 500ppb, and 1000ppb. 5 mLs of sample are then analyzed on the headspace analyzer and the results are used to calculate a dilution, if necessary, for the sample.

10.6.4.3 Dilutions should be done just prior to the GC/MS analysis of the sample. Dilutions are made in volumetric flasks or in a Luerlok syringe. Calculate the volume of reagent water required for the dilution. Fill the syringe with reagent water, compress the water to vent any residual air and adjust the water volume to the desired amount. Adjust the plunger to the mark and inject the proper aliquot of sample into the syringe. If the dilution required would use less than 5 µL of sample then serial dilutions must be made in volumetric flasks.

10.6.4.3.1 The diluted concentration is to be estimated to be in the upper half of the calibration range. The upper range will be defined as the mid-range calibration point and above. **NOTE:** TestAmerica Pittsburgh considers a good dilution for regular waters and soils to be > or = 200 ng on column and for low level waters a good dilution is considered to be > or = 50 ng on column.

10.6.5 Sample Analysis Procedure

10.6.6 All analysis conditions for samples must be the same as for the continuing calibration standards (including purge time and flow, desorb time and temperature, column temperatures, multiplier setting etc.).

10.6.7 All samples must be analyzed as part of a batch. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The batch also must contain a MS/MSD, a LCS, and a method blank.

10.6.7.1 If there is insufficient time in the 12-hour tune period to analyze 20 samples, the batch may be continued into the next 12 hour tune

period. However, if any instrument corrective action is required, or if a period of greater than 12 hours (SW-8260B) from the preceding BFB tune has passed, a new batch must be started. In other words a QC batch may be kept open for two adjacent and uninterrupted tune periods where both pass all BFB, CCAL, blank and LCS criteria up to a maximum of 24 hours. For medium level soils the batch is defined at the sample preparation stage. For method 624 the batch tune period is 24 hours.

10.6.7.2 Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

10.6.7.3 It is not necessary to reanalyze batch QC with the reanalyses of samples. However, any reruns must be as part of a valid batch.

10.6.8 For manual integration practices refer to TestAmerica corporate SOP, CA-Q-S-002, Acceptable Manual Integration Practices. For DoD and all other projects the following criteria must be met:

When manual integrations are performed, raw data records shall include a complete audit trail for those manipulations, raw data output showing the results of manual integration (i.e., chromatograms of manually integrated peaks), and notation of rationale, date, and name or initials of person performing manual integration operation (electronic signature is acceptable). DoD QSM, Version 3, Clarification 50 and 57.

Case Narrative. For DoD the case narrative shall provide: identification of **samples and analytes** for which manual integration was necessary. DoD QSM, Version 3, Appendix DoD-A and DoD QSM 4.1, Appendix E.

10.6.9 Retention time criteria for samples

Retention time windows must be established and verified once per ICAL and at the beginning of the analytical shift as per DoD QSM, Version 3, Appendix DoD-B, Table B-3 and DoD QSM 4.1 Appendix F, Table F-1. If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

10.6.9.1 If the retention time of any internal standard in any sample varies by more than 0.1 minute from the preceding continuing calibration

standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
Retention Time window position establishment for each analyte and surrogate	Once per ICAL	Position shall l be set using the midpoint standard of the initial calibration curve.	NA	NA
Evaluation of relative retention times (RRT)	With each sample	RRT of each target analyte in each calibration standard within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	Flagging criteria are not appropriate.

10.7 Water Samples

10.7.1 All samples and standard solutions must be at ambient temperature before analysis.

10.7.2 Fill a syringe with the sample. If a dilution is necessary it may be made in the syringe if the sample aliquot is ≥ 5 µL. Check and document the pH of the remaining sample.

10.7.3 Add 250 ng of each internal and surrogate standard (10 µL of a 25 µg/mL solution, refer to Tables 6 and 7). The internal standards and the surrogate standards may be mixed and added as one spiking solution (this results in a 50 µg/L solution for a standard 5 mL sample, and a 10 µg/L solution for low level analyses, when added to a 25 mL sample aliquot). Inject the sample into the purging chamber. Note: Low level analyses on instruments that sample directly from the VOA vial (i.e., Archons) use a 5 ml sample volume. Therefore, 1.0 µL of a 250 µg/mL solution of internal standards and surrogates are added to the sample for the regular 5 mL waters and 1uL of a 50 ug/mL solution is added for low level waters.

10.7.3.1 For TCLP samples use 125 uL of TCLP leachate with 4.875 mL reagent water and spike with 8 µL of the 25 µg/mL spiking solution.

(Note that TCLP reporting limits will be 40 times higher than the corresponding aqueous limits).

10.7.4 Purge the sample for eleven minutes (the trap must be ≤ 35□C).

10.7.5 After purging is complete, desorb the sample, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for 5-10 minutes to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

10.7.6 Desorb and bake time and temperature are optimized for the type of trap in use. The same conditions must be used for samples and standards.

10.8 Methanol Extracted Soils

10.8.1 Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add 100 µL for a 5 mL purge methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard. Load the sample onto the purge and trap device and analyze the same as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

10.9 Liquid wastes that are soluble in methanol and insoluble in water.

10.9.1 Pipette 1 mL of the sample into a tared vial. Use a top-loading balance. Record the weight to the nearest 0.01 gram. In order to produce an accurate weight to volume relationship take the weight of the liquid sample divided by 1.0 grams to determine a dilution factor which will be applied to reflect this relationship accurately.

10.9.2 Quickly add 8 mL of methanol, then add 1 mL of surrogate spiking solution to bring the final volume to 10 mL. Cap the vial and shake for 2 minutes to mix thoroughly. For a MS/MSD, 7 mL of methanol, 1 mL of surrogate solution, and 1 mL of matrix spike solution is used.

10.9.3 Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add 100 µL for a 5 mL purge methanolic extract (from Section 11.6.2) to the syringe. Add internal standard. Load the sample onto the purge and trap device and analyze the same as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

10.10 Aqueous and Low level Soil Sample Analysis (Purge and Trap units that sample directly from the VOA vial)

10.10.1 Units which sample from the VOA vial should be equipped with a module which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

10.10.2 If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise the internal and surrogate standards must be added to the vial. Note: Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to be analyzed as soils.

10.10.3 Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

10.10.4 For aqueous samples, check the pH of the sample remaining in the VOA vial after analysis is completed with narrow range pH paper. If the pH is greater than 2, a nonconformance memo should be initiated.

10.11 Low-Level Solids Analysis using discrete autosamplers:

Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846 and is not permitted within a number of programs including the PADEP programs.

This method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogates, internal standards, and if applicable, the matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40^{o}C.

10.11.1 Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.

10.11.2 Weigh out 5 g (or other appropriate aliquot) of sample into a disposable culture tube or other purge vessel. Record the weight to the nearest 0.01 g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 1.0 g. If the sample is contaminated with analytes such that a purge amount less than 1.0 g is appropriate, use the medium level method described in section 10.8.

10.11.3 Connect the purge vessel to the purge and trap device.

10.11.4 Rinse a 5 mL gas-tight syringe with organic free water, and fill. Compress to 5 mL. Add surrogate/internal standard (and matrix spike solutions if required.). Add directly to the sample from 11.8.2.

10.11.5 The above steps should be performed rapidly and without interruption to avoid loss of volatile organics.

10.11.6 Add the heater jacket or other heating device and start the purge and trap unit.

10.11.7 Soil samples that have low IS recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect.

10.12 Initial review and corrective actions

10.12.1 If the retention time for any internal standard in the continuing calibration changes by more than 0.5 minutes from the mid-level initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

10.12.2 If the internal standard response in the continuing calibration is more than 200% or less than 50% of the response in the mid-level of the initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

10.12.3 Any samples that do not meet the internal standard criteria for the continuing calibration must be evaluated for validity. Samples that are reported with internal standard exceedances must have documentation supporting matrix effect. Where the matrix effect is well established it may be reported with narration, otherwise the samples must be reanalyzed to confirm matrix effect is required. If the internal standard exceedance is deemed to be due to an instrumental problem, instrument maintenance will be done and all affected samples must be reanalyzed after the problem is corrected.

10.12.4 The surrogate standard recoveries are evaluated to ensure that they are within limits. See section 9.4 for corrective actions for surrogate recoveries.

10.13 Dilutions

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be

in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

10.13.1 Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than half the height of the internal standards, or if individual non target peaks are less than twice the height of the internal standards, then the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgment.

10.13.2 Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

11 CALCULATIONS / DATA REDUCTION

11.1 Qualitative identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards, from the hardcopy printout of the "clean" reference spectrum book or from the NIST Library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

11.1.1 The sample component retention time must compare to within at least ±0.06 RRT units of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

11.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

11.1.3 The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80 percent.)

11.1.4 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst, the identification is correct, then the analyst shall report that identification and proceed with quantitation.

11.1.5 The characteristic ions of a compound must maximize in the same scan or within one scan of each other.

11.2 Tentatively Identified Compounds (TICs)

If the client requests components not associated with the calibration standards, a search of the NIST library may be made for the purpose of tentative identification. Guidelines are:

11.2.1 Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

11.2.2 The relative intensities of the major ions should agree to within 20%. (Example: If an ion shows an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%).

11.2.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

11.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

11.2.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the spectrum because of background contamination or coeluting peaks. (Data system reduction programs can sometimes create these discrepancies.)

11.2.6 Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual inspection of the sample with the nearest library searches should the analyst assign a tentative identification.

11.3 Calculations.

11.3.1 Response factor (RF):

Equation 1

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the specific internal standard

C_{is} = Concentration of the specific internal standard, ng

C_x = Concentration of the compound being measured, ng

Relative Retention Time (RRT) – is the ration of the retention time of a compound to that of a standard (such as an internal standard).

$$RRT = \frac{RT_C}{RT_{is}}$$

Where,

RT_C = Retention time for the volatile target compounds in the continuing calibration.

RT_{is} = Retention time for the internal standard in calibration standard or in a sample.

11.3.2 Standard deviation (SD):

Equation 2

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(Xi - X)^2}{N - 1}}$$

X_i = Value of X at i through N

N = Number of points

X = Average value of X_i

11.3.3 Percent relative standard deviation (%RSD):

Equation 3

$$\%RSD = \frac{\text{Standard Deviation}}{\overline{RF_i}} \times 100$$

$\overline{RF_i}$ = Mean of RF values in the curve

11.3.4 Percent deviation between the initial calibration and the continuing calibration (%D):

Equation 4

$$\% \text{ Deviation} = \frac{RRFic - RRFcc}{RRFic} \times 100$$

11.3.5 Percent drift between the initial calibration and the continuing calibration:

Equation 5

$$\% \text{ Drift} = \frac{C_{expected} - C_{found}}{C_{expected}} \times 100$$

Where

$C_{expected}$ = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

11.3.6 Target compound and surrogate concentrations:

Concentrations in the sample may be determined from linear or second order (quadratic) curve fitted to the initial calibration points, or from the average response factor of the initial calibration points. Average response factor may only be used when the % RSD of the response factors in the initial calibration is $\leq$ 15%.

Calculation of concentration using Average Response Factors

Equation 6

$$\text{Concentration } \mu g / L = \frac{x}{RF}$$

Calculation of concentration using Linear fit

Equation 7

$$\text{Concentration } \mu g / L = A + Bx$$

Calculation of concentration using Quadratic fit

Equation 8

$$\text{Concentration } \mu g / L = A + Bx + Cx^2$$

x is defined in equations 8, 9 and 10

A is a constant defined by the intercept

B is the slope of the curve

C is the curvature

Calculation of **x** for Water and water-miscible waste:

Equation 9

$$x = \frac{(A_x)(I_s)(D_f)}{(A_{is})(V_o)}$$

Where:

A_x = Area of characteristic ion for the compound being measured (secondary ion quantitation is allowed only when there are sample interferences with the primary ion)

A_{is} = Area of the characteristic ion for the internal standard

I_s = Amount of internal standard added in ng

$$\text{Dilution Factor} = D_f = \frac{\text{Total volume purged (mL)}}{\text{Volume of original sample used (mL)}}$$

V_o = Volume of water purged, mL

Calculation of **x** for Medium level soils:

Equation 10

$$x = \frac{(A_x)(I_s)(V_t)(1000)(D_f)}{(A_{is})(V_a)(W_s)(D)}$$

Where:

A_x, I_s, D_f, A_{is}, same as for water.

V_t = Volume of total extract, mL

V_a = Volume of extract added for purging, µL

W_s = Weight of sample extracted, g

$$D = \frac{100 - \%\text{moisture}}{100}$$

Calculation of **x** for Low level soils:

Equation 11

$$x = \frac{(A_x)(I_s)}{(A_{is})(W_s)(D)}$$

Where:

A_x, I_s, A_{is}, same as for water.

D is as for medium level soils

W_s = Weight of sample added to the purge vessel, g

Calculation of TICs: The calculation of TICs (tentatively identified compounds) isidentical to the above calculations with the following exceptions:

A_x = Area in the total ion chromatogram for the compound being measured

A_{is} = Area of the total ion chromatogram for the nearest internal standard without interference

RF = 1

In other words, the concentration is equal to **x** as defined in equations 8, 9 and 10.

11.3.7 MS/MSD Recovery and RPD Calculation:

Equation 12

$$\textbf{Matrix Spike Recovery, \%} = \frac{SSR - SR}{SA} \times 100$$

SSR = Spike sample result

SR = Sample result

SA = Spike added

Relative % Difference calculation for the MS/MSD

Equation 13

$$\textbf{RPD} = \frac{|\textbf{MSR - MSDR}|}{\frac{1}{2}(\textbf{MSR + MSDR})} \times 100$$

Where:

RPD = Relative percent difference

MSR = Matrix spike result

MSDR = Matrix spike duplicate result

12 METHOD PERFORMANCE

12.1 Method Detection Limit

Generally, the laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA SOP # PT-QA-007. (MDL) studies must be acceptable before analysis of samples may begin. MDLs should be analyzed for low level and soils and aqueous samples. For non-standard analytes, a MDL study or MDL Verification must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. At a minimum, a standard at the reporting limit must be analyzed to demonstrate the capability of the method.

12.2 Initial Demonstration

Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check/LCS samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest. The QC check sample is made up at 20 µg/L. (Some compounds will be at higher levels, refer to the calibration standard levels for guidance.)

12.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

12.2.2 The performance of all four QC check samples must meet all method requirements for LCSs.

12.2.3 If any analyte does not meet the acceptance criteria, check the acceptance limits in the reference methods (Table 6 of Method 8260B). If the recovery or precision is outside the limits in the reference methods, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.3 Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13 POLLUTION PREVENTION

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

13.2 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

13.3 This method does not contain any specific modifications that serve to minimize or prevent pollution.

14 WASTE MANAGEMENT

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001 (or CHP manual). The following waste streams are produced when this method is carried out.

14.1.1 Aqueous waste generated from analysis. This material may have a pH of less than 2.0. This waste is collected in containers identified as "Acid Waste", Waste #33. It is neutralized to a pH between 6 and 9 and disposed down a lab sink.

14.1.2 Solvent waste generated from analysis. This waste is placed in containers identified as "Vials & Extracts", Waste #7.

14.1.3 Solid waste generated from analysis. This waste is placed in trash containers and disposed with other building trash.

14.1.4 Expired Standards. This waste is placed in container identified as "Mixed Flammable Solvent Waste", Waste #3.

15 REFERENCES / CROSS REFERENCES

15.1 SW-846, 8000B, Determinative Chromatographic Separations, Revision 2, December 1996.

15.2 SW-846, Test Methods for Evaluating Solid Waste, Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260B, , Revision 2, December 1996.

15.3 SW-846, Method 5030B Purge-And-Trap For Aqueous Samples, Revision 2, December 1996.

15.4 SW-846, Method 5035 Closed-System Purge-And-Trap And Extraction For Volatile Organics In Soil And Waste Samples, Revision 0, December 1996.

15.5 40 CFR Chapter I Part 136, Appendix A, Method 624, 7-1-1997 Edition.

15.6 USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, OSWER 9240.1-05A-P, PG99-963-506, EPA540/R-99/008, October 1999.

15.7 SOP # PT-QA-025, Implementation of DoD QSM Version 3 January 2006, current version.

15.8 SOP # CA-Q-S-002, Acceptable Manual Integration Practices, current version.

15.9 Pittsburgh Laboratory Quality Assurance Manual, PT-LQAM, current version.

15.10 SOP #PT-QA-029, QA/QC Requirements for DoD QSM.

15.11 SOP #PT-QA-007, Detection Limits.

15.12 SOP # PT-QA-011, Data Recording Requirements.

15.13 SOP # PT-QA-015, Maintaining Time Integrity.

15.14 SOP #PT-QA-016, Nonconformance An Corrective Action.

15.15 SOP #PT-QA-018, Technical Data Review Requirements.

15.16 SOP # PT-QA-021, Quality Assurance Program.

15.17 SOP #PT-QA-022, Equipment Maintenance.

15.18 SOP #PT-QA-027, Sample Receiving And Chain Of Custody.

16 METHOD MODIFICATIONS

16.1 Modifications from SW-846 Method 8260B

16.1.1 Ion 119 is used as the quantitation ion for chlorobenzene-d5.

16.1.2 A relative retention time window of ±0.06 RT units is used for all components.

16.1.3 The quantitation and qualifier ions for some compounds have been added to the list of those which are recommended in SW-846 in order to improve the reliability of qualitative identification.

16.2 Modification from Method 5035

16.2.1 Presence of residual chlorine is not tested for water samples in section 8.2

16.2.2 Soils samples are not preserved with sodium bisulfate in section 8.4 for low level soils. Refer to sections 8.4 and 8.9.

16.2.3 Flow diagram for Field bisulfate preservation procedure was removed.

17 ATTACHMENTS

17.1 Figure –1 Flow diagram - Initial Demonstration and MDL

17.2 Appendix A, Section 19, Method 624 Requirements

17.3 Tables:

Table 1 - Primary Standard and Reporting Limits for SW846 8260B

Table 2 - Appendix IX Standard and Reporting Limits for SW846 8260B

Table 3 - Primary Standard Calibration Levels

Table 4 - Appendix IX Standard Calibration Levels

Table 4A - Calibration Standard Concentration and Preparation

Table 4-1 – 8260 ICAL Control List

Table 4-2 – 8260 ICAL Control List (South Carolina)

Table 5 - Reportable Analytes for Standard Tests

Table 6 - Internal Standards

Table 6A – Internal Standards with Corresponding Assigned Analytes for Quantitation

Table 7 - Surrogate Standards

Table 8 - Matrix Spike / LCS Standards

Table 9 - BFB Tune Criteria

Table 10 - SPCC Compounds and Minimum Response Factors

Table 11 - CCC Compounds

Table 12 - Characteristic Ions

Table 13 - QC Acceptance Criteria Method 8260B

Table 14 – TestAmerica Pittsburgh VOA Dilution Calculation Table

Table A-1 - Method 624 Analytes and Reporting Limits

Table A-2 - Method 624 QC Acceptance Criteria

Table B-1 - DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-3 - DoD QSM Version3: Requirements for Organic Analysis by GC/MS - Methods 8260 and 8270

18 REVISION HISTORY

18.1 Revision 11, 07/14/08:

18.1.1 Updated to new SOP format

18.1.2 Sodium bisulfate removed.

18.1.3 Sections 8.5-8.7, Terra Core added.

18.1.4 Section 9.5 use of sand for Method Blank added.

18.1.5 Section 10.1 calibration standards updated, using 7 levels.

18.1.6 Section 10.3.1, Tune criteria updated to be consistent with Pittsburgh Laboratory Quality Assurance Manual (PT-LQAM).

18.1.7 Section 10.4.11 changed to: The acceptance criteria are 75-125% for most compounds and 50-150% for poor method performers. The poor performers are footnoted in Tables 3 and 4. Any compound not listed will fall into the 50-150% criteria until knowledge of the compound can be developed. **For DoD second source must be ± 25% for all compounds, refer to SOP PT-QA-025.**

18.1.8 Section 10.5 continuing calibration levels updated.

18.1.9 Calibration levels updated, areas are highlighted. Standards tables updated.

18.1.10 SOP and method references updated.

18.2 Revision 12, 11/04/08:

18.2.1 Updated Table 4-1 SPCC designations.

18.2.2 Updated SOP references. Updated Safety section to match Corp SOP format along with sections 13 and 14 Pollution Prevention/Waste Management.

18.3 Revision 13:

18.3.1 Added Section 8.15 concerning Regulatory Requirements for Acrolein, Acrylonitrile and 2-Chloroethyl-vinyl ether in relationship to Holding Times and Preservation.

18.3.2 Added text to section 10.9.1 concerning the application of a dilution factor in accurately reflect the volume to weight relationship.

18.3.3 Updated spike amounts and volumes in section 10.7.3.1 for TCLP.

18.3.4 Removed references and requirements for DoD Version 2.2, this was a typo, Pitt never performed this version.

18.3.5 Updated Table 4-1.

18.3.6 Added to section 9.6.5: Use of marginal exceedances are not permitted for South Carolina work

18.3.7 Added to section 10.4. Note: South Carolina can only be analyzed using linear calibration, quadratic is not allowed.

18.3.8 Added references to DoD QSM 4.1, SOP PT-QA-029.

18.4 Revision 14

18.4.1 In section 7.2.6 corrected the unit to read ng/mL.

18.4.2 In section 10.4.3 added reference to Table 6A – Internal Standards with Corresponding Assigned Analytes for Quantitation.

18.4.3 In section 10.4.11 corrected grammar from criteria is to criteria are.

18.4.4 Under section 10.5.3.2.4 added reference to Table 4-2 8260 ICAL Control List (South Carolina). Footnote 3 under Table 4-2 had the following statement added: The most common poor purging List 1 compounds are Carbon tetrachloride, cis-1,3-Dichloropropene and trans-1,3-Dichloropropene.

18.4.5 In section 17, added reference to Table 4-1 8260 ICAL Control List; Table 4-2 8260 ICAL Control List (South Carolina); Table 6A – Internal Standards with Corresponding Assigned Analytes for Quantitation.

18.4.6 Added a **NOTE** in section 19.4.1 to clarify the CCAL concentration when analyzing 8260B and 624 samples together. Noted that a 10 ug/L standard will be used for calibration instead of a 20 ug/L and that all criteria for both Methods must be met in order to analyze samples.

18.4.7 Removed reference to OVAP in sections 8.9.1, 8.10.2 and 10.11.

18.4.8 Removed the DoD QSM 3.0 tables and added them to DoD QSM 3.0 SOP PT-QA-025.

18.4.9 Added reference to DoD QSM 4.1 and SOP PT-QA-029 in section 1.2

18.4.10 In section 1.4 changed 200 ug/L to 250 ug/L as per the VOA group.

18.4.11 Specified the ± 20% DoD QSM 4.1 criteria for the ICV in section 10.4.11.

18.4.12 In section 10.6.8 added reference to DoD QSM 4.1 Appendix E.

18.4.13 In section 10.6.9 added reference to DoD QSM 4.1 Appendix F, Table F-1.

18.4.14 In section 10.6.4.3.1 changed 250 ng to 200 ng as per the VOA group.

18.5 Revision 15:

18.5.1 Fixed Typos for two compounds in Tables 4-1 and 4-2: 1,1,2-Trichloro-1,2,2-Trifluoroethane and 1,2-Dibromoethane.

18.5.2 Deleted SPCC and Min FR 0.1 for ,1,2-Dichloroethane in Tables 4-1 and 4-2.

18.5.3 Updated foot note in Table 4-2 to meet SC requirements: List 2 compounds – All compounds must meet 70-130% with the exception of the identified poor purging compounds which are identified as Carbon tetrachloride, cis-1,3-Dichloropropene and trans-1,3-Dichloropropene. Any compounds outside of the 70-130% range (0r 40% for poor purgers) must be flagged in the data and narrated.

18.5.4 Added SOP references.

18.6 Revision 16

18.6.1 Hexane added to Tables 1 and A1.

18.7 Revision 17

18.7.1 Under section 9.3.8, added a NOTE concerning the analysis of Calgon Samples.

18.7.2 Under section 9.5.5, noted that an LCS/LCSD will be analyzed for Safety Kleen.

18.7.3 Under section 9.6.4, noted that an LCS/LCSD will be analyzed for Calgon samples when the parent sample for the MS/MSD requires a 5X or greater dilution.

18.7.4 In section 10.4.6.5, corrected 0.990 to ≥ 0.990.

18.7.5 Updated Table 6A with additional compounds listed under the appropriate internal standard. Corrected the 3rd internal to read 1,4-Dichlorobenzene-d4 instead of 1,2-Dichlorobenzene-d4.

18.7.6 Added Table 14 VOA Dilution Calculation Table in Section 17 and after Table 13.

18.7.7 Added a **NOTE** under section 10.4.6.5 to indicate that sporadic marginal failures are not allowed for South Carolina regulatory compliance samples.

18.7.8 Corrected Table Reference letters from B to A in sections 19.1, 19.2.3, 19.4.1 and 19.5.3.

Figure 1 - Flow diagram - Initial Demonstration and MDL

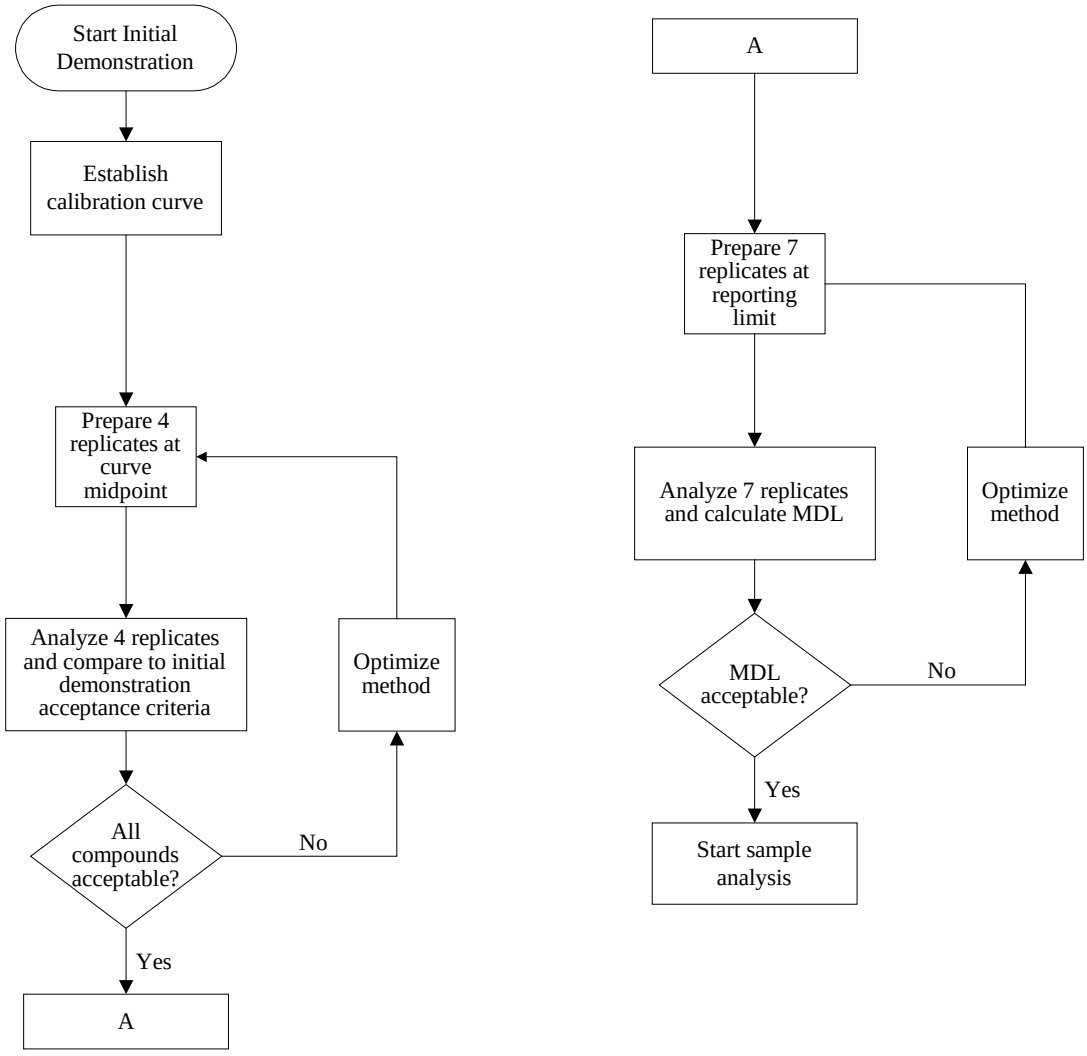


Table 1
Primary Standard and Reporting Limits for SW846 8260B

Compound	CAS Number	Low Level water µg/L	5 mL Water µg/L	Low soil µg/kg	Med. Soil µg/kg
Dichlorodifluoromethane	75-71-8	1	5	5	250
Chloromethane	74-87-3	1	5	5	250
Bromomethane	74-83-9	1	5	5	250
Vinyl chloride	75-01-4	1	5	5	250
Chloroethane	75-00-3	1	5	5	250
Trichlorofluoromethane	75-69-4	1	5	5	250
Acetone	67-64-1	10	20	20	1000
Trichlorotrifluoroethane	76-13-1	1	5	5	250
Carbon disulfide	75-15-0	1	5	5	250
Methylene chloride	75-09-2	1	5	5	250
1,1-Dichloroethene	75-35-4	1	5	5	250
1,1-Dichloroethane	75-34-3	1	5	5	250
trans-1,2-Dichloroethene	156-60-5	1	5	5	250
Methyl tert-butyl ether (MTBE)	1634-04-4	1	5	5	250
cis-1,2-Dichloroethene	156-59-2	1	5	5	250
1,2-Dichloroethene (Total)	540-59-0	1	5	5	250
Chloroform	67-66-3	1	5	5	250
1,2-Dichloroethane	107-06-2	1	5	5	250
Dibromomethane	74-95-3	1	5	5	250
2-Butanone	78-93-3	5	20	20	1000
1,1,1-Trichloroethane	71-55-6	1	5	5	250
Carbon tetrachloride	56-23-5	1	5	5	250
Bromodichloromethane	75-27-4	1	5	5	250
1,2-Dichloropropane	78-87-5	1	5	5	250
cis-1,3-Dichloropropene	10061-01-5	1	5	5	250
Trichloroethene	79-01-6	1	5	5	250
Dibromochloromethane	124-48-1	1	5	5	250
1,2-Dibromoethane	106-93-4	1	5	5	250
1,2,3-Trichloropropane	96-18-4	1	5	5	250
1,1,2-Trichloroethane	79-00-5	1	5	5	250
Benzene	71-43-2	1	5	5	250
trans-1,3-Dichloropropene	10061-02-6	1	5	5	250
Bromoform	75-25-2	1	5	5	250
4-Methyl-2-pentanone	108-10-1	5	20	20	1000
2-Hexanone	591-78-6	5	20	20	1000
Tetrachloroethene	127-18-4	1	5	5	250
Toluene	108-88-3	1	5	5	250
1,1,2,2-Tetrachloroethane	79-34-5	1	5	5	250
1,1,1,2-Tetrachloroethane	630-20-6	1	5	5	250

Table 1

Primary Standard and Reporting Limits for SW846 8260B

Compound	CAS Number	Low Level water µg/L	5 mL Water µg/L	Low soil µg/kg	Med. Soil µg/kg
1,2-Dibromo-3-chloropropane	96-12-8	1	5	5	250
Chlorobenzene	108-90-7	1	5	5	250
Ethylbenzene	100-41-4	1	5	5	250
Styrene	100-42-5	1	5	5	250
m and p Xylenes		2	10	10	500
o-xylene	95-47-6	1	5	5	250
Total xylenes	1330-20-7	3	15	15	750
p-Isopropyltoluene	99-87-6	1	5	5	250
Methylcyclohexane	108-87-2	1	5	5	250
1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	1	5	5	250
Methyl acetate	79-20-9	1	5	5	250
Cyclohexane	110-82-7	1	5	5	250
1,3-Dichlorobenzene	541-73-1	1	5	5	250
1,4-Dichlorobenzene	106-46-7	1	5	5	250
1,2-Dichlorobenzene	95-50-1	1	5	5	250
Isopropylbenzene	98-82-8	1	5	5	250
Bromobenzene	108-86-1	1	5	5	250
n-Propylbenzene	103-65-1	1	5	5	250
2-Chlorotoluene	95-49-8	1	5	5	250
4-Chlorotoluene	106-43-4	1	5	5	250
1,3,5-Trimethylbenzene	108-67-8	1	5	5	250
tert-Butylbenzene	98-06-6	1	5	5	250
1,2,4-Trimethylbenzene	95-63-6	1	5	5	250
sec-Butylbenzene	135-98-8	1	5	5	250
n-Butylbenzene	104-51-8	1	5	5	250
1,2,4-Trichlorobenzene	120-82-1	1	5	5	250
Naphthalene	91-20-3	1	5	5	250
Hexachlorobutadiene	87-68-3	1	5	5	250
1,2,3-Trichlorobenzene	87-61-6	1	5	5	250
Hexane	110-54-3	1	5	5	250

[1] Reporting limits listed for soil/sediment are based on wet weight. The reporting limits calculated by the laboratory for soil/sediment, calculated on dry weight basis, will be higher.

Table 2
Appendix IX Standard and Reporting Limits for SW846 8260B

Compound	CAS Number	Low level water µg/L	5 mL Water µg/L	Low Soil µg/kg	Medium Soil µg/mL
Allyl Chloride	107-05-1	1	5	5	250
Acetonitrile	75-05-8	20	100	100	5000
Acrolein	107-02-8	20	100	100	5000
Chloroprene	126-99-8	1	5	5	250
Iodomethane	74-88-4	1	5	5	250
Propionitrile	107-12-0	2	10	10	500
Methacrylonitrile	126-98-7	1	5	5	250
Isobutanol	78-83-1	40	200	200	10000
Iodomethane	74-88-4	1	5	5	250
Methyl methacrylate	80-62-6	1	5	5	250
Acrylonitrile	107-13-1	20	100	100	5000
Ethylmethacrylate	97-63-2	1	5	5	250
2-Chloroethyl vinyl ether[1]	110-75-8	2	10	10	500
tert-Butyl Alcohol	75-65-0	40	200	200	10,000
1,4-Dioxane	123-91-1	200	1000	1000	50000
Vinyl acetate	108-05-4	1	5	5	250
t-1,4-Dichloro-2-butene	110-57-6	1	5	5	250

Table 3

Primary Standard Calibration Levels, Standard 5 mL purge (Low Level Calibration Levels)

Compound	Calibration Level (ug/L)						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
1,2-Dichloroethane-d4 (Surrogate)	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Toluene-d8 (Surrogate)	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
4-Bromofluorobenzene (Surrogate)	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Dichlorodifluoromethane *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Chloromethane *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Bromomethane *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Vinyl chloride *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Chloroethane *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Trichlorofluoromethane *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Acetone *	5 (2)	10 (10)	25 (10)	40 (30)	50 (40)	125 (70)	250 (80)
Carbon disulfide *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Methylene chloride	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Isopropylbenzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,1-Dichloroethene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,1-Dichloroethane	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
trans-1,2-Dichloroethene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,1,1,2-Tetrachloroethane	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Methyl tert-butyl ether (MTBE) *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,2-Dibromo-3-chloropropane *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
cis-1,2-Dichloroethene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Chloroform	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,2-Dichloroethane	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Dibromomethane	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
2-Butanone *	5 (2)	10 (10)	25 (20)	40 (15)	50 (40)	125 (70)	250 (80)
1,1,1-Trichloroethane	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Carbon tetrachloride	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Bromodichloromethane	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,2-Dichloropropane	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
cis-1,3-Dichloropropene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Trichloroethene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Dibromochloromethane	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,2-Dibromoethane	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,2,3-Trichloropropane	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,1,2-Trichloroethane	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Benzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
trans-1,3-Dichloropropene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Bromoform	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)

Table 3

Primary Standard Calibration Levels, Standard 5 mL purge (Low Level Calibration Levels)

Compound	Calibration Level (ug/L)						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
4-Methyl-2-pentanone *	5 (2)	10 (10)	25 (20)	40 (30)	50 (40)	125 (70)	250 (80)
2-Hexanone *	5 (2)	10 (10)	25 (20)	40 (30)	50 (40)	125 (70)	250 (80)
Tetrachloroethene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Toluene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,1,2,2-Tetrachloroethane	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Chlorobenzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Ethylbenzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Styrene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
m and p Xylenes	10 (2)	20 (10)	50 (20)	80 (30)	100 (40)	125 (70)	500 (80)
o-xylene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,3-Dichlorobenzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,4-Dichlorobenzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,2-Dichlorobenzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Isopropylbenzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Bromobenzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
n-Propylbenzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
2-Chlorotoluene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
4-Chlorotoluene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,3,5-Trimethylbenzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
tert-Butylbenzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,2,4-Trimethylbenzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
sec-Butylbenzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
n-Butylbenzene	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,2,4-Trichlorobenzene *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Naphthalene *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Hexachlorobutadiene *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
1,2,3-Trichlorobenzene *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)

For medium level soils the above standard concentrations will be multiplied by 50.

Table 4
Appendix IX Standard Calibration Levels, Standard 5 mL purge (Low Level Calibration Levels)

Compound	Calibration Level (ug/L)						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Allyl Chloride *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Acetonitrile *	100 (20)	200 (100)	500 (200)	800 (300)	1000 (400)	2500 (700)	5000 (800)
Chloroprene *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Propionitrile *	10 (2)	20 (10)	50 (20)	80 (30)	100 (40)	250 (70)	500 (80)
Methacrylonitrile *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	125 (35)	250 (40)
Isobutanol *	200 (40)	400 (200)	1000 (400)	1600 (600)	2000 (800)	5000 (1400)	10000 (1600)
Methyl methacrylate *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	250 (35)	50 (40)
Acrolein *	100 (20)	125 (25)	150 (30)	175 (35)	200 (40)	225 (45)	250 (50)
1,4-Dioxane *	1000 (200)	2000 (1000)	5000(2000)	8000 (3000)	10000 (4000)	25000 (7000)	50000 (8000)
tert-Butyl alcohol *	200 (40)	400 (200)	1000 (400)	1600 (600)	2000 (800)	5000 (1400)	10000 (1600)
Acrylonitrile *	100 (20)	125 (25)	150 (30)	175 (35)	200 (40)	225 (45)	250 (50)
Ethylmethacrylate *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	250 (35)	50 (40)
2-Chloroethyl vinyl ether*	10 (2)	20 (10)	50 (20)	80 (30)	100 (40)	250 (70)	500 (80)
Vinyl Acetate *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	250 (35)	50 (40)
t-1,4-Dichloro-2-butene*	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	250 (35)	50 (40)
Iodomethane *	5 (1)	10 (5)	25 (10)	40 (15)	50 (20)	250 (35)	50 (40)

* Poor method performers (see section 10.4.11)

For medium level soils the above standard concentrations will be multiplied by 50.

Table 4A – Calibration Standard Concentration and Preparation

Standard Level 8260B Water or Soil 5mL syringe

STD	INT (25ug/mL)	SURR (25ug/mL)	VOA (25ug/mL)	Acetonitrile (1000ug/mL)	Methanol Added
5ppb	10ul	1ul	1ul	0.5ul	122.5ul
10ppb	10ul	2ul	2ul	1ul	120ul
25ppb	10ul	5ul	5ul	2.5ul	112.5ul
40ppb	10ul	8ul	8ul	4ul	105ul
50ppb	10ul	10ul	10ul	5ul	100ul
125ppb	10ul	25ul	25ul	12.5ul	62.5ul
250ppb	10ul	50ul	50ul	25ul	0

8260B App IX Water/Soil 5mL syringe

STD	INT 25ug/mL	App IX 25ug/mL	2CEVE 50ug/mL	A&A 25ug/mL	TBA 1000ug/mL	n-Heptane 25ug/mL
5ppb	10ul	1ul	1ul	20ul	1ul	1ul
10ppb	10ul	2ul	2ul	25ul	2ul	2ul
25ppb	10ul	5ul	5ul	30ul	5ul	5ul
40ppb	10ul	8ul	8ul	35ul	8ul	8ul
50ppb	10ul	10ul	10ul	40ul	10ul	10ul
125ppb	10ul	25ul	25ul	45ul	25ul	25ul
250ppb	10ul	50ul	50ul	50ul	50ul	50ul

Table 4A – Calibration Standard Concentration and Preparation Cont.

Dupont 5mL syringe

STD	INT 25ug/mL	Dupont VOA 25ug/mL	Dupont Acrylates 25ug/mL
5ppb	10ul	1ul	1ul
10ppb	10ul	2ul	2ul
25ppb	10ul	5ul	5ul
40ppb	10ul	8ul	8ul
50ppb	10ul	10ul	10ul
125ppb	10ul	25ul	25ul
250ppb	10ul	50ul	50ul

CLP OLM04.1/3.1/3.2 Water & Soil 5mL syringe

STD	INT (25ug/mL)	SURR (25ug/mL)	VOA (25ug/mL)	Methanol Added
10ppb	10ul	2ul	2ul	80ul
20ppb	10ul	4ul	4ul	70ul
50ppb	10ul	10ul	10ul	60ul
100ppb	10ul	20ul	20ul	40ul
200ppb	10ul	40ul	40ul	0

Table 4A – Calibration Standard Concentration & Preparation Cont.

624 & Low Level 8260B Water 25mL syringe

STD	INT 25ug/mL	SURR (25ug/mL)	VOA (25ug/mL)	Acetonitrile (1000ug/mL)	Ketone 25ug/mL	Methanol Added
1ppb	10ul	1ul	1ul	0.5ul	4ul	140ul
5ppb	10ul	5ul	5ul	2.5ul	5ul	120ul
10ppb	10ul	10ul	10ul	5.0ul	10ul	105ul
15ppb	10ul	15ul	15ul	7.5ul	15ul	88ul
20ppb	10ul	20ul	20ul	10ul	20ul	70ul
35ppb	10ul	35ul	35ul	17.5ul	35ul	17.5ul
40ppb	10ul	40ul	40ul	20ul	40ul	0

8260B Low Level App IX Water 25mL syringe

STD	INT 25ug/mL	App IX (Various)	2CEVE 50ug/mL	A&A 25ug/mL	TBA 1000ug/mL
1ppb	10ul	1ul	1ul	20ul	1ul
5ppb	10ul	5ul	5ul	25ul	5ul
10ppb	10ul	10ul	10ul	30ul	10ul
15ppb	10ul	15ul	15ul	35ul	15ul
20ppb	10ul	20ul	20ul	40ul	20ul
35ppb	10ul	35ul	35ul	45ul	45ul
40ppb	10ul	40ul	40ul	50ul	50ul

Table 4-1
8260 ICAL Control List

Compound	SW-846	Control	SPCC	Comments
1,1-Dichloroethene	8260B	CCC [1]		
Chloroform	8260B	CCC		
Ethylbenzene	8260B	CCC		
Toluene	8260B	CCC		
Vinyl Chloride	8260B	CCC		
1,2-Dichloropropane	8260B	CCC		
1,1,1-Trichloroethane	8260B	1		
1,1,2,2-Tetrachloroethane	8260B	SPCC	SPCC[3]	Min RF 0.3
1,1,2-Trichloroethane	8260B	1		
1,1-Dichloroethane	8260B	SPCC		Min RF 0.1
1,2-Dichlorobenzene	8260B	1		
1,2-Dichloroethane	8260B	1		
1,3-Dichlorobenzene	8260B	1		
1,4-Dichlorobenzene	8260B	1		
Benzene	8260B	1		
Bromodichloromethane	8260B	1		
Bromoform	8260B	SPCC	SPCC	Min RF 0.1
Bromomethane (Methyl Bromide)	8260B	2		
Carbon Tetrachloride	8260B	1		
Chlorobenzene	8260B	SPCC	SPCC	Min RF 0.3
Cis-1,3-Dichloropropene	8260B	1		
Dibromochloromethane	8260B	1		
Styrene	8260B	1		
Tetrachloroethene	8260B	1		
Trans-1,3-Dichloropropene	8260B	1		
Trichloroethene	8260B	1		
Xylenes (total)	8260B	2		
1,2,4-Trichlorobenzene	8260B	2		
1,1,2-Trichloro-1,2,2-Trifluoroethane	8260B	2[4]		
1,2-Dibromo-3-Chloropropane	8260B	2		
1,2-Dibromoethane	8260B	2		
1,2-Dichloroethene (total)	8260B	2		
2-Butanone (MEK)	8260B	2		
2-Hexanone	8260B	2		
4-Methyl-2-Pentanone	8260B	2		
Acetone	8260B	2		
Carbon Disulfide	8260B	2		

Table 4-1
8260 ICAL Control List

Compound	SW-846	Control	SPCC	Comments
Chloroethane	8260B	2		
Chloromethane (Methyl Chloride)	8260B	SPCC	SPCC	Min RF 0.1
Cis-1,2-Dichloroethene	8260B	2		
Cyclohexane	8260B	2		
Dichlorodifluoromethane	8260B	2		
Isopropylbenzene	8260B	2		
Methyl Acetate	8260B	2		
Methyl Tert-Butyl Ether (MTBE)	8260B	2		
Methylcyclohexane	8260B	2		
Methylene Chloride	8260B	2		
Trans-1,2-Dichloroethene	8260B	2		
Trichlorofluoromethane	8260B	2		
1,1,1,2-Tetrachloroethane	8260B	2		
1,2-Dichloropropene	8260B	2		
1,2,3-Trichlorobenzene	8260B	2		
1,2,3-Trichloropropane	8260B	2		
1,2,4-Trimethylbenzene	8260B	2		
1,2-Dibromoethane (EDB)	8260B	2		
1,3,5-Trimethylbenzene	8260B	2		
1,3-Dichloropropane	8260B	2		
1,4-Dioxane	8260B	2		APPIX
2,2-Dichloropropane	8260B	2		
2-Butanone (MEK)	8260B	2		
2-Chloroethyl Vinyl Ether	8260B	2		APPIX
2-Chlorotoluene	8260B	2		
4-Chlorotoluene	8260B	2		
4-Methyl-2-Pentanone (MIBK)	8260B	2		
Acetonitrile	8260B	2		APPIX
Acrolein	8260B	2		APPIX
Acrylonitrile	8260B	2		APPIX
Ally Chloride	8260B	2		APPIX
Bromobenzene	8260B	2		
Bromochloromethane	8260B	2		
Chlorodibromomethane	8260B	2		
Chloroprene	8260B	2		APPIX
Dibromomethane (Methylene Bromide)	8260B	2		
Dichlorobromomethane	8260B	2		
Ethyl Methacrylate	8260B	2		APPIX

Table 4-1
8260 ICAL Control List

Compound	SW-846	Control	SPCC	Comments
Hexachlorobutadiene	8260B	2		
Iodomethane (Methyl Iodide)	8260B	2		APPIX
Isobutanol	8260B	2		APPIX
Isobutyl Alcohol	8260B	2		APPIX
m-Dichlorobenzene	8260B	2		
Methacrylonitrile	8260B	2		APPIX
Methyl Methacrylate	8260B	2		
m-Xylene & p-Xylene	8260B	2		
Naphthalene	8260B	2		
n-Butylbenzene	8260B	2		
n-Propylbenzene	8260B	2		
o-Dichlorobenzene	8260B	2		
o-Xylene	8260B	2		
p-Dichlorobenzene	8260B	2		
p-Isopropyltoluene	8260B	2		
Propionitrile	8260B	2		APPIX
Sec-Butylbenzene	8260B	2		
Tert-Butylbenzene	8260B	2		
Tetrachloroethene	8260B	2		
Traas-1,4-Dichloro-2-butene	8260B	2		APPIX
Vinyl Acetate	8260B	2		APPIX

[1] CCC'S Must Be <20% No Exceptions

[2] SPCC's Must Pass Minimum RF Requirements

[3] List 1 Can Have Up To 2 Compounds Above 25%D But Must Be <40%.

[4] List 2 Compounds Can Be Over 40%D, However If The %D Is >50% (Too High) It Can Be Narrated As Long As The Compound(S) Are ND In The Samples; If The Compounds >50%D (Too Low) This Compound Cannot Be Analyzed For On That Particular CCAL.

Narrative Issues:

- All %RSD that >30% must be narrated. This may be changed with the development of a calibration summary sheet.
- All %Diff or %Drift >25% must be narrated.
- Any other criteria exceedance aside from these should be narrated.
- Using an average response factor curve for a %RDS ≥30% should be narrated.
- If a list two compound > 50% D or Drift and is out high and this compound is not found in the associated samples it may be reported with narration.

  Note: These criterion are subject to project-specific criteria which may vary depending on project needs.

Table 4-2
8260 ICAL Control List (South Carolina)

Compound	SW-846	Control	SPCC	Comments
1,1-Dichloroethene	8260B	CCC [1]		
Chloroform	8260B	CCC		
Ethylbenzene	8260B	CCC		
Toluene	8260B	CCC		
Vinyl Chloride	8260B	CCC		
1,2-Dichloropropane	8260B	CCC		
1,1,1-Trichloroethane	8260B	1		
1,1,2,2-Tetrachloroethane	8260B	SPCC	SPCC[3]	Min RF 0.3
1,1,2-Trichloroethane	8260B	1		
1,1-Dichloroethane	8260B	SPCC		Min RF 0.1
1,2-Dichlorobenzene	8260B	1		
1,2-Dichloroethane	8260B	1		
1,3-Dichlorobenzene	8260B	1		
1,4-Dichlorobenzene	8260B	1		
Benzene	8260B	1		
Bromodichloromethane	8260B	1		
Bromoform	8260B	SPCC	SPCC	Min RF 0.1
Bromomethane (Methyl Bromide)	8260B	2		
Carbon Tetrachloride	8260B	1		
Chlorobenzene	8260B	SPCC	SPCC	Min RF 0.3
Cis-1,3-Dichloropropene	8260B	1		
Dibromochloromethane	8260B	1		
Styrene	8260B	1		
Tetrachloroethene	8260B	1		
Trans-1,3-Dichloropropene	8260B	1		
Trichloroethene	8260B	1		
Xylenes (total)	8260B	2		
1,2,4-Trichlorobenzene	8260B	2		
1,1,2-Trichloro-1,2,2-Trifluoroethane	8260B	2[4]		
1,2-Dibromo-3-Chloropropane	8260B	2		
1,2-Dibromoethane	8260B	1		
1,2-Dichloroethene (total)	8260B	1		
2-Butanone (MEK)	8260B	2		
2-Hexanone	8260B	2		
4-Methyl-2-Pentanone	8260B	2		
Acetone	8260B	2		
Carbon Disulfide	8260B	2		
Chloroethane	8260B	2		

Table 4-2
8260 ICAL Control List (South Carolina)

Compound	SW-846	Control	SPCC	Comments
Chloromethane (Methyl Chloride)	8260B	SPCC	SPCC	Min RF 0.1
Cis-1,2-Dichloroethene	8260B	1		
Cyclohexane	8260B	1		
Dichlorodifluoromethane	8260B	2		
Isopropylbenzene	8260B	1		
Methyl Acetate	8260B	2		
Methyl Tert-Butyl Ether (MTBE)	8260B	1		
Methylcyclohexane	8260B	2		
Methylene Chloride	8260B	1		
Trans-1,2-Dichloroethene	8260B	1		
Trichlorofluoromethane	8260B	2		
1,1,1,2-Tetrachloroethane	8260B	2		
1,2-Dichloropropene	8260B	1		
1,2,3-Trichlorobenzene	8260B	2		
1,2,3-Trichloropropane	8260B	1		
1,2,4-Trimethylbenzene	8260B	1		
1,2-Dibromoethane (EDB)	8260B	1		
1,3,5-Trimethylbenzene	8260B	1		
1,3-Dichloropropane	8260B	1		
1,4-Dioxane	8260B	--		APPIX
2,2-Dichloropropane	8260B	2		
2-Butanone (MEK)	8260B	2		
2-Chloroethyl Vinyl Ether	8260B	--		APPIX
2-Chlorotoluene	8260B	1		
4-Chlorotoluene	8260B	1		
4-Methyl-2-Pentanone (MIBK)	8260B	2		
Acetonitrile	8260B	--		APPIX
Acrolein	8260B	--		APPIX
Acrylonitrile	8260B	--		APPIX
Ally Chloride	8260B	--		APPIX
Bromobenzene	8260B	2		
Bromochloromethane	8260B	2		
Chlorodibromomethane	8260B	2		
Chloroprene	8260B	--		APPIX
Dibromomethane (Methylene Bromide)	8260B	1		
Dichlorobromomethane	8260B	1		
Ethyl Methacrylate	8260B	--		APPIX
Hexachlorobutadiene	8260B	2		

Table 4-2
8260 ICAL Control List (South Carolina)

Compound	SW-846	Control	SPCC	Comments
Iodomethane (Methyl Iodide)	8260B	--		APPIX
Isobutanol	8260B	--		APPIX
Isobutyl Alcohol	8260B	--		APPIX
m-Dichlorobenzene	8260B	1		
Methacrylonitrile	8260B	--		APPIX
Methyl Methacrylate	8260B	2		
m-Xylene & p-Xylene	8260B	2		
Naphthalene	8260B	2		
n-Butylbenzene	8260B	2		
n-Propylbenzene	8260B	2		
o-Dichlorobenzene	8260B	1		
o-Xylene	8260B	2		
p-Dichlorobenzene	8260B	1		
p-Isopropyltoluene	8260B	1		
Propionitrile	8260B	--		APPIX
Sec-Butylbenzene	8260B	2		
Tert-Butylbenzene	8260B	2		
Tetrachloroethene	8260B	1		
Trans-1,4-Dichloro-2-butene	8260B	--		APPIX
Vinyl Acetate	8260B	--		APPIX

[1] CCC'S Must Be <20% No Exceptions

[2] SPCC's Must Pass Minimum RF Requirements

[3] List 1 Can Have Up To 2 Compounds Above 25%D But Must Be <40%. The most common poor purging List 1 compounds are Carbon tetrachloride, cis-1,3-Dichloropropene and trans-1,3-Dichloropropene.

[4] **List 2 compounds – All compounds must meet 70-130% with the exception of the identified poor purging compounds which are identified as Carbon tetrachloride, cis-1,3-Dichloropropene and trans-1,3-Dichloropropene. Any compounds outside of the 70-130% range (0r 40% for poor purgers) must be flagged in the data and narrated.**

Narrative Issues:

- All %RSD that >30% must be narrated. This may be changed with the development of a calibration summary sheet.
- All %Diff or %Drift >25% must be narrated.
- Any other criteria exceedance aside from these should be narrated.
- Using an average response factor curve for a %RDS ≥30% should be narrated.
- If a list two compound > 50% D or Drift and is out high and this compound is not found in the associated samples it may be reported with narration.

  Note: These criterion are subject to project-specific criteria which may vary depending on project needs.

Table 5
Reportable Analytes for TestAmerica Standard Tests

Compound	CAS Number	624	8260	Appendix IX	CLP 4.2
Dichlorodifluoromethane	75-71-8		X	X	X
Chloromethane	74-87-3	X	X	X	X
Bromomethane	74-83-9	X	X	X	X
Vinyl chloride	75-01-4	X	X	X	X
Chloroethane	75-00-3	X	X	X	X
Trichlorofluoromethane	75-69-4	X	X	X	X
Acrolein	107-02-8			X	
Acetone	67-64-1		X	X	X
Iodomethane	74-88-4			X	
Carbon disulfide	75-15-0		X	X	X
Methylene chloride	75-09-2	X	X	X	X
tert-Butyl alcohol	75-65-0			X	
1,1-Dichloroethene	75-35-4	X	X	X	X
1,1-Dichloroethane	75-34-3	X	X	X	X
trans-1,2-Dichloroethene	156-60-5	X	X	X	X
Acrylonitrile	107-13-1			X	
Methyl tert-butyl ether (MTBE)	1634-04-4	X	X	X	X
cis-1,2-Dichloroethene	156-59-2		X	X	X
Chloroform	67-66-3	X	X	X	X
1,2-Dichloroethane	107-06-2	X	X	X	X
Dibromomethane	74-95-3		X	X	
2-Butanone	78-93-3		X	X	X
1,4-Dioxane	123-91-1			X	
1,1,1-Trichloroethane	71-55-6	X	X	X	X
Carbon tetrachloride	56-23-5	X	X	X	X
Bromodichloromethane	75-27-4	X	X	X	X
1,2-Dichloropropane	78-87-5	X	X	X	X
cis-1,3-Dichloropropene	10061-01-5	X	X	X	X
Trichloroethene	79-01-6	X	X	X	X
Dibromochloromethane	124-48-1	X	X	X	X
1,2-Dibromoethane	106-93-4		X	X	X
1,2,3-Trichloropropane	96-18-4		X	X	
1,1,2-Trichloroethane	79-00-5	X	X	X	X
Benzene	71-43-2	X	X	X	X
Ethylmethacrylate	97-63-2			X	
trans-1,3-Dichloropropene	10061-02-6	X	X	X	X
Bromoform	75-25-2	X	X	X	X

Table 5
Reportable Analytes for TestAmerica Standard Tests

Compound	CAS Number	624	8260	Appendix IX	CLP 4.2
4-Methyl-2-pentanone	108-10-1		X	X	X
2-Hexanone	591-78-6		X	X	X
Tetrachloroethene	127-18-4	X	X	X	X
Toluene	108-88-3	X	X	X	X
1,1,2,2-Tetrachloroethane	79-34-5	X	X	X	X
2-Chloroethyl vinyl ether	110-75-8	X		X	
Vinyl acetate	108-05-4			X	
Chlorobenzene	108-90-7	X	X	X	X
Ethylbenzene	100-41-4	X	X	X	X
Styrene	100-42-5		X	X	X
t-1,4-Dichloro-2-butene	110-57-6			X	
m and p Xylenes			X	X	
o-xylene	95-47-6		X	X	
Total xylenes	1330-20-7		X	X	X
1,3-Dichlorobenzene	541-73-1	X	X		X
1,4-Dichlorobenzene	106-46-7	X	X		X
1,2-Dichlorobenzene	95-50-1	X	X		X
1,2-Dichloroethene (total)	540-59-0		X		
2,2-Dichloropropane	590-20-7		X	X	
Bromochloromethane	74-97-5		X		
1,1-Dichloropropene	563-58-6		X		
1,3-Dichloropropane	142-28-9		X		
1,1,1,2-Tetrachloroethane	630-20-6		X	X	
Isopropylbenzene	98-82-8		X		X
Bromobenzene	108-86-1		X		
n-Propylbenzene	103-65-1		X		
2-Chlorotoluene	95-49-8		X		
4-Chlorotoluene	106-43-4		X		
1,3,5-Trimethylbenzene	108-67-8		X		
tert-Butylbenzene	98-06-6		X		
1,2,4-Trimethylbenzene	95-63-6		X		
sec-butylbenzene	135-98-8		X		
4-Isopropyltoluene	99-87-6		X		
n-Butylbenzene	104-51-8		X		
1,2-Dibromo-3-chloropropane	96-12-8		X		X
1,2,4-Trichlorobenzene	120-82-1		X		X
Napthalene	91-20-3		X		
Hexachlorobutadiene	87-68-3		X		

Table 5
Reportable Analytes for TestAmerica Standard Tests

Compound	CAS Number	624	8260	Appendix IX	CLP 4.2
1,2,3-Trichlorobenzene	87-61-6		X		
Methylcyclohexane	108-87-2		X		X
1,1,2-Trichloro-1,2,2-Triflroroethane	76-13-1		X		X
Methyl Acetate	79-20-9		X		X
Allyl Chloride	107-05-1			X	
Acetonitrile	75-05-8			X	
Chloroprene	126-99-8			X	
Propionitrile	107-12-0			X	
Methacrylonitrile	126-98-7			X	
Isobutanol	78-83-1			X	
Methyl methacrylate	80-62-6			X	

Table 6
Internal Standards

Internal Standard Compound	Standard Concentration µg/mL	Quantitation ion (m/z)
Fluorobenzene	25	96
Chlorobenzene-d5	25	119
1,4-Dichlorobenzene-d4	25	152

Notes:

1) 10 µL of the internal standard is added to the sample. This results in a concentration of each internal in the sample of 50µg/L for a standard 5 mL purge Method 8260B, or 10 µg/L for low level Method 8260B waters (which uses a 25 ml sample aliquot), Method 624. For instruments that sample directly from the VOA vial, 10 µL of a 5 µg/mL internal standard solution is added to low level Method 8260B waters, and Method 624 since the instrument uses a 5 ml sample volume.
2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

Table 6A
Internal Standards with Corresponding Assigned Analytes for Quantitation

1st Internal - Fluorobenzene	2nd Internal – Chlorobenzene-d5	3rd Internal – 1,4-Dichlorobenzene-d4
1,1,1-Trichloroethane	1,1,1,2-Tetrachloroethane	1,1,2,2-Tetrachloroethane
1,1,2-Trichloro-1,2,2-Trifluoroethane	1,1,2-Trichloroethane	1,2,3-Trichlorobenzene
1,1-Dicloroethane	1,2-Dibromoethane (EDB)	1,2,3-Trichloropropane
1,1-Dichloroethene	1,3-Dichloropropane	1,2,4-Trichlorobenzene
1,1-Dichloropropene	2-Hexanone	1,2,4-Trimethylbenzene
1,2-Dichloroethane	4-Methyl-2-pentanone (MIBK)	1,2-Dibromo-3-chloropropane
1,2-Dichloroethene (total)	Bromoform	1,2,-Dichlorobenzene
1,2,-Dichloropropane	Chlorobenzene	1,3,5-Trimethylbenzene
1,4-Dioxane	Chlorodibromomethane	1,3-Dichlorobenzene
2,2-Dichloropropane	Ethyl methacrylate	1,4-Dichlorobenzene
2-Butanone (MEK)	Ethylbenzene	2-Chlorotoluene
2-Chloroethyl vinyl ether	Isopropylbenzene	4-Chlorotoluene
Acetone	m-Xylene & p-Xylene	Bromobenezene
Acetonitrile	o-Xylene	Hexachlorobutadiene
Acrolein	Styrene	Naphthalene
Acrylonitrile	Tetratchloroethene	n-Butylbenzene
Allyl chloride (3-Chloro-1-propene)	Toluene	n-Propylbenzene
Benzene	trans-1,3-Dichloropropene	p-Isopropyltoluene
Bromochloromethane	Xylenes (total)	sec-Butylbenzene
Bromodichloromethane	Ethyl acrylate	trans-1,4-Dicloro-2-butene
Bromomethane (Methyl bromide)	2-Nitropropane	tert-Butylbenzene
Carbon disulfide	Cyclohexanol	Dichloroethyl ether [bis(2-Chloroethyl) ether]
Carbon tetrachloride	2-Chlorobenzotrifluoride	1,3,5-Trichlorobenzene
Chloroethane	3-Chlorobenzotrifluoride	Benzyl chloride
Chloroform	4-Chlorobenzotrifluoride	2,3;2,4-Dichlorotoluene
Chloromethane (Methyl chloride)	4-Bromofluorobenzene (surrogate)	2,4; 2,5; 2,6-Dichlorotoluene
Chloroprene	Toluene-d8 (surrogate)	3-Chlorotoluene
cis-1,2-Dichloroethene		2,4-Dichlorobenzotrichloride
cis-1,3-Dichloropropene		2,5-Dichlorobenzotrichloride
Cyclohexane		3,4-Dichlorobenzotrichloride
Dibromomethane (Methylene bromide)		2,3,6-Trichlorotoluene
Dichlorodifluoromethane		2,4,5-Trichlorotoluene
Ethyl ether		
Hexane		
Iodomethane (Methyl iodide)		
Isobutyl alcohol		

1st Internal - Fluorobenzene	2nd Internal – Chlorobenzene-d5	3rd Internal – 1,4-Dichlorobenzene-d4
Methacrylonitrile		
Methyl acetate		
Methyl methacrylate		
Methyl tert-butyl ether (MTBE)		
Methylcyclohexane		
Methylene chloride		
Propionitrile		
tert-Butyl alcohol (2-Methyl-2-propanol)		
Tetrahydrofuran		
trans-1,2-Dichloroethene		
Trichloroethene		
Trichlorofluoromethane		
Vinyl Acetate		
Vinyl Chloride		
Vinyl Bromide		
2,2,4-Trimethylpentane (Isooctane)		
1,2-Epoxybutane		
n-Butanol		
n-Heptane		
Dichlorofluoromethane		
Dibromofluoromethane (surrogate)		
1,2-Dichlorobenzene-d4 (surrogate)		

Table 7
Surrogate Standards

Surrogate Compounds	Standard Concentration µg/mL
1,2-Dichloroethane-d_4	25
Dibromofluoromethane	25
Toluene-d_8	25
4-Bromofluorobenzene	25

Notes:

1) 10 µL of the surrogate standard is added to the sample. This results in a concentration of each surrogate in the sample of 50µg/L for a standard 5 mL purge Method 8260B, or 10 µg/L for low level Method 8260B waters (which uses a 25 ml sample aliquot), Method 624. For instruments that sample directly from the VOA vial, 10 µL of a 5 µg/mL surrogate solution is added to low level Method 8260B waters, and Method 624 since the instrument uses a 5 ml sample volume.
2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.
3) Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 8
Matrix Spike / LCS Compounds

Compound	Standard Concentration µg /mL
1,1-Dichloroethene	25
Trichloroethene	25
Toluene	25
Benzene	25
Chlorobenzene	25

Notes:

1) 10 µL of the standard is added to the LCS or matrix spiked sample. This results in a concentration of each spike analyte in the sample of 50µg/L for a standard 5 mL purge Method 8260B water or 10 µg/L for a low level Method 8260B sample when added to a 25 ml sample aliquot.
2) Recovery and precision limits for LCS and MS/MSD are generated from historical data and are maintained by the QA department.

Table 9
BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15% to 40% of Mass 95
75	30% to 60% of Mass 95
95	Base Peak, 100% Relative Abundance
96	5% to 9% of Mass 95
173	Less Than 2% of Mass 174
174	Greater Than 50% of Mass 95
175	5% to 9% of Mass 174
176	Greater Than 95%, But Less Than 101% of Mass 174
177	5% to 9% of Mass 176

Table 10
SPCC Compounds and Minimum Response Factors

Compound	8260B Min. RF
Chloromethane	0.100
1,1-Dichloroethane	0.100
Bromoform	>0.100
1,1,2,2-Tetrachloroethane	0.300
Chlorobenzene	0.300

Table 11
CCC compounds

Compound	Max. %RSD from Initial Calibration	Max. %D for continuing calibration
Vinyl Chloride	≤30.0	≤20.0
1,1-Dichloroethene	≤30.0	≤20.0
Chloroform	≤30.0	≤20.0
1,2-Dichloropropane	≤30.0	≤20.0
Toluene	≤30.0	≤20.0
Ethylbenzene	≤30.0	≤20.0

Table 12
Characteristic ions

Compound	Primary*	Secondary	Tertiary
1,2-Dichloroethane-d_4 (Surrogate)	65	102	
Dichlorodifluoromethane	85	87	50, 101,103
Chloromethane (Methyl chloride)	50	52	49
Vinyl chloride	62	64	61
Bromomethane (Methyl bromide)	94	96	79
Chloroethane	64	66	49
Trichlorofluoromethane	101	103	66
1,1-Dichloroethene	96	61	98
Acrolein	56	55	58
Iodomethane (Methyl iodide)	142	127	141
Carbon disulfide	76	78	
Trichlorotrifluoroethane	151	101	153
Cyclohexane	56	69	84
Acetone	43	58	
Methylene chloride	84	49	51, 86
tert-Butyl alcohol	59	74	
trans-1,2-Dichloroethene	96	61	98
Acrylonitrile	53	52	51
Methyl tert butyl ether (MTBE)	73	41	
Hexane	57	43	
1,1-Dichloroethane	63	65	83
cis-1,2-Dichloroethene	96	61	98
2-Butanone (MEK)	43	57	72**
Tetrahydrofuran (THF)	42	71	
Chloroform	83	85	47
1,2-Dichloroethane	62	64	98
Dibromomethane (Methylene bromide)	93	174	95, 172, 176
1,4-Dioxane	88	58	
Vinyl acetate	43	86	
1,1,1-Trichloroethane	97	99	117
Carbon tetrachloride	117	119	121
Benzene	78	52	77
Trichloroethene	130	95	97, 132
1,2-Dichloropropane	63	65	41
Bromodichloromethane	83	85	129
2-Chloroethyl vinyl ether	63	65	106
cis-1,3-Dichloropropene	75	77	39
trans-1,3-Dichloropropene	75	77	39

Table 12
Characteristic ions

Compound	Primary*	Secondary	Tertiary
1,1,2-Trichloroethane	97	83	85, 99
Chlorodibromomethane	129	127	131
Bromoform	173	171	175, 252
1,2,3-Trichloropropane	75	110	77, 112, 97
Toluene-d_8 (Surrogate)	98	70	100
4-Bromofluorobenzene (Surrogate)	95	174	176
Toluene	91	92	65
4-Methyl-2-pentanone (MIBK)	43	58	57, 100
Tetrachloroethene	164	166	131
Ethyl methacrylate	69	41	99, 86, 114
2-Hexanone	43	58	57, 100
Chlorobenzene	112	114	77
Ethylbenzene	106	91	
Xylenes	106	91	
Styrene	104	103	78, 51, 77
Dichlorobenzene (all isomers)	146	148	111
trans 1,4-Dichloro-2-butene	53	75	89, 77, 124
1,1,2,2-Tetrachloroethane	83	85	131, 133
Allyl Chloride	76	41	78
Acetonitrile	40	41	
Dichlorofluoromethane	67	69	
Isopropyl ether	87	59	45
Chloroprene	53	88	90
n-Butanol	56	41	42
Propionitrile	54	52	55
Methacrylonitrile	41	67	52
Isobutanol (Isobutyl alcohol)	41	43	74
Methyl methacrylate	41	69	100
1,1,1,2-Tetrachloroethane	131	133	119
1,2-Dibromo-3-chloropropane	157	155	75
Ethyl ether	59	74	
Ethyl Acetate	43	88	61
2-Nitropropane	41	43	46
Cyclohexanone	55	42	98
Isopropylbenzene	105	120	
Dibromochloromethane	129	208	
1,2,4-Trichlorobenzene	180	182	145
1,1,2-Trichloro-1,2,2-trifluoroethane	101	151	
1,2-Dibromoethane	107	109	

Table 12
Characteristic ions

Compound	Primary*	Secondary	Tertiary
Methyl acetate	43	74	
Methylcyclohexane	83	55	
1,2,3-Trichlorobenzene	180	182	145
1,2,4-Trimethylbenzene	105	120	
1,3,5-Trimethylbenzene	105	120	
1,3-Dichloropropane	76	78	
2,2-Dichloropropane	77	97	
2-Chlorotoluene	126	91	
4-Chlorotoluene	126	91	
Bromobenzene	156	158	77
Bromochloromethane	128	49	130
Hexachlorobutadiene	225	260	227
m-Xylene & p-Xylene	106	91	
Naphthalene	128		
n-Butylbenzene	91	134	
n-Propylbenzene	120	91	
o-Xylene	106	91	
p-Isopropyltoluene	119	134	
sec-Butylbenzene	105	134	
tert-Butylbenzene	119	91	134
Tetrachloroethene	164	129	131

* The primary ion should be used for quantitation unless interferences are present, in which case a secondary ion may be used.
** m/z 43 may be used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

Table 13 - 8260B QC Acceptance Criteria															
	Water	LCS			MS			Soil	LCS			MS		
Compound	AMT ug/L	LCL	UCL	RPD	LCL	UCL	RPD	AMT ug/kg	LCL	UCL	RPD	LCL	UCL	RPD
Acetone	40	10	141	32	10	141	32	40	20	150	40	20	150	40
Benzene	40	80	120	20	80	120	20	40	77	120	20	77	120	20
Bromodichloromethane	40	71	119	20	71	119	20	40	70	125	21	70	125	21
Bromoform	40	49	137	20	49	137	20	40	53	140	23	53	140	23
Bromomethane	40	45	150	23	45	150	23	40	25	150	40	25	150	40
2-Butanone	40	31	139	35	31	139	35	40	35	149	36	35	149	36
Carbon disulfide	40	62	126	20	62	126	20	40	50	127	23	50	127	23
Carbon tetrachloride	40	63	139	25	63	139	25	40	69	122	22	69	122	22
Chlorobenzene	40	83	120	20	83	120	20	40	79	120	20	79	120	20
Dibromochloromethane	40	64	124	20	64	124	20	40	70	132	20	70	132	20
Chloroethane	40	33	150	24	33	150	24	40	22	150	40	22	150	40
Chloroform	40	77	119	20	77	119	20	40	72	120	25	72	120	25
Chloromethane	40	49	133	20	49	133	20	40	44	131	27	44	131	27
Cyclohexane	40	69	124	20	69	124	20	40	64	130	21	64	130	21
1,2-Dibromo-3-chloropropane	40	28	150	20	28	150	20	40	35	136	40	35	136	40
1,2-Dibromoethane	40	57	124	20	57	124	20	40	70	131	20	70	131	20
1,2-Dichlorobenzene	40	75	125	20	75	125	20	40	71	124	22	71	124	22
1,3-Dichlorobenzene	40	76	125	21	76	125	21	40	75	118	20	75	118	20
1,4-Dichlorobenzene	40	76	123	20	76	123	20	40	77	116	20	77	116	20
Dichlorodifluoromethane	40	28	140	20	28	140	20	40	25	150	34	25	150	34
1,1-Dichloroethane	40	77	122	22	77	122	22	40	66	124	23	66	124	23
1,2-Dichloroethane	40	63	140	25	63	140	25	40	61	127	23	61	127	23
cis-1,2-Dichloroethene	40	82	116	20	82	116	20	40	80	118	20	80	118	20
trans-1,2-Dichloroethene	40	78	120	20	78	120	20	40	77	121	20	77	121	20
1,1-Dichloroethene	40	69	127	20	69	127	20	40	59	129	25	59	129	25
1,2-Dichloropropane	40	75	114	20	75	114	20	40	72	122	20	72	122	20
cis-1,3-Dichloropropene	40	74	123	20	74	123	20	40	73	120	20	73	120	20
trans-1,3-Dichloropropene	40	63	122	20	63	122	20	40	74	129	20	74	129	20
Ethylbenzene	40	79	124	25	79	124	25	40	78	125	21	78	125	21
2-Hexanone	40	35	129	24	35	129	24	40	32	150	32	32	150	32
Isopropylbenzene	40	73	130	20	73	130	20	40	70	133	22	70	133	22

Table 13 - 8260B QC Acceptance Criteria														
	Water	LCS			MS			Soil	LCS			MS		
Compound	AMT ug/L	LCL	UCL	RPD	LCL	UCL	RPD	AMT ug/kg	LCL	UCL	RPD	LCL	UCL	RPD
Methyl acetate	40	34	127	29	34	127	29	40	27	142	40	10	150	50
Methylcyclohexane	40	67	120	20	67	120	20	40	66	135	23	50	150	50
Methylene chloride	40	75	120	20	75	120	20	40	58	127	28	65	134	20
4-Methyl-2-pentanone	40	33	135	29	33	135	29	40	44	148	30	37	146	39
Methyl tert-butyl ether	40	53	122	20	53	122	20	40	48	132	36	47	131	45
Styrene	40	78	124	22	78	124	22	40	83	129	20	73	121	22
1,1,2,2-Tetrachloroethane	40	59	136	20	59	136	20	40	60	139	24	38	138	20
Tetrachloroethene	40	78	126	25	78	126	25	40	78	129	20	73	120	25
Toluene	40	80	124	20	80	124	20	40	78	124	21	60	134	26
1,2,4-Trichlorobenzene	40	35	150	30	35	150	30	40	51	136	40	48	131	30
1,1,1-Trichloroethane	40	69	134	24	69	134	24	40	67	126	31	71	121	24
1,1,2-Trichloroethane	40	75	126	23	75	126	23	40	70	128	22	61	125	23
Trichloroethene	40	80	120	20	80	120	20	40	76	119	21	52	143	26
Trichlorofluoromethane	40	14	150	20	14	150	20	40	20	150	40	21	153	20
1,1,2-Trichloro-1,2,2-trifluoroethane	40	70	131	30	70	131	30	40	55	130	37	53	146	30
Vinyl chloride	40	57	128	26	57	128	26	40	63	124	27	43	138	25
Xylenes (total)	120	81	121	20	81	121	20	120	83	126	20	75	121	20
4-Bromofluorobenzene	40	75	120		75	120		40	63	120		63	120	
1,2-Dichloroethane-d4	40	62	123		62	123		40	52	124		52	124	
Toluene-d8	40	80	120		80	120		40	72	127		72	127	
Dibromofluoromethane	40	80	120		80	120		40	68	121		68	121	

These limits are established based on internal laboratory data.

Table 14 - TestAmerica Pittsburgh VOA Dilution Calculation Table

Matrix	Dilution Required	Dilution Formula
Soil	1.25	4.00g/5mL
	1.67	3.00g/5mL
	2	2.50g/5mL
	2.5	2.00g/5mL
	4	1.25g/5mL
	5	1.00g/5mL
Methanol	2	50uL(5.00g/5mL)/5mL P&T
	4	25uL(5.00g/5mL)/5mL P&T
	5	20uL(5.00g/5mL)/5mL P&T
	10	10uL(5.00g/5mL)/5mL P&T
	20	5uL(5.00g/5mL)/5mL P&T
	25	100uL(1mL(5.00g/5mL)/25mL)/5mL P&T
	50	50uL(1mL(5.00g/5mL)/25mL)/5mL P&T
	100	25uL(1mL(5.00g/5mL)/25mL)/5mL P&T
25mL Water	2	(12.5mL/25mL)/5mL P&T
	4	(6.25mL/25mL)/5mL P&T
	5	(5 mL/25mL)/5mL P&T
	10	(2.5mL/25mL)/5mL P&T
	12.5	(2 mL/25mL)/5mL P&T
	20	(1.25mL/25mL)/5mL P&T

Matrix	Dilution Required	Dilution Formula
	40	(625uL/25mL)/5mL P&T
	50	(500uL/25mL)/5mL P&T
	100	(250uL/25mL)/5mL P&T
	125	(200uL/25mL)/5mL P&T
	150	(500uL(5mL/15mL)/25mL)/5mL P&T
	200	(125uL/25mL)/5mL P&T
	250	(100uL/25mL)/5mL P&T
	400	(62.5uL/25mL)/5mL P&T
	500	(50uL/25mL)/5mL P&T
	1000	(25uL/25mL)/5mL P&T
	1250	(20uL/25mL)/5mL P&T
	1500	(50uL(5mL/15mL)/25mL)/5mL P&T
	2000	(12.5uL/25mL)/5mL P&T
	2500	(10uL/25mL)/5mL P&T
	4000	(25uL/100mL)/5mL P&T
	5000	(5uL/25mL)/5mL P&T
	8000	(12.5uL/100mL)/5mL P&T
	10000	(2.5mL(25uL/25mL)/25mL)/5mL P&T
	12500	(2.5mL(20uL/25mL)/25mL)/5mL P&T
	15000	(2.5mL(500uL(100uL/5mL)/15mL)/25mL)/5mL P&T
	20000	(2.5mL(12.5uL/25mL)/25mL)/5mL P&T
	25000	(2.5mL(10uL/25mL)/25mL)/5mL P&T

Matrix	Dilution Required	Dilution Formula
	50000	(2.5mL(5uL/25mL)/25mL)/5mL P&T
	100000	(2.5mL(10uL/100mL)/25mL)/5mL P&T
5mL Water	2	(2.5mL/5mL)/5mL P&T
	4	(1.25mL/5mL)/5mL P&T
	5	(1mL/5mL)/5mL P&T
	8	(625uL/5mL)/5mL P&T
	10	(500uL/5mL)/5mL P&T
	12.5	(2mL/25mL)/5mL P&T
	20	(250uL/5mL)/5mL P&T
	40	(125uL/5mL)/5mL P&T
	50	(100uL/5mL)/5mL P&T
	80	(62.5uL/5mL)/5mL P&T
	100	(50uL/5mL)/5mL P&T
	125	(200uL/25mL)/5mL P&T
	150	(5mL(100uL/5mL)/15mL)/5mL P&T
	200	(25uL/5mL)/5mL P&T
	250	(100uL/25mL)/5mL P&T
	400	(25uL/10mL)/5mL P&T
	500	(50uL/25mL)/5mL P&T
	800	(12.5uL/10mL)/5mL P&T
	1000	(25uL/25mL)/5mL P&T
	1250	(20uL/25mL)/5mL P&T

Matrix	Dilution Required	Dilution Formula
	1500	(500uL(100uL/5mL)/15mL)/5mL P&T
	2000	(12.5uL/25mL)/5mL P&T
	2500	(10uL/25mL)/5mL P&T
	4000	(25uL/100mL)/5mL P&T
	5000	(5uL/25mL)/5mL P&T
	8000	(12.5uL/100mL)/5mL P&T
	10000	(2.5mL(25uL/25mL)/25mL)/5mL P&T
	12500	(2.5mL(20uL/25mL)/25mL)/5mL P&T
	15000	(2.5mL(500uL(100uL/5mL)/15mL)/25mL)/5mL P&T
	20000	(2.5mL(12.5uL/25mL)/25mL)/5mL P&T
	25000	(2.5mL(10uL/25mL)/25mL)/5mL P&T
	50000	(2.5mL(5uL/25mL)/25mL)/5mL P&T
	100000	(500uL(10uL/100mL)/5mL)/5mL P&T

NOTE: Primary dilutions are contained within the innermost parentheses. Secondary and/or Tertiary dilutions bracket the primary dilutions.

19 REQUIREMENTS FOR EPA 624

19.1 Method 624 is required for demonstration of compliance with NPDES wastewater discharge permits. This method can be applied only to aqueous matrices. The standard analyte list and reporting limits are listed in Table A-1.

19.1.1 The tune period for this method is defined as 24 hours after passing a 25 ug/ml BFB.

19.1.2 The initial calibration curve for this method requires at least three points.

19.2 Sample concentrations are calculated using the average RRF from the initial calibration curve.

19.2.1 Each target analyte is assigned to the closest eluting internal standard.

19.2.2 Initial demonstration of Proficiency

19.2.3 The spiking level for the four replicate initial demonstration of proficiency is 20 µg/L. The acceptance criteria are listed in Table A-2.

19.3 Initial calibration curve requirements:

19.3.1 Target compounds listed in Method 624 must have RSD ≤ 35%.

19.3.2 If this requirement cannot be met, a regression curve must be constructed for the non-compliant compounds. There is no correlation coefficient requirement for the regression curve.

19.3.3 For compounds not listed in Method 624, the average response factor will be used for quantitation.

19.3.4 The initial calibration is verified daily by the analysis of a 20 ug/L second source QC Check Standard.

19.4 Continuing calibration verification requirements:

19.4.1 The continuing calibration standard is the daily QC Check Standard. The acceptance criteria are listed in Table A-2. **NOTE: If 8260B and 624 samples are analyzed together the concentration of the CCAL will be 10 ug/L. The**

CCAL will need to pass criteria for both Method 8260B and 624 in order to analyze for both methods using the same CCAL.

19.5 LCS and MS/MSD requirements

19.5.1 The daily 20 ug/L QC Check Standard also serves as the LCS.

19.5.2 The MS and MSD will be 20 ug/L for all compounds.

19.5.3 The recovery limits for MS/MSD and LCS recovery are listed in Table A-2.

19.5.4 The LCS and MS are required for 5% of the samples.

19.6 Method clarifications, modifications and additions

19.6.1 Section 5.2.2 of the source method describes the trap packing materials as Tenax GC, Methyl silicone, silica gel and coconut charcoal. TestAmerica routinely employs the Supelco VOCARB 3000, which consists of Carbopack B and Carboxen 1000 and 1001.

19.6.2 Section 5.3.2 of the source method describes a packed analytical column. TestAmerica routinely employs capillary columns when performing this method.

19.6.3 The source method provides a suggested list of compounds for internal and surrogate standards. TestAmerica Pittsburgh uses the internal standards and surrogates found in Tables 6 and 7.

19.7 When informed that the samples are from a potential chlorinated site, residual chlorine will be checked using total residual chlorine strips. If residual chlorine is detected, the Project Manager will be immediately informed and corrective action will be initiated.

Table A-1.
Method 624 Analytes and Reporting Limits

Analytes	CAS Number	µg/L
Benzene	71-43-2	1
Bromodichloromethane	75-27-4	1
Bromoform	75-25-2	1
Bromomethane	74-83-9	1
Carbon tetrachloride	56-23-5	1
Chlorobenzene	108-90-7	1
Chloroethane	75-00-3	1
2-Chloroethyl vinyl ether *	110-75-8	2
Chloroform	67-66-3	1
Chloromethane	74-87-3	1
Dibromochloromethane	124-48-1	1
1,2-Dichlorobenzene	95-50-1	1
1,3-Dichlorobenzene	541-73-1	1
1,4-Dichlorobenzene	106-46-7	1
1,1-Dichloroethane	75-34-3	1
1,2-Dichloroethane	107-06-2	1
1,1-Dichloroethene	75-35-4	1
trans-1,2-Dichloroethene	156-60-5	1
1,2-Dichloropropane	78-87-5	1
cis-1,3-Dichloropropene	10061-01-5	1
trans-1,3-Dichloropropene	10061-02-6	1
Ethylbenzene	100-41-4	1
Methylene chloride	75-09-2	1
1,1,2,2-Tetrachloroethane	79-34-5	1
Tetrachloroethene	127-18-4	1
Toluene	108-88-3	1
1,1,1-Trichloroethane (1,1,1-Trichloroethene)	71-55-6	1
1,1,2-Trichloroethane (1,1,2-Trichloroethene)	79-00-5	1
Trichloroethene (Trichloroethane)	79-01-6	1
Trichlorofluoromethane	75-69-4	1
Vinyl chloride	75-01-4	1
Hexane[1]	110-54-3	1

2-Chloroethylvinyl ether degrades under acidic conditions and cannot be determined in an acid preserved sample.
[1] Not part of 624 PP standard list.

Table A-2.
Method 624 QC Acceptance Criteria

Analytes	Daily QC Check acceptance criteria %Recovery	Mean recovery, 4 replicate initial demonstration acceptance criteria (20µg/L spike)	Standard deviation, 4 replicate initial demonstration acceptance criteria (20µg/L spike)	Matrix spike acceptance criteria (% Recovery)
Benzene	64-136	15.2-26.0	6.9	37-151
Bromodichloromethane	65-135	10.1-28.0	6.4	35-155
Bromoform	71-129	11.4-31.1	5.4	45-169
Bromomethane	14-186	D-41.2	17.9	D-242
Carbon tetrachloride	73-127	17.2-23.5	5.2	70-140
Chlorobenzene	66-134	16.4-27.4	6.3	37-160
Chloroethane	38-162	8.4-40.4	11.4	14-230
2-Chloroethyl vinyl ether	0-224	D-50.4	25.9	D-305
Chloroform	67-133	13.7-24.2	6.1	51-138
Chloromethane	D-204	D-45.9	19.8	D-273
Dibromochloromethane	67-133	13.8-26.6	6.1	53-149
1,2-Dichlorobenzene	63-137	11.8-34.7	7.1	18-190
1,3-Dichlorobenzene	73-127	17.0-28.8	5.5	59-156
1,4-Dichlorobenzene	63-137	11.8-34.7	7.1	18-190
1,1-Dichloroethane	72-128	14.2-28.5	5.1	59-155
1,2-Dichloroethane	68-132	14.3-27.4	6.0	49-155
1,1-Dichloroethene	50-150	3.7-42.3	9.1	D-234
trans-1,2-Dichloroethene	69-131	13.6-28.5	5.7	54-156
1,2-Dichloropropane	34-166	3.8-36.2	13.8	D-210
cis-1,3-Dichloropropene	24-176	1.0-39.0	15.8	D-227
trans-1,3-Dichloropropene	50-150	7.6-32.4	10.4	17-183
Ethylbenzene	59-141	17.4-26.7	7.5	37-162
Methylene chloride	60-140	D-41.0	7.4	D-221
1,1,2,2-Tetrachloroethane	60-140	13.5-27.2	7.4	46-157
Tetrachloroethene	73-127	17.0-26.6	5.0	64-148
Toluene	74-126	16.6-26.7	4.8	47-150
1,1,1-Trichloroethane (1,11-Trichloroehene)	75-125	13.7-30.1	4.6	52-162
1,1,2-Trichloroethane (1,1,2-Trichloroethene)	71-129	14.3-27.1	5.5	52-150
Trichloroethene (Trichloroethane)	66-134	18.6-27.6	6.6	71-157
Trichlorofluoromethane	48-152	8.9-31.5	10.0	17-181
Vinyl chloride	4-196	D-43.5	20.0	D-251

D = MDL for the particular analyte
Note: These limits are based on method 624. The QC check acceptance criteria in percent recovery is calculated from the concentration range given in the method where the QC sample concentration is at 20 ug/L. For instance for Benzene the method states a concentration range of 12.8-27.2 ug/L. 12.8/20 *100 = 64 and 27.2/20 * 100 = 136, therefore these conversions in percent recovery is listed in the above table.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Semivolatile Organic Analysis by GCMS

Method(s): SW-846 8270C and EPA 625

Approvals (Signature/Date):

11/17/09	11/17/09
Sharon Bacha Date	Steve Jackson Date
Technical Manager	Health & Safety Coordinator
11/17/09	11/17/09
Nasreen K. DeRubeis Date	Larry Matko Date
Quality Assurance Manager	Laboratory Manager

1. SCOPE AND APPLICATION

1.1. This method is based upon SW846 8270C, and is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from solid and aqueous matrices. The modifications presented in Attachment A may be followed for analysis of wastewater following method 625. Direct injection of a sample may be used in limited applications. Refer to Tables 1 through 4 for the list of compounds applicable for this method. Note that the compounds are listed in approximate retention time order. Additional compounds may be amenable to this method. If non-standard analytes are required, they must be validated by the procedures described in section 12 before sample analysis.

1.2. The following compounds may require special treatment when being determined by this method:

- Benzidine can be subject to oxidative losses during solvent concentration and exhibits poor chromatography. Neutral extraction should be performed if this compound is expected.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be distinguished from diphenylamine.
- Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
- Hexachlorophene is not amenable to analysis by this method.
- 3-Methylphenol cannot be separated from 4-methylphenol by the conditions specified in this method.

1.3. The standard reporting limit (SRL) of this method for determining an individual compound is approximately 0.33 mg/kg (wet weight) for soil/sediment samples, 1 - 200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for groundwater samples. Some compounds have higher reporting limits. Refer to Tables 1 and 2 for specific SRLs. Reporting limits will be proportionately higher for sample extracts that require dilution.

1.4. For DoD QSM Version 3 additional requirements, refer to SOP PT-QA-025 and for DoD QSM Version 4.1 requirements, refer to SOP PT-QA-029.

1.5. Analytes, Matrix(s), and Reporting Limits:

1.5.1. This method is used to determine semivolatile organic compounds in a variety of matrices: water, soil, sediment, sludge, waste and tissue samples.

1.5.2. Reporting Limits are listed in Tables 1 through 2D.

2. SUMMARY OF METHOD

2.1. Aqueous samples are extracted with methylene chloride using a separatory funnel, a continuous extractor or Accelerated One-Step™. Solid samples are extracted with methylene chloride / acetone using sonication, soxhlet, accelerated soxhlet or pressurized fluid extraction. Waste dilution is used for samples that are miscible with the solvent. The extract is dried and concentrated to a final volume as defined for the matrix in the extraction SOP. Extraction procedures are detailed in SOP# PT-OP-001. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of characteristic ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

3. DEFINITIONS

3.1. CCC (Calibration Check Compounds) - A subset of target compounds used to evaluate the calibration stability of the GC/MS system. A maximum percent deviation of the CCC's is specified for calibration acceptance.

3.2. SPCC (System Performance Check Compounds) - Target compounds designated to monitor chromatographic performance, sensitivity, and compound instability or degradation on active sites. Minimum response factors are specified for acceptable performance.

3.3. Batch - The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process to the extent possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the TestAmerica Pittsburgh QC Program document (QA-003/PT-QA-021) for further details of the batch definition.

3.4. Method Blank - An analytical control consisting of all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

3.5. LCS (Laboratory Control Sample) - A blank spiked with the parameters of interest that is carried through the entire analytical procedure. Analysis of this sample with acceptable recoveries of the spiked materials demonstrates that the laboratory techniques for this method are acceptable.

3.6. MS (Matrix Spike)- aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

3.7. MSD (Matrix Spike Duplicate)- a second aliquot of the same sample as the matrix spike (above) that is spiked in order to determine the precision of the method.

3.8. PT-LQAM – Pittsburgh laboratory quality assurance manual.

3.9. Method Code QL – Quantims (LIMS) Method code for 8270C.

3.10. Method Code 42 – Quantims (LIMS) Method code for 8270C low level.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If an interference is detected it is necessary to determine if the source of interference is in the preparation and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.2. The use of high purity reagents, solvents, and gases helps to minimize interference problems.

4.3. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample.

4.4. Contamination by carryover can occur whenever high-level and low-level samples are

sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.5. Phthalate contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of

getting cut. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.4. Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers should be kept closed unless transfers are being made.

5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Pittsburgh associate. The situation must be reported immediately to a laboratory supervisor or EH&S coordinator

6. EQUIPMENT AND SUPPLIES

6.1. Gas Chromatograph/Mass Spectrometer System: An analytical system complete with a temperature-programmable gas chromatograph suitable for split/split less injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

6.2. Column: 30 m x 0.32 mm I.D. (or 0.25 mm I.D.) 0.5-µm film thickness silicon-coated fused-silica capillary column (J & W Scientific DB-5.625 or equivalent). Alternate columns are acceptable if they provide acceptable performance.

6.3. Mass Spectrometer: Capable of scanning from 35 to 500 AMU every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 6 when 50 ng of the GC/MS tuning standard is injected through the GC.

6.4. GC/MS Interface: Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.5. Data System: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended.

6.6. Syringe: 10 µL Hamilton Laboratory grade syringes or equivalent.

6.7. Carrier gas: Ultra high purity helium.

7. REAGENTS AND STANDARDS

7.1. A minimum of seven calibration points are prepared. The low point should be at or below the reporting limit. Refer to Tables 12 through 13 for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit and the high standard defines the range of the calibration.

7.2. An Internal Standard solution is prepared. Compounds in the I.S. Mix are: acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10. The standard is stored at -10ºC ± 2 ºC.

7.2.1. Internal Standards are added to all standards and extracts to result in 40ng injected onto the column. For example, if the volume of an extract used was 200 µL, 20 µL of a 400 µg/mL internal standard solution would be added for a 1 µL injection. For low level analysis internal standards are added to all standards and extracts to result in 8 ng injected onto the column. For example, if the volume of an extract being analyzed is 100 uL, 1 µL of a 400 µg/mL internal standard solution would be added for a 2 µL injection.

7.3. Surrogate Standard Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. Surrogate compounds and levels are listed in Table 11.

7.4. GC/MS Tuning Standard: A methylene chloride solution containing 50 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared. Pentachlorophenol, benzidine, and DDT, should also be included in the Tuning Standard at 50 µg/mL. The standard is stored according to manufacturer recommendations.

7.5. Laboratory Control Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. LCS compounds and levels are listed in Tables 9 and 10.

7.6. Matrix Spike Solution: Prepare as indicated in the preparative methods. See preparation SOP. The matrix spike compounds and levels are the same as the LCS compounds.

7.7. The standards listed in 7.1 to 7.6 should be refrigerated at $\leq 6^{o}$C when not in use.

Refrigeration at -10°C to -20°C may be used if it can be demonstrated that analytes do not fall out of solution at this temperature. The standards must be replaced at least once a year. The continuing calibration standard must be replaced every week and is stored at 4 °C ± 2°C.

7.8. Standard Stock Solutions: See attachment "Standard Preparation Logbook Record".

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Reference appropriate facility SOPs and PT- LQAM for sample bottle preservation.

8.2. Samples are stored at 4 ± 2°C. Samples and extracts should be stored in suitable glass containers with Teflon lined caps. The extracts are stored at -10 °C ± 2°C (Extracts will normally be stored for 30 days after invoicing.)

8.3. Water samples are extracted within seven days of sampling and the extracts are analyzed within forty days of extraction. Solids, sludges, and organic liquids are extracted within fourteen days of sampling and the extracts are analyzed within forty days of extraction.

9. QUALITY CONTROL

9.1. See Document QA-0003 "TestAmerica Pittsburgh Quality Control Program" for additional detail. **For DoD QSM requirements and exceptions to requirements refer to SOP PT-QA-025, and Table B-1 and B-3. For DoD QSM 4.1 refer to SOP PT-QA-029.**

9.2. Initial Demonstration of Capability

9.2.1. For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin. Refer to the flow chart in section 17.2.

9.2.2. For non-standard analytes an MDL study should be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.3. Control Limits

For DoD quality control requirements and acceptance criteria see SOP PT-QA-025 and PT-QA-029. In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates, MS and LCS Precision limits for matrix spikes / matrix spike duplicates are mean relative percent difference +/- 3 standard deviations.

9.3.1. These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported unless the dilution is more than 10X.

9.3.2. Routine 8270, QL and 42 Method Codes - Surrogates will be considered DIL, NC (Diluted out – can not be calculated) at 11X or above. Any dilution between a straight run and 10X run will be reported. Straight runs up to a 5X we should be able to see surrogates. If surrogates are outside QC limits and no obvious matrix is visible, these samples will go back for reextraction provided there are no technical reasons why reextraction should not be done. Project Manager approval will be required if technical judgment is used not to reextract. If surrogates are outside QC for dilutions 6X through 10X a NCM will be generated noting surrogates are out due to dilution.

9.3.3. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.3.4. Refer to the QC program document (QA-003/PT-QA-021) for further details of control limits.

9.4. Method Blank

9.4.1. A method blank is prepared and analyzed with each batch of samples. The method blank consists of reagent water for aqueous samples, and sodium sulfate for soil samples (Refer to SOP No. PT-OP-001 for details). Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher. Refer to the TestAmerica Pittsburgh QC Program document (QA-003/PT-QA-021) for further details on the corrective actions. **For DoD requirements see PT-QA-025, Implementation of the DoD QSM**

Versions 3, January 2006. **For DoD Version 4.1 requirements see SOP PT-QA-029.**

- If the analyte is a common laboratory contaminant (phthalate esters), the data may be reported with qualifiers if the concentration of the analyte is less than five times the RL. Such action must be taken in consultation with the client.

- Reanalysis of any samples with reportable concentrations of analytes found in the method blank is required unless other actions are agreed with the client.

- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.4.2. The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.4.3. If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B", and appropriate comments may be made in a narrative to provide further documentation.

9.4.4. Sample results are NOT to be blank subtracted.

9.5. Instrument Blank

9.5.1. Instruments must be evaluated for contamination during each 12 hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of methylene chloride with the internal standards added. It is evaluated in the same way as the method blank.

9.6. Laboratory Control Sample (LCS)

9.6.1. A laboratory control sample (LCS) is prepared and analyzed with every batch of

samples. The LCS is spiked with all target compounds listed unless specified otherwise by a client or agency. All control analytes must be within established control limits (Table 9). The compounds must be spiked at a concentration appropriate for the chosen method of analysis, see Tables 9 through 10 for routine 8270 and low level (method codes 42 and QL). For DoD LCS control limits and requirements see SOP PT-QA-025 (Version 3) or SOP PT-QA-029 (Version 4.1).

9.6.2. If any control analyte (Table 9) in the LCS is outside the laboratory established historical control limits, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. The analyst should consult with the PM and QA Manager to ensure that reporting with narration is acceptable with the client and program. Where this is approved a non-conformance memo will be created including all evidence that the associated samples are not affected.

- If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.6.3. Ongoing monitoring of the LCS provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.7. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every batch of samples. The MS/MSD is spiked with the same analytes as the LCS (full analyte spike). Compare the percent recovery and relative percent difference (RPD) of the control analytes to that in the laboratory specific historically generated limits. (Table 9)

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for

accepting the batch must be documented.

- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.

- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.8. Surrogates

9.8.1. Every sample, blank, and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. Surrogate compounds must be spiked at appropriate level chosen for the method of analysis, see Table 11 for 8270 routine and low level surrogates. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 11.

9.8.2. If any surrogates are outside control (Table 15A and 15B) limits the following corrective actions must take place (except for dilutions):

- Check all calculations for error.

- Ensure that instrument performance is acceptable.

- Recalculate the data and/or reanalyze the extract if either of the above checks reveal a problem.

- Re-extract and reanalyze the sample or flag the data as “Estimated Concentration” if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to

demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.8.3. If the sample with surrogate recoveries outside the recovery limits was a sample used for an MS/MSD and the surrogate recoveries in the MS/MSD are also outside of the control limits, then the sample, the MS, and the MSD do not require reanalysis as this phenomenon would indicate a possible matrix problem.

9.8.4. If the surrogates were within control limits in the sample and the MS/MSD surrogates are outside QC limits, the MS/MSD confirm matrix interference and sample and MS/MSD will not be reextracted. If the surrogates are outside QC limits in the sample but the MS/MSD surrogates are within QC limits, the sample will be reextracted and reanalyzed. If there is a trending pattern with the samples, analyst will use technical judgment whether to reextract or not.

9.8.5. If the sample is reanalyzed and the surrogate recoveries in the reanalysis are acceptable, then the problem was within the analyst's control and only the reanalyzed data should be reported. (Unless the reanalysis was outside holding times, in which case reporting both sets of results may be appropriate.)

9.8.6. If the reanalysis does confirm the original results, the original analysis is reported and the data flagged as estimated due to matrix effect.

9.8.7. Routine 8270, QL and 42 Method Codes - Surrogates will be considered DIL, NC (Diluted out – can not be calculated) at 11X or above. Any dilution between a straight run and 10X run will be reported. Straight runs up to a 5X we should be able to see surrogates. If surrogates are outside QC limits and no obvious matrix is visible, these samples will go back for reextraction provided there are no technical reasons why reextraction should not be done. Project Manager approval will be required if technical judgment is used not to reextract. If surrogates are outside QC for dilutions 6X through 10X a NCM will be generated noting surrogates are out due to dilution.

9.8.8. **For DoD work the QSM indicates that all surrogate exceedances must be re-prepped and reanalyzed for confirmation of all matrix effects**.

9.9. Nonconformance and Corrective Action

9.9.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA

Manager.

9.10. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.11. TestAmerica Pittsburgh QC Program

Further details of QC and corrective action guidelines are presented in the TestAmerica Pittsburgh QC Program documented in Policy QA-003/PT-QA-021.

10. PROCEDURE

10.1. CALIBRATION AND STANDARDIZATION

10.1.1. For DoD QSM Version 3 calibration requirements refer to SOP PT-QA-025. For DoD QSM, Version 4.1 calibration requirements refer to SOP PT-QA-029.

10.1.2. Summary

10.1.2.1. The instrument is tuned for DFTPP, calibrated initially with a six-point calibration curve, and verified each 12-hour shift with one or more continuing calibration standard(s). Recommended instrument conditions are listed in Table 5.

10.1.3. All standards and extracts are allowed to warm to room temperature before injecting.

10.1.4. Instrument Tuning

Prior to any GCMS analytical sequence, including calibration, the instrument parameters for the tune and subsequent sample analyses within that sequence must be set. Prior to tuning/auto-tuning the mass spec, the parameters may be adjusted within the specifications set by the manufacturer or the analytical method. These generally do not need any adjustment but it may be required based on the current instrument performance. If the tune verification does not pass it may be necessary to clean the source or perform additional maintenance. Any maintenance is documented in the maintenance log.

At the beginning of every twelve hour shift when analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria (Table 6) is achieved for DFTPP (decafluorotriphenylphosphine).

10.1.4.1. Inject 50 ng of the GC/MS tuning standard (Section 7.4) into the GC/MS system. Part of the purpose of the tune is to demonstrate sensitivity and analyzing solutions at higher concentrations does not support this purpose. Tune failures may be due to saturation and a lower DFTPP concentration may be warranted. Obtain a mass spectra of DFTPP and confirm that all the key m/z criteria in Table 6 are achieved. Acceptable means of passing DFTPP are as follows:

10.1.4.2. Tune evaluations usually utilize the "Autofind" function and are set up to look at the apex +/- 1 scan and average the three scans. Background correction is required prior to the start of the peak but no more than 20 scans before. Background correction cannot include any part of the target peak. The peak apex, or the scan immediately before the apex, or the scan immediately after the apex, or the average of these three scans may be used.

10.1.4.3. Other Options or if Auto Tune Fails:

10.1.4.3.1. Sometimes the instrument does not always correctly identify the apex on some peaks when the peak is not perfectly shaped. In this case, manually identify and average the apex peak +/- 1 scan and background correct as in 10.1.4.2. This is consistent with EPA 8270.

10.1.4.3.2. Or the scan across the peak at one half peak height may be averaged and background corrected. This is consistent with Standard EPA 625.

10.1.4.3.3. A single scan at the Apex (only) may also be used for the evaluation of the tune. For SW 846 and EPA 600 series methods, background correction is still required.

10.1.4.3.4. Adjustments such as adjustments to the repeller and ion focus lenses, adjusting the EM Voltage, etc. may be made prior to tune verification as long as all of the subsequent injections in the 12 hour tune cycle are analyzed under the same MS tune settings and it is

documented in the run sequence log and/or maintenance log that an adjustment was made. Excessive adjusting (more than 2 tries) without clear documentation is not allowed. Necessary maintenance is performed and documented in instrument log.

10.1.4.3.5. Cleaning the source or other maintenance may be performed and then follow steps for tune evaluation above. Note: If significant maintenance was performed, see methods 8000B or 8000C then the instrument may require recalibration prior to proceeding.

10.1.4.3.6. Tune evaluation printouts must include the chromatogram and spectra as well as the Tune evaluation information. In addition, the verifications must be sent directly to the printer or pdf file (no screen prints for DFTPP tunes). This ability should be built into the instrument software.

10.1.4.3.7. Since the limits are expressed in whole percentages, the results may be rounded to whole percentage before comparing to criteria when assessing the tune verification against the tune requirements. However, the comparison to the criteria is usually done automatically by the software and if the printout says “Fail” then there would have to be documentation of the hand calculation on the raw data and comparison to the criteria if the lab intends to still accept the tune. In most cases the analyst is better off performing an adjustment and rerunning the tune standard.

10.1.4.3.8. All MS tune settings must remain constant between running the tune check and all other samples. It is recommended that a separate tune method not be used, however a separate method may be used as long as the MS conditions between the methods are the same as the sample analysis method and tracked so any changes that are made to the analysis method are also made to the tune method.

10.1.4.3.9. If the instrument has a built in macro that checks the DFTPP, use of this macro with no manual manipulation is also acceptable and preferred (assuming, of course that the correct ion ratios are being checked).

10.1.4.3.10. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

10.1.4.4. The GC/MS tuning standard must also be used to evaluate the inertness of the chromatographic system. The tailing factor for Benzidine and pentachlorophenol must be calculated. Benzidine must have a tailing factor that is less than 3 and pentachlorophenol must have a tailing factor that is less than 5. If DDT is an analyte of interest, it must be included in the tuning standard, and its breakdown must be ≤ 20%. The DDT breakdown check minimum frequency is daily prior to analysis of samples. The entire calculation must be included on the raw data. Refer to section 12 for the appropriate calculations.

10.1.5. Initial Calibration

10.1.5.1. Internal Standard Calibration Procedure: Internal standards are listed in Table 7. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation. For DoD initial calibration requirements refer to SOP PT-QA-025 (Version 3) or SOP PT-QA-029 (Version 4.1).

10.1.5.2. Compounds should be assigned to the IS with the closest retention time.

10.1.5.3. Prepare calibration standards at a minimum of eight concentration levels for each target compound and all surrogates. Six standards must be used for a quadratic least squares calibration. It may also be useful to analyze six calibration levels and use the lower five for most analytes and the upper five for analytes that have poor

response. In either case, the lowest standard must be at or below the reporting limit and the use of only five standards requires a linear curve technique to be used. Add the internal standard mixture to result in 40 ng on column. (For example, if the volume of the calibration standard used is 1 mL, add 100 µL of the 400 µg/mL internal standard solution for a 1 µL injection). The concentrations of all analytes are listed in tables 12 and 13. For low level analysis internal standards are added to all standards and extracts to result in 8 ng injected onto the column. For example, if the volume of an extract being analyzed is 100 uL, 1 µL of a 400 µg/mL internal standard solution would be added for a 2 µL injection.

10.1.5.4. Analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in section 12 and verify that the SPCC and CCC criteria in section 10.1.5.5 and 10.1.5.6 are met. **No sample analysis may be performed unless these criteria are met.**

10.1.5.5. System Performance Check Compounds (SPCCs): The minimum average RF for semivolatile SPCCs is 0.050. If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

SPCC Compounds:

N-nitroso-di-n-propylamine
Hexachlorocyclopentadiene
2,4-Dinitrophenol
4-Nitrophenol

10.1.5.6. Calibration Check Compounds (CCCs): The %RSD of the response factors for each CCC in the initial calibration must be less than 30% for the initial calibration to be considered valid. This criterion must be met before sample analysis begins. Problems similar to those listed under SPCCs could affect this criterion.

10.1.5.6.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.1.5.6.2. CCC Compounds:

Phenol
Acenaphthene
1,4-Dichlorobenzene
N-nitrosodiphenylamine
2-Nitrophenol
Pentachlorophenol
2,4-Dichlorophenol
Fluoranthene
Hexachlorobutadiene
Di-n-octylphthalate
4-Chloro-3-methylphenol
Benzo(a)pyrene
2,4,6-Trichlorophenol

10.1.5.7. Note: the laboratory may not use the "grand mean" rule. The following are guidelines that are used for routine SW-846 analysis within the laboratory, however these guidelines are subject to program and project specific requirements.

10.1.5.8. Where a target compound is ≤15% RSD an average response factor curve may be used. If the 15% RSD criteria is exceeded for a non-CCC target compound the analyst must assess the curve and attempt to apply a "best-fit" curve function. The first step of the assessment is to find out if the quadratic curve will have a correlation coefficient of ≥ .995. If it does not, then use the average response factor. If it does, then review where the quadratic curve intercepts the y- axis in comparison to the MDL and origin. Also review the shape of the curve. Does it overlap itself or have other potential problems? These steps should all be used in deciding when a quadratic curve or average response factor curve would be best.

10.1.5.9. Where a quadratic or polynomial curve is used R must be ≥.995 for a curve to be considered to be an acceptable fit.

10.1.5.10. All linear curves for non-CCC compounds that exceed 15% RSD or

best-fit curve functions that have R < .995 are in exceedance of guidance criteria and must be evaluated for corrective action. Any non-CCC compound being reported from a curve that does not meet either the 15% RSD criteria or the R = .995 for a "best-fit" curve will be narrated as a non-conformance.

10.1.6. The following exceptions may be reportable with narration depending on the project DQO's and data usability requirements:

10.1.6.1. Where a target compound is ≥15% but ≤30% an average response factor curve may still be used if the analyst shows that the average response factor is an acceptable fit over the range of use. A graphical representation of the curve should be presented for documentation. However, if the quadratic curve is clearly a better fit it should be used.

10.1.6.2. Compound list will be divided into two lists: List 1 (reliable performers) and List 2 (poor performers). List 1 compounds should always have a %RSD less than 30% or correlation coefficient of .995 with an allowance of up to four sporadic marginal failures for semivolatiles. Sporadic marginal failures for these compounds should be </= 40% or .990. Sporadic marginal failures require a print out of the curve with narration.

10.1.6.3. List 2 compounds is comprised of the list of known poor performers. For List 2 analytes, where the %RSD is ≤15% an average response factor will be used. For %RSDs >15% and ≤60% the best fit curve will be selected. For these compounds a print out of the curve will be provided as a graphical documentation of curve performance.

10.1.6.4. Documentation: Raw target curve summary with all compounds set to average response factor will be provided. If quadratic or polynomial equations are used a reprint of the curve table will be provided to show the correlation coefficient for the "best fit" equation. And as noted above, compounds that need additional documentation to demonstrate the curve fit will have a graphical presentation of the curve provided for reference.

10.1.6.5. Any analyte not on List 1 or List 2 would be held to specific criteria

based on project specific requirements.

10.1.6.6. Any non-CCC compound being reported from a curve that does not meet either the 15% RSD criteria or the R = .995 for a "best-fit" curve will be narrated as a non-conformance.

10.1.6.7. All %RSDs that are >30% must be narrated and when using an average response factor curve for a %RSD >30 % should also be narrated.

10.1.7. Weighting of data points

In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.1.8. If time remains in the 12 hour period initiated by the DFTPP injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.1.9. Quantitation is performed using the calibration curve or average response factor from the initial curve, not the continuing calibration.

10.1.10. **Second Source Calibration Verification Requirements:**

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Second source calibration verification	Once after each initial calibration	Value of second source for all analytes within ± 30% of expected value (initial source) for all work except DoD. For DoD work all analytes must be within ± 25% of expected value. The exception to this requirement	Correct problem and verify second source standard. Rerun second source verification. If that fails, correct problem and repeat	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until calibration has been verified.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
		is for poor performers: 2-Naphthylamine and Benzaldehyde. For these compounds the criteria is 50-150. **Note:** 2-Naphthylamine and Benzaldehyde are not DoD compounds.	initial calibration.		

10.2. Continuing Calibration

10.2.1. At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. A 50 ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 6.

10.2.2. Following a successful DFTPP analysis the continuing calibration standard(s) are analyzed. The standards must contain all semivolatile analytes, including all required surrogates. A mid level calibration standard is used for the continuing calibration.

10.2.3. The following criteria must be met for the continuing calibration to be acceptable:

- The SPCC compounds must have a response factor of ≥ 0.05.
- The percent difference or drift of the CCC compounds from the initial calibration must be $\leq 20\%$. (see section 12 for calculations)
- List 1 compounds that are Non CCC's must be $\leq 25\%$ differences or drift with the allowance of up to four which must be $\leq 40\%$.
- List 2 target compounds including Appendix IX will be accepted where the % difference or drift is $\leq 50\%$.
- Where a List 2 target compound is out high by > 50% and the compound is ND in the samples, the samples may be reported with narration.
- If a list 1 compound is not found in the sample, a CCV(out high) of up to 50%D or drift, may be accepted with narration subject to determination

that it is acceptable for the specific project.

- Any compound with a %D or Drift >25% must be narrated.
- The internal standard response must be within 50-200% of the response in the mid level of the initial calibration.
- The internal standard retention times must be within 30 seconds of the retention times in the mid-level of the initial calibration.

10.2.3.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.2.4. Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the DFTPP have passed. (A sample *injected* less than 12 hours after the DFTPP is acceptable.)

10.3. **Sample Preparation**

Samples are prepared following the procedure in SOP # PT-OP-001.

10.4. **Sample Analysis**

10.4.1. Calibrate the instrument as described in section 10. Depending on the target compounds required by the client, it may be necessary to use more than one calibration standard.

10.4.2. All samples must be analyzed using the same instrument conditions as the preceding continuing calibration standard.

10.4.3. Add internal standard to the extract to result in 40 ng injected on column (for example, 1 µL of a 2000µL/mL internal standard solution in 100 µL of extract for a 2 µL injection). Mix thoroughly before injection into the instrument. For low level analysis internal standards are added to all standards and extracts to result in 8 ng injected onto the column. For example, if the volume of an extract being analyzed is 100 uL, 1 µL of a 400 µg/mL internal standard solution would be added for a 2 µL injection.

10.4.4. Inject the sample extract into the GC/MS system using the same injection

technique as used for the standards.

10.4.5. The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in section 12. Quantitation is based on the initial calibration, not the continuing calibration.

10.4.6. Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst or automatically by the data system. For manual integration practices refer to TestAmerica corporate SOP, CA-Q-S-002, Acceptable Manual Integration Practices. For DoD and all other projects the following criteria must be met:

When manual integrations are performed, raw data records shall include a complete audit trail for those manipulations, raw data output showing the results of manual integration (i.e., chromatograms of manually integrated peaks), and notation of rationale, date, and name or initials of person performing manual integration operation (electronic signature is acceptable). DoD QSM, Version 3, Clarification 50 and 57.

Case Narrative. For DoD the case narrative shall provide: identification of **samples and analytes** for which manual integration was necessary. DoD QSM, Version 3, Appendix DoD-A and DoD QSM, Version 4.1, Appendix DoD-E.

10.4.7. Target compounds identified by the data system are evaluated using the criteria listed in section 11.0.

10.4.8. Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, TIC) may be performed if required by the client. They are evaluated using the criteria in section 11.0. At least 20 TICs will be generated.

10.5. Tissue analysis follows the same procedure as other samples as described in this SOP.

10.6. Initial review and corrective actions

10.6.1. If the retention time for any internal standard in the continuing calibration changes by more than 0.5 minutes from the mid-level initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

10.6.2. If the internal standard response in the continuing calibration is more than 200% or less than 50% of the response in the mid-level of the initial calibration standard, the chromatography will be reviewed and if in the technical judgment of the analyst obvious matrix interference is observed and the chromatographic system returns within control, samples will be reported as is if not reanalysis of samples analyzed while the system was malfunctioning is required.

10.6.3. Any samples that do not meet the internal standard criteria for the continuing calibration must be evaluated for validity. Samples that are reported with internal standard exceedances must have documentation supporting matrix effect. Where the matrix effect is well established it may be reported with narration, otherwise the samples must be reanalyzed to confirm matrix effect is required. If the internal standard exceedance is deemed to be due to an instrumental problem, instrument maintenance will be done and all affected samples must be reanalyzed after the problem is corrected

10.6.4. The surrogate standard recoveries are evaluated to ensure that they are within limits. See section 9.8 for corrective actions for surrogate recoveries.

10.7. Dilutions

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, based on analyst technical judgment, the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

10.7.1. Routine 8270, QL and 42 Method Codes - Surrogates will be considered DIL, NC (Diluted out – can not be calculated) at 11X or above. Any dilution between a straight run and 10X run will be reported. Straight runs up to a 5X we should be able to see surrogates. If surrogates are outside QC limits and no obvious matrix is visible, these samples will go back for reextraction provided there are no technical reasons why reextraction should not be done. Project Manager approval will be required if technical judgment is used not to reextract. If surrogates are outside QC for dilutions 6X through 10X a NCM will be generated noting surrogates are out due to dilution.

If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are less than

two times the height of the internal standards, the sample should be reanalyzed at a more concentrated dilution. If viscosity of the sample is in question, as per analyst technical judgment, the lowest possible dilution will be done in order for the autosampler to function properly due to viscosity. This requirement is approximate and subject to analyst judgment. For example, samples containing organic acids may need to be analyzed at a higher dilution to avoid destroying the column.

10.7.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

10.8. Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, refrigerate them at 4 $\pm$ 2^{o}C, protected from light in screw cap vials equipped with unpierced Teflon lined septa.

10.9. Retention time criteria for samples

Retention time windows must be established and verified once per ICAL and at the beginning of the analytical shift as per DoD QSM, Version 3, Appendix DoD-B, Table B-3 and DoD QSM, Version 4.1, Appendix DoD-F, Table F-4. If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

10.9.1. If the retention time of any internal standard in any sample varies by more than 0.1 minute from the preceding continuing calibration standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
Retention Time window position establishment for each analyte and surrogate	Once per ICAL	Position shall l be set using the midpoint standard of the initial calibration curve.	NA	NA
Evaluation of relative retention times (RRT)	With each sample	RRT of each target analyte in each calibration standard within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	Flagging criteria are not appropriate.

10.10. Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to the facility specific SOP for determination of percent moisture.

10.11. Procedural Variations

10.11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. Any unauthorized deviations from this procedure must also be documented as a non-conformance, with a cause and corrective action described.

10.12. Troubleshooting Guide

10.12.1. Daily Instrument Maintenance

In addition to the checks listed in the instrument maintenance schedule in the TestAmerica Pittsburgh Laboratory Quality Assurance Manual (LQAM), the following daily maintenance should be performed.

10.12.1.1. Clip Column as necessary.

10.12.1.2. Install new or cleaned injection port liner as necessary.

10.12.1.3. Install new septum as necessary.

10.12.1.4. Perform mass calibration as necessary.

10.12.2. Major Maintenance

A new initial calibration is necessary following major maintenance. Major maintenance includes changing the column, cleaning the ion volume or repeller, cleaning the source, and replacing the multiplier. Refer to the manufacturer's manual for specific guidance.

11. CALCULATIONS / DATA REDUCTION

11.1. Qualitative identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards, referencing the hardcopy "clean" spectra reference book or from the NBS library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- The sample component relative retention time must compare to ± 0.06 RRT units of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.
- All ions present in the standard mass spectra at a relative intensity greater than 30% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.
- The characteristic ions of a compound must maximize in the same scan or within one scan of each other.
- The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%.)

11.1.1. If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

11.2. Mass chromatogram searches:

Certain compounds are unstable in the calibration standard and cannot be calibrated in the normal way. In particular, the compound hexachlorophene (CAS 70-30-4) falls into this category, and is required for Appendix IX analysis. For this analyte a mass chromatogram search is made.

11.2.1. Hexachlorophene

Display the mass chromatograms for mass 196 and mass 198 for the region of the chromatogram from at least 2 minutes before chrysene-d12 to at least 4 minutes after chrysene-d12. If peaks for both ions coincide then the analyst evaluates the spectrum for the presence of hexachlorophene. No quantitation is possible.

11.3. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches shall the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30% and 70%.)
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or presence of coeluting compounds.

- Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

- Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

11.4. Anyone evaluating data is trained to know how to handle isomers with identical mass spectra and close elution times. These include:

Dichlorobenzenes
Methylphenols
Trichlorophenols
Phenanthrene, anthracene
Fluoranthene, pyrene
Benzo(b) and (k)fluoranthene
Chrysene, benzo(a)anthracene

Extra precautions concerning these compounds are to more closely scrutinize retention time vs. the calibration standard and also to check that all isomers have distinct retention times.

The compounds which may be analyzed by 8270C include some problem compounds would be the poor responders or compounds that chromatograph poorly. Included in this category would be:

Benzoic acid
Chloroanilines
Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol
3,3'-Dichlorobenzidine
Benzyl alcohol
4,6-Dinitro-2-methylphenol

Manually checking the integrations would be appropriate for these compounds.

11.5. **Calculations**

11.5.1. Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

$\overline{RF}$ = Mean of RFs from intial caibration for a compound

SD = Standard deviation of RFs from initial calibration for a compound,

$$\text{SD} = \sqrt{\sum_{i=1}^{N} \frac{\left(RFi - \overline{RF}\right)^2}{N-1}}$$

RFi = RF for each of the calibration levels

N = Number of RF values

11.5.2. Continuing calibration percent drift

$$\%Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

C_{actual} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

11.5.3. Concentration in the extract

The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration.

11.5.4. Average response factor

If the average of all the %RSDs of the response factors in the initial calibration is $\leq$ 15%, the average response factor from the initial calibration may be used for quantitation.

$$\boldsymbol{RF} = \frac{\boldsymbol{A_x C_{is}}}{\boldsymbol{A_{is} C_x}} \qquad mean\ \overline{RF} = \sum_{i=1}^{n} RF_i / n$$

Where:

$\mathbf{A_x}$ = Area of the characteristic ion for the compound to be measured

$\mathbf{A_{is}}$ = Area of the characteristic ion for the specific internal standard

$\mathbf{C_{is}}$ = Concentration of the specific internal standard, ng

$\mathbf{C_x}$ = Concentration of the compound being measured, ng

11.5.5. **Relative Retention Time (RRT)** – is the ration of the retention time of a compound to that of a standard (such as an internal standard).

$$RRT = \frac{RT_C}{RT_{is}}$$

Where,

RT_C = Retention time for the volatile tragert compounds in the continuing calibration.

RT_{is} = Retention time for the internal standard in calibrtion standard or in a sample.

11.5.6. Linear fit

$$C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$$

C_{ex}= Concentration in extract, µg/mL

R_x= Response for analyte

R_{is}= Response for internal standard

C_{is}= Concentration of internal standard

A= Intercept

B= Slope

11.5.7. Quadratic fit

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}}{R_{is}}\right)$$

C = Curvature

11.5.8. The concentration in the sample is then calculated:

11.5.8.1. Aqueous Calculation

$$\text{Concentration, } \mu g / L = \frac{C_{ex} V_t}{V_o}$$

Where:

V_t = Volume of total extract, µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1 mL extract will mean V_t = 10,000 µL. If half of the base/neutral extract and half of the acid extract are combined, V_t = 2,000.)

V_o = Volume of water extracted (mL)

C_{ex} = *Result from linear or quadratic fit*

11.5.8.2. Sediment/Soil, Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis:

$$\text{Concentration, } \mu g / kg = \frac{C_{ex} V_t}{W_s D}$$

W_s = Weight of sample extracted or diluted in grams

D = (100 - % moisture in sample)/100, for a dry weight basis or 1 for a wet weight basis

11.5.9. MS/MSD percent recovery calculation.

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

S_{SR} = Spike sample result

S_R=Sample result

S_A = Spike added

11.5.10. Relative % Difference calculation for the MS/MSD

$$RPD = \frac{|MS_R - MSD_R|}{(MS_R + MSD_R)/2} \times 100$$

RPD = Relative percent difference

MS_R = Matrix spike result

MSD_R = Matrix spike duplicate result

11.5.11. Relative response factor calculation.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

A_x=Area of the characteristic ion for the compound being measured

A_{is}=Area of the characteristic ion for the specific internal standard

C_x=Concentration of the compound being measured (µg/L)

C_{is} =Concentration of the specific internal standard (µg/L)

11.5.12. Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

A_x=Area of the total ion chromatogram for the compound being measured

A_{is}=Area of the total ion chromatogram for the nearest internal standard without interference

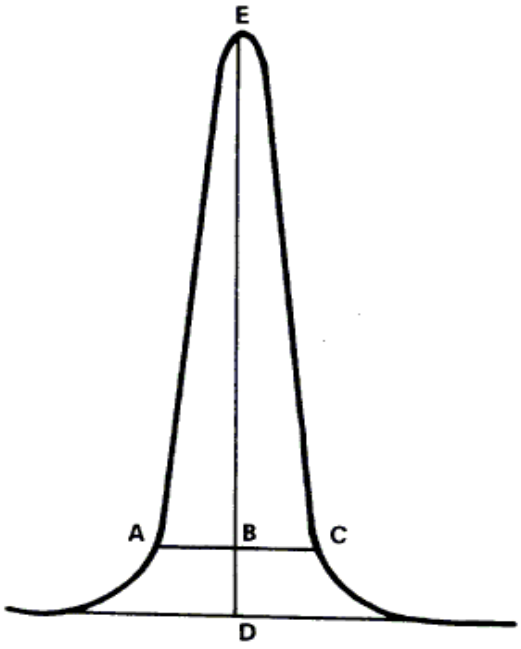
RF=1

11.5.13. Percent DDT breakdown

$$\%\ \text{DDT breakdown} = \frac{\text{DDEarea} + \text{DDDarea}}{\text{DDTarea} + \text{DDEarea} + \text{DDarea}}$$

The total ion current areas are used for this calculation

11.5.14. Tailing Factor Calculation



TAILING FACTOR= $\frac{BC}{AB}$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

12. METHOD PERFORMANCE

12.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of

interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is defined in SOP # PT-QA-007. MDLs for the analytes of interest are performed as per SOP PT-QA-007. For NELAC MDLs are verified annually. For DoD MDLs are verified quarterly. For DoD QSM 4.1 refer to SOP PT-QA-029.

12.2. Also for DoD QSM 4.1 LOQs (Limit of Quantitation) or RL is verified quarterly.

12.3. Initial Demonstration

Each laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of LCS containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check or LCS mix to cover all analytes of interest. IDOC is analyzed for each new analyst.

12.3.1. Four aliquots of the QC check sample or LCS are analyzed using the same procedures used to analyze samples, including sample preparation.

12.3.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria for the LCS. Current limits are maintained in LIMS.

12.3.3. If any analyte does not meet the acceptance criteria the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.4. Non-standard analytes

For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

12.5. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

12.6. Data Quality Objectives (DQO). Refer to project-specific Quality Assurance plans for DQO information.

13. POLLUTION CONTROL

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Pittsburgh Health and Safety Facility Addendum. The following waste streams are produced when this method is carried out.

14.1.1. Solvent waste generated from cleaning operations and out of specification standards. This waste is placed in a waste container identified as "Methylene Chloride Waste", Waste #2 or "Mixed Flammable Solvent Waste", Waste #3.

14.1.2. Sample extracts in vials. This waste is placed in containers identified as "Vials & Extracts", Waste #7.

14.1.3. Sylon Waste. This waste is collected in a container identified as "Sylon (5%) / TolueneWaste", Waste #20.

15. REFERENCES / CROSS-REFERENCES

15.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique, Method 8270C, Revision 3, December 1996.

15.2. J. W. Eichelberger, L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography/Mass Spectrometry," Analytical Chemistry, 47, 995 (1975).

15.3. SOP # PT-QA-025, Implementation of DoD QSM Version 3 January 2006, current

version.

15.4. USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, OSWER 9240.1-05A-P, PG99-963-506, EPA540/R-99/008, October 1999.

15.5. SOP # PT-OP-001, Extraction and Cleanup of Organic Compounds from Waters and Solids, based on SW-846 3500 series, 3600 series, and Method 8151A.

15.6. SOP # PT-QA-007, Determination of Method Detection Limits (MDL).

15.7. SOP # CA-Q-S-002, Acceptable Manual Integration Practices.

15.8. Pittsburgh Laboratory Quality Assurance Manual (PT-LQAM).

15.9. SOP # PT-QA-029, Implementation of DoD QSM Version 4.1 April 2009, current version.

16. METHOD MODIFICATIONS

16.1. Modifications from Reference Method

16.1.1. A relative retention time window of ± 0.06 RRT units is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

16.1.2. The quantitation and qualifier ions for some compounds have been added to the list of those which are recommended in SW-846 in order to improve the reliability of qualitative identification.

17. ATTACHMENTS

17.1. Attachment A - Modifications Required For Analysis Of Wastewater Following Method 625

17.2. Appendix A - Routine Calibration Criteria For Most Projects Using SW-846 8270C – For DoD refer to DoD SOP PT-QA-025 (Version 3) or SOP PT-QA-029 (Version 4.1).

17.3. Attachment B – Standard Preparation Logs

17.4. Appendix B – EPA Memo Regarding Method 625 Modifications

17.5. Appendix C – DoD QSM QA/QC Requirements

18. REVISION HISTORY

18.1. Revision 8, 11/16/07:

18.1.1. Modifications in this version of SOP are highlighted throughout the procedure in Revision 8.

18.1.2. 8270C low level analysis added to this SOP. Calibration levels, internal standard levels and spike levels, dilution requirements and reporting limits were all updated for method codes 42 and QL.

18.1.3. SOP format updated to TestAmerica SOP format.

18.2. Revision 9, 07/28/08

18.2.1. Safety section updated to new format. Section numbers in Procedure updated to reflect current format.

18.2.2. Section10.1.4 updated the tune criteria to be consistent with Corp policy and PT-LQAM.

18.2.3. Section 10.1.10 updated for second source requirement for DoD. For DoD compounds listed in QSM Version 3 all compounds must meet the ± 25% criteria except for the two compounds listed in this section, which are not DoD compounds.

18.2.4. 8270C revision number and date added in References. Manual integration SOP reference updated.

18.2.5. Caprolactam reporting limit changed for to 5 mg/l and 170 ug/kg for method code 42 LL BNA and 50 and 1700 for method code QL BNA.

18.3. Revision 10, 09/09/09

18.3.1. Added the SOP reference PT-QA-029 for DoD version 4.1 requirements where reference to PT-QA-025 is found in this SOP.

18.3.2. Removed Table 12 and renumbered Table 12A as Table 12. Also removed Low Level from the Table title.

18.3.3. Removed Table 15 and removed Low Level from Table 15B.

18.3.4. Removed Tables 14 and 14-A.

18.3.5. Updated the Standard References in Attachment B.

18.3.6. Added Level 7 at 30 ug/ml to Tables 12 and 13.

18.4. Revision 11

18.4.1. Updated cross reference in section 10.1.4.3.1 to section 10.1.4.2.

Appendix A – Calibration Criteria

This Appendix summarizes routine calibration criteria for most projects using SW-846 8270C. It is superceded by project specific requirements that may specify project specific DQOs. The purpose of this section is to identify exceedances, which are typically reportable with narration for most projects, and exceedances, which are not normally reportable except with permission of the client in advance. The criteria presented are based on SW-846 and national functional guidelines for data validation and data usability. This document is also written into a work instruction. **For DoD requirements refer to SOP PT-QA-025 (Version 3) and SOP PT-QA-029 (Version 4.1)**.

INITIAL CALIBRATION

Number of Points

1) An eight-point curve is required for use of average response factor.

2) A six-point curve is required for use of quadratic curves.

3) A graphical print out of the curve should be included in the data for all quadratic curves to demonstrate that it is a good fit and has been reviewed for "fit".

4) The analyst will routinely run eight standards for their calibration.

   - All eight may be used for the average response factor curve (5 required).
   - At least six must be used for the quadratic curve.
   - The lowest standard must be less than or equal to the project RL.

Initial Calibration Criteria

1) All CCCs must be ≤ 30% RSD in order for the curve to be acceptable and the CCC's may use an average response factor curve. Where the term target compound is used below it refers to non-CCC's

2) Where a target compound is ≤ 15% RSD an average response factor curve may be used.

3) Where a target compound is ≥ 15% but ≤ 30% the analyst will review the curve techniques to select a "best fit" curve. An average response factor curve may be used if

the analyst shows that the average response factor is an acceptable fit in the range that the curve is being used. A graphical representation of the curve should be presented for documentation. If the quadratic is clearly a better fit it must be used.

4) Where a quadratic or polynomial curve is used R must be ≥ .995

5) Compound list will be divided into two lists: list one (reliable performers) and list two (poor performers). **List one compounds should always have a %RSD less than 30 percent or correlation coefficient of .995 with an allowance for up to two sporadic marginal failures for volatiles and four for semivolatiles.** Sporadic marginal failures for these compounds should be </= 40% or .990. Sporadic marginal failures require a print out of the curve.

6) List two compounds are comprised of the list of known poor performers. **List two analytes may use an average response factor curve, where the %RSD is ≤ 15% and where the %RSDs > 15% and ≤ 60% a "best fit" curve will be selected. For these compounds (%RSD > 15%) a print out of the curve will be provided as a graphical documentation of curve performance and of "best-fit" selection**.

7) Documentation: Raw target curve summary with all compounds set to average response factor will be provided. If quadratic or polynomial equations are used a reprint of the curve table will be provided to show the correlation coefficient for the "best fit" equations. And as noted above, compounds that need additional documentation to demonstrate the curve fit will have a graphical presentation of the curve provided for reference.

8) Any analyte not on list one or list two would be held to specific criteria based on project specific requirements.

Minimum RRF Criteria

1) SPCCs must have an RRF ≥ 0.050

2) All other target compounds must have an RRF of ≥ 0.010,

Continuing Calibration Verification

The continuing calibration verification requirements for DoD work are listed in SOP PT-QA-025 (version #) or SOP PT-QA-029 (version 4.1).

Calculation Type

1) Average Response factor curves should be verified using a %Difference Equation. The %Difference Equation compares the RRF factor calculated for the Calibration Verification Standard to the Average RRF of the Curve.

2) The Quadratic Curves should be verified using a %Drift Equation. The %Drift Equation compares the measured value of the Calibration Verification Standard to the theoretical value of the standard.

% Diff. & % Drift Criteria

1) CCCs must be ≤ 20% Diff.

2) List 1 compounds that are Non CCC's must be ≤ 25% Diff or Drift

3) Up to 2 Volatile and 4 Semivolatile compounds that are List 1 analytes may exceed the 25% criteria but must be ≤ 40%.

4) List 2 Target Analytes including Appendix IX compounds will be accepted where the % difference or % Drift ≤ 50%.

5) Where a CCV is out high by > 50% and the compound is ND in the samples, the samples may be reported with narration.

RRF Criteria

1) SPCCs must be ≥ 0.05

2) All other compounds must be ≥ 0.01

Narrative Issues:

1) All %RSD that > 30% must be narrated.

2) All % D or Drift > 25% must be narrated.

3) Any other criteria exceedances aside from these should be narrated

4) Using an average response factor curve for a % RSD ≥ 30% must be narrated.

5) If a list 1 compound is not found in the sample, up to 50% D or Drift may be accepted with narration subject to determination that it is acceptable for the specific project.

6) If a list 2 compound is > 50% D or Drift (out high) and it is not found in the samples it may be reported with narration.

Note: These criterions are subject to project specific criteria, which may vary, depending on project compounds of concern and the usability needs of the project.

COMPOUND	SW846	LIST	QC TYPE
2,4,6-Trichlorophenol	8270C	**CCC**	**CCC**
2,4-Dichlorophenol	8270C	**CCC**	**CCC**
2-Nitrophenol	8270C	**CCC**	**CCC**
4-Chloro-3-methylphenol	8270C	**CCC**	**CCC**
Acenaphthene	8270C	**CCC**	**CCC**
Benzo(a)pyrene	8270C	**CCC**	**CCC**
Fluoranthene	8270C	**CCC**	**CCC**
Pentachlorophenol	8270C	**CCC**	**CCC**
Phenol	8270C	**CCC**	**CCC**
Di-n-octyl phthalate	8270C	**CCC**	**CCC**
Hexachlorobutadiene	8270C	**CCC**	**CCC**
N-Nitrosodiphenylamine	8270C	**CCC**	**CCC**
1,4-Dichlorobenzene	8270C	**CCC**	**CCC**
2,4,5-Trichlorophenol	8270C	1	
2,4-Dimethylphenol	8270C	1	
2,4-Dinitrotoluene	8270C	1	
2,6-Dinitrotoluene	8270C	1	
2-Chloronaphthalene	8270C	1	
2-Chlorophenol	8270C	1	
2-Methylnaphthalene	8270C	1	
2-Methylphenol	8270C	1	
4-Bromophenyl phenyl ether	8270C	1	
4-Chlorophenyl phenyl ether	8270C	1	
4-Methylphenol	8270C	1	
Acenaphthylene	8270C	1	
Anthracene	8270C	1	
Benzo(a)anthracene	8270C	1	
Benzo(b)fluoranthene	8270C	1	
Benzo(k)fluoranthene	8270C	1	
bis(2-Chloroethoxy)methane	8270C	1	
bis(2-Chloroethyl) ether	8270C	1	
Chrysene	8270C	1	

COMPOUND	SW846	LIST	QC TYPE
Dibenzofuran	8270C	1	
Fluorene	8270C	1	
Hexachlorobenzene	8270C	1	
Hexachloroethane	8270C	1	
Isophorone	8270C	1	
Naphthalene	8270C	1	
Nitrobenzene	8270C	1	
N-Nitrosodi-n-propylamine	8270C	**1**	**SPCC**
Phenanthrene	8270C	1	
Pyrene	8270C	1	
3&4 Methylphenol total	8270C	1	
1,2,4-Trichlorobenzene	8270C	1	
Benzo(ghi)perylene	8270C	1	
2,4-Dinitrophenol	8270C	**2**	**SPCC**
2-Nitroaniline	8270C	2	
3,3'-Dichlorobenzidine	8270C	2	
3-Nitroaniline	8270C	2	
4,6-Dinitro-2-methylphenol	8270C	2	
4-Chloroaniline	8270C	2	
4-Nitroaniline	8270C	2	
4-Nitrophenol	8270C	**2**	**SPCC**
bis(2-Ethylhexyl) phthalate	8270C	2	
Butyl benzyl phthalate	8270C	2	
Carbazole	8270C	2	
Dibenz(a,h)anthracene	8270C	2	
Diethyl phthalate	8270C	2	
Dimethyl phthalate	8270C	2	
Di-n-butyl phthalate	8270C	2	
Hexachlorocyclopentadiene	8270C	**2**	**SPCC**
Indeno(1,2,3-cd)pyrene	8270C	2	
1,2,4,5-Tetrachlorobenzene	8270C	2	
1,2-Dichlorobenzene	8270C	2	
1,2-Diphenylhydrazine	8270C	2	
1,3,5-Trinitrobenzene	8270C	2	
1,3-Dichlorobenzene	8270C	2	
1,3-Dinitrobenzene	8270C	2	
1,4-Dioxane	8270C	2	

COMPOUND	SW846	LIST	QC TYPE
1,4-Naphthoquinone	8270C	2	
1-Methylnaphthalene	8270C	2	
1-Naphthylamine	8270C	2	
2,2'-oxybis(1-Chloropropane)	8270C	2	
2,3,4,6-Tetrachlorophenol	8270C	2	
2,3,5,6-Tetrachlorophenol	8270C	2	
2,6-Dichlorophenol	8270C	2	
2-Acetylaminofluorene	8270C	2	
2-Methyl-4,6-dinitrophenol	8270C	2	
2-Naphthylamine	8270C	2	
2-Picoline	8270C	2	
2-sec-Butyl-4,6-dinitrophenol	8270C	2	
3,3'-Dimethylbenzidine	8270C	2	
3-Methylcholanthrene	8270C	2	
4,4'-Methylenebis(2-chloroaniline)	8270C	2	
4,6-Dinitro-o-cresol	8270C	2	
4-Aminobiphenyl	8270C	2	
4-Nitroquinoline-1-oxide	8270C	2	
5-Nitro-o-toluidine	8270C	2	
6-Methylchrysene	8270C	2	
7,12-Dimethylbenz(a)anthracene	8270C	2	
a,a-Dimethylphenethylamine	8270C	2	
alpha,alpha-Dimethylphenethylamine	8270C	2	
Aniline	8270C	2	
Aramite	8270C	2	
Aramite (total)	8270C	2	
Benzenethiol	8270C	2	
Benzidine	8270C	2	
bis(2-Chloroisopropyl) ether	8270C	2	
Chlorobenzilate	8270C	2	
Cresols (total)	8270C	2	
Diallate	8270C	2	
Dibenz(a,h)acridine	8270C	2	
Dibenzo(a,h)anthracene	8270C	2	
Dimethoate	8270C	2	
Dinoseb	8270C	2	
Disulfoton	8270C	2	

COMPOUND	SW846	LIST	QC TYPE
Ethyl methanesulfonate	8270C	2	
Famphur	8270C	2	
Hexachloropropene	8270C	2	
Isodrin	8270C	2	
Isosafrole	8270C	2	
Kepone	8270C	2	
m-Dinitrobenzene	8270C	2	
Methapyrilene	8270C	2	
Methyl methanesulfonate	8270C	2	
Methyl parathion	8270C	2	
N-Nitrosodiethylamine	8270C	2	
N-Nitrosodimethylamine	8270C	2	
N-Nitrosodi-n-butylamine	8270C	2	
N-Nitrosomethylethylamine	8270C	2	
N-Nitrosomorpholine	8270C	2	
N-Nitrosopiperidine	8270C	2	
N-Nitrosopyrrolidine	8270C	2	
O,O,O-Triethyl phosphorothioate	8270C	2	
o-Toluidine	8270C	2	
Parathion	8270C	2	
p-Chloroaniline	8270C	2	
p-Chlorobenzilate	8270C	2	
p-Chloro-m-cresol	8270C	2	
p-Dimethylaminoazobenzene	8270C	2	
Pentachlorobenzene	8270C	2	
Pentachloroethane	8270C	2	
Pentachloronitrobenzene	8270C	2	
Phenacetin	8270C	2	
Phorate	8270C	2	
p-Nitroaniline	8270C	2	
p-Phenylene diamine	8270C	2	
Pronamide	8270C	2	
Pyridine	8270C	2	
Safrole	8270C	2	
Sulfotepp	8270C	2	
Thionazin	8270C	2	
1,1'-Biphenyl	8270C	*	

COMPOUND	SW846	LIST	QC TYPE
Acetophenone	8270C	*	
Atrazine	8270C	*	
Benzaldehyde	8270C	*	
Caprolactam	8270C	*	
Benzoic acid	8270C	*	
Benzyl alcohol	8270C	*	
Indene	8270C	*	
Quindine	8270C	*	
1,4-Oxathiane	8270C	*	
Dimethyl Disulfide	8270C	*	
p-chlorophenyl metyl sulfide	8270C	*	
p-chlorophenyl metyl sulfone	8270C	*	
p-chloropheyny methyl sulfoxide	8270C	*	
Hexachlorophene	8270C	TIC	

* SPECIFIC CRITERIA WOULD BE IMPLEMENTED ON A PROJECT SPECIFIC BASIS WHEN REQUIRED.

Tables

Table 1
TestAmerica Pittsburgh Primary Standard[1] and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Pyridine	110-86-1	20	660
N-nitrosodimethylamine	62-75-9	10	330
Aniline	62-53-3	10	330
Phenol	108-95-2	10	330
Bis(2-chloroethyl)ether	111-44-4	10	330
2-Chlorophenol	95-57-8	10	330
1,3-Dichlorobenzene	541-73-1	10	330
1,4-Dichlorobenzene	106-46-7	10	330
Benzyl alcohol	100-51-6	10	330
1,2-Dichlorobenzene	95-50-1	10	330
2-Methylphenol	95-48-7	10	330
2,2'-oxybis(1-chloropropane)[2]	108-60-1	10	330
4-Methylphenol	106-44-5	10	330
N-Nitroso-di-n-propylamine	621-64-7	10	330
Hexachloroethane	67-72-1	10	330
Nitrobenzene	98-95-3	10	330
Isophorone	78-59-1	10	330
2-Nitrophenol	88-75-5	10	330
2,4-Dimethylphenol	105-67-9	10	330
Benzoic acid	65-85-0	50	1600
Bis(2-chloroethoxy)methane	111-91-1	10	330
2,4-Dichlorophenol	120-83-2	10	330
1,2,4-Trichlorobenzene	120-82-1	10	330
Naphthalene	91-20-3	10	330
4-Chloroaniline	106-47-8	10	330
Hexachlorobutadiene	87-68-3	10	330
4-Chloro-3-methylphenol	59-50-7	10	330
2-Methylnaphthalene	91-57-6	10	330
Hexachlorocyclopentadiene	77-47-4	50	1600
2,4,6-Trichlorophenol	88-06-2	10	330
2,4,5-Trichlorophenol	95-95-4	10	330
2-Chloronaphthalene	91-58-7	10	330
2-Nitroaniline	88-74-4	50	1600
Dimethyl phthalate	131-11-3	10	330
Acenaphthylene	208-96-8	10	330

Table 1
TestAmerica Pittsburgh Primary Standard[1] and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
3-Nitroaniline	99-09-2	50	1600
Acenaphthene	83-32-9	10	330
2,4-Dinitrophenol	51-28-5	50	1600
4-Nitrophenol	100-02-7	50	1600
Dibenzofuran	132-64-9	10	330
2,4-Dinitrotoluene	121-14-2	10	330
2,6-Dinitrotoluene	606-20-2	10	330
Diethylphthalate	84-66-2	10	330
4-Chlorophenyl phenyl ether	7005-72-3	10	330
Fluorene	86-73-7	10	330
4-Nitroaniline	100-01-6	50	1600
4,6-Dinitro-2-methylphenol	534-52-1	50	1600
4-Phenylenediamine	106-50-3	200	6600
N-Nitrosodiphenylamine	86-30-6	10	330
Azobenzene	103-33-3	10	330
4-Bromophenyl phenyl ether	101-55-3	10	330
Hexachlorobenzene	118-74-1	10	330
Pentachlorophenol	87-86-5	50	1600
Phenanthrene	85-01-8	10	330
Anthracene	120-12-7	10	330
Carbazole	86-74-8	10	330
Di-n-butyl phthalate	84-74-2	10	330
Fluoranthene	206-44-0	10	330
Benzidine	92-87-5	100	3300
Pyrene	129-00-0	10	330
Butyl benzyl phthalate	85-68-7	10	330
3,3'-Dichlorobenzidine	91-94-1	50	1600
Benzo(a)anthracene	56-55-3	10	330
Bis(2-ethylhexyl)phthalate	117-81-7	10	330
Chrysene	218-01-9	10	330
Di-n-octylphthalate	117-84-0	10	330
Benzo(b)fluoranthene	205-99-2	10	330
Benzo(k)fluoranthene	207-08-9	10	330
Benzo(a)pyrene	50-32-8	10	330
Indeno(1,2,3-cd)pyrene	193-39-5	10	330
Dibenz(a,h)anthracene	53-70-3	10	330
Benzo(g,h,i)perylene	191-24-2	10	330
Atrazine	1912-24-9	10	330
1,4-Dioxane	123-91-1	10	330
Benzaldehyde	100-52-7	10	330

Table 1
TestAmerica Pittsburgh Primary Standard[1] and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Acetophenone	98-68-2	10	330
Caprolactam	105-60-2	10	330
1,1-Biphenyl	92-52-4	10	330
2-Naphthylamine	91-59-8	10	330

1 The TestAmerica Pittsburgh primary standard is the standard normally used at TestAmerica Pittsburgh. Additional standards, such as the Appendix IX standard may be necessary to include all target analytes required for some clients.

2 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

TestAmerica Pittsburgh Appendix IX[1] Routine Standard Reporting Limits

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
2-Picoline	109-06-8	20	660
N-Nitrosomethylethylamine	10595-95-6	10	330
Methyl methanesulfonate	66-27-3	10	330
N-Nitrosodiethylamine	55-18-5	10	330
Ethyl methanesulfonate	62-50-0	10	330
Pentachloroethane	76-01-7	50	1600
Acetophenone	98-86-2	10	330
N-Nitrosopyrrolidine	930-55-2	10	330
N-Nitrosomorpholine	59-89-2	10	330
o-Toluidine	95-53-4	20	660
3-Methylphenol	108-39-4	10	330
N-Nitrosopiperidine	100-75-4	10	330
o,o,o-Triethyl-Phosphorothioate[2]	126-68-1	50	1600
a,a-Dimethyl-phenethylamine	122-09-8	50	1600
2,6-Dichlorophenol	87-65-0	10	330
Hexachloropropene	1888-71-7	100	3300
p-Phenylenediamine	106-50-3	100	3300
n-Nitrosodi-n-butylamine	924-16-3	10	330
Safrole	94-59-7	20	660
1,2,4,5-Tetrachlorobenzene	95-94-3	10	330
Isosafrole	120-58-1	20	660
1,4-Dinitrobenzene	100-25-4	10	330
1,4-Naphthoquinone	130-15-4	50	1600
1,3-Dinitrobenzene	99-65-0	10	330
Pentachlorobenzene	608-93-5	10	330
1-Naphthylamine	134-32-7	10	330
2-Naphthylamine	91-59-8	10	330
2,3,4,6-Tetrachlorophenol	58-90-2	10	330
5-Nitro-o-toluidine	99-55-8	20	660
Thionazin[2]	297-97-2	50	1600
1,3,5-Trinitrobenzene	99-35-4	50	1600
Sulfotepp[2]	3689-24-5	50	1600
Phorate[2]	298-02-2	50	1600
Phenacetin	62-44-2	20	660
Diallate[3]	2303-16-4	20	660
Dimethoate[2]	60-51-5	20	660
4-Aminobiphenyl	92-67-1	50	1600

Pentachloronitrobenzene	82-68-8	50	1600
Pronamide	23950-58-5	20	660
Disulfoton[2]	298-04-4	50	1600
2-secbutyl-4,6-dinitrophenol (Dinoseb)	88-85-7	20	660
Methyl Parathion[2]	298-00-0	10	330
4-Nitroquinoline-1-oxide	56-57-5	100	3300
Parathion[2]	56-38-2	50	1600
Methapyrilene	91-80-5	50	1600
Aramite	140-57-8	50	1600
Isodrin[3]	465-73-6	10	330
Kepone	143-50-0	40	1300
Famphur[2]	52-85-7	100	3300
p-(Dimethylamino)azobenzene	60-11-7	20	660
p-Chlorobenzilate[3]	510-15-6	10	330
3,3'-Dimethylbenzidine	119-93-7	50	1600
2-Acetylaminofluorene	53-96-3	20	660
Dibenz(a,j)acridine	224-42-0	20	660
7,12-Dimethylbenz(a)anthracene	57-97-6	20	660
3-Methylcholanthrene	56-49-5	50	1600

[1] The Appendix IX standard contains additional analytes required for the Appendix IX list. The TestAmerica Pittsburgh primary standard must also be analyzed to include all of the Appendix IX list.

[2] May also be analyzed by method 8141A, which can achieve lower reporting limits.

[3] May also be analyzed by method 8081A, which can achieve lower reporting limits

Table 2 A 8270C Water Low Level Method Code 42 Reporting Limits	
Compound	**Reporting Limit ug/L**
a,a-Dimethylphenethylamine	1
Acenaphthene	0.2
Acenaphthylene	0.2
Acetophenone	1
2-Acetylaminofluorene	1
4-Aminobiphenyl	1
Aniline	1
Anthracene	0.2
Aramite	1
Aramite (total)	1
Atrazine	1
Benzaldehyde	1
Benzenethiol	1
Benzidine	20
Benzo(a)anthracene	0.2
Benzo(b)fluoranthene	0.2
Benzo(k)fluoranthene	0.2
Benzoic acid	5
Benzo(ghi)perylene	0.2
Benzo(a)pyrene	0.2
Benzotrichloride	10
Benzyl alcohol	1
1,1'-Biphenyl	1
Biphenyl	1
bis(2-Chloroethoxy)methane	1
bis(2-Chloroethyl) ether	0.2
bis(2-Chloroisopropyl) ether	0.2
bis(2-Ethylhexyl) phthalate	1
Bis(4-hydroxyphenyl)methane	1
Bis(2-hydroxyphenyl)methane	1
2-Bromonaphthalene	1
4-Bromophenyl phenyl ether	1
Butyl benzyl phthalate	1

Table 2 A 8270C Water Low Level Method Code 42 Reporting Limits	
Compound	**Reporting Limit ug/L**
Caprolactam	5
Carbaryl	1
Carbazole	0.2
p-Chloroaniline	1
4-Chloroaniline	1
Chlorobenzilate	1
p-Chlorobenzilate	1
4-Chloro-3-methylphenol	1
p-Chloro-m-cresol	1
2-Chloronaphthalene	0.2
2-Chlorophenol	1
4-Chlorophenyl phenyl ether	1
Chrysene	0.2
6-Methylchrysene	1
Cresols (total)	1
Diallate	1
Dibenz(a,h)acridine	1
Dibenz(a,h)anthracene	0.2
Dibenzo(a,h)anthracene	0.2
Dibenzofuran	1
1,2-Dibromo-3-chloropropane	1
Di-n-butyl phthalate	1
1,2-Dichlorobenzene	0.2
o-Dichlorobenzene	0.2
1,3-Dichlorobenzene	0.2
m-Dichlorobenzene	0.2
1,4-Dichlorobenzene	0.2
p-Dichlorobenzene	0.2
3,3'-Dichlorobenzidine	1
2,3-Dichlorophenol	1
2,4-Dichlorophenol	0.2
2,6-Dichlorophenol	0.2
2,5-Dichlorophenol	1
Diethyl phthalate	1
Dimethoate	1

Table 2 A 8270C Water Low Level Method Code 42 Reporting Limits	
Compound	**Reporting Limit ug/L**
p-Dimethylaminoazobenzene	1
N,N-Dimethylaniline	1
7,12-Dimethylbenz(a)anthracene	1
3,3'-Dimethylbenzidine	10
alpha,alpha-Dimethylphenethylamine	1
2,4-Dimethylphenol	1
Dimethyl phthalate	1
m-Dinitrobenzene	1
1,3-Dinitrobenzene	1
2-Methyl-4,6-dinitrophenol	5
4,6-Dinitro-o-cresol	5
4,6-Dinitro-2-methylphenol	5
2,4-Dinitrophenol	5
2,4-Dinitrotoluene	1
2,6-Dinitrotoluene	1
2-sec-Butyl-4,6-dinitrophenol	1
Dinoseb	1
Di-n-octyl phthalate	1
1,4-Dioxane	0.2
1,2-Diphenylhydrazine	0.2
1,2-Diphenylhydrazine (as Azobenzene)	0.2
Disulfoton	1
Ethyl methanesulfonate	1
Famphur	10
Fluoranthene	0.2
Fluorene	0.2
Hexachlorobenzene	0.2
Hexachlorobutadiene	0.2
Hexachlorocyclopentadiene	1
Hexachloroethane	1
Hexachlorophene	--
Hexachloropropene	1
Indeno(1,2,3-cd)pyrene	0.2
Isodrin	1
Isophorone	1

Table 2 A 8270C Water Low Level Method Code 42 Reporting Limits	
Compound	**Reporting Limit ug/L**
Isosafrole	1
Kepone	4
Methapyrilene	1
3-Methylcholanthrene	1
4,4'-Methylenebis(2-chloroaniline)	1
Methyl methanesulfonate	1
2-Methylnaphthalene	0.2
1-Methylnaphthalene	0.2
Methyl parathion	1
2-Methylphenol	1
3-Methylphenol	1
4-Methylphenol	1
3-Methylphenol & 4-Methylphenol	1
Naphthalene	0.2
1,4-Naphthoquinone	1
1-Naphthylamine	1
2-Naphthylamine	1
2-Nitroaniline	5
3-Nitroaniline	5
4-Nitroaniline	5
p-Nitroaniline	5
Nitrobenzene	0.2
4-Nitrobiphenyl	1
2-Nitrophenol	1
4-Nitrophenol	5
4-Nitroquinoline-1-oxide	10
N-Nitrosodi-n-butylamine	1
N-Nitrosodiethylamine	1
N-Nitrosodimethylamine	1
N-Nitrosodiphenylamine	0.2
N-Nitrosodiphenylamine (1)	0.2
N-Nitrosodi-n-propylamine	0.2
N-Nitrosomethylethylamine	1
N-Nitrosomorpholine	1
N-Nitrosopiperidine	1

Table 2 A
8270C Water Low Level Method Code 42 Reporting Limits

Compound	Reporting Limit ug/L
N-Nitrosopyrrolidine	1
5-Nitro-o-toluidine	10
Octachlorocyclopentene	1
Octachlorostyrene	1
2,2'-oxybis(1-Chloropropane)	0.2
Parathion	1
Pentachlorobenzene	1
Pentachloroethane	2
Pentachloronitrobenzene	1
Pentachlorophenol	1
Phenacetin	1
Phenanthrene	0.2
Phenol	0.2
p-Phenylene diamine	40
Phorate	1
2-Picoline	1
Pronamide	1
Pyrene	0.2
Pyridine	1
Safrole	1
Sevin	1
Sulfotepp	1
1,2,4,5-Tetrachlorobenzene	1
2,3,4,6-Tetrachlorophenol	1
2,3,5,6-Tetrachlorophenol	1
1,2,3,4-Tetrahydronaphthalene	1
Thionazin	1
o-Toluidine	1
1,2,4-Trichlorobenzene	0.2
2,4,5-Trichlorophenol	1
2,4,6-Trichlorophenol	1
O,O,O-Triethyl phosphorothioate	1
Trifluralin	1
1,3,5-Trinitrobenzene	1
1-Nitronaphthalene	1

Table 2 A **8270C Water Low Level Method Code 42 Reporting Limits**	
Compound	**Reporting Limit ug/L**
1,2,3,4-Tetrachlorobenzene	1
3&4 Methylphenol total	1

Table 2 B 8270C Soil Low Level Method Code 42 Reporting Limits	
Compuound	**Reporting Limit ug/kg**
a,a-Dimethylphenethylamine	33
Acenaphthene	6.7
Acenaphthylene	6.7
Acetophenone	33
2-Acetylaminofluorene	33
4-Aminobiphenyl	33
Aniline	33
Anthracene	6.7
Aramite	33
Aramite (total)	33
Atrazine	33
Benzaldehyde	33
Benzenethiol	330
Benzidine	670
Benzo(a)anthracene	6.7
Benzo(b)fluoranthene	6.7
Benzo(k)fluoranthene	6.7
Benzoic acid	170
Benzo(ghi)perylene	6.7
Benzo(a)pyrene	6.7
Benzyl alcohol	33
1,1'-Biphenyl	33
bis(2-Chloroethoxy)methane	33
bis(2-Chloroethyl) ether	6.7
bis(2-Chloroisopropyl) ether	6.7
bis(2-Ethylhexyl) phthalate	33
4-Bromophenyl phenyl ether	33
Butyl benzyl phthalate	33
Caprolactam	170
Carbazole	6.7
4-Chloroaniline	33
Chlorobenzilate	33
4-Chloro-3-methylphenol	33

Table 2 B 8270C Soil Low Level Method Code 42 Reporting Limits	
Compuound	**Reporting Limit ug/kg**
2-Chloronaphthalene	6.7
2-Chlorophenol	33
4-Chlorophenyl phenyl ether	33
Chrysene	6.7
6-Methylchrysene	33
Diallate	33
Dibenz(a,h)acridine	33
Dibenz(a,h)anthracene	6.7
Dibenzo(a,h)anthracene	6.7
Dibenzofuran	33
Di-n-butyl phthalate	33
1,2-Dichlorobenzene	6.7
1,3-Dichlorobenzene	6.7
1,4-Dichlorobenzene	6.7
3,3'-Dichlorobenzidine	33
2,4-Dichlorophenol	6.7
2,6-Dichlorophenol	6.7
Diethyl phthalate	33
O,O-Diethyl-O-(2-pyrazinyl) phosphorothioate	33
Dimethoate	33
p-Dimethylaminoazobenzene	33
7,12-Dimethylbenz(a)anthracene	33
3,3'-Dimethylbenzidine	170
alpha,alpha-Dimethylphenethylamine	33
2,4-Dimethylphenol	33
Dimethyl phthalate	33
m-Dinitrobenzene	33
1,3-Dinitrobenzene	33
4,6-Dinitro-2-methylphenol	170
2,4-Dinitrophenol	170
2,4-Dinitrotoluene	33
2,6-Dinitrotoluene	33
Dinoseb	33
Di-n-octyl phthalate	33
1,4-Dioxane	6.7

Table 2 B 8270C Soil Low Level Method Code 42 Reporting Limits	
Compuound	**Reporting Limit ug/kg**
1,2-Diphenylhydrazine	6.7
Disulfoton	33
Ethyl methanesulfonate	33
Famphur	330
Fluoranthene	6.7
Fluorene	6.7
Hexachlorobenzene	6.7
Hexachlorobutadiene	6.7
Hexachlorocyclopentadiene	33
Hexachloro-1,3-cyclopentadiene	33
Hexachloroethane	33
Hexachlorophene	--
Hexachloropropene	33
Indeno(1,2,3-cd)pyrene	6.7
Isodrin	33
Isophorone	33
Isosafrole	33
Kepone	1300
Methapyrilene	33
3-Methylcholanthrene	33
4,4'-Methylenebis(2-chloroaniline)	33
Methyl methanesulfonate	33
2-Methylnaphthalene	6.7
1-Methylnaphthalene	6.7
Methyl parathion	33
2-Methylphenol	33
4-Methylphenol	33
3-Methylphenol & 4-Methylphenol	33
Naphthalene	6.7
1,4-Naphthoquinone	33
1-Naphthylamine	33
2-Naphthylamine	33
2-Nitroaniline	170
3-Nitroaniline	170
4-Nitroaniline	170

Table 2 B 8270C Soil Low Level Method Code 42 Reporting Limits	
Compuound	**Reporting Limit ug/kg**
Nitrobenzene	6.7
2-Nitrophenol	33
4-Nitrophenol	170
4-Nitroquinoline-1-oxide	170
N-Nitrosodi-n-butylamine	33
N-Nitrosodiethylamine	33
N-Nitrosodimethylamine	33
N-Nitrosodiphenylamine (1)	6.7
N-Nitrosodiphenylamine	6.7
N-Nitrosodi-n-propylamine	6.7
N-Nitrosomethylethylamine	33
N-Nitrosomorpholine	33
N-Nitrosopiperidine	33
N-Nitrosopyrrolidine	33
N-Nitro-o-toluidine	33
5-Nitro-o-toluidine	33
2,2'-oxybis(1-Chloropropane)	6.7
Parathion	33
Pentachlorobenzene	33
Pentachloroethane	33
Pentachloronitrobenzene	33
Pentachlorophenol	33
Phenacetin	33
Phenanthrene	6.7
Phenol	6.7
p-Phenylene diamine	670
Phorate	33
2-Picoline	33
Pronamide	33
Pyrene	6.7
Pyridine	33
Safrole	33
Sulfotepp	33
1,2,4,5-Tetrachlorobenzene	33
2,3,4,6-Tetrachlorophenol	33

Table 2 B **8270C Soil Low Level Method Code 42 Reporting Limits**	
Compuound	**Reporting Limit ug/kg**
2,3,5,6-Tetrachlorophenol	33
Tetraethyldithiopyrophosphate	33
Thionazin	33
1,2,4-Trichlorobenzene	6.7
2,4,5-Trichlorophenol	33
2,4,6-Trichlorophenol	33
O,O,O-Triethyl phosphorothioate	33
1,3,5-Trinitrobenzene	33

Table 2 C 8270C Low Level Water Method Code QL Reporting Limits	
Compound	**Reporting Limit ug/L**
a,a-Dimethylphenethylamine	10
Acenaphthene	2
Acenaphthylene	2
Acetophenone	10
2-Acetylaminofluorene	10
4-Aminobiphenyl	10
Aniline	10
Anthracene	2
Aramite	10
Aramite (total)	10
Atrazine	10
Benzaldehyde	10
Benzenethiol	10
Benzidine	200
Benzo(a)anthracene	2
Benzo(b)fluoranthene	2
Benzo(k)fluoranthene	2
Benzoic acid	50
Benzo(ghi)perylene	2
Benzo(a)pyrene	2
Benzotrichloride	100
Benzyl alcohol	10
1,1'-Biphenyl	10
Biphenyl	10
bis(2-Chloroethoxy)methane	10
bis(2-Chloroethyl) ether	2
bis(2-Chloroisopropyl) ether	2
bis(2-Ethylhexyl) phthalate	10
2-Bromonaphthalene	10
4-Bromophenyl phenyl ether	10
Butyl benzyl phthalate	10
Caprolactam	50
Carbaryl	10

Table 2 C 8270C Low Level Water Method Code QL Reporting Limits	
Compound	**Reporting Limit ug/L**
Carbazole	2
p-Chloroaniline	10
4-Chloroaniline	10
Chlorobenzilate	10
p-Chlorobenzilate	10
4-Chloro-3-methylphenol	10
p-Chloro-m-cresol	10
2-Chloronaphthalene	2
2-Chlorophenol	10
4-Chlorophenyl phenyl ether	10
Chrysene	2
6-Methylchrysene	10
Cresols (total)	10
Diallate	10
Dibenz(a,h)acridine	10
Dibenz(a,h)anthracene	2
Dibenzo(a,h)anthracene	2
Dibenzofuran	10
1,2-Dibromo-3-chloropropane	10
Di-n-butyl phthalate	10
1,2-Dichlorobenzene	2
o-Dichlorobenzene	2
1,3-Dichlorobenzene	2
m-Dichlorobenzene	2
1,4-Dichlorobenzene	2
p-Dichlorobenzene	2
3,3'-Dichlorobenzidine	10
2,4-Dichlorophenol	2
2,6-Dichlorophenol	2
Diethyl phthalate	10
Dimethoate	10
p-Dimethylaminoazobenzene	10
N,N-Dimethylaniline	10
7,12-Dimethylbenz(a)anthracene	10
3,3'-Dimethylbenzidine	100

Table 2 C 8270C Low Level Water Method Code QL Reporting Limits	
Compound	**Reporting Limit ug/L**
alpha,alpha-Dimethylphenethylamine	10
2,4-Dimethylphenol	10
Dimethyl phthalate	10
m-Dinitrobenzene	10
1,3-Dinitrobenzene	10
2-Methyl-4,6-dinitrophenol	50
4,6-Dinitro-o-cresol	50
4,6-Dinitro-2-methylphenol	50
2,4-Dinitrophenol	50
2,4-Dinitrotoluene	10
2,6-Dinitrotoluene	10
2-sec-Butyl-4,6-dinitrophenol	10
Dinoseb	10
Di-n-octyl phthalate	10
1,4-Dioxane	2
Diphenylamine	2
1,2-Diphenylhydrazine	2
1,2-Diphenylhydrazine (as Azobenzene)	2
Disulfoton	10
Ethyl methanesulfonate	10
Famphur	100
Fluoranthene	2
Fluorene	2
Hexachlorobenzene	2
Hexachlorobutadiene	2
Hexachlorocyclopentadiene	10
Hexachloroethane	10
Hexachlorophene	--
Hexachloropropene	10
Indeno(1,2,3-cd)pyrene	2
Isodrin	10
Isophorone	10
Isosafrole	10
Kepone	40
Methapyrilene	10

Table 2 C 8270C Low Level Water Method Code QL Reporting Limits	
Compound	**Reporting Limit ug/L**
3-Methylcholanthrene	10
4,4'-Methylenebis(2-chloroaniline)	10
Methyl methanesulfonate	10
2-Methylnaphthalene	2
1-Methylnaphthalene	2
Methyl parathion	10
2-Methylphenol	10
3-Methylphenol	10
4-Methylphenol	10
3-Methylphenol & 4-Methylphenol	10
Naphthalene	2
1,4-Naphthoquinone	10
1-Naphthylamine	10
2-Naphthylamine	10
2-Nitroaniline	50
3-Nitroaniline	50
4-Nitroaniline	50
p-Nitroaniline	50
Nitrobenzene	2
4-Nitrobiphenyl	10
2-Nitrophenol	10
4-Nitrophenol	50
4-Nitroquinoline-1-oxide	100
N-Nitrosodi-n-butylamine	10
N-Nitrosodiethylamine	10
N-Nitrosodimethylamine	10
N-Nitrosodiphenylamine	2
N-Nitrosodiphenylamine (1)	2
N-Nitrosodi-n-propylamine	2
N-Nitrosomethylethylamine	10
N-Nitrosomorpholine	10
N-Nitrosopiperidine	10
N-Nitrosopyrrolidine	10
5-Nitro-o-toluidine	100
2,2'-oxybis(1-Chloropropane)	2

Table 2 C 8270C Low Level Water Method Code QL Reporting Limits	
Compound	**Reporting Limit ug/L**
Parathion	10
Pentachlorobenzene	10
Pentachloroethane	20
Pentachloronitrobenzene	10
Pentachlorophenol	10
Phenacetin	10
Phenanthrene	2
Phenol	2
p-Phenylene diamine	400
Phorate	10
2-Picoline	10
Pronamide	10
Pyrene	2
Pyridine	10
Safrole	10
Sevin	10
Sulfotepp	10
1,2,4,5-Tetrachlorobenzene	10
2,3,4,6-Tetrachlorophenol	10
2,3,5,6-Tetrachlorophenol	10
1,2,3,4-Tetrahydronaphthalene	10
Thionazin	10
o-Toluidine	10
1,2,4-Trichlorobenzene	2
2,4,5-Trichlorophenol	10
2,4,6-Trichlorophenol	10
O,O,O-Triethyl phosphorothioate	10
Trifluralin	10
1,3,5-Trinitrobenzene	10
1-Nitronaphthalene	10
3&4 Methylphenol total	10

Table 2 D 8270C Low Level Soil Method Code QL Reporting Limits	
Compound	**Reporting Limit ug/L**
a,a-Dimethylphenethylamine	330
Acenaphthene	67
Acenaphthylene	67
Acetophenone	330
2-Acetylaminofluorene	330
4-Aminobiphenyl	330
Aniline	330
Anthracene	67
Aramite	330
Aramite (total)	330
Atrazine	330
Benzaldehyde	330
Benzenethiol	330
Benzidine	6700
Benzo(a)anthracene	67
Benzo(b)fluoranthene	67
Benzo(k)fluoranthene	67
Benzoic acid	1700
Benzo(ghi)perylene	67
Benzo(a)pyrene	67
Benzyl alcohol	330
1,1'-Biphenyl	330
bis(2-Chloroethoxy)methane	330
bis(2-Chloroethyl) ether	67
bis(2-Chloroisopropyl) ether	67
bis(2-Ethylhexyl) phthalate	330
4-Bromophenyl phenyl ether	330
Butyl benzyl phthalate	330
Caprolactam	1700
Carbazole	67
p-Chloroaniline	330
4-Chloroaniline	330
Chlorobenzilate	330
p-Chlorobenzilate	330
4-Chloro-3-methylphenol	330

Table 2 D 8270C Low Level Soil Method Code QL Reporting Limits	
Compound	**Reporting Limit ug/L**
p-Chloro-m-cresol	330
2-Chloronaphthalene	67
2-Chlorophenol	330
4-Chlorophenyl phenyl ether	330
Chrysene	67
6-Methylchrysene	330
Diallate	330
Dibenz(a,h)acridine	330
Dibenz(a,h)anthracene	67
Dibenzo(a,h)anthracene	67
Dibenzofuran	330
Di-n-butyl phthalate	330
1,2-Dichlorobenzene	67
o-Dichlorobenzene	67
1,3-Dichlorobenzene	67
m-Dichlorobenzene	67
1,4-Dichlorobenzene	67
p-Dichlorobenzene	67
3,3'-Dichlorobenzidine	330
2,4-Dichlorophenol	67
2,6-Dichlorophenol	67
Diethyl phthalate	330
O,O-Diethyl-O-(2-pyrazinyl) phosphorothioate	330
Dimethoate	330
p-Dimethylaminoazobenzene	330
7,12-Dimethylbenz(a)anthracene	330
3,3'-Dimethylbenzidine	1700
alpha,alpha-Dimethylphenethylamine	330
2,4-Dimethylphenol	330
Dimethyl phthalate	330
m-Dinitrobenzene	330
1,3-Dinitrobenzene	330
4,6-Dinitro-o-cresol	1700
2-Methyl-4,6-dinitrophenol	1700

Table 2 D 8270C Low Level Soil Method Code QL Reporting Limits	
Compound	**Reporting Limit ug/L**
4,6-Dinitro-2-methylphenol	1700
2,4-Dinitrophenol	1700
2,4-Dinitrotoluene	330
2,6-Dinitrotoluene	330
2-sec-Butyl-4,6-dinitrophenol	330
Dinoseb	330
Di-n-octyl phthalate	330
1,4-Dioxane	67
1,2-Diphenylhydrazine (as Azobenzene)	67
1,2-Diphenylhydrazine	67
Disulfoton	330
Ethyl methanesulfonate	330
Famphur	3300
Fluoranthene	67
Fluorene	67
Hexachlorobenzene	67
Hexachlorobutadiene	67
Hexachlorocyclopentadiene	330
Hexachloro-1,3-cyclopentadiene	330
Hexachloroethane	330
Hexachlorophene	--
Hexachloropropene	330
Indeno(1,2,3-cd)pyrene	67
Isodrin	330
Isophorone	330
Isosafrole	330
Kepone	13000
Methapyrilene	330
3-Methylcholanthrene	330
4,4'-Methylenebis(2-chloroaniline)	330
Methyl methanesulfonate	330
2-Methylnaphthalene	67
1-Methylnaphthalene	67
Methyl parathion	330
2-Methylphenol	330

Table 2 D 8270C Low Level Soil Method Code QL Reporting Limits	
Compound	**Reporting Limit ug/L**
4-Methylphenol	330
3-Methylphenol & 4-Methylphenol	330
Naphthalene	67
1,4-Naphthoquinone	330
1-Naphthylamine	330
2-Naphthylamine	330
2-Nitroaniline	1700
3-Nitroaniline	1700
m-Nitroaniline	1700
4-Nitroaniline	1700
p-Nitroaniline	1700
Nitrobenzene	67
2-Nitrophenol	330
4-Nitrophenol	1700
4-Nitroquinoline-1-oxide	1700
N-Nitrosodi-n-butylamine	330
N-Nitrosodiethylamine	330
N-Nitrosodimethylamine	330
N-Nitrosodiphenylamine (1)	67
N-Nitrosodiphenylamine	67
N-Nitrosodi-n-propylamine	67
N-Nitrosomethylethylamine	330
N-Nitrosomorpholine	330
N-Nitrosopiperidine	330
N-Nitrosopyrrolidine	330
5-Nitro-o-toluidine	330
2,2'-oxybis(1-Chloropropane)	67
Parathion	330
Pentachlorobenzene	330
Pentachloroethane	330
Pentachloronitrobenzene	330
Pentachlorophenol	330
Phenacetin	330
Phenanthrene	67
Phenol	67

Table 2 D 8270C Low Level Soil Method Code QL Reporting Limits	
Compound	**Reporting Limit ug/L**
p-Phenylene diamine	6700
Phorate	330
2-Picoline	330
Pronamide	330
Pyrene	67
Pyridine	330
Safrole	330
Sulfotepp	330
1,2,4,5-Tetrachlorobenzene	330
2,3,4,6-Tetrachlorophenol	330
2,3,5,6-Tetrachlorophenol	330
Tetraethyldithiopyrophosphate	330
Thionazin	330
o-Toluidine	330
1,2,4-Trichlorobenzene	67
2,4,5-Trichlorophenol	330
2,4,6-Trichlorophenol	330
O,O,O-Triethyl phosphorothioate	330
1,3,5-Trinitrobenzene	330
3&4 Methylphenol total	330

Table 3

Reportable Analytes for TestAmerica Pittsburgh Standard Tests, Primary Standard

Analyte	CAS Number	Routinely Calibrated Compounds	TCLP	TCL	Appendix IX
Pyridine	110-86-1	X	X		X
N-nitrosodimethylamine	62-75-9	X			X
Aniline	62-53-3	X			X
Phenol	108-95-2	X		X	X
Bis(2-chloroethyl)ether	111-44-4	X		X	X
2-Chlorophenol	95-57-8	X		X	X
1,3-Dichlorobenzene	541-73-1	X		X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X
Benzyl alcohol	100-51-6	X			X
1,2-Dichlorobenzene	95-50-1	X		X	X
2-Methylphenol	95-48-7	X	X	X	X
2,2'-oxybis(1-chloropropane)[1]	180-60-1	X		X	X
4-Methylphenol	106-44-5	X	X	X	X
N-Nitroso-di-n-propylamine	621-64-7	X		X	X
Hexachloroethane	67-72-1	X	X	X	X
Nitrobenzene	98-95-3	X	X	X	X
Isophorone	78-59-1	X		X	X
2-Nitrophenol	88-75-5	X		X	X
2,4-Dimethylphenol	105-67-9	X		X	X
Benzoic acid	65-85-0	X			
Bis(2-chloroethoxy)methane	111-91-1	X		X	X
2,4-Dichlorophenol	120-83-2	X		X	X
1,2,4-Trichlorobenzene	120-82-1	X		X	X
Naphthalene	91-20-3	X		X	X
4-Chloroaniline	106-47-8	X		X	X
Hexachlorobutadiene	87-68-3	X	X	X	X
4-Chloro-3-methylphenol	59-50-7	X		X	X
2-Methylnaphthalene	91-57-6	X		X	X
Hexachlorocyclopentadiene	77-47-4	X		X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	X	X
2-Chloronaphthalene	91-58-7	X		X	X
2-Nitroaniline	88-74-4	X		X	X
Dimethyl phthalate	131-11-3	X		X	X
Acenaphthylene	208-96-8	X		X	X
3-Nitroaniline	99-09-2	X		X	X
Acenaphthene	83-32-9	X		X	X

Table 3

Reportable Analytes for TestAmerica Pittsburgh Standard Tests, Primary Standard

Analyte	CAS Number	Routinely Calibrated Compounds	TCLP	TCL	Appendix IX
2,4-Dinitrophenol	51-28-5	X		X	X
4-Nitrophenol	100-02-7	X		X	X
Dibenzofuran	132-64-9	X		X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X		X	X
Diethylphthalate	84-66-2	X		X	X
4-Chlorophenyl phenyl ether	7005-72-3	X		X	X
Fluorene	86-73-7	X		X	X
4-Nitroaniline	100-01-6	X		X	X
4,6-Dinitro-2-methylphenol	534-52-1	X		X	X
N-Nitrosodiphenylamine	86-30-6	X		X	X
Azobenzene[4]	103-33-3	X			
4-Bromophenyl phenyl ether	101-55-3	X		X	X
Hexachlorobenzene	118-74-1	X	X	X	X
Pentachlorophenol	87-86-5	X	X	X	X
Phenanthrene	85-01-8	X		X	X
Anthracene	120-12-7	X		X	X
Carbazole	86-74-8	X		X	
Di-n-butyl phthalate	84-74-2	X		X	X
Fluoranthene	206-44-0	X		X	X
Benzidine	92-87-5				
Pyrene	129-00-0	X		X	X
Butyl benzyl phthalate	85-68-7	X		X	X
3,3'-Dichlorobenzidine	91-94-1	X		X	X
Benzo(a)anthracene	56-55-3	X		X	X
Bis(2-ethylhexyl)phthalate	117-81-7	X		X	X
Chrysene	218-01-9	X		X	X
Di-n-octylphthalate	117-84-0	X		X	X
Benzo(b)fluoranthene	205-99-2	X		X	X
Benzo(k)fluoranthene	207-08-9	X		X	X
Benzo(a)pyrene	50-32-8	X		X	X
Indeno(1,2,3-cd)pyrene	193-39-5	X		X	X
Dibenz(a,h)anthracene	53-70-3	X		X	X
Benzo(g,h,i)perylene	191-24-2	X		X	X
Atrazine	1912-24-9	X		X	
1,4-Dioxane	123-91-1	X		X	
Benzaldehyde	100-52-7	X		X	
Acetophenone	98-68-2	X		X	
Caprolactam	105-60-2	X		X	

Table 3

Reportable Analytes for TestAmerica Pittsburgh Standard Tests, Primary Standard

Analyte	CAS Number	Routinely Calibrated Compounds	TCLP	TCL	Appendix IX
1,1-Biphenyl	92-52-4	X		X	
2-Naphthylamine	91-59-8	X		X	

[1] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether
[2] Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 4

Reportable analytes for TestAmerica Pittsburgh Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	Appendix IX
2-Picoline	109-06-8	X
N-Nitrosomethylethylamine	10595-95-6	X
Methyl methanesulfonate	66-27-3	X
N-Nitrosodiethylamine	55-18-5	X
Ethyl methanesulfonate	62-50-0	X
Pentachloroethane	76-01-7	X
Acetophenone	98-86-2	X
N-Nitrosopyrrolidine	930-55-2	X
N-Nitrosomorpholine	59-89-2	X
o-Toluidine	95-53-4	X
3-Methylphenol	108-39-4	X
N-Nitrosopiperidine	100-75-4	X
o,o,o-Triethyl-Phosphorothioate[2]	126-68-1	X
a,a-Dimethyl-phenethylamine	122-09-8	X
2,6-Dichlorophenol	87-65-0	X
Hexachloropropene	1888-71-7	X
p-Phenylenediamine	106-50-3	X
n-Nitrosodi-n-butylamine	924-16-3	X
Safrole	94-59-7	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X
Isosafrole	120-58-1	X
1,4-Dinitrobenzene	100-25-4	
1,4-Naphthoquinone	130-15-4	X
1,3-Dinitrobenzene	99-65-0	X
Pentachlorobenzene	608-93-5	X
1-Naphthylamine	134-32-7	X
2-Naphthylamine	91-59-8	X
2,3,4,6-Tetrachlorophenol	58-90-2	X
5-Nitro-o-toluidine	99-55-8	X
Thionazin[2]	297-97-2	X
1,3,5-Trinitrobenzene	99-35-4	X
Sulfotepp[2]	3689-24-5	X
Phorate[2]	298-02-2	X
Phenacetin	62-44-2	X
Diallate	2303-16-4	X
Dimethoate[2]	60-51-5	X
4-Aminobiphenyl	92-67-1	X
Pentachloronitrobenzene	82-68-8	X
Pronamide	23950-58-5	X

Table 4

Reportable analytes for TestAmerica Pittsburgh Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	Appendix IX
Disulfoton[2]	298-04-4	X
2-secbutyl-4,6-dinitrophenol (Dinoseb)[2]	88-85-7	X
Methyl parathion[2]	298-00-0	X
4-Nitroquinoline-1-oxide	56-57-5	X
Parathion[2]	56-38-2	X
Isodrin[3]	465-73-6	X
Kepone	143-50-0	X
Famphur[2]	52-85-7	X
Methapyrilene	91-80-5	X
Aramite	140-57-8	X
p-(Dimethylamino)azobenzene	60-11-7	X
p-Chlorobenzilate[3]	510-15-6	X
3,3'-Dimethylbenzidine	119-93-7	X
2-Acetylaminofluorene	53-96-3	X
Dibenz(a,j)acridine	224-42-0	
7,12-Dimethylbenz(a)anthracene	57-97-6	X
3-Methylcholanthrene	56-49-5	X
Hexachlorophene[4]	70-30-4	X
Diphenylamine[5]	122-39-4	X

[2] May also be analyzed by method 8141A, which can achieve lower reporting limits.

[3] May also be analyzed by method 8081A, which can achieve lower reporting limits

[4] Hexachlorophene is a required analyte for Appendix IX. This compound is not stable, and therefore not included in the calibration standard. The characteristic ions for hexachlorophene are searched for in the chromatogram.

[5] Diphenylamine is a required compound for Appendix IX. N-nitrosodiphenylamine decomposes in the injection port to form diphenylamine. Therefore these two compounds cannot be distinguished. Diphenylamine is not included in the calibration standard.

Table 5

Suggested Instrumental Conditions

Mass Range	35-500 amu
Scan Time	≤1 second/scan
Initial Column Temperature/Hold Time	40°C for 2 minutes
Column Temperature Program	40 - 320°C at 11.5°C/min
Final Column Temperature/Hold Time	320°C (until at least one minute after benzo(g,h,i)perylene has eluted)
Total Run time	0.5 min based on the last compound of cont. Cal.
Injector Temperature	250 - 300°C
Transfer Line Temperature	250 - 300°C
Source Temperature	According to manufacturer's specifications
Injector	Grob-type, split / splitless
Sample Volume	1 or 2 µl
Carrier Gas	Helium at 30 cm/sec

Table 6

DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30 - 60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40 - 60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5 - 9% of mass 198
275	10 - 30% of mass 198
365	>1% of mass 198
441	Present, but less than mass 443
442	>40% of mass 198
443	17 - 23% of mass 442

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
N-nitrosodimethylamine	74	42	
Pyridine	79	52	
2-Fluorophenol (Surrogate Standard)	112	64	63
Phenol-d6 (Surrogate Standard)	99	42	71
Acetophenone	105	77	51
Aniline	93	66	
Benzaldehyde	77	105	106
Phenol	94	65	66
Bis(2-chloroethyl)ether	93	63	95
2-Chlorophenol	128	64	130
1,3-Dichlorobenzene	146	148	111
1,4-Dichlorobenzene-d4 (Internal Standard)	152	150	115
1,4-Dichlorobenzene	146	148	111
Benzyl Alcohol	108	79	77
Caprolactam	113	55	56
1,2-Dichlorobenzene	146	148	111
2-Methylphenol	108	107	79
2,2'-oxybis(1-chloropropane)[1]	45	77	121
4-Methylphenol	108	107	79
N-Nitroso-di-n-propylamine	70	42	101,130
Hexachloroethane	117	201	199
Nitrobenzene-d5 (Surrogate Standard)	82	128	54
1,1-Biphenyl	154	153	76
Nitrobenzene	77	123	65
Isophorone	82	95	138
2-Naphthylamine	143	115	116
2-Nitrophenol	139	65	109
2,4-Dimethylphenol	107	121	122
Benzoic Acid	122	105	77
Bis(2-chloroethoxy)methane	93	95	123
2,4-Dichlorophenol	162	164	98
1,2,4-Trichlorobenzene	180	182	145
Naphthalene-d8 (Internal Standard)	136	68	54
Atrazine	200	173	215
Naphthalene	128	129	127
4-Chloroaniline	127	129	65
Hexachlorobutadiene	225	223	227
4-Chloro-3-methylphenol	107	144	142
2-Methylnaphthalene	142	141	115

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
Hexachlorocyclopentadiene	237	235	272
2,4,6-Trichlorophenol	196	198	200
2,4,5-Trichlorophenol	196	198	200
2-Fluorobiphenyl (Surrogate Standard)	172	171	170
2-Chloronaphthalene	162	164	127
2-Nitroaniline	65	92	138
Dimethylphthalate	163	194	164
Acenaphthylene	152	151	153
2,6-Dinitrotoluene	165	89	63
Acenaphthene-d10 (Internal Standard)	164	162	160
3-Nitroaniline	138	108	92
Acenaphthene	153	152	154
2,4-Dinitrophenol	184	63	154
Dibenzofuran	168	139	84
4-Nitrophenol	139	109	65
2,4-Dinitrotoluene	165	63	89
Diethylphthalate	149	177	150
Fluorene	166	165	167
4-Chlorophenylphenylether	204	206	141
4-Nitroaniline	138	92	108
4,6-Dinitro-2-methylphenol	198	51	105
N-Nitrosodiphenylamine	169	168	167
2,4,6-Tribromophenol (Surrogate Standard)	330	332	141
Azobenzene	77	182	105
4-Bromophenylphenylether	248	250	141
Hexachlorobenzene	284	142	249
Pentachlorophenol	266	264	268
Phenanthrene-d10 (Internal Standard)	188	94	80
Phenanthrene	178	179	176
Anthracene	178	179	176
Carbazole	167	166	168
Di-n-butylphthalate	149	150	104
Fluoranthene	202	101	203
Benzidine	184	92	185
Pyrene	202	200	203
Terphenyl-d14 (Surrogate Standard)	244	122	212
Butylbenzylphthalate	149	91	206
Benzo(a)Anthracene	228	229	226
Chrysene-d12 (Internal Standard)	240	120	236

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
3,3'-Dichlorobenzidine	252	254	126
Chrysene	228	226	229
Bis(2-ethylhexyl)phthalate	149	167	279
Perylene-d12 (Internal Standard)	264	260	265
Di-n-octylphthalate	149	167	43
Benzo(b)fluoranthene	252	253	125
Benzo(k)fluoranthene	252	253	125
Benzo(a)pyrene	252	253	125
Indeno(1,2,3-cd)pyrene	276	138	277
Dibenz(a,h)anthracene	278	139	279
Benzo(g,h,i)perylene	276	138	277

Table 8

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
2-Picoline	93	66	92
N-Nitrosomethylethylamine	88	42	43
Methyl methanesulfonate	80	79	65
N-Nitrosodiethylamine	102	44	57
Ethyl methanesulfonate	79	109	97
Pentachloroethane	117	119	167
Acetophenone	105	77	120
N-Nitrosopyrrolidine	100	41	42
N-Nitrosomorpholine	116	56	86
o-Toluidine	106	107	77
3-Methylphenol	108	107	77
N-Nitrosopiperidine	114	42	55
o,o,o-Triethyl-Phosphorothioate	198	121	93
a,a-Dimethyl-phenethylamine	58	91	
2,6-Dichlorophenol	162	164	63
Hexachloropropene	213	215	211
p-Phenylenediamine	108	80	107
n-Nitrosodi-n-butylamine	84	57	41
Safrole	162	104	77
1,2,4,5-Tetrachlorobenzene	216	214	218
Isosafrole 1	162	104	131
Isosafrole 2	162	104	131
1,4-Dinitrobenzene	168	75	122
1,4-Naphthoquinone	158	104	102
1,3-Dinitrobenzene	168	75	76
Pentachlorobenzene	250	248	252
1-Naphthylamine	143	115	116
2-Naphthylamine	143	115	116
2,3,4,6-Tetrachlorophenol	232	230	131
5-Nitro-o-toluidine	152	77	106
Thionazin	97	96	143
1,3,5-Trinitrobenzene	213	75	120
Sulfotepp	97	322	202
Phorate	121	75	260
Phenacetin	108	179	109
Diallate	86	43	234
Dimethoate	87	93	125
4-Aminobiphenyl	169	168	170
Pentachloronitrobenzene	237	142	214
Pronamide	173	175	255

Table 8

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
Disulfoton	88	97	89
2-secbutyl-4,6-dinitrophenol (Dinoseb)	211	163	147
Methyl parathion	109	125	263
4-Nitroquinoline-1-oxide	190	128	160
Parathion	109	97	291
Isodrin	193	66	195
Kepone	272	274	237
Famphur	218	125	93
Methapyrilene	58	97	72
Aramite 1	185	135	63
Aramite 2	185	135	63
p-(Dimethylamino)azobenzene	120	225	77
p-Chlorobenzilate	251	139	253
3,3'-Dimethylbenzidine	212	213	211
2-Acetylaminofluorene	181	180	223
Dibenz(a,j)acridine	279	280	277
7,12-Dimethylbenz(a)anthracene	256	241	120
3-Methylcholanthrene	268	252	253

Table 9
8270C Routine LCS and Spike Control Compounds and Control Limits

Water			LCS			Spike		
Compound	**Units**	**Spike Level**	**LCL**	**UCL**	**RPD**	**LCL**	**UCL**	**RPD**
Acenaphthene	ug/L	50	40	97	32	31	131	39
4-Bromophenyl phenyl ether	ug/L	50	40	105	40	51	125	37
Butyl benzyl phthalate	ug/L	50	39	105	35	37	132	63
4-Chloro-3-methylphenol	ug/L	50	38	100	32	31	127	83
2-Chlorophenol	ug/L	50	38	97	31	10	129	139
1,4-Dichlorobenzene	ug/L	50	38	94	33	18	107	60
2,4-Dinitrotoluene	ug/L	50	37	103	32	41	130	53
Hexachloroethane	ug/L	50	35	96	43	10	111	63
4-Methylphenol	ug/L	100	33	106	34	28	125	77
Naphthalene	ug/L	50	38	98	39	29	118	45
4-Nitrophenol	ug/L	50	30	112	39	10	163	118
N-Nitrosodi-n-propylamine	ug/L	50	36	102	36	39	122	47
Pentachlorophenol	ug/L	50	13	120	56	10	165	98
Phenol	ug/L	50	36	98	35	10	135	115
Pyrene	ug/L	50	39	108	38	37	132	45
1,2,4-Trichlorobenzene	ug/L	50	39	97	32	10	142	52
Soil			**LCS**			**Spike**		
Compound	**Units**	**Spike Level**	**LCL**	**UCL**	**RPD**	**LCL**	**UCL**	**RPD**
Acenaphthene	ug/kg	1665	38	112	51	15	130	50
4-Bromophenyl phenyl ether	ug/kg	1665	46	120	81	27	136	48
Butyl benzyl phthalate	ug/kg	1665	47	115	54	27	130	48
4-Chloro-3-methylphenol	ug/kg	1665	39	111	52	16	128	52
2-Chlorophenol	ug/kg	1665	38	109	62	16	120	54
1,4-Dichlorobenzene	ug/kg	1665	36	107	57	20	105	62
2,4-Dinitrotoluene	ug/kg	1665	35	117	50	15	132	49
Hexachloroethane	ug/kg	1665	40	106	53	13	111	63
4-Methylphenol	ug/kg	3333	41	117	87	17	131	50
Naphthalene	ug/kg	1665	44	109	64	10	140	56
4-Nitrophenol	ug/kg	1665	30	125	43	10	154	88
N-Nitrosodi-n-propylamine	ug/kg	1665	36	114	45	30	118	51
Pentachlorophenol	ug/kg	1665	21	127	52	10	136	123
Phenol	ug/kg	1665	36	110	55	19	119	50
Pyrene	ug/kg	1665	43	118	48	10	168	69
1,2,4-Trichlorobenzene	ug/kg	1665	37	111	58	21	118	49

Table 9A
Low Level 8270C (Spike Method Code 42) - LCS and Spike Control Compounds and Control Limits

Water			LCS			Spike		
Compound	**Units**	**Spike Level**	**LCL**	**UCL**	**RPD**	**LCL**	**UCL**	**RPD**
Acenaphthene	ug/L	20	35	96	41	35	96	41
4-Bromophenyl phenyl ether	ug/L	20	39	94	40	39	94	40
Butyl benzyl phthalate	ug/L	20	33	106	40	33	106	40
4-Chloro-3-methylphenol	ug/L	20	41	99	42	41	99	42
2-Chlorophenol	ug/L	20	39	93	39	39	93	39
1,4-Dichlorobenzene	ug/L	20	36	91	41	36	91	41
2,4-Dinitrotoluene	ug/L	20	37	120	39	37	120	39
Hexachloroethane	ug/L	20	38	91	39	38	91	39
4-Methylphenol	ug/L	40	41	92	41	41	92	41
Naphthalene	ug/L	20	40	89	43	40	89	43
4-Nitrophenol	ug/L	20	39	110	42	39	110	42
N-Nitrosodi-n-propylamine	ug/L	20	41	96	43	41	96	43
Pentachlorophenol	ug/L	20	23	108	42	23	108	42
Phenol	ug/L	20	38	95	39	38	95	39
Pyrene	ug/L	20	30	106	42	30	106	42
1,2,4-Trichlorobenzene	ug/L	20	35	95	45	35	95	45
Soil			**LCS**			**Spike**		
Compound	**Units**	**Spike Level**	**LCL**	**UCL**	**RPD**	**LCL**	**UCL**	**RPD**
Acenaphthene	ug/kg	667	34	107	36	34	107	36
4-Bromophenyl phenyl ether	ug/kg	667	37	105	20	37	105	20
Butyl benzyl phthalate	ug/kg	667	35	110	34	35	110	34
4-Chloro-3-methylphenol	ug/kg	667	37	114	31	37	114	31
2-Chlorophenol	ug/kg	667	45	99	40	45	99	40
1,4-Dichlorobenzene	ug/kg	667	39	103	39	39	103	39
2,4-Dinitrotoluene	ug/kg	667	42	118	33	42	118	33
Hexachloroethane	ug/kg	667	40	102	37	40	102	37
4-Methylphenol	ug/kg	1334	40	113	42	40	113	42
Naphthalene	ug/kg	667	38	103	25	38	103	25
4-Nitrophenol	ug/kg	667	24	132	37	24	132	37
N-Nitrosodi-n-propylamine	ug/kg	667	39	111	32	39	111	32
Pentachlorophenol	ug/kg	667	18	117	37	18	117	37
Phenol	ug/kg	667	44	100	40	44	100	40
Pyrene	ug/kg	667	28	116	28	28	116	28
1,2,4-Trichlorobenzene	ug/kg	667	38	103	40	38	103	40
All samples are spiked with full analytes and the above compounds are the control analytes.								

Table 9B
Low Level 8270C (Spike Method Code QL)- LCS and Spike Control Compounds and Control Limits

Water			LCS			Spike		
Compound	**Units**	**Spike Level**	**LCL**	**UCL**	**RPD**	**LCL**	**UCL**	**RPD**
Acenaphthene	ug/L	200	40	97	32	31	131	39
4-Bromophenyl phenyl ether	ug/L	200	40	105	40	51	125	37
Butyl benzyl phthalate	ug/L	200	39	105	35	37	132	63
4-Chloro-3-methylphenol	ug/L	200	38	100	32	31	127	83
2-Chlorophenol	ug/L	200	38	97	31	10	129	139
1,4-Dichlorobenzene	ug/L	200	38	94	33	18	107	60
2,4-Dinitrotoluene	ug/L	200	37	103	32	41	130	53
Hexachloroethane	ug/L	200	35	96	43	10	111	63
4-Methylphenol	ug/L	400	33	106	34	28	125	77
Naphthalene	ug/L	200	38	98	39	29	118	45
4-Nitrophenol	ug/L	200	30	112	39	10	163	118
N-Nitrosodi-n-propylamine	ug/L	200	36	102	36	39	122	47
Pentachlorophenol	ug/L	200	13	120	56	10	165	98
Phenol	ug/L	200	36	98	35	10	135	115
Pyrene	ug/L	200	39	108	38	37	132	45
1,2,4-Trichlorobenzene	ug/L	200	39	97	32	10	142	52
Soil			**LCS**			**Spike**		
Compound	**Units**	**Spike Level**	**LCL**	**UCL**	**RPD**	**LCL**	**UCL**	**RPD**
Acenaphthene	ug/kg	6667	38	112	51	15	130	50
4-Bromophenyl phenyl ether	ug/kg	6667	46	120	81	27	136	48
Butyl benzyl phthalate	ug/kg	6667	47	115	54	27	130	48
4-Chloro-3-methylphenol	ug/kg	6667	39	111	52	16	128	52
2-Chlorophenol	ug/kg	6667	38	109	62	16	120	54
1,4-Dichlorobenzene	ug/kg	6667	36	107	57	20	105	62
2,4-Dinitrotoluene	ug/kg	6667	35	117	50	15	132	49
Hexachloroethane	ug/kg	6667	40	106	53	13	111	63
4-Methylphenol	ug/kg	13334	41	117	87	17	131	50
Naphthalene	ug/kg	6667	44	109	64	10	140	56
4-Nitrophenol	ug/kg	6667	30	125	43	10	154	88
N-Nitrosodi-n-propylamine	ug/kg	6667	36	114	45	30	118	51
Pentachlorophenol	ug/kg	6667	21	127	52	10	136	123
Phenol	ug/kg	6667	36	110	55	19	119	50
Pyrene	ug/kg	6667	43	118	48	10	168	69
1,2,4-Trichlorobenzene	ug/kg	6667	37	111	58	21	118	49

All samples are spiked with full analytes and the above compounds are the control analytes.
Samples extracted for QL method are prepared at the time of analysis at a 10X dilution. All control limits are subject to change.

Table 10

TCLP LCS Compounds

LCS Compounds	Spiking Level, ng/µL in extract[1]
1,4-Dichlorobenzene	100
2,4-Dinitrotoluene	100
Hexachlorobenzene	100
Hexachlorobutadiene	100
Hexachloroethane	100
2-Methylphenol	100
3 & 4-Methylphenol	200
Nitrobenzene	100
Pentachlorophenol	100
Pyridine	100
2,4,5-Trichlorophenol	100
2,4,6-Trichlorophenol	100

[1] Levels are 50 ng/µL if 2 µL injection is used

Recovery limits for the LCS and for matrix spikes are generated from historical data and are maintained by the QA department.

Table 11

8270C Surrogate Compounds

Surrogate Compounds	Routine 8270C Spiking Concentration, ug/mL	Low Level 8270C Spiked Method Code 42	Low Level 8270C Spiked Method Code QL
Nitrobenzene-d5	100	20	200
2-Fluorobiphenyl	100	20	200
Terphenyl-d14	100	20	200
1,2-Dichlorobenzene-d4[1]	100	20	200
Phenol-d6	150	30	300
2-Fluorophenol	150	30	300
2,4,6-Tribromophenol	150	30	300
2-Chlorophenol-d4[1]	150	30	300

[1] Included in standard mix, but not routinely evaluated for method 8270C

Samples extracted for QL method are prepared at the time of analysis at a 10X dilution.

Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 12 - Calibration Levels, ug/ml (for 2ul injection)

Analytes	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8
Pyridine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
N-nitrosodimethylamine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Aniline	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Phenol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Bis(2-chloroethyl)ether	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2-Chlorophenol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
1,3-Dichlorobenzene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
1,4-Dichlorobenzene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Benzyl alcohol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
1,2-Dichlorobenzene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2-Methylphenol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2,2'-oxybis(1-chloropropane)[1]	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
4-Methylphenol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
N-Nitroso-di-n-propylamine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Hexachloroethane	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Nitrobenzene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Isophorone	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2-Nitrophenol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2,4-Dimethylphenol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Benzoic acid	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Bis(2-chloroethoxy)methane	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2,4-Dichlorophenol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
1,2,4-Trichlorobenzene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Naphthalene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
4-Chloroaniline	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Hexachlorobutadiene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
4-Chloro-3-methylphenol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2-Methylnaphthalene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Hexachlorocyclopentadiene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2,4,6-Trichlorophenol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2,4,5-Trichlorophenol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2-Chloronaphthalene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2-Nitroaniline	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Dimethyl phthalate	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Acenaphthylene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
3-Nitroaniline	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Acenaphthene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2,4-Dinitrophenol	1.0	2.0	5.0	10.0	15.0	20.0	30.0	40.0
4-Nitrophenol	1.0	2.0	5.0	10.0	15.0	20.0	30.0	40.0

Table 12 - Calibration Levels, ug/ml (for 2ul injection)

Analytes	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8
Dibenzofuran	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2,4-Dinitrotoluene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2,6-Dinitrotoluene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Diethylphthalate	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
4-Chlorophenyl phenyl ether	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Fluorene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
4-Nitroaniline	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
4,6-Dinitro-2-methylphenol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
N-Nitrosodiphenylamine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Azobenzene[2]	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
4-Bromophenyl phenyl ether	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Hexachlorobenzene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Pentachlorophenol	1.0	2.0	5.0	10.0	15.0	20.0	30.0	40.0
Phenanthrene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Anthracene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Carbazole	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Di-n-butyl phthalate	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Fluoranthene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Benzidine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Pyrene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Butyl benzyl phthalate	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
3,3'-Dichlorobenzidine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Benzo(a)anthracene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Bis(2-ethylhexyl)phthalate	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Chrysene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Di-n-octylphthalate	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Benzo(b)fluoranthene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Benzo(k)fluoranthene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Benzo(a)pyrene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Indeno(1,2,3-cd)pyrene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Dibenz(a,h)anthracene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Benzo(g,h,i)perylene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0

[1] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether.
[2]Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 13 - Calibration Levels, Appendix IX Standard, µg/mL (for 2ul injection)

Analytes	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8
2-Picoline	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
N-Nitrosomethylethylamine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Methyl methanesulfonate	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
N-Nitrosodiethylamine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Ethyl methanesulfonate	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Pentachloroethane	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Acetophenone	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
N-Nitrosopyrrolidine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
N-Nitrosomorpholine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
o-Toluidine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
3-Methylphenol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
N-Nitrosopiperidine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
o,o,o-Triethyl-Phosphorothioate	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
a,a-Dimethyl-phenethylamine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2,6-Dichlorophenol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Hexachloropropene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
p-Phenylenediamine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
n-Nitrosodi-n-butylamine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Safrole	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
1,2,4,5-Tetrachlorobenzene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Isosafrole 1 + 2	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
1,4-Dinitrobenzene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
1,4-Naphthoquinone	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
1,3-Dinitrobenzene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Pentachlorobenzene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
1-Naphthylamine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2-Naphthylamine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2,3,4,6-Tetrachlorophenol	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
5-Nitro-o-toluidine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Thionazin	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
1,3,5-Trinitrobenzene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Sulfotepp	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Phorate	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Phenacetin	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Diallate 1 + 2	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Dimethoate	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
4-Aminobiphenyl	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Pentachloronitrobenzene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0

Table 13 - Calibration Levels, Appendix IX Standard, µg/mL (for 2ul injection)

Analytes	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8
Pronamide	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Disulfoton	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2-secbutyl-4,6-dinitrophenol (Dinoseb)	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Methyl parathion	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
4-Nitroquinoline-1-oxide	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Parathion	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Isodrin	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Kepone	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Famphur	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Methapyrilene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Aramite 1 and 2	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
p-(Dimethylamino)azobenzene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
p-Chlorobenzilate	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
3,3'-Dimethylbenzidine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
2-Acetylaminofluorene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
Dibenz (a,j)acridine	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
7,12-Dimethylbenz(a)anthracene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0
3-Methylcholanthrene	0.2	1.0	2.0	5.0	10.0	20.0	30.0	40.0

Note: Tables 14 and 14A were removed.

Table 15A
Method 8270C Low Level (Method Code 42) Surrogate QC Acceptance Criteria

	Water			Soil		
Compound	**AMT ug/L**	**LCL**	**UCL**	**AMT ug/kg**	**LCL**	**UCL**
2-Fluorobiphenyl	20	19	107	667	28	108
2-Fluorophenol	30	10	111	1000	28	107
2,4,6-Tribromophenol	30	16	122	1000	21	116
Nitrobenzene-d5	20	23	112	667	27	110
Phenol-d5	30	15	112	1000	30	112
Terphenyl-d14	20	10	132	667	21	130

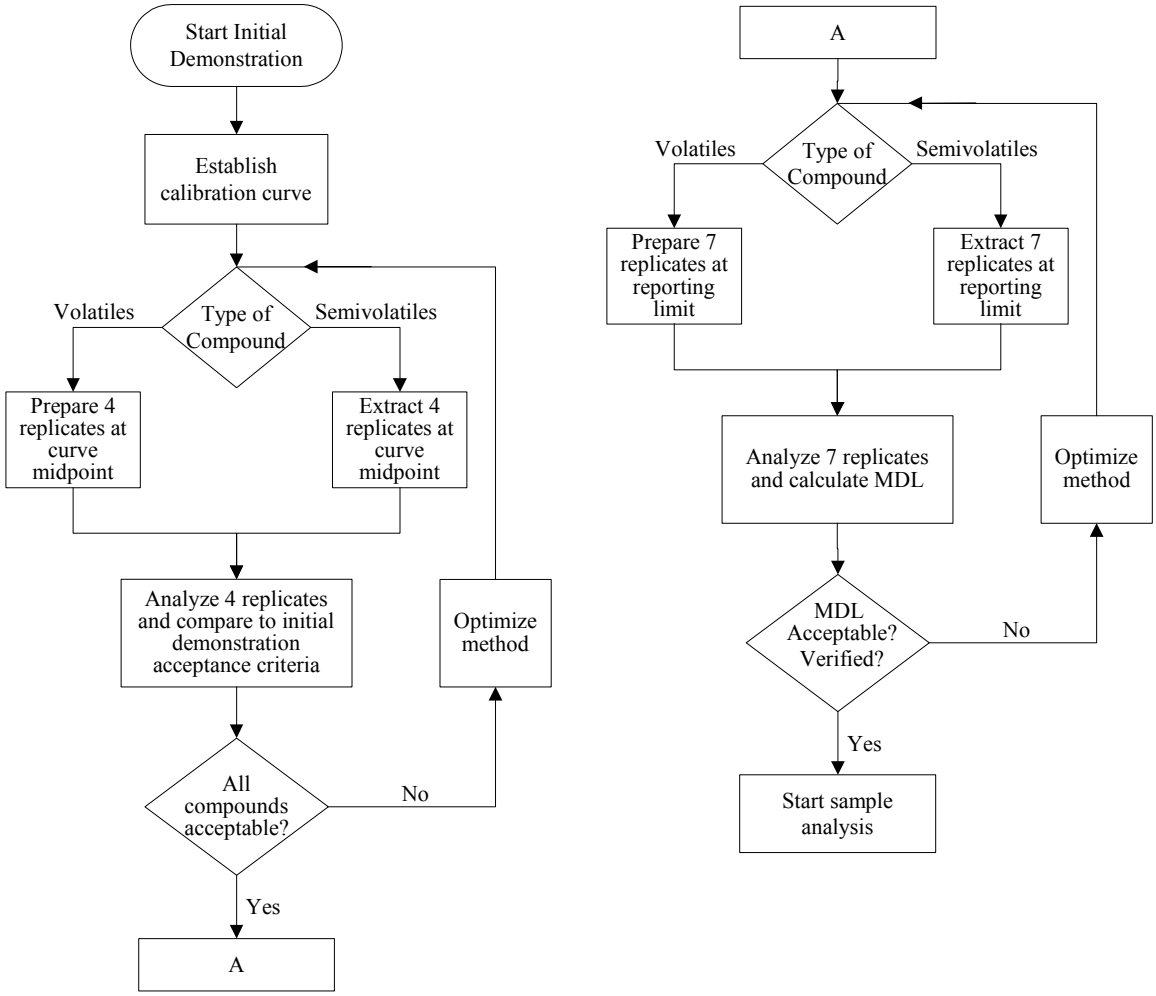
Table 15B
Method 8270C (Method Code QL) Surrogate QC Acceptance Criteria

	Water			Soil		
Compound	**AMT ug/L**	**LCL**	**UCL**	**AMT ug/kg**	**LCL**	**UCL**
2-Fluorobiphenyl	200	27	104	6667	20	109
2-Fluorophenol	300	17	102	10000	10	113
2,4,6-Tribromophenol	300	20	107	10000	10	117
Nitrobenzene-d5	200	33	103	6667	18	106
Phenol-d5	300	25	107	10000	18	113
Terphenyl-d14	200	14	127	6667	10	138

The acceptance criteria listed above is based on laboratory generated data and are subject to change.

Samples extracted for QL method are prepared at the time of analysis at a 10X dilution

17.2 Initial demonstration and MDL[i]



[i] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

ATTACHMENT A

MODIFICATIONS REQUIRED FOR ANALYSIS OF WASTEWATER FOLLOWING METHOD 625

19. REQUIREMENTS FOR METHOD 625

19.1. Method 625 is required for demonstration of compliance with NPDES wastewater discharge permits. The standard analyte list and reporting limits are listed in Table A-1.

19.2. This method can be applied only to aqueous matrices.

19.3. EPA has approved modification to method 625: one extraction can be done. In using single pH extractions for 625 the laboratory should analyze a series of LCSs and have the recovery and precision data filed and readily available. Refer to Appendix A.

19.4. The tune period for this method is defined as 24 hours.

19.5. Initial calibration curve requirements:

19.5.1. The initial calibration curve for this method requires at least three points.

19.5.2. Target compounds must have RSD ≤ 35%.

19.5.3. If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds.

19.6. Continuing calibration verification requirements: All target compounds must have %D ≤ 20%.

19.7. Matrix Spike and LCS requirements:

19.7.1. A full analyte spike is required for method 625. The spiking levels are given in Table A-2.

19.8. The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to 20 samples per month, at least one spiked sample per month is required. The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control.

19.8.1. If any parameter fails the acceptance criteria for recovery, a QC check standard containing each parameter that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of single-component parameters in must be measured in the sample, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

Table A-1

TestAmerica Pittsburgh Method 625 Standard Reporting List and Reporting Limits

Analytes	CAS Number	Aqueous µg/L
Phenol	108-95-2	10
Bis(2-chloroethyl)ether	111-44-4	10
2-Chlorophenol	95-57-8	10
1,3-Dichlorobenzene	541-73-1	10
1,4-Dichlorobenzene	106-46-7	10
1,2-Dichlorobenzene	95-50-1	10
2,2'-oxybis(1-chloropropane)	108-60-1	10
N-Nitroso-di-n-propylamine	621-64-7	10
Hexachloroethane	67-72-1	10
Nitrobenzene	98-95-3	10
Isophorone	78-59-1	10
2-Nitrophenol	88-75-5	10
2,4-Dimethylphenol	105-67-9	10
Bis(2-chloroethoxy)methane	111-91-1	10
2,4-Dichlorophenol	120-83-2	10
1,2,4-Trichlorobenzene	120-82-1	10
Naphthalene	91-20-3	10
Hexachlorobutadiene	87-68-3	10
4-Chloro-3-methylphenol	59-50-7	10
Hexachlorocyclopentadiene	77-47-4	50
2,4,6-Trichlorophenol	88-06-2	10
2-Chloronaphthalene	91-58-7	10
Dimethyl phthalate	131-11-3	10
Acenaphthylene	208-96-8	10
Acenaphthene	83-32-9	10
2,4-Dinitrophenol	51-28-5	50
4-Nitrophenol	100-02-7	50
2,4-Dinitrotoluene	121-14-2	10
2,6-Dinitrotoluene	606-20-2	10
Diethylphthalate	84-66-2	10
4-Chlorophenyl phenyl ether	7005-72-3	10
Fluorene	86-73-7	10
4,6-Dinitro-2-methylphenol	534-52-1	50
N-Nitrosodiphenylamine	86-30-6	10
4-Bromophenyl phenyl ether	101-55-3	10
Hexachlorobenzene	118-74-1	10
Pentachlorophenol	87-86-5	50

Table A-1

TestAmerica Pittsburgh Method 625 Standard Reporting List and Reporting Limits

Analytes	CAS Number	Aqueous µg/L
Phenanthrene	85-01-8	10
Anthracene	120-12-7	10
Di-n-butyl phthalate	84-74-2	10
Fluoranthene	206-44-0	10
Benzidine	92-87-5	100
Pyrene	129-00-0	10
Butyl benzyl phthalate	85-68-7	10
3,3'-Dichlorobenzidine	91-94-1	50
Benzo(a)anthracene	56-55-3	10
Bis(2-ethylhexyl)phthalate	117-81-7	10
Chrysene	218-01-9	10
Di-n-octylphthalate	117-84-0	10
Benzo(b)fluoranthene	205-99-2	10
Benzo(k)fluoranthene	207-08-9	10
Benzo(a)pyrene	50-32-8	10
Indeno(1,2,3-cd)pyrene	193-39-5	10
Dibenz(a,h)anthracene	53-70-3	10
Benzo(g,h,i)perylene	191-24-2	10

Table A-2
Method 625 LCS and MS Compounds and Spike Concentrations

LCS Compounds	Spiking Level, ng in injected 2 µL injection
Phenol	100
Bis(2-chloroethyl)ether	100
2-Chlorophenol	100
1,3-Dichlorobenzene	100
1,4-Dichlorobenzene	100
1,2-Dichlorobenzene	100
2,2'-oxybis(1-chloropropane)	100
N-Nitroso-di-n-propylamine	100
Hexachloroethane	100
Nitrobenzene	100
Isophorone	100
2-Nitrophenol	100
2,4-Dimethylphenol	100
Bis(2-chloroethoxy)methane	100
2,4-Dichlorophenol	100
1,2,4-Trichlorobenzene	100
Naphthalene	100
Hexachlorobutadiene	100
4-Chloro-3-methylphenol	100
Hexachlorocyclopentadiene	100
2,4,6-Trichlorophenol	100
2-Chloronaphthalene	100
Dimethyl phthalate	100
Acenaphthylene	100
Acenaphthene	100
2,4-Dinitrophenol	100
4-Nitrophenol	100
2,4-Dinitrotoluene	100
2,6-Dinitrotoluene	100
Diethylphthalate	100
4-Chlorophenyl phenyl ether	100
Fluorene	100
4,6-Dinitro-2-methylphenol	100
N-Nitrosodiphenylamine	100
4-Bromophenyl phenyl ether	100
Hexachlorobenzene	100
Pentachlorophenol	100

Table A-2 Method 625 LCS and MS Compounds and Spike Concentrations	
LCS Compounds	Spiking Level, ng in injected 2 µL injection
Phenanthrene	100
Anthracene	100
Di-n-butyl phthalate	100
Fluoranthene	100
Benzidine	100
Pyrene	100
Butyl benzyl phthalate	100
3,3'-Dichlorobenzidine	100
Benzo(a)anthracene	100
Bis(2-ethylhexyl)phthalate	100
Chrysene	100
Di-n-octylphthalate	100
Benzo(b)fluoranthene	100
Benzo(k)fluoranthene	100
Benzo(a)pyrene	100
Indeno(1,2,3-cd)pyrene	100
Dibenz(a,h)anthracene	100
Benzo(g,h,i)perylene	100

TABLE A-3 Method 625 LCS and MS Compounds and Spike Concentrations	
Surrogate Compounds	Spiking Level, ug/L in extract
Nitrobenzene-d5	50
2-Fluorobiphenyl	50
Terphenyl-d14	50
2-Fluorophenol	50
2,4,6-Tribromophenol	50
Phenol-d_5	50

Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

TABLE A-4. METHOD 625 LCS, MS AND SURROGATE QC ACCEPTANCE CRITERIA

Compound	MDL[1] (ug/L)	LCS			Matrix Spike		
		LCL	UCL	RPD	LCL	UCL	RPD
1,2,4-Trichlorobenzene	1.377	31	110	37	31	110	37
1,2-Dichlorobenzene	1.361	32	129	20	32	129	20
1,2-Diphenylhydrazine	1.339	30	125	25	30	125	25
1,3-Dichlorobenzene	1.269	1	172	35	1	172	35
1,4-Dichlorobenzene	1.317	28	110	36	28	110	36
2,2'-oxybis(1-Chloropropane)	1.715	50	150	50	50	150	50
2,4,6-Trichlorophenol	1.497	46	135	27	46	135	27
2,4-Dichlorophenol	1.335	42	115	44	42	115	44
2,4-Dimethylphenol	1.833	32	119	20	32	119	20
2,4-Dinitrophenol	14.763	1	191	53	1	191	53
2,4-Dinitrotoluene	1.289	47	131	32	47	131	32
2,6-Dinitrotoluene	1.4	50	158	20	50	158	20
2-Chloronaphthalene	1.429	60	118	20	60	118	20
2-Chlorophenol	1.389	19	124	43	19	124	43
2-Methyl-4,6-dinitrophenol	9.644	10	181	40	10	181	40
2-Nitrophenol	2.99	29	182	32	29	182	32
3,3'-Dichlorobenzidine	25.023	1	162	56	1	162	56
4-Bromophenyl phenyl ether	1.238	53	127	20	53	127	20
4-Chloro-3-methylphenol	1.314	29	124	55	29	124	55
4-Chlorophenyl phenyl ether	1.629	25	158	27	25	158	27
4-Nitrophenol	1.775	19	144	34	19	144	34
Acenaphthene	1.556	39	118	35	39	118	35
Acenaphthylene	1.822	33	145	23	33	145	23
Anthracene	1.195	27	133	22	27	133	22
Benzidine	1.998	1	140	50	1	140	50
Benzo(a)anthracene	0.932	33	143	23	33	143	23

TABLE A-4. METHOD 625 LCS, MS AND SURROGATE QC ACCEPTANCE CRITERIA

Compound	MDL[1] (ug/L)	LCS			Matrix Spike		
		LCL	UCL	RPD	LCL	UCL	RPD
Benzo(a)pyrene	2.503	17	163	31	17	163	31
Benzo(b)fluoranthene	0.857	24	159	28	24	159	28
Benzo(ghi)perylene	0.997	1	219	50	1	219	50
Benzo(k)fluoranthene	1.101	11	162	31	11	162	31
bis(2-Chloroethoxy)methane	3.45	33	184	30	33	184	30
bis(2-Chloroethyl) ether	1.44	12	158	30	12	158	30
bis(2-Ethylhexyl) phthalate	0.907	8	158	31	8	158	31
Butyl benzyl phthalate	1.011	1	152	35	1	152	35
Chrysene	0.953	17	168	31	17	168	31
Dibenzo(a,h)anthracene	1.039	1	227	55	1	227	55
Diethyl phthalate	1.13	1	114	24	1	114	24
Dimethyl phthalate	1.251	1	112	22	1	112	22
Di-n-butyl phthalate	1.104	1	118	24	1	118	24
Di-n-octyl phthalate	0.948	4	146	29	4	146	29
Fluoranthene	1.124	26	137	23	26	137	23
Fluorene	1.548	59	121	20	59	121	20
Hexachlorobenzene	1.261	57	128	22	57	128	22
Hexachlorobutadiene	1.47	36	116	32	36	116	32
Hexachlorocyclopentadiene	6.259	1	138	54	1	138	54
Hexachloroethane	1.371	30	110	33	30	110	33
Indeno(1,2,3-cd)pyrene	0.998	1	171	37	1	171	37
Isophorone	1.404	21	196	37	21	196	37
Naphthalene	1.5	21	133	23	21	133	23
Nitrobenzene	1.455	45	130	50	45	130	50
N-Nitrosodimethylamine	1.694	1	230	47	1	230	47
N-Nitrosodi-n-propylamine	1.538	30	115	36	30	115	36

TABLE A-4. METHOD 625 LCS, MS AND SURROGATE QC ACCEPTANCE CRITERIA

Compound	MDL[1] (ug/L)	LCS			Matrix Spike		
		LCL	UCL	RPD	LCL	UCL	RPD
N-Nitrosodiphenylamine	4.191	5	138	68	5	138	68
Pentachlorophenol	0.816	10	140	56	10	140	56
Phenanthrene	1.068	54	120	20	54	120	20
Phenol	1.98	10	131	43	10	131	43
Pyrene	0.941	46	130	31	46	130	31
Surrogates:							
2-Fluorobiphenyl		30	110		30	110	
2-Fluorophenol		13	110		13	110	
2,4,6-Tribromophenol		21	122		21	122	
Nitrobenzene-d5		32	112		32	112	
Phenol-d5		10	113		10	113	
Terphenyl-d14		10	144		10	144	

Note: The control limits are derived from laboratory generated data.

[1] The MDL listed are subject to change.

Attachment B
Standard Preparation

TestAmerica Pittsburgh

Standards Preparation Logbook Record

Sep-09-2009

Logbook: \\pitsvr01\stdslog\GCMS Semi-Volatile.std

BNA0890-09, +LLSSTD0.4(0.2ug/ml) Analyst: piccolinov

Solvent: Methylene chloride Lot No.: BNA0803-09 Volume (ml): 1.0000
Date Prep./Opened: 07-01-2009
Date Expires(1): 08-31-2009 (6 Months)
Date Reviewed: 08-18-2009 by bozike

Parent Std No.: BNA0854-08, 4,6dn2mphenol 100ug/ml Aliquot Amount (ml): 0.0080

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
4,6-Dinitro-2-methylphenol	100.00	0.8000

Parent Std No.: BNA0855-08, 4 nitrophenol 100ug/ml Aliquot Amount (ml): 0.0080

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
4-Nitrophenol	20.000	0.1600

Parent Std No.: BNA0856-08, 2,4 dinitrophenol 100ug/ml Aliquot Amount (ml): 0.0080

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
2,4-Dinitrophenol	20.000	0.1600

Parent Std No.: BNA0857-08, benzoic acid 100ug/ml Aliquot Amount (ml): 0.0080

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Benzoic Acid	100.00	0.8000

Parent Std No.: BNA0858-08, pentachlorophenol 100ug/ml Aliquot Amount (ml): 0.0080

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Pentachlorophenol	100.00	0.8000

Parent Std No.: BNA0866-09, LOW LEVEL Stock 40ug/ml Aliquot Amount (ml): 0.0050

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Indene	40.000	0.2000
2,4,6-Tribromophenol	40.000	0.2000
2-Chlorophenol-d4	40.000	0.2000
2-Fluorophenol	40.000	0.2000
Phenol-d5	40.000	0.2000
1,2-Dichlorobenzene-d4	40.000	0.2000
2-Fluorobiphenyl	40.000	0.2000
Nitrobenzene-d5	40.000	0.2000
p-Terphenyl-d14	40.000	0.2000

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3,3'-Dichlorobenzidine	40.000	0.2000
3,3'-dimethylbenzidine	40.000	0.2000
Benzidine	40.000	0.2000
1-Methylnaphthalene	40.000	0.2000
2,3,4,6-Tetrachlorophenol	40.000	0.2000
2,3,5,6-Tetrachlorophenol	40.000	0.2000
2-Naphthylamine	40.000	0.2000
7,12-Dimethylbenz(a)anthracene	40.000	0.2000
Methyl methanesulfonate	40.000	0.2000
N-Nitroso-di-n-butylamine	40.000	0.2000
1,4 Dioxane	40.000	0.2000
1,2,4,5-Tetrachlorobenzene	40.000	0.2000
Acetophenone	40.000	0.2000
Atrazine	40.000	0.2000
Benzaldehyde	40.000	0.2000
Biphenyl	40.000	0.2000
Caprolactam	40.000	0.2000
l-Nitrosopyrrolidine	40.000	0.2000
Aniline	40.000	0.2000
Benzoic Acid	40.000	0.2000
Benzyl Alcohol	40.000	0.2000
Pyridine	40.000	0.2000
N-Nitrosodiphenylamine	40.000	0.2000
2,6-Dichlorophenol	40.000	0.2000
1,2,4-Trichlorobenzene	40.000	0.2000
1,2-Dichlorobenzene	40.000	0.2000
1,3-Dichlorobenzene	40.000	0.2000
1,4-Dichlorobenzene	40.000	0.2000
2,4,5-Trichlorophenol	40.000	0.2000
2,4,6-Trichlorophenol	40.000	0.2000
2,4-Dichlorophenol	40.000	0.2000
2,4-Dimethylphenol	40.000	0.2000
2,4-Dinitrophenol	40.000	0.2000
2,4-Dinitrotoluene	40.000	0.2000
2,6-Dinitrotoluene	40.000	0.2000
2-Chloroisopropyl Ether	40.000	0.2000
2-Chloronaphthalene	40.000	0.2000
2-Chlorophenol	40.000	0.2000
2-Methyl-4,6-Dinitrophenol	40.000	0.2000
2-Methylnaphthalene	40.000	0.2000
2-Nitroaniline	40.000	0.2000
2-Nitrophenol	40.000	0.2000
3-Nitroaniline	40.000	0.2000
4-Bromodiphenyl Ether	40.000	0.2000
4-Chloro-3-Methylphenol	40.000	0.2000
4-Chloroaniline	40.000	0.2000
4-Chlorodiphenyl Ether	40.000	0.2000
4-Nitroaniline	40.000	0.2000
4-Nitrophenol	40.000	0.2000
Acenaphthene	40.000	0.2000
Acenaphthylene	40.000	0.2000

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Anthracene	40.000	0.2000
Azobenzene	40.000	0.2000
Benz(A)Anthracene	40.000	0.2000
Benzo(A)Pyrene	40.000	0.2000
Benzo(B)Fluoranthene	40.000	0.2000
Benzo(ghi)Perylene	40.000	0.2000
Benzo(K)Fluoranthene	40.000	0.2000
Benzyl Butyl Phthalate	40.000	0.2000
Bis(2-Chloroethoxy)Methane	40.000	0.2000
Bis(2-Chloroethyl)Ether	40.000	0.2000
Bis(2-Ethylhexyl)Phthalate	40.000	0.2000
Carbazole	40.000	0.2000
Chrysene	40.000	0.2000
Dibenz(A,H)Anthracene	40.000	0.2000
Dibenzofuran	40.000	0.2000
Dibutyl Phthalate	40.000	0.2000
Diethyl Phthalate	40.000	0.2000
Dimethyl Phthalate	40.000	0.2000
Dioctyl Phthalate	40.000	0.2000
Fluoranthene	40.000	0.2000
Fluorene	40.000	0.2000
Hexachloro-1,3-butadiene	40.000	0.2000
Hexachlorobenzene	40.000	0.2000
Hexachlorocyclopentadiene	40.000	0.2000
Hexachloroethane	40.000	0.2000
Indeno(1,2,3-cd)Pyrene	40.000	0.2000
Isophorone	40.000	0.2000
N-Nitrosodi-N-propylamine	40.000	0.2000
N-Nitrosodimethylamine	40.000	0.2000
Naphthalene	40.000	0.2000
Nitrobenzene	40.000	0.2000
O-Cresol	40.000	0.2000
P-Cresol	40.000	0.2000
Pentachlorophenol	40.000	0.2000
Phenanthrene	40.000	0.2000
Phenol	40.000	0.2000
Pyrene	40.000	0.2000

Reviewed By: _____

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TestAmerica Pittsburgh

Standards Preparation Logbook Record

Sep-09-2009

Logbook: \\pitsvr01\stdslog\GCMS Semi-Volatile.std

BNA0891-09, +LLSSTD2.0(1.0ug/ml) Analyst: piccolinov

Solvent: Methylene chloride Lot No.: BNA0803-09 Volume (ml): 1.0000
Date Prep./Opened: 07-01-2009
Date Expires(1): 08-31-2009 (6 Months)
Date Reviewed: 08-18-2009 by bozike

Parent Std No.: BNA0854-08, 4,6dn2mphenol 100ug/ml Aliquot Amount (ml): 0.0100

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
4,6-Dinitro-2-methylphenol	100.00	1.0000

Parent Std No.: BNA0855-08, 4 nitrophenol 100ug/ml Aliquot Amount (ml): 0.0100

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
4-Nitrophenol	20.000	0.2000

Parent Std No.: BNA0856-08, 2,4 dinitrophenol 100ug/ml Aliquot Amount (ml): 0.0100

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
2,4-Dinitrophenol	20.000	0.2000

Parent Std No.: BNA0857-08, benzoic acid 100ug/ml Aliquot Amount (ml): 0.0100

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Benzoic Acid	100.00	1.0000

Parent Std No.: BNA0858-08, pentachlorophenol 100ug/ml Aliquot Amount (ml): 0.0100

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Pentachlorophenol	100.00	1.0000

Parent Std No.: BNA0866-09, LOW LEVEL Stock 40ug/ml Aliquot Amount (ml): 0.0250

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Benzyl Alcohol	40.000	1.0000
Pyridine	40.000	1.0000
N-Nitrosodiphenylamine	40.000	1.0000
2,6-Dichlorophenol	40.000	1.0000
1,2,4-Trichlorobenzene	40.000	1.0000
1,2-Dichlorobenzene	40.000	1.0000
1,3-Dichlorobenzene	40.000	1.0000
1,4-Dichlorobenzene	40.000	1.0000
2,4,5-Trichlorophenol	40.000	1.0000

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2,4,6-Trichlorophenol	40.000	1.0000
2,4-Dichlorophenol	40.000	1.0000
2,4-Dimethylphenol	40.000	1.0000
2,4-Dinitrophenol	40.000	1.0000
2,4-Dinitrotoluene	40.000	1.0000
2,6-Dinitrotoluene	40.000	1.0000
2-Chloroisopropyl Ether	40.000	1.0000
2-Chloronaphthalene	40.000	1.0000
2-Chlorophenol	40.000	1.0000
2-Methyl-4,6-Dinitrophenol	40.000	1.0000
2-Methylnaphthalene	40.000	1.0000
2-Nitroaniline	40.000	1.0000
2-Nitrophenol	40.000	1.0000
3-Nitroaniline	40.000	1.0000
4-Bromodiphenyl Ether	40.000	1.0000
4-Chloro-3-Methylphenol	40.000	1.0000
4-Chloroaniline	40.000	1.0000
4-Chlorodiphenyl Ether	40.000	1.0000
4-Nitroaniline	40.000	1.0000
4-Nitrophenol	40.000	1.0000
Acenaphthene	40.000	1.0000
Acenaphthylene	40.000	1.0000
Anthracene	40.000	1.0000
Azobenzene	40.000	1.0000
Benz(A)Anthracene	40.000	1.0000
Benzo(A)Pyrene	40.000	1.0000
Benzo(B)Fluoranthene	40.000	1.0000
Benzo(ghi)Perylene	40.000	1.0000
Benzo(K)Fluoranthene	40.000	1.0000
Benzyl Butyl Phthalate	40.000	1.0000
Bis(2-Chloroethoxy)Methane	40.000	1.0000
Bis(2-Chloroethyl)Ether	40.000	1.0000
Bis(2-Ethylhexyl)Phthalate	40.000	1.0000
Carbazole	40.000	1.0000
Chrysene	40.000	1.0000
Dibenz(A,H)Anthracene	40.000	1.0000
Dibenzofuran	40.000	1.0000
Dibutyl Phthalate	40.000	1.0000
Diethyl Phthalate	40.000	1.0000
Dimethyl Phthalate	40.000	1.0000
Dioctyl Phthalate	40.000	1.0000
Fluoranthene	40.000	1.0000
Fluorene	40.000	1.0000
Hexachloro-1,3-butadiene	40.000	1.0000
Hexachlorobenzene	40.000	1.0000
Hexachlorocyclopentadiene	40.000	1.0000
Hexachloroethane	40.000	1.0000
Indeno(1,2,3-cd)Pyrene	40.000	1.0000
Isophorone	40.000	1.0000
N-Nitrosodi-N-propylamine	40.000	1.0000
N-Nitrosodimethylamine	40.000	1.0000

Reviewed By: _____

Naphthalene	40.000	1.0000
Nitrobenzene	40.000	1.0000
O-Cresol	40.000	1.0000
P-Cresol	40.000	1.0000
Pentachlorophenol	40.000	1.0000
Indene	40.000	1.0000
2,4,6-Tribromophenol	40.000	1.0000
2-Chlorophenol-d4	40.000	1.0000
2-Fluorophenol	40.000	1.0000
Phenol-d5	40.000	1.0000
1,2-Dichlorobenzene-d4	40.000	1.0000
2-Fluorobiphenyl	40.000	1.0000
Nitrobenzene-d5	40.000	1.0000
p-Terphenyl-d14	40.000	1.0000
3,3'-Dichlorobenzidine	40.000	1.0000
3,3'-dimethylbenzidine	40.000	1.0000
Benzidine	40.000	1.0000
1-Methylnaphthalene	40.000	1.0000
2,3,4,6-Tetrachlorophenol	40.000	1.0000
2,3,5,6-Tetrachlorophenol	40.000	1.0000
2-Naphthylamine	40.000	1.0000
7,12-Dimethylbenz(a)anthracene	40.000	1.0000
Methyl methanesulfonate	40.000	1.0000
N-Nitroso-di-n-butylamine	40.000	1.0000
1,4 Dioxane	40.000	1.0000
1,2,4,5-Tetrachlorobenzene	40.000	1.0000
Acetophenone	40.000	1.0000
Atrazine	40.000	1.0000
Benzaldehyde	40.000	1.0000
Biphenyl	40.000	1.0000
Caprolactam	40.000	1.0000
!-Nitrosopyrrolidine	40.000	1.0000
Aniline	40.000	1.0000
Benzoic Acid	40.000	1.0000
Phenanthrene	40.000	1.0000
Phenol	40.000	1.0000
Pyrene	40.000	1.0000

Reviewed By: _____

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TestAmerica Pittsburgh

Standards Preparation Logbook Record

Sep-09-2009

Logbook: \\pitsvr01\stdslog\GCMS Semi-Volatile.std

BNA0974-09, +LLSSTD4.0(2.0ug/ml) Analyst: bungardf

Solvent: Methylene chloride
Date Prep./Opened: 08-09-2009
Date Expires(1): 08-16-2009 (1 Week)

Volume (ml): 1.0000

Parent Std No.: BNA0854-08, 4,6dn2mphenol 100ug/ml Aliquot Amount (ml): 0.0300

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
4,6-Dinitro-2-methylphenol	100.00	3.0000

Parent Std No.: BNA0855-08, 4 nitrophenol 100ug/ml Aliquot Amount (ml): 0.0300

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
4-Nitrophenol	20.000	0.6000

Parent Std No.: BNA0856-08, 2,4 dinitrophenol 100ug/ml Aliquot Amount (ml): 0.0300

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
2,4-Dinitrophenol	20.000	0.6000

Parent Std No.: BNA0857-08, benzoic acid 100ug/ml Aliquot Amount (ml): 0.0300

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Benzoic Acid	100.00	3.0000

Parent Std No.: BNA0858-08, pentachlorophenol 100ug/ml Aliquot Amount (ml): 0.0300

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Pentachlorophenol	100.00	3.0000

Parent Std No.: BNA0866-09, LOW LEVEL Stock 40ug/ml Aliquot Amount (ml): 0.0500

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Indene	40.000	2.0000
2,4,6-Tribromophenol	40.000	2.0000
2-Chlorophenol-d4	40.000	2.0000
2-Fluorophenol	40.000	2.0000
Phenol-d5	40.000	2.0000
1,2-Dichlorobenzene-d4	40.000	2.0000
2-Fluorobiphenyl	40.000	2.0000
Nitrobenzene-d5	40.000	2.0000
p-Terphenyl-d14	40.000	2.0000
3,3'-Dichlorobenzidine	40.000	2.0000

Reviewed By: _____

Page 1 of 3

3,3'-dimethylbenzidine	40.000	2.0000
Benzidine	40.000	2.0000
1-Methylnaphthalene	40.000	2.0000
2,3,4,6-Tetrachlorophenol	40.000	2.0000
2,3,5,6-Tetrachlorophenol	40.000	2.0000
2-Naphthylamine	40.000	2.0000
7,12-Dimethylbenz(a)anthracene	40.000	2.0000
Methyl methanesulfonate	40.000	2.0000
N-Nitroso-di-n-butylamine	40.000	2.0000
1,4 Dioxane	40.000	2.0000
1,2,4,5-Tetrachlorobenzene	40.000	2.0000
Acetophenone	40.000	2.0000
Atrazine	40.000	2.0000
Benzaldehyde	40.000	2.0000
Biphenyl	40.000	2.0000
Caprolactam	40.000	2.0000
!-Nitrosopyrrolidine	40.000	2.0000
Aniline	40.000	2.0000
Benzoic Acid	40.000	2.0000
Benzyl Alcohol	40.000	2.0000
Pyridine	40.000	2.0000
N-Nitrosodiphenylamine	40.000	2.0000
2,6-Dichlorophenol	40.000	2.0000
1,2,4-Trichlorobenzene	40.000	2.0000
1,2-Dichlorobenzene	40.000	2.0000
1,3-Dichlorobenzene	40.000	2.0000
1,4-Dichlorobenzene	40.000	2.0000
2,4,5-Trichlorophenol	40.000	2.0000
2,4,6-Trichlorophenol	40.000	2.0000
2,4-Dichlorophenol	40.000	2.0000
2,4-Dimethylphenol	40.000	2.0000
2,4-Dinitrophenol	40.000	2.0000
2,4-Dinitrotoluene	40.000	2.0000
2,6-Dinitrotoluene	40.000	2.0000
2-Chloroisopropyl Ether	40.000	2.0000
2-Chloronaphthalene	40.000	2.0000
2-Chlorophenol	40.000	2.0000
2-Methyl-4,6-Dinitrophenol	40.000	2.0000
2-Methylnaphthalene	40.000	2.0000
2-Nitroaniline	40.000	2.0000
2-Nitrophenol	40.000	2.0000
3-Nitroaniline	40.000	2.0000
4-Bromodiphenyl Ether	40.000	2.0000
4-Chloro-3-Methylphenol	40.000	2.0000
4-Chloroaniline	40.000	2.0000
4-Chlorodiphenyl Ether	40.000	2.0000
4-Nitroaniline	40.000	2.0000
4-Nitrophenol	40.000	2.0000
Acenaphthene	40.000	2.0000
Acenaphthylene	40.000	2.0000
Anthracene	40.000	2.0000

Reviewed By: _____

Azobenzene	40.000	2.0000
Benz(A)Anthracene	40.000	2.0000
Benzo(A)Pyrene	40.000	2.0000
Benzo(B)Fluoranthene	40.000	2.0000
Benzo(ghi)Perylene	40.000	2.0000
Benzo(K)Fluoranthene	40.000	2.0000
Benzyl Butyl Phthalate	40.000	2.0000
Bis(2-Chloroethoxy)Methane	40.000	2.0000
Bis(2-Chloroethyl)Ether	40.000	2.0000
Bis(2-Ethylhexyl)Phthalate	40.000	2.0000
Carbazole	40.000	2.0000
Chrysene	40.000	2.0000
Dibenz(A,H)Anthracene	40.000	2.0000
Dibenzofuran	40.000	2.0000
Dibutyl Phthalate	40.000	2.0000
Diethyl Phthalate	40.000	2.0000
Dimethyl Phthalate	40.000	2.0000
Dioctyl Phthalate	40.000	2.0000
Fluoranthene	40.000	2.0000
Fluorene	40.000	2.0000
Hexachloro-1,3-butadiene	40.000	2.0000
Hexachlorobenzene	40.000	2.0000
Hexachlorocyclopentadiene	40.000	2.0000
Hexachloroethane	40.000	2.0000
Indeno(1,2,3-cd)Pyrene	40.000	2.0000
Isophorone	40.000	2.0000
N-Nitrosodi-N-propylamine	40.000	2.0000
N-Nitrosodimethylamine	40.000	2.0000
Naphthalene	40.000	2.0000
Nitrobenzene	40.000	2.0000
O-Cresol	40.000	2.0000
P-Cresol	40.000	2.0000
Pentachlorophenol	40.000	2.0000
Phenanthrene	40.000	2.0000
Phenol	40.000	2.0000
Pyrene	40.000	2.0000

Reviewed By: _____

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TestAmerica Pittsburgh

Standards Preparation Logbook Record

Sep-09-2009

Logbook: \\pitsvr01\stdslog\GCMS Semi-Volatile.std

BNA0892-09, +LLSSTD10(5ug/ml) Analyst: piccolinov

Solvent: Methylene chloride Lot No.: BNA0803-09 Volume (ml): 1.0000
Date Prep./Opened: 07-01-2009
Date Expires(1): 08-31-2009 (6 Months)
Date Reviewed: 08-18-2009 by bozike

Parent Std No.: BNA0854-08, 4,6dn2mphenol 100ug/ml Aliquot Amount (ml): 0.0500

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
4,6-Dinitro-2-methylphenol	100.00	5.0000

Parent Std No.: BNA0855-08, 4 nitrophenol 100ug/ml Aliquot Amount (ml): 0.0500

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
4-Nitrophenol	20.000	1.0000

Parent Std No.: BNA0856-08, 2,4 dinitrophenol 100ug/ml Aliquot Amount (ml): 0.0500

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
2,4-Dinitrophenol	20.000	1.0000

Parent Std No.: BNA0857-08, benzoic acid 100ug/ml Aliquot Amount (ml): 0.0500

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Benzoic Acid	100.00	5.0000

Parent Std No.: BNA0858-08, pentachlorophenol 100ug/ml Aliquot Amount (ml): 0.0500

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Pentachlorophenol	100.00	5.0000

Parent Std No.: BNA0866-09, LOW LEVEL Stock 40ug/ml Aliquot Amount (ml): 0.1250

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Indene	40.000	5.0000
2,4,6-Tribromophenol	40.000	5.0000
2-Chlorophenol-d4	40.000	5.0000
2-Fluorophenol	40.000	5.0000
Phenol-d5	40.000	5.0000
1,2-Dichlorobenzene-d4	40.000	5.0000
2-Fluorobiphenyl	40.000	5.0000
Nitrobenzene-d5	40.000	5.0000
p-Terphenyl-d14	40.000	5.0000

Reviewed By: _____

Page 1 of 3

3,3'-Dichlorobenzidine	40.000	5.0000
3,3'-dimethylbenzidine	40.000	5.0000
Benzidine	40.000	5.0000
1-Methylnaphthalene	40.000	5.0000
2,3,4,6-Tetrachlorophenol	40.000	5.0000
2,3,5,6-Tetrachlorophenol	40.000	5.0000
2-Naphthylamine	40.000	5.0000
7,12-Dimethylbenz(a)anthracene	40.000	5.0000
Methyl methanesulfonate	40.000	5.0000
N-Nitroso-di-n-butylamine	40.000	5.0000
1,4 Dioxane	40.000	5.0000
1,2,4,5-Tetrachlorobenzene	40.000	5.0000
Acetophenone	40.000	5.0000
Atrazine	40.000	5.0000
Benzaldehyde	40.000	5.0000
Biphenyl	40.000	5.0000
Caprolactam	40.000	5.0000
!-Nitrosopyrrolidine	40.000	5.0000
Aniline	40.000	5.0000
Benzoic Acid	40.000	5.0000
Benzyl Alcohol	40.000	5.0000
Pyridine	40.000	5.0000
N-Nitrosodiphenylamine	40.000	5.0000
2,6-Dichlorophenol	40.000	5.0000
1,2,4-Trichlorobenzene	40.000	5.0000
1,2-Dichlorobenzene	40.000	5.0000
1,3-Dichlorobenzene	40.000	5.0000
1,4-Dichlorobenzene	40.000	5.0000
2,4,5-Trichlorophenol	40.000	5.0000
2,4,6-Trichlorophenol	40.000	5.0000
2,4-Dichlorophenol	40.000	5.0000
2,4-Dimethylphenol	40.000	5.0000
2,4-Dinitrophenol	40.000	5.0000
2,4-Dinitrotoluene	40.000	5.0000
2,6-Dinitrotoluene	40.000	5.0000
2-Chloroisopropyl Ether	40.000	5.0000
2-Chloronaphthalene	40.000	5.0000
2-Chlorophenol	40.000	5.0000
2-Methyl-4,6-Dinitrophenol	40.000	5.0000
2-Methylnaphthalene	40.000	5.0000
2-Nitroaniline	40.000	5.0000
2-Nitrophenol	40.000	5.0000
3-Nitroaniline	40.000	5.0000
4-Bromodiphenyl Ether	40.000	5.0000
4-Chloro-3-Methylphenol	40.000	5.0000
4-Chloroaniline	40.000	5.0000
4-Chlorodiphenyl Ether	40.000	5.0000
4-Nitroaniline	40.000	5.0000
4-Nitrophenol	40.000	5.0000
Acenaphthene	40.000	5.0000
Acenaphthylene	40.000	5.0000

Reviewed By: _____

Anthracene	40.000	5.0000
Azobenzene	40.000	5.0000
Benz(A)Anthracene	40.000	5.0000
Benzo(A)Pyrene	40.000	5.0000
Benzo(B)Fluoranthene	40.000	5.0000
Benzo(ghi)Perylene	40.000	5.0000
Benzo(K)Fluoranthene	40.000	5.0000
Benzyl Butyl Phthalate	40.000	5.0000
Bis(2-Chloroethoxy)Methane	40.000	5.0000
Bis(2-Chloroethyl)Ether	40.000	5.0000
Bis(2-Ethylhexyl)Phthalate	40.000	5.0000
Carbazole	40.000	5.0000
Chrysene	40.000	5.0000
Dibenz(A,H)Anthracene	40.000	5.0000
Dibenzofuran	40.000	5.0000
Dibutyl Phthalate	40.000	5.0000
Diethyl Phthalate	40.000	5.0000
Dimethyl Phthalate	40.000	5.0000
Dioctyl Phthalate	40.000	5.0000
Fluoranthene	40.000	5.0000
Fluorene	40.000	5.0000
Hexachloro-1,3-butadiene	40.000	5.0000
Hexachlorobenzene	40.000	5.0000
Hexachlorocyclopentadiene	40.000	5.0000
Hexachloroethane	40.000	5.0000
Indeno(1,2,3-cd)Pyrene	40.000	5.0000
Isophorone	40.000	5.0000
N-Nitrosodi-N-propylamine	40.000	5.0000
N-Nitrosodimethylamine	40.000	5.0000
Naphthalene	40.000	5.0000
Nitrobenzene	40.000	5.0000
O-Cresol	40.000	5.0000
P-Cresol	40.000	5.0000
Pentachlorophenol	40.000	5.0000
Phenanthrene	40.000	5.0000
Phenol	40.000	5.0000
Pyrene	40.000	5.0000

Reviewed By: _____

TestAmerica Pittsburgh

Standards Preparation Logbook Record

Sep-09-2009

Logbook: \\pitsvr01\stdslog\GCMS Semi-Volatile.std

BNA0893-09, +LLSSTD20(10ug/ml) Analyst: piccolinov

Solvent: Methylene chloride Lot No.: BNA0803-09 Volume (ml): 1.0000
Date Prep./Opened: 07-01-2009
Date Expires(1): 08-31-2009 (6 Months)
Date Reviewed: 08-18-2009 by bozike

Parent Std No.: BNA0854-08, 4,6dn2mphenol 100ug/ml Aliquot Amount (ml): 0.0500

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
4,6-Dinitro-2-methylphenol	100.00	5.0000

Parent Std No.: BNA0855-08, 4 nitrophenol 100ug/ml Aliquot Amount (ml): 0.0500

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
4-Nitrophenol	20.000	1.0000

Parent Std No.: BNA0856-08, 2,4 dinitrophenol 100ug/ml Aliquot Amount (ml): 0.0500

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
2,4-Dinitrophenol	20.000	1.0000

Parent Std No.: BNA0857-08, benzoic acid 100ug/ml Aliquot Amount (ml): 0.0500

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Benzoic Acid	100.00	5.0000

Parent Std No.: BNA0858-08, pentachlorophenol 100ug/ml Aliquot Amount (ml): 0.0500

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Pentachlorophenol	100.00	5.0000

Parent Std No.: BNA0866-09, LOW LEVEL Stock 40ug/ml Aliquot Amount (ml): 0.2500

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Indene	40.000	10.000
2,4,6-Tribromophenol	40.000	10.000
2-Chlorophenol-d4	40.000	10.000
2-Fluorophenol	40.000	10.000
Phenol-d5	40.000	10.000
1,2-Dichlorobenzene-d4	40.000	10.000
2-Fluorobiphenyl	40.000	10.000
Nitrobenzene-d5	40.000	10.000
p-Terphenyl-d14	40.000	10.000

Reviewed By: _____

Page 1 of 3

Anthracene	40.000	10.000
Azobenzene	40.000	10.000
Benz(A)Anthracene	40.000	10.000
Benzo(A)Pyrene	40.000	10.000
Benzo(B)Fluoranthene	40.000	10.000
Benzo(ghi)Perylene	40.000	10.000
Benzo(K)Fluoranthene	40.000	10.000
Benzyl Butyl Phthalate	40.000	10.000
Bis(2-Chloroethoxy)Methane	40.000	10.000
Bis(2-Chloroethyl)Ether	40.000	10.000
Bis(2-Ethylhexyl)Phthalate	40.000	10.000
Carbazole	40.000	10.000
Chrysene	40.000	10.000
Dibenz(A,H)Anthracene	40.000	10.000
Dibenzofuran	40.000	10.000
Dibutyl Phthalate	40.000	10.000
Diethyl Phthalate	40.000	10.000
Dimethyl Phthalate	40.000	10.000
Dioctyl Phthalate	40.000	10.000
Fluoranthene	40.000	10.000
Fluorene	40.000	10.000
Hexachloro-1,3-butadiene	40.000	10.000
Hexachlorobenzene	40.000	10.000
Hexachlorocyclopentadiene	40.000	10.000
Hexachloroethane	40.000	10.000
Indeno(1,2,3-cd)Pyrene	40.000	10.000
Isophorone	40.000	10.000
N-Nitrosodi-N-propylamine	40.000	10.000
N-Nitrosodimethylamine	40.000	10.000
Naphthalene	40.000	10.000
Nitrobenzene	40.000	10.000
O-Cresol	40.000	10.000
P-Cresol	40.000	10.000
Pentachlorophenol	40.000	10.000
Phenanthrene	40.000	10.000
Phenol	40.000	10.000
Pyrene	40.000	10.000

Reviewed By: _____

TestAmerica Pittsburgh

Standards Preparation Logbook Record

Sep-09-2009

Logbook: \\pitsvr01\stdslog\GCMS Semi-Volatile.std

BNA0894-09, +LLSSTD40(20ug/ml) Analyst: piccolinov

Solvent: Methylene chloride Lot No.: BNA0803-09 Volume (ml): 1.0000
Date Prep./Opened: 07-01-2009
Date Expires(1): 08-31-2009 (6 Months)
Date Reviewed: 08-18-2009 by bozike

Parent Std No.: BNA0866-09, LOW LEVEL Stock 40ug/ml Aliquot Amount (ml): 0.5000

1,2,4-Trichlorobenzene	40.000	20.000
1,2-Dichlorobenzene	40.000	20.000
1,3-Dichlorobenzene	40.000	20.000
1,4-Dichlorobenzene	40.000	20.000
2,4,5-Trichlorophenol	40.000	20.000
2,4,6-Trichlorophenol	40.000	20.000
2,4-Dichlorophenol	40.000	20.000
2,4-Dimethylphenol	40.000	20.000
2,4-Dinitrophenol	40.000	20.000
2,4-Dinitrotoluene	40.000	20.000
2,6-Dinitrotoluene	40.000	20.000
2-Chloroisopropyl Ether	40.000	20.000
2-Chloronaphthalene	40.000	20.000
2-Chlorophenol	40.000	20.000
2-Methyl-4,6-Dinitrophenol	40.000	20.000
2-Methylnaphthalene	40.000	20.000
2-Nitroaniline	40.000	20.000
2-Nitrophenol	40.000	20.000

Hexachloroethane	40.000	20.000
Indeno(1,2,3-cd)Pyrene	40.000	20.000
Isophorone	40.000	20.000
N-Nitrosodi-N-propylamine	40.000	20.000
N-Nitrosodimethylamine	40.000	20.000
Naphthalene	40.000	20.000
Nitrobenzene	40.000	20.000
O-Cresol	40.000	20.000
P-Cresol	40.000	20.000
Pentachlorophenol	40.000	20.000
Phenanthrene	40.000	20.000
Phenol	40.000	20.000
Pyrene	40.000	20.000

TestAmerica Pittsburgh

Standards Preparation Logbook Record

Sep-09-2009

Logbook: \\pitsvr01\stdslog\GCMS Semi-Volatile.std

BNA0895-09, +LLSSTD60(30ug/ml) Analyst: piccolinov

Solvent: Methylene chloride Lot No.: BNA0803-09 Volume (ml): 1.0000
Date Prep./Opened: 07-01-2009
Date Expires(1): 08-31-2009 (6 Months)
Date Reviewed: 08-18-2009 by bozike

Parent Std No.: BNA0866-09, LOW LEVEL Stock 40ug/ml Aliquot Amount (ml): 0.7500

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Indene	40.000	30.000
2,4,6-Tribromophenol	40.000	30.000
2-Chlorophenol-d4	40.000	30.000
2-Fluorophenol	40.000	30.000
Phenol-d5	40.000	30.000

1,2,4-Trichlorobenzene	40.000	30.000
1,2-Dichlorobenzene	40.000	30.000
1,3-Dichlorobenzene	40.000	30.000
1,4-Dichlorobenzene	40.000	30.000
2,4,5-Trichlorophenol	40.000	30.000
2,4,6-Trichlorophenol	40.000	30.000
2,4-Dichlorophenol	40.000	30.000
2,4-Dimethylphenol	40.000	30.000
2,4-Dinitrophenol	40.000	30.000
2,4-Dinitrotoluene	40.000	30.000
2,6-Dinitrotoluene	40.000	30.000
2-Chloroisopropyl Ether	40.000	30.000
2-Chloronaphthalene	40.000	30.000
2-Chlorophenol	40.000	30.000
2-Methyl-4,6-Dinitrophenol	40.000	30.000
2-Methylnaphthalene	40.000	30.000
2-Nitroaniline	40.000	30.000
2-Nitrophenol	40.000	30.000
3-Nitroaniline	40.000	30.000
4-Bromodiphenyl Ether	40.000	30.000
4-Chloro-3-Methylphenol	40.000	30.000
4-Chloroaniline	40.000	30.000
4-Chlorodiphenyl Ether	40.000	30.000
4-Nitroaniline	40.000	30.000
4-Nitrophenol	40.000	30.000
Acenaphthene	40.000	30.000
Acenaphthylene	40.000	30.000

Hexachloroethane	40.000	30.000
Indeno(1,2,3-cd)Pyrene	40.000	30.000
Isophorone	40.000	30.000
N-Nitrosodi-N-propylamine	40.000	30.000
N-Nitrosodimethylamine	40.000	30.000
Naphthalene	40.000	30.000
Nitrobenzene	40.000	30.000
O-Cresol	40.000	30.000
P-Cresol	40.000	30.000
Pentachlorophenol	40.000	30.000
Phenanthrene	40.000	30.000
Phenol	40.000	30.000
Pyrene	40.000	30.000

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Standards Preparation Logbook Record

Sep-09-2009

Logbook: \\pitsvr01\stdslog\GCMS Semi-Volatile.std

BNA0896-09, +LLSSTD80(40ug/ml) Analyst: piccolinov

Solvent: Methylene chloride Lot No.: BNA0803-09 Volume (ml): 1.0000
Date Prep./Opened: 07-01-2009
Date Expires(1): 08-31-2009 (6 Months)
Date Reviewed: 08-18-2009 by bozike

Parent Std No.: BNA0866-09, LOW LEVEL Stock 40ug/ml Aliquot Amount (ml): 1.0000

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
N-Nitroso-di-n-butylamine	40.000	40.000
1,4 Dioxane	40.000	40.000
1,2,4,5-Tetrachlorobenzene	40.000	40.000
Acetophenone	40.000	40.000
Atrazine	40.000	40.000
Benzaldehyde	40.000	40.000
Biphenyl	40.000	40.000
Caprolactam	40.000	40.000
!-Nitrosopyrrolidine	40.000	40.000
Aniline	40.000	40.000
Benzoic Acid	40.000	40.000
Benzyl Alcohol	40.000	40.000
Pyridine	40.000	40.000
N-Nitrosodiphenylamine	40.000	40.000
2,6-Dichlorophenol	40.000	40.000
1,2,4-Trichlorobenzene	40.000	40.000
1,2-Dichlorobenzene	40.000	40.000

3-Nitroaniline	40.000	40.000
4-Bromodiphenyl Ether	40.000	40.000
4-Chloro-3-Methylphenol	40.000	40.000
4-Chloroaniline	40.000	40.000
4-Chlorodiphenyl Ether	40.000	40.000
4-Nitroaniline	40.000	40.000
4-Nitrophenol	40.000	40.000
Acenaphthene	40.000	40.000
Acenaphthylene	40.000	40.000
Anthracene	40.000	40.000
Azobenzene	40.000	40.000
Benz(A)Anthracene	40.000	40.000
Benzo(A)Pyrene	40.000	40.000
Benzo(B)Fluoranthene	40.000	40.000
Benzo(ghi)Perylene	40.000	40.000
Benzo(K)Fluoranthene	40.000	40.000
Benzyl Butyl Phthalate	40.000	40.000
Bis(2-Chloroethoxy)Methane	40.000	40.000
Bis(2-Chloroethyl)Ether	40.000	40.000
Bis(2-Ethylhexyl)Phthalate	40.000	40.000
Carbazole	40.000	40.000
Chrysene	40.000	40.000
Dibenz(A,H)Anthracene	40.000	40.000
Dibenzofuran	40.000	40.000
Dibutyl Phthalate	40.000	40.000
Diethyl Phthalate	40.000	40.000
Dimethyl Phthalate	40.000	40.000
Dioctyl Phthalate	40.000	40.000
Fluoranthene	40.000	40.000
Fluorene	40.000	40.000
Hexachloro-1,3-butadiene	40.000	40.000
Hexachlorobenzene	40.000	40.000
Indene	40.000	40.000
2,4,6-Tribromophenol	40.000	40.000
2-Chlorophenol-d4	40.000	40.000
2-Fluorophenol	40.000	40.000
Phenol-d5	40.000	40.000

Hexachloroethane	40.000	40.000
Indeno(1,2,3-cd)Pyrene	40.000	40.000
Isophorone	40.000	40.000
N-Nitrosodi-N-propylamine	40.000	40.000
N-Nitrosodimethylamine	40.000	40.000
Naphthalene	40.000	40.000
Nitrobenzene	40.000	40.000
O-Cresol	40.000	40.000
P-Cresol	40.000	40.000
Pentachlorophenol	40.000	40.000
Phenanthrene	40.000	40.000
Phenol	40.000	40.000
Pyrene	40.000	40.000

TestAmerica Pittsburgh

Standards Preparation Logbook Record

Sep-09-2009

Logbook: \\pitsvr01\stdslog\GCMS Semi-Volatile.std

BNA0817-09, LL2nd source verif sstd20(10ug/ml) Analyst: piccolinov

Solvent: Methylene chloride Lot No.: bna0803-09 Volume (ml): 1.0000
Date Prep./Opened: 06-06-2009
Date Expires(1): 07-31-2009 (6 Months)

Parent Std No.: BNA0233-09, Indene Aliquot Amount (ml): 0.0100
Parent Date Expires(1): 01-12-2010 Parent Date Expires(2): 09-29-2010

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Indene	1,000.0	10.000

Parent Std No.: BNA0568-09, Equity SS 8270 Benzidines Mix Aliquot Amount (ml): 0.0050
Parent Date Expires(1): 03-20-2010 Parent Date Expires(2): 08-31-2010

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
3,3'-Dichlorobenzidine	2,000.0	10.000
3,3'-Dimethylbenzidine	2,000.0	10.000
Benzidine	2,000.0	10.000

Parent Std No.: BNA0569-09, Equity SS N-Nitrosodiphenylamine Aliquot Amount (ml): 0.0020
Parent Date Expires(1): 07-31-2009 Parent Date Expires(2): 07-31-2009

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
N-Nitrosodiphenylamine	5,000.0	10.000

Parent Std No.: BNA0570-09, Equity SS 8270 Calibration Mix Aliquot Amount (ml): 0.0100
Parent Date Expires(1): 03-20-2010 Parent Date Expires(2): 11-30-2010

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
64 Compounds	1,000.0	10.000

Parent Std No.: BNA0571-09, Equity SS 8270 Calibration Mix 4 Aliquot Amount (ml): 0.0050
Parent Date Expires(1): 07-31-2009 Parent Date Expires(2): 07-31-2009

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Aniline	2,000.0	10.000
Benzoic Acid	2,000.0	10.000
Benzyl Alcohol	2,000.0	10.000
Pyridine	2,000.0	10.000

Parent Std No.: BNA0572-09, 2,6 Dichlorophenol Aliquot Amount (ml): 0.0100
Parent Date Expires(1): 03-20-2010 Parent Date Expires(2): 06-20-2012

7-compounds	2,000.0	10.000

Parent Std No.: BNA0656-09, 1,4 Dioxane 2nd source — Aliquot Amount (ml): 0.0100
Parent Date Expires(1): 04-21-2010 Parent Date Expires(2): 02-25-2014

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
1,4 Dioxane	1,000.0	10.000

Parent Std No.: BNA0695-09, 1,2,4,5-Tetrachlorobenzene 2nd source — Aliquot Amount (ml): 0.0100
Parent Date Expires(1): 05-02-2010 Parent Date Expires(2): 09-09-2013

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
1,2,4,5-Tetrachlorobenzene	1,000.0	10.000

Parent Std No.: BNA0752-09, Equity SS CLP OLM04 Semivolatiles — Aliquot Amount (ml): 0.0050
Parent Date Expires(1): 05-21-2010 Parent Date Expires(2): 03-31-2011

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
Acetophenone	2,000.0	10.000
Atrazine	2,000.0	10.000
Benzaldehyde	2,000.0	10.000
Biphenyl	2,000.0	10.000
Caprolactam	2,000.0	10.000

Parent Std No.: BNA0816-09, N-Nitrosopyrrolidine 2nd source — Aliquot Amount (ml): 0.0100
Parent Date Expires(1): 06-06-2010 Parent Date Expires(2): 06-11-2014

Component	Initial Conc (ug/ml)	Final Conc (ug/ml)
N-Nitrosopyrrolidine	1,000.0	10.000

Appendix B– EPA Memo Regarding Method 625 Modification

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MEMORANDUM

OFFICE OF WATER

SUBJECT: **Recommended Approved Modifications to EPA Method 625**

FROM: Richard Reding, Chief
Engineering & Analytical Support Branch, EAD, OST

TO: Quality Assurance Managers
ATP Coordinators
NPDES Coordinators

DATE: November 1, 2006

The 304(h) methods branch recommends allowing several modifications to EPA Method 625 for environmental permitting and compliance monitoring under the EPA's Clean Water Act (CWA) programs. This memorandum does not address laboratory certification requirements that states have mandated.

The text in "Protocol for EPA Approval of Alternate Test Procedures for Organic and Inorganic Analytes in Wastewater and Drinking Water" Section 1.3.2 allows flexibility in the modification of "front end techniques" of the test method provided all criteria in this section and **all QC in the method are** met and documented. This protocol can be downloaded at http://www.epa.gov/waterscience/methods.

Recommendations on Method Modifications to EPA Method 625 when Capillary Columns are used:

1. **Combining sample extracts before analysis**

If the analytes can be reliably identified and quantified in the combined extracts, the extracts may be combined. If, however, the identification and quantitation of any analyte is adversely affected by another analyte, a surrogate, or an interferant, the extracts must be analyzed separately. If there is ambiguity, the extracts must be analyzed separately.

2. **Reverse order of pH extraction**

The pH extraction sequence may be reversed to better separate acid and neutral components. Neutral components may be extracted with either acid or base components.

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Previously, neither of these modifications has been used with Method 625 primarily because of limitations of the resolving power of the packed columns used. In 1985, EPA Region 3 Central Regional Lab requested a modification to method 625 as an alternate test procedure (ATP). Although the approval was for limit use by EPA's Region 3, Central Regional Laboratory only, this modification has come to be used throughout the laboratory community (see attached memo).

Why allow these modifications? Following the base-neutral than acid extraction sequence of method 625 in some cases demonstrated the decomposition of some analytes under basic conditions. Organochlorine pesticides may dechlorinate; phthalate esters may exchange; phenols may react to form tannates. These reactions increase with increasing pH. Reversing the extraction pH sequence may better separate acid and neutral waste components.

Other Recommended Modifications to Method 625

A smaller sample volume may be used to minimize matrix interferences provided matrix interferences are demonstrated and documented.

Alternate surrogate and internal standard concentrations other than those specified in the method are acceptable provided that method performance is not degraded;

An alternate calibration curve and a calibration check other than those specified in the method;

A different solvent for the calibration standards to match the solvent of the final extract.

Other Method Flexibility News

We are revising the "Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring" often referred to as the "Pumpkin Book". Many of the recommendations in the revised "Pumpkin Book" cover ways to mitigate matrix effects.

More explicit flexibility to make changes in approved methods without prior EPA approval is now described at 40 CFR Part 136.6. Such changes are only allowed if the modified method produces equivalent performance for the analyte(s) of interest, and the equivalent performance is documented. It is essential to consult the full text at 40 CFR 136.6 before undertaking method modifications.

Please feel free to forward this information. If you have any questions regarding this memorandum, please contact Lemuel Walker of EASB/EAD/OST by email at walker.lemuel@epa.gov.

cc Lemuel Walker
ATP Coordinator

Appenidx C

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-1 Summary of QC Check Definitions, Purpose, and Evaluation – Organics (GC/MS)

QC Check	Definition	Purpose	Evaluation
Breakdown Check 8081A: Endrin, DDT 8270C: DDT	Analysis of s standard solution containing Endrin and DDT. Area counts of these compounds and their breakdown products are evaluated to assess instrument conditions.	To verify the inertness of the injection port because DDT and Endrin are easily degraded in the injection port.	If degradation of either DDT or Endrin exceeds method–specified criteria, corrective action must be taken before proceeding with calibration.
Confirmation of positive results (organics only)	Use of alternative analytical techniques (another method, dissimilar column, or different detector such as MS detector) to validate the presence of target analytes identified.	To verify the identification of an analyte.	This is a required QC procedure. All positive results must be confirmed.
CCV	This verification of the initial calibration that is required during the course of analysis at periodic intervals. Continuing calibration applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models.	To verify that instrument response is reliable, and has not changed significantly from the current ICAL.	If the values for the analytes are outside the acceptance criteria, the initial calibration may not be stable. Results associated with out-of-control CCV results require reanalysis or flagging.
Demonstrate Acceptable Analyst Capability	Analyst runs QC samples in series to establish his/her ability to produce data of acceptable accuracy and precision.	To establish the analysts' ability to produce data of acceptable accuracy and precision.	The average recovery and standard deviation of the replicate must be within designated acceptance criteria.
Duplicate Sample	Two identical portions of material collected for chemical analysis, and identified by unique alphanumeric codes. The duplicate may be portioned from the same sample, or may be two identical samples taken from the same site. The two portions are taken and prepared and analyzed identically.	To provide information on the heterogeneity of the sample matrix or to determine the precision of the intralaboratory analytical process for a specific sample matrix.	To provide information on the heterogeneity of the sample matrix. The greater the heterogeneity of the matrix, the greater the RPD between the sample and the duplicate.
ICAL	Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method.	To establish a calibration curve for the quantification of the analytes of interest.	Statistical procedures are used to determine the relationship between the signal response and the known concentration of analytes of interest. The ICAL must be successful before any samples or other QC check samples can be analyzed.

Appenidx C

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-1 Summary of QC Check Definitions, Purpose, and Evaluation – Organics (GC/MS)

QC Check	Definition	Purpose	Evaluation
Internal Standards	A known amount of standard added to all standards and samples as a reference for evaluating and controlling the precision and bias of the applied analytical method.	To verify that the analytical system is in control.	Any sample associated with out-of-control results must be reanalyzed.
LCS containing all analytes required to be reported	A QC standard of known composition prepared using reagent free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern.	To evaluate method performance by assessing the ability of the lab/analyst to successfully recover the target analytes from a control (clean) matrix.	This is a required QC Check. The inability to achieve acceptable recoveries in the LCS indicate problems with the accuracy/bias of the measurement system.
MS	A sample prepared by adding a know amount of targeted analyte(s) to an aliquot of a specific environmental sample.	To assess the performance of the method as applied to a particular matrix.	The lack of acceptable recoveries in the matrix spike often points to problems with the sample matrix. One test of this is a comparison to the LCS recoveries. If the corresponding LCS recoveries are within acceptable limits, a matrix effect is likely. The lab should not correct for recovery; only report the results of the analyses and the associated MS results and indicate that the results from these analyses have increased uncertainty.
MSD	A 2nd replicate MS prepared in the lab, spiked with an identical, known amount of targeted analyte(s), and analyzed to obtain a measure of the precision of the recovery for each analyte.	To assess the performance of the method as applied to a particular matrix and provide information of the homogeneity of the matrix.	When compared to the MS, the MSD will provide information on the heterogeneity of the sample matrix.
MDL Verification Check	A low-level spike taken through the prep and analytical steps at approximately 2x the MDL used to verify that the laboratory can detect analytes at the calculated MDL.	To validate the MDL on an ongoing basis	If the MDL verification check fails, reprep/reanalyze at a higher level to set a higher MDL or the MDL study must be repeated.
MB	A sample of a matrix similar to the batch of associated samples in which no target analytes or interferences are present at concentrations that impact the analytical results.	To assess background interferences or contamination in the analytical system that might lead to high bias or false positive data.	This QC is used to measure lab accuracy/bias. The MB could indicate whether contamination is occurring during sample prep and analysis. If analytes are detected > ½ RL, reanalyze or B-Flag results for all samples in prep batch. For common

Appenidx C

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-1 Summary of QC Check Definitions, Purpose, and Evaluation – Organics (GC/MS)

QC Check	Definition	Purpose	Evaluation
			lab contaminants, no analytes detected > RL. See DoD Box D-5; & Sec. D.1.1.1
MDL Study	The process to determine the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.	To determine the lowest concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.	MDLs must be established prior to sample analysis. The RL or LOQ is at least 3x the MDL. Used in combination with the MDL verification check to validate the MDL on an ongoing basis.
RT window position establishment for each analyte (chromatographic methods only)	Determination of the placement of the RT window (start/stop time) of each analyte or group of analytes as it elutes through the chromatographic column so that analyte identification can be made during sample analysis. This is done during the initial calibration.	To identify analytes of interest	Incorrect window position may result in false negatives, require additional manual integrations, and/or cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified.
RT window verification for each analyte (chromatographic methods only)	A standard is used to verify that the width and position of the RT windows are valid so that accurate analyte identification can be made during sample analysis.	To minimize the occurrence of both false positive and false negative results at each calibration verification.	The peaks from the standard used are compared to the RT window established during the ICAL to verify that the analytes of interest still fall within the window.
Second source calibration verification	A standard obtained or prepared from a source independent of the source of standards for the initial calibration. Its concentration should be at or near the middle of the calibration range. It is done after the initial calibration.	To verify the accuracy of the initial calibration.	The concentration of the 2nd source calibration verification, determined from the analysis, is compared to the known value of the standard to determine the accuracy of the ICAL. This independent verification of the ICAL must be acceptable before sample analysis can begin.
Surrogate spike (organic analysis only)	A pure substance with properties that mimic the analyte of interest. Surrogates are compounds unlikely to be found in environmental samples to evaluate analytical efficiency by measuring their % Recovery.	To assess the ability of the method to successfully recover specific non-target analytes from an actual matrix.	Whereas the MS is normally done on a batch-specific basis, the surrogate spike is done on a sample-specific basis. Taken with the information derived from other spikes (LCS; MS), the bias in the analytical system can be determined.

Appenidx C

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-1 Summary of QC Check Definitions, Purpose, and Evaluation – Organics (GC/MS)

QC Check	Definition	Purpose	Evaluation
Tuning (MS methods only)	The analysis of a standard compound to verify the mass spectrometer meets standard mass spectra abundance criteria prior to sample analysis.	To verify the proper working of the mass spectrometer.	Proper tuning of the mass spectrometer must be verified prior to sample analysis .

Notes:

1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.

2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.

3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-3: Organic Analysis by GC/MS - Methods 8270

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
IDOC	Per Instrument/Analyst	DoD acceptance criteria if available; otherwise method specific criteria.	Correct / Repeat for those analytes which failed criteria.	NA
MDL	Annually or quarterly MDL Checks performed	40 CFR 136B; MDL verification checks must produce a signal at least 3x the instrument's noise level.	Run MDL check at higher level and set MDL higher or reconduct MDL study.	NA
Tuning	Prior to calibration and every 12 hours during sample analysis	Refer to method specific ion criteria.	Retune instrument and verify. Rerun affected samples.	NA
Breakdown check DDT (8270C only)	Daily prior to analysis of samples	Degradation $\leq$ 20% for DDT (Benzidine & PCP should be present at their normal response and no peak tailing should be observed).	Correct problem then repeat breakdown check.	NA
ICAL	Initial 5-point calibration prior to sample analysis	1. Average RF for SPCCs: SVOCs - $\geq$ 0.050 2. RSD for RFs for CCCs: SVOCs - $\leq$ 30% and one option below. **Option 1:** RSD for each analyte $\leq$ 15% **Option 2:** linear least squares regression: r $\geq$ 0.995 **Option 3:** non-linear regression: Coefficient of determination (COD) $r^2 \geq 0.99$ (6 points shall be used for 2nd order, 7 points shall be used for 3rd order)	Correct problem then repeat initial calibration.	NA
2nd Source calibration verification	Once after each initial calibration	Value of 2nd source for all analytes within $\pm$ 25% of expected value - See SOP Section 10.1.10 for exception and DoD SOP.	Correct problem and verify 2nd source standard. Rerun, if that fails, correct problem and repeat ICAL.	NA
RT window position	Once per ICAL	Position shall be set using midpoint standard of the initial calibration	NA	NA

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-3: Organic Analysis by GC/MS - Methods 8270

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
establishment for each analyte		curve.		
Evaluation of Relative RT (RRT)	With each sample	RRT of each target analyte in each calibration standard within ± 0.06 RRT units.	Correct problem, then rerun ICAL	NA
Calibration verification (CV)	Daily, before sample analysis, and every 12 hours of analysis time	1. Average RF for SPCCs: SVOCs - ≥ 0.050 2. %Difference for CCCs: SVOCs - ≤ 20% D (Note: D = difference when using RFs or drift when using least squares regression or non-linear calibration) All calibration analytes must be within 20% D, with no individual analytes (except CCC's) > 25% D	Correct problem, rerun CV, if fails, repeat ICAL (Data associated with an unacceptable CCV may be fully usable under the following conditions: 1. CCV (high bias) and samples ND, then raw data may be reported with appropriate flag 2. CCV (low bias) and samples exceed maximum regulatory limit/decision level (DoD Box 60: Project specific permission from appropriate DoD personnel is required to report data generated from a run with noncompliant CCV.)	Apply J-flag to all results associated with the analytical batch for all analytes > 20%D and < 25% D. Identify in case narrative analytes > 20% D.) Apply Q-flag if no sample material remains and analyte exceeds criteria
Internal Standards verification	In all field samples and standards	RT ± 30 seconds from RT of the midpoint standard in the ICAL EICP area within -50% to +100% of ICAL midpoint standard.	Inspect mass spectrometer and GC for malfunctions. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	Apply Q-flag to analytes associated with the non-compliant IS.
MB	One per prep batch	No analytes detected > ½ RL For common lab contaminants, no analytes > RL	Correct problem, then see criteria in box D-5; if required, reprep/reanalyze MB and all associated samples.	Apply B-flag to all results for the contaminated analyte for all samples in the associated prep batch.
LCS (containing all analytes to be reported)	One LCS per prep batch	DoD specified QC criteria, if available	Correct problem, reprep/reanalyze the LCS and all samples in the associated prep batch for all failed analytes, if sufficient sample is available.	Apply Q-flag to specific analyte(s) in all samples in the prep batch.

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-3: Organic Analysis by GC/MS - Methods 8270

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
			available.	
MS	One per prep batch per matrix	For matrix evaluation, use DoD specified QC criteria for LCS.	Examine the project-specific DQOs. Contact client for additional corrective action measures.	Apply J-flag to specific analyte(s) in the parent sample.
MSD or Sample Duplicate	One per prep batch per matrix	RPD $\leq$ 30% (between MS and MSD or sample and sample duplicate).	Examine the project-specific DQOs. Contact client for additional corrective action measures.	Apply J-flag to specific analyte(s) in the parent sample.
Surrogate	All field and QC samples	DoD specified QC criteria if available, otherwise method specific criteria or lab's own in-house criteria.	For QC and field samples, correct problem, reprep/reanalyze all failed samples in the associated prep batch if sufficient sample material is available.	Apply J-flag for specific analyte(s) in all field samples collected from the same site matrix as the parent. Apply Q-flag to QC samples for specific analyte(s)
Results reported between LOD and LOQ			Apply J-flag to all results between LOD (MDL) and LOQ (RL)	
Manual Integration	When manual integrations are performed	Raw data shall include a complete audit trail for those manipulations, raw data output showing the results of the MI (i.e., chromatograms of manually integrated peaks), and notation of rationale, date, and signature/initials of person performing manual operation.		Apply M-flag to MI data

Notes:

1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.

2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.

3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Chlorinated Pesticides

Method: SW-846 8081B

Approvals (Signature/Date):

7/14/2010	6/30/2010
Sharon Bacha Date	Steve Jackson Date
Technical Manager	Health & Safety Manager/Coordinator
07/15/10	6/29/2010
Nasreen DeRubeis Date	Larry Matko Date
Quality Assurance Manager	Laboratory Director

1.0 Scope and Application

1.1 This standard operating procedure (SOP) describes the determination of chlorinated pesticides using the methodology described in EPA SW-846 Method 8081B.

1.2 This SOP is applicable to the gas chromatographic (GC) analysis of extracts of soil, sediment, tissue, oil, waste and water samples. Table 1 lists the compounds that can be determined by this method and their associated routine reporting limits (RLs).

1.3 This SOP does not include the procedures for extracting soil and water samples. Refer to SOP PT-OP-001 for sample extraction procedures. For specific DoD quality control requirements refer to SOP # PT-QA-025, Implementation of the DoD QSM Version 3, January 2006 and Appendix I in this SOP. For DoD V4.1 refer to SOP PT-QA-029.

1.4 Analytes, Matrix(s), and Reporting Limits: See Table 1 for analytes and reporting limits by matrix.

2.0 Summary of Method

2.1 Sample Preparation

2.1.1 Chlorinated pesticides are typically extracted from a one-liter water sample with methylene chloride using a separatory funnel (Method 3510C). Detailed instructions are given in SOP PT-OP-001. The methylene chloride extract is exchanged to hexane as described in SOP PT-OP-001.

2.1.2 Chlorinated pesticides are typically extracted from a 15-gram soil/tissue/sediment subsample into a 50:50 acetone-methylene chloride solution by automated soxtherm (Method 3541). The extract is dried and exchanged to hexane. Detailed instructions are given in SOPs PT-OP-001.

2.1.3 SOP PT-OP-001 provides instructions for the concentration and cleanup of sample extracts. Carboprep 90 Cleanup is used to clean extracts that show color. Sulfur is removed if observed. All extracts are in hexane and the final extract volume is 20 mL for soils and 40 mL for waters.

2.2 Analysis

2.2.1 Samples are analyzed using a gas chromatograph equipped with dual columns and dual electron capture detectors (ECDs).

2.2.2 The instrument is calibrated using external standards. Compounds are identified by their retention time on the columns.

2.2.3 Positive results from the primary column are confirmed with a second, dissimilar column.

3.0 Definitions

3.1 Single-Component Pesticides: A pesticide formulation that consists of a single chemical compound. Most of the analytes determined by this procedure are single-compound pesticides.

3.2 Multi-Component Pesticides: A pesticide formulation that consists of more than one chemical compound. Toxaphene and Technical Chlordane are production mixtures of multiple compounds. Toxaphene is manufactured by the chlorination of camphenes, which produces a variety of compounds, not all of which are chromatographically resolved. Technical Chlordane is produced by the chlorination of a mixture of camphenes and pinenes.

3.3 Chlordane: As just described, Technical Chlordane (CAS# 12789-03-6) is a mixture of compounds. Method 8081B, Section 11.6.2 notes that it includes at least 11 major components and 30 minor components, and adds “the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.” The laboratory has found that manufacturing lots of Technical Chlordane produced at different times or at different production facilities have different ratios of the key components. For this reason, it is more common to analyze for the major components of technical Chlordane (α-Chlordane, γ-Chlordane, and heptachlor) instead of analyzing for the total mixture. For the purpose of reporting results under this SOP, the following compounds are reported. Alpha-chlordane (cis-chlordane) CAS # 5103-71-9 and gamma-chlordane (trans-chlordane) CAS # 5103-74-2. The laboratory may also report chlordane (not otherwise specified) or, n.o.s under CAS# 57-74-9.

3.4 The quality control terms used in this procedure are consistent with SW-846 terminology. Definitions are provided in the glossary of the TestAmerica Pittsburgh Laboratory Quality Assurance Manual (PT-LQAM).

4.0 Interferences

4.1 Contamination by carryover can occur when a low concentration sample is analyzed immediately following a high concentration sample. It is the laboratory's policy to evaluate and reanalyze when necessary any samples that follow an unusually concentrated sample and that show detectable levels of the same compounds that appeared in the preceding concentrated sample.

4.2 Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3 Sulfur will interfere, and, when observed, is removed using cleanup procedures described in SOP PT-OP-001.

4.4 Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), Carboprep 90 Cleanup and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # PT-OP-001. Use of hexane / acetone as the extraction solvent (rather than acetone / methylene chloride) may reduce the amount of interferences extracted.

4.5 Carboprep 90 Cleanup

4.5.1 This cleanup may be performed prior to analyses for PCBs if the sample extract has some color.

4.5.2 Cartridge Method

4.5.2.1 Put approximately 2 ml of sample extract into a test tube and mark the sample volume on the tube.

4.5.2.2 Condition the cartridge by adding 2 ml of methylene chloride and allowing it to drip through the cartridge. Do not allow the cartridge packing to go dry in this or any subsequent step, until the final rinse has been completed.

4.5.2.3 Add 2 ml of hexane/methylene chloride (80%/20%) mixture and allow it to drip through the cartridge until almost empty.

4.5.2.4 Add the sample extract to the cartridge and place the test tube under the cartridge to collect the liquid as it drips through.

4.5.2.5 Rinse 3 times with 2 ml aliquots of hexane/methylene chloride (80%/20%) mixture, while not allowing the cartridge to go dry. After the final rinse, use a pipette bulb to force out all of the remaining liquid in the cartridge.

4.5.2.6 Concentrate the sample extract back down to the original volume according to the mark on the test tube. The extract is now ready for analysis.

4.5.3 Quick Method

4.5.3.1 Add a half scoop of Carboprep 90 to approximately 2 ml of sample extract. Shake for one minute and allow the extract to settle. Pipette out an aliquot of the clear extract for analysis.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.1.2 The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.3 There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.1.4 The ECD contains a ^{63}Ni radioactive source. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the facility's radioactive material license. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Radiation Safety Officer shall be immediately notified and a letter sent to the Colorado Department of Public Health and Environment.

5.1.5 As a safety precaution, all standards, samples, and extracts are handled in an approved fume hood.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and Symptoms of Exposure
Acetone	Flammable	1000 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200 ppm (TWA)	A slight irritant to the mucous membranes. Toxic effects are exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness, and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
(1) Exposure limit refers to the OSHA regulatory exposure limit.			

6 Equipment and Supplies

6.1 An analytical system complete with a gas chromatograph and dual ECD (Ni-63) detectors is required. A data system capable of measuring peak area and/or height is required.

6.2 An analytical balance capable of weighing to 0.0100g.

6.3 Columns

6.3.1 Primary Column: MR1, 30 m X 0.53 mm id

6.3.2 Secondary Column: MR2, 30 m X 0.53 mm id

6.3.3 Additional columns that can be used for confirmation include 30 m X 0.53 mm id RTx5, RTx50 or RTx1701.

6.4 Autosampler vials, crimp-top cap with PTFE-faced septa

6.5 Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7 Reagents and Standards

7.1 Reagents

7.1.1 Hexane, pesticide grade

7.1.2 Carrier gas, ≥ 99.99999% pure hydrogen or helium

7.1.3 Make-up gas, ≥ 99.99980% pure nitrogen

7.2 Standards

7.2.1 Storage of Stock Standards

7.2.1.1 Commercial standards are received in flame-sealed ampoules or neat, 100% concentration, solutions. Stock standards are stored refrigerated at ≤ 6 ºC. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

7.2.1.2 Dilutions from stock standards cannot have a later expiration date than the date assigned to the parent stock solutions. Stock standards are monitored for signs of degradation or evaporation. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem. Kepone extracted from samples or in standards exposed to water or methanol may produce peaks with broad tails that elute later than the standard by up to 1 minute. This shift is presumably the result of the formation of a hemi-acetal from the ketone functionality and may seriously affect the ability to identify this compound on the basis of retention time. For this reason, analysis for Kepone using Method 8081B is not performed by TestAmerica Pittsburgh. Method 8270D is the method of choice for this compound. Endosulfan I and II appear to degrade in the presence of methanol. Gamma-BHC appears to degrade in the presence of acetone.

7.3 Calibration Stock Standards

7.3.1 All calibration stock standards are obtained from commercial sources.

NOTE: The availability of the specific commercial standard solutions upon which the following sections are based may change at any time. As a result, it may be necessary to alter the dilution scheme presented herein to accommodate changes in stock standard concentrations. All such changes are documented in the standards preparation records.

7.3.2 Routine Pesticide A and B Mix Stock Standard

Custom Pesticide Mix A	
Compound	**Concentration (µg/mL)**
TCMX (surrogate)	100
4,4'-DDD	100
4,4'-DDT	100

Custom Pesticide Mix A	
Compound	**Concentration (µg/mL)**
α-BHC	100
DCB (surrogate)	100
Dieldrin	100
Endosulfan I	100
Endrin	100
γ-BHC (Lindane)	100
Heptachlor	100
Methoxychlor	200
Custom Pesticide Mix B	
4,4'DDE	100
Aldrin	100
α-Chlordane	100
β-BHC	100
δ-BHC	100
Endosulfan II	100
Endosulfan Sulfate	100
Endrin aldehyde	100
Endrin ketone	100
γ-Chlordane	100
Heptachlor epoxide	100

7.3.3 Surrogate Stock Standard

7.3.3.1 The surrogate stock standard contains decachlorobiphenyl (DCB) at 1000 µg/mL and tetrachloro-m-xylene (TCMX) is contained in a separate stock standard at 2000 µg/mL.

7.3.4 Toxaphene Stock, 1000 µg/mL

7.3.4.1 The Toxaphene stock standard contains a specific production mixture of Toxaphene. This mixture does not necessarily match all possible production mixtures that could be found in the environment. This can present problems for Toxaphene quantitation (see Section 12).

7.3.5 Chlordane Stock, 100 µg/mL

7.3.5.1 The Toxaphene stock standard contains a specific production mixture of Toxaphene. This mixture does not necessarily match all possible production mixtures that could be found in the environment. This can present problems for Toxaphene quantitation (see Section 12).

7.3.5.2 The Chlordane stock contains Technical Chlordane (CAS# 12789-03-6).

7.3.6 Appendix IX Calibration Stock

7.3.6.1 The Appendix IX stock calibration mixture contains the compounds at the concentrations listed in the following table.

Appendix IX Mix 1 and Mix 2 Calibration Stock Standard

Mix 1 Compounds	Concentration (µg/mL)
Chlorobenside	50
Dacthal (DCPA)	50
Hexachlorobenzene	25
Hexachlorocyclopentadiene	50
Mirex	20
Isodrin	10
Oxychlordane isomer	10
Mix 2 Compounds	**Concentration (µg/mL)**
2,4-DDD	10
2,4-DDE	10
2,4-DDT	10
Chlorobenzilate	100
cis-Nonachlor	10
DCB (surrogate)	10
Diallate	200
Hexachlorobutadiene	10
TCMX (surrogate)	10
trans-Nonachlor	10

7.3.7 Non-Routine Compounds

7.3.7.1 Other, non-routine compounds not listed in this section may be requested by a client and may be added to this procedure.

7.3.7.2 In these cases, all stock solutions will be obtained from commercial sources and will be verified with a second-source standard as described in Section 7.5.

7.3.7.3 Non-routine standards will be stored and treated as described in Section 7.2.1.

7.3.7.4 Subsequent dilutions of specially requested compounds will be determined in a manner

consistent with the client's recommendations for number of calibration points, inclusion of reporting limit, and concentration range adequate to represent the linearity of the instrument.

7.3.7.5 These specially requested, non-routine compounds either may be added to the dilution scheme used for routine compounds or may be prepared as a separate calibration.

7.3.7.6 All standards preparation for non-routine compounds shall be documented using the same method that is used for routine compounds.

7.4 Working Level Calibration Standards

7.4.1 The single peak pesticide stock standards are purchased as certified standards in two separate solutions in 50%hexane/50% toluene, which are combined prior to standard preparation (See Section 7.3.2). An intermediate stock standard is prepared by diluting 1.0 mL of each of the appropriate stock mixtures (Custom Pesticide Mix A and B) to 10.0 mL in hexane. The intermediate stock mix concentrations are 10 ug/mL for all compounds except methoxychlor, which is 20 ug/mL. The working standards are prepared by diluting the volume noted in the Table listed below to a 40.0 mL final volume in hexane except for the Level 3 standard, which is taken to a 100 mL final volume in hexane. (See Table below.)

7.4.2 Toxaphene and Technical Chlordane stock standards are purchased certified solutions at 100 ug/mL. The mid level (Level 3) Toxaphene calibration standard is prepared by diluting 0.40 mL of the stock standard mix to 40 mL in hexane. The mid level (Level 3) Technical Chlordane calibration standard is prepared by diluting 0.10 mL of the stock standard mix to 40 mL in hexane. (See Table below.)

Preparation of Calibration Standards

Compound	Calibration Level (µg/mL)[1]					
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Aldrin	0.001	0.005	0.025	0.050	0.100	0.200
α-BHC	0.001	0.005	0.025	0.050	0.100	0.200
β-BHC	0.001	0.005	0.025	0.050	0.100	0.200
δ-BHC	0.001	0.005	0.025	0.050	0.100	0.200
γ-BHC (Lindane)	0.001	0.005	0.025	0.050	0.100	0.200
4,4'-DDD	0.001	0.005	0.025	0.050	0.100	0.200
4,4'-DDE	0.001	0.005	0.025	0.050	0.100	0.200
4,4'-DDT	0.001	0.005	0.025	0.050	0.100	0.200
Dieldrin	0.001	0.005	0.025	0.050	0.100	0.200
Endosulfan I	0.001	0.005	0.025	0.050	0.100	0.200
Endosulfan II	0.001	0.005	0.025	0.050	0.100	0.200
Endosulfan Sulfate	0.001	0.005	0.025	0.050	0.100	0.200

Preparation of Calibration Standards						
Compound	Calibration Level (µg/mL)[1]					
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Endrin	0.001	0.005	0.025	0.050	0.100	0.200
Endrin Aldehyde	0.001	0.005	0.025	0.050	0.100	0.200
Endrin ketone	0.001	0.005	0.025	0.050	0.100	0.200
Heptachlor	0.001	0.005	0.025	0.050	0.100	0.200
Heptachlor Epoxide	0.001	0.005	0.025	0.050	0.100	0.200
Methoxychlor	0.002	0.010	0.050	0.100	0.200	0.400
Toxaphene			1.0			
Chlordane (tech.)			0.250			

[1]These calibration levels are prepared by adding 4, 20, 250, 200, 400 and 800 µL of the stock standard concentrations listed above. The mid-level Toxaphene and Chlordane calibration levels are prepared by adding 40 µL and 100 µL, respectively. **NOTE:** These amounts are subject to change as the concentration of the purchased standards changes.

7.4.3 Appendix IX Working Level Calibration Standards

7.4.3.1 The following volumes of the Appendix IX intermediate stock standard are diluted with hexane to a final volume of 25.0 mL. The following table summarizes the final compound concentration ranges for each calibration level. The concentration for each compound at each level is given in Table 3.

Appendix IX Mix 1 and 2 Working Level Calibration Standards		
Level	Volume of Stock Std (mL)	Final Compound Concentration Range (µg/mL)
1	0.005	0.0004 - 0.002
2	0.025	0.002 – 0.01
3*	0.20	0.05 – 0.25
4	0.25	0.02 – 0.10
5	0.50	0.04 – 0.20
6	1.0	0.08 – 0.40
* *This level is used as the CCV.*		

7.5 Second-Source Standards for Initial Calibration Verification (ICV)

7.5.1 The second-source stock standards are purchased from a vendor different from the one that supplied the stock calibration standards.

7.5.2 Routine Pesticide AB Mix ICV Stock Standard, 2,000 µg/mL

7.5.2.1 Commercial standards containing all single-component pesticide compounds are obtained from a vendor different from the one that supplied the calibration stock standard. Typically, the standards are obtained from Restek.

7.5.3 Appendix IX ICV Stock Standard

7.5.3.1 Commercial standards are obtained at the same concentrations as shown for the calibration stock standards in Section 7.3, but from a different vendor (typically AccuStandard).

7.5.4 Routine Pesticide ICV Working Level Standard, 0.025 µg/mL

7.5.4.1 The working level ICV standard for the routine pesticide compounds is prepared by diluting the ICV intermediate standard (Section 7.4) in hexane follows:

Routine Pesticide Second-Source ICV Working Level Standard		
Volume of Intermediate Standard (mL)	**Final Volume (mL)**	**Final Concentration (µg/mL)**
0.100	100	0.025

7.5.5 Appendix IX ICV Working Level Standard

7.5.5.1 The working level ICV standard for the Appendix IX compounds is prepared by diluting 0.040 mL of the second-source Appendix IX stock standard (Section 7.5.3) with hexane to a final volume of 40 mL. The following table lists the final concentration of each pesticide:

Appendix IX Second Source ICV Working Level Standard	
Mix 1	**Final Concentration (µg/mL)**
Chlorobenside	0.05
Dacthal (DCPA)	0.05
Hexachlorobenzene	0.025
Hexachlorocyclopentadiene	0.05

Appendix IX Second Source ICV Working Level Standard	
Mix 1	**Final Concentration (µg/mL)**
Mirex	0.01
Isodrin	0.02
Oxychlordane isomer	0.01
Mix 2	**Final Concentration (µg/mL)**
2,4-DDD	0.025
2,4-DDE	0.025
2,4-DDT	0.025
Chlorobenzilate	0.250
cis-Nonachlor	0.025
DCB (surrogate)	0.500
Diallate	0.025
Hexachlorobutadiene	0.025
TCMX (surrogate)	0.025
trans-Nonachlor	0.025

7.6 Continuing Calibration Verification (CCV) Standards

7.6.1 The Level 3 AB mix working calibration standard (Section 7.4.1 and 7.4.2) and the Level 3 Appendix IX working calibration standard (Section 7.5.5) are used as the CCV standard.

7.7 RL Standard

7.7.1 The lowest concentration calibration standard (i.e., Level 1) is used as the RL standard.

7.8 Laboratory Control Standard (LCS) Spike Solution, 1.0 µg/mL

7.8.1 The working LCS spike solution is prepared by diluting 0.100 mL of a commercially purchased (2000 µg/mL) AB mix stock standard in acetone to a final volume of 200 mL in a volumetric flask, as summarized in the table below.

7.8.2 The LCS for batches of aqueous samples is prepared by adding 1.0 mL of the LCS spike solution to one liter of reagent water. The LCS for batches of aqueous samples is prepared by adding 0.025 mL of the LCS spike solution to one liter of reagent water for analyses. The LCS for batches of soil samples is prepared by adding 0.5 mL of the LCS spiking solution to 15 g of Sodium sulfate.

LCS Spiking Solution

Volume of AB Mix Stock (mL)	Conc. of AB Mix Stock (µg/mL)	Final Volume (mL)	Final Concentration (µg/mL)
0.100	2000	200	1.0

7.9 Matrix Spike (MS) Spike Solution, 1.0 µg/mL

7.9.1 The working matrix spike solution is the same as the LCS spike solution. Matrix spikes (MS and MSD) are prepared by adding 1.0 mL of the working spike solution to one liter of an aqueous sample, 0.025 mL of the working spike solution to one liter of an aqueous sample and 0.5 mL of the working spike solution to a 15-gram solid subsample.

7.10 Surrogate Spike Solution, 0.8 µg/mL for TCMX and 1.6 µg/mL for DCB

7.10.1 The surrogate stock solution, containing 200 µg/mL each of decachlorobiphenyl and tetrachloro-m-xylene (TCMX), is purchased from commercial sources.

7.10.2 The working surrogate spike solution is prepared in a volumetric flask by adding 0.8 mL of the TCMX stock solution and 1.6 mL of the DCB stock solution and diluting to a final volume of 200 mL with acetone.

7.10.3 For aqueous sample batches, 1.0 mL of the surrogate spike solution is added to each one-liter sample and QC sample. For low-level aqueous sample batches, 0.025 mL of the surrogate spike solution is added to each one-liter sample and QC sample. For soil sample batches, 0.5 mL of the surrogate spike solution is added to each 15-gram soil subsample and QC sample. For tissue sample batches, 0.2 mL of the surrogate spike solution is added to each 15-gram tissue subsample and QC sample.

7.11 Column Degradation Mix (EVAL B)

7.11.1 The DDT/endrin breakdown stock standard solution is obtained from commercial sources, with endrin at a concentration of 100 µg/mL, and 4,4'-DDT at 200 µg/mL.

7.11.2 The working EVAL B solution is prepared in a volumetric flask, by diluting 0.05 mL of the stock solution to 200 mL in hexane, as summarized in the following table:

Column Degradation Mix (Eval B Std) Spike Solution			
Compound	**Volume of Stock (mL)**	**Final Volume (mL)**	**Final Concentration (µg/mL)**
Endrin	0.05	200	0.025
4,4'-DDT			0.05

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Water samples are collected in pre-cleaned, amber glass bottles fitted with a Teflon-lined cap. To achieve routine reporting limits, a full one liter of sample is required. Additional one-liter portions are needed to satisfy the requirements for matrix spikes and duplicate matrix spikes.

8.2 Soil samples are collected in 8-ounce, pre-cleaned, wide-mouth jars with a Teflon-lined lid.

8.3 Samples are stored at 4 ± 2 °C.

8.4 Extracts are refrigerated at ≤ 6 °C.

Matrix	Sample Container	Min. Sample Size	Preservation	Extraction Holding Time	Analysis Holding Time
Waters	Amber glass	1 Liter	Cool 4 $\pm$ 2°C	7 Days	40 Days from extraction
Soils	Glass	30 grams	Cool 4 $\pm$ 2°C	14 Days	40 Days from extraction

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica PT-QA-021, Quality Control Program.

9.1.2 Refer to the TestAmerica Pittsburgh QC Program document (PT-QA-021) for further details on criteria and corrective actions.

9.1.3 For specific DoD quality control requirements refer to SOP # PT-QA-025, Implementation of the DoD QSM Version 3, January 2006 and Appendix I in this SOP. For DoD V4.1 refer to SOP PT-QA-029.

9.1.4 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.

9.1.5 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP PT-QA-016. This is in addition to the corrective actions described in the following sections.

9.2 Initial Performance Studies

Before analyzing samples, the laboratory must establish a method detection limit (MDL). In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument he/she will be using. On-going proficiency must be demonstrated by each analyst on an annual basis. See Section 13 for more details on detection limit studies, initial demonstrations of capability, and analyst training and qualification.

9.3 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. The method blank

must be run on each instrument that is used to analyze samples from the same preparation batch. See QC SOP PT-QA-021 for further details.

9.4 Method Blank (MB)

At least one method blank must be processed with each preparation batch. The method blank for batches of aqueous samples consists of 1.0 liter of reagent water, and for batches of soil samples, consists of 15 grams of sodium sulfate, both of which are free of any of the analyte(s) of interest. The method blank is processed and analyzed just as if it were a field sample.

Acceptance Criteria: The method blank must not contain any analyte of interest at or above the reporting limit or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher. Wherever blank contamination is greater than 1/10 the concentrations found in the samples and/or 1/10 of the regulatory limit it is potentially at a level of concern and should be handled as a non-conformance. Blank contamination should always be assessed against project specific requirements. Such action must be taken in consultation with the client.

Corrective Action: Re-extraction and reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples. If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.5 Laboratory Control Sample (LCS)

At least one LCS must be processed with each preparation batch. For aqueous sample batches, the LCS consists of reagent water to which all the analyte(s) of interest are added at a known concentration. For soil sample batches, the LCS consists of sodium sulfate to which all the analyte(s) of interest are added at a known concentration. See Section 7.8 for the preparation of LCSs. The LCS is carried through the entire analytical procedure just as if it were a sample. TestAmerica Pittsburgh uses a full-analyte spike for its LCS. For specific DoD quality control requirements refer to SOP # PT-QA-025 and DoD QSM Appendix I in this SOP. For DoD V4.1 refer to SOP PT-QA-029.

See Table 7 for Laboratory generated Control Limits.

Acceptance Criteria: All analytes are spiked and list of control analytes are used to control the batch. The control analytes must meet the LCS control limits. For DoD follow SOP PT-QA-029. The recovery results for the LCS must fall within the established control limits. Control limits are set at ± 3 standard deviations around the

historical mean. Where required, project-specific limits may be used in place of historical limits. Current control limits are maintained in the LIMS. Corrective action will normally be repreparation and reanalysis of the batch.

Marginal Exeedance limits are not used unless required by a project. When there are more than 11 analytes in the LCS, then NELAC allows a specified number of results to fall beyond the LCS control limit (3 standard deviations), but within the marginal exceedance (ME) limits, which are set at ± 4 standard deviations around the mean of historical data. The number of marginal exceedances is based on the number of analytes in the LCS, as shown in the following table:

# of Analytes in LCS	# of Allowed MEs
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

If more analytes exceed the LCS control limits than is allowed, or if any analyte exceeds the ME limits, the LCS fails and corrective action is necessary. Marginal exceedances must be random. If the same analyte repeatedly fails the LCS control limits, it is an indication of a systematic problem. The source of the error must be identified and corrective action taken. When using list of control compounds, all those compounds must be within acceptable limits.

Corrective Action: If LCS recoveries are outside of the established control limits, the system is out of control and corrective action must occur. The recoveries for control analytes must be within the limit. If recoveries are above the upper control limit and the analyte(s) of interest is not detected in samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative. In other circumstances, the entire batch must be re-prepared and reanalyzed.

9.5.1 Use of marginal exceedances is not permitted for South Carolina work for LCS. For SC work the LCS limits must be 70-130% at a maximum. Same limits or lab calculated limits

can be used for MS/MSD. If limits are calculated for LCS, they must be within 70-130 % range.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

One MS/MSD pair must be processed with each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of all target analytes have been added. It is prepared in a manner similar to the LCS, but uses a real sample matrix in place of the blank matrix. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked exactly as the MS) that is prepared and analyzed along with the sample and matrix spike. Refer to Section 7.9 for preparation of matrix spikes. Some programs allow spikes to be reported for project-related samples only. Samples identified as field blanks cannot be used for the MS/MSD analysis. TestAmerica Pittsburgh uses a full-analyte spike for its MS/MSD. For specific DoD quality control requirements refer to SOP # PT-QA-025, Implementation of the DoD QSM Version 3, January 2006 and Appendix I in this SOP. For DoD V4.1 refer to SOP PT-QA-029.

See Table 7 for Laboratory generated Control Limits.

Acceptance Criteria: The recovery results for the MS and MSD must fall within the established control limits, which are set at ± 3 standard deviations around the historical mean. The relative percent difference (RPD) between the MS and MSD must be less than the established RPD limit, which is set at 3 standard deviations above the historical mean. Current control limits are maintained in the LIMS. For SC work lab generated limits can be used for MS/MSD or same limits as LCS can be used for MS/MSD, 70-130%.

Corrective Action: If analyte recovery or RPD falls outside the acceptance range, but the associated LCS recovery is in control, and all other QC criteria (e.g., continuing calibration verification) are met, then there is no evidence of analytical problems, and qualified results may be reported. The situation must be described in an NCM and in the final report case narrative. In other circumstances, the batch must be re-prepared and reanalyzed.

9.7 Surrogate Spikes

Every calibration standard, field sample, and QC sample (i.e., method blank, LCS, LCSD, MS, and MSD) is spiked with DCB and TCMX surrogate compounds. Refer to Section 7.10 for preparation of the surrogate spike solution. See Table 7 for Laboratory generated Control Limits.

Acceptance Criteria: The recovery of each surrogate must fall within established statistical limits, which are set at ± 3 standard deviations around the historical mean.

Corrective Action: If surrogate recoveries in the method blank are outside the established limits, verify calculations, standard solutions, and acceptable instrument performance. High surrogate recoveries in the blank might be acceptable if the surrogate recoveries for the field samples and other QC samples in the batch are acceptable. Low surrogate recoveries in the blank require re-preparation and reanalysis of the associated samples, unless sample surrogate recoveries are acceptable and targeted compounds are not detected.

For field samples and QC, both DCB and TCMX are evaluated. If one surrogate fails to fall within the control limits and the other surrogate is within the control limits, the data is considered reportable with an NCM and narration in the final report.

If a surrogate recovery fails, verify calculations, standard solutions, and acceptable instrument performance. High recoveries may be due to a co-eluting matrix interference, which can be confirmed by examining the sample chromatogram. Low recoveries may be due to adsorption by the sample matrix (i.e., clay particles, peat or organic material in the sample). Recalculate the data and/or reanalyze the extract if the checks reveal a problem.

If matrix interference is not obvious from the initial analysis, it is necessary to re-prepare / reanalyze a sample only once to demonstrate that poor surrogate recovery is due to a matrix effect, as long as it can be shown that the analytical system was in control.

10.0 Calibration and Standardization

10.1 TestAmerica Pittsburgh gas chromatograph instrument systems are computer controlled to automatically inject samples and process the resulting data.

10.1.1 Use the ChemStation chromatography data system to set up GC conditions for calibration. See Table 2 for typical operating conditions.

10.1.2 Transfer calibration standard solutions into autosampler vials and load into the GC autosampler. Use the ChemStation software to set up the analytical sequence.

10.1.3 Unprocessed calibration data are transferred to the TARGET DB database for processing. After processing the calibration data, print the calibration report and review it using the calibration review checklist (GC and HPLC Data Review Checklist - ICAL). Submit the calibration report to a qualified peer or the group leader for final review. The completed calibration reports are scanned and stored as Adobe Acrobat files on the

Public Drive.

10.2 Column Degradation Evaluation

10.2.1 Each day of operation and at the beginning of each 12 hour shift, before any calibration or calibration verification standards are analyzed, the column degradation evaluation mix (EVAL B) must be analyzed. In addition, some programs require injection of the degradation evaluation mix more frequently. Unless otherwise specified in an approved project plan, the degradation check must be performed whether or not 4,4'-DDT, Endrin, or degradation compounds are designated as target analytes. The purpose of the evaluation is to determine whether instrument/column maintenance is needed. The preparation of this standard is described in Section 7.11.

10.2.2 The results of the analysis of the EVAL B standard solution are used to calculate column degradation in terms of DDT percent breakdown (%B) and Endrin %B as follows:

$$\text{DDT } \%B = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}} \times 100\% \qquad \textit{Equation 1}$$

Where A_{DDD}, A_{DDE}, and A_{DDT} are the peak responses for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT, respectively, in the EVAL B chromatogram.

$$\text{Endrin } \%B = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_{E}} \times 100\% \qquad \textit{Equation 2}$$

Where A_{EK}, A_{EA}, and A_{E} are the peak responses for endrin ketone, endrin aldehyde, and endrin, respectively, in the EVAL B chromatogram.

10.2.3 Acceptance Criteria

10.2.3.1 The %D for each of these two compounds, 4,4'-DDT and Endrin, must be less than 15%

10.2.4 Corrective Action

10.2.4.1 If the breakdown of 4,4'-DDT and/or Endrin exceeds the 15% limit, corrective action must be taken. This action may include any or all of the following:

- Replacing the injection port liner or the glass wool.
- Cutting off a portion of the injection end of the column or guard column.
- Replacing the GC column or guard column
- Replacing the y-splitter.

10.2.4.2 After taking the appropriate corrective action, the degradation evaluation standard must be reanalyzed and must pass acceptance criteria before conducting any calibration events

10.3 The laboratory uses six calibration levels (as shown in Table 3) for the single-component pesticides. The lowest point on the calibration curve is at or below the reporting limit (RL). The highest standard defines the highest sample extract concentration that may be reported without dilution. The preparation of the calibration standards is described in Section 7.4.

10.4 All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

Calibration for the multi-peak component analytes, Toxaphene and Technical Chlordane, is a single-point calibration. If requested by a client, a calibration for the multi-component analyte(s) can be conducted using a minimum of five calibration levels. The samples would then be analyzed using the full calibration curve that brackets the quantitation range. **For specific DoD quality control requirements refer to SOP # PT-QA-025, Implementation of the DoD QSM Version 3, January 2006 and Appendix I in this SOP.** For DoD V4.1 refer to SOP PT-QA-029.

NOTE: Generally, it is NOT acceptable to remove points from a calibration. If calibration acceptance criteria are not met, the normal corrective action is to examine conditions such as instrument maintenance and accuracy of calibration standards. Any problems found must be fixed and documented in the run log or maintenance log. Then the calibration standard(s) must be reanalyzed.

10.4.1 If no problems are found or there is documented evidence of a problem with a calibration point (e.g., obvious mis-injection explained in the run log), then one point might be rejected, but only if all of the following conditions are met:

- The rejected point is the highest or lowest on the curve, i.e., the remaining points used for calibration must be contiguous; and
- The lowest remaining calibration point is still at or below the project reporting limit; and
- The highest remaining calibration point defines the upper concentration of the working range, and all samples producing results above this concentration are diluted and reanalyzed; and
- The calibration must still have the minimum number of calibration levels required by the method, i.e., five levels for calibrations modeled with average calibration factors or linear regressions, or six levels for second-order curve fits.

NOTE: Second order curves are not allowed for South Carolina work.

10.5 External Standard Calibration

10.5.1 External standard calibration involves the comparison of instrument responses (e.g., peak area or peak height) from the target compounds in the sample to the responses of the target compounds in the calibration standards. The ratio of the detector response to the amount or concentration of target analyte in the calibration standard is defined as the calibration factor (CF), as follows:

$$CF = \frac{A_S}{C_S} \qquad \textit{Equation 3}$$

Where:

A_s = Peak area (or height) of the analyte or surrogate in the calibration standard.

C_s = Concentration of the analyte or surrogate, in ng/mL, in the injected calibration standard.

10.6 Establishing the Calibration Function

Calibrations are modeled either as average calibration factors or as calibration curves, using a systematic approach to selecting the optimum calibration function. Start with the simplest model, i.e., a straight line through the origin and progress through the other options until the calibration acceptance criteria are met.

10.6.1 Linear Calibration Using Average Calibration Factor

Tabulate the peak area response for each target analyte in each calibration level against the concentration injected. For each analyte in each calibration standard, calculate the calibration factor (CF) as shown in Equation 3 above. The calibration factor is a measure of the slope of the calibration line, assuming that the line passes through the origin. Under ideal conditions, the factors calculated for each calibration level will not vary with the concentration of the standard. In practice, some variation can be expected. When the variation, measured as the relative standard deviation, is relatively small (e.g., ≤ 20%), the use of the straight line through the origin model is generally appropriate.

For each target analyte, calculate the average calibration factor as follows:

$$AverageCalibrationFactor = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n} \qquad \textit{Equation 4}$$

Where:

CF_i = Calibration factor for the i^{th} calibration level.

n = The number of calibration levels.

The relative standard deviation (RSD) is calculated as follows:

$$RSD = \frac{SD}{\overline{CF}} \times 100\% \qquad \textit{Equation 5}$$

Where SD is the standard deviation of the average CF, which is calculated as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(CF_i - \overline{CF}\right)^2}{n-1}} \qquad \textit{Equation 6}$$

10.6.2 Evaluation of the Average Calibration Factor

The calibration relationship can be graphically represented as a line through the origin with a slope equal to the average calibration factor. Examine the residuals, i.e., the difference between the actual calibration points and the plotted line. Particular attention should be paid to the residuals for the highest points, and if the residual values are relatively large, a linear regression should be considered.

Note: The use of grand average (evaluation of the average response over all the compounds) is no longer allowed. Each compound must meet the RSD criteria.

Acceptance Criteria: The RSD must be ≤ 20%.

Corrective Action: If the RSD exceeds the limit, linearity through the origin cannot be assumed, and a least-squares linear regression should be attempted.

10.6.3 Linear Calibration Using Least-Squares Regression

Calibration using least-squares linear regression produces a straight line that does not necessarily pass through the origin. The calibration relationship is constructed by performing a linear regression of the instrument response (peak area or peak height) versus the concentration of the standards. The instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). A weighted least squares regression may be used if at least three multi-point calibrations have been performed. The weighting used is the reciprocal of the square of the standard deviation. The regression produces the slope and intercept terms for a linear equation in the following form:

$$y = ax + b \qquad \textit{Equation 7}$$

Where:

y = Instrument response (peak area or height).

x = Concentration of the target analyte in the calibration standard.

a = Slope of the line.

b = The y-intercept of the line.

For an external standard calibration, the above equation takes the following form:

$$A_s = aC_s + b \qquad \textit{Equation 8}$$

To calculate the concentration in an unknown sample extract, the regression equation (Equation 6) is solved for concentration, resulting in the following equation, where C_s is now C_e, the concentration of the target analyte in the unknown sample extract.

$$C_e = \frac{A_e - b}{a} \qquad \textit{Equation 9}$$

Where:

A_s = Area of the chromatographic peak for the target analyte in the calibration standard.

A_e = Area of the chromatographic peak for the target analyte in the sample extract.

a = Slope of the line as determined by the least-squares regression.

C_s = Concentration of the target analyte in the calibration standard.

C_e = Concentration of the target analyte in the sample extract.

b = Intercept of the line as determined by the least-squares regression.

10.6.4 Linear Regression Evaluation

With an unweighted linear regression, points at the lower end of the calibration curve have less weight in determining the curve than points at the high concentration end of the curve. For this reason, inverse weighting of the linear function is recommended to optimize the accuracy at low concentrations. Note that the August 7, 1998 EPA memorandum “Clarification Regarding Use of SW-846 Methods”, Attachment 2, Page 9, includes the statement “The Agency further recommends the use of a weighted regression over the use of an unweighted regression.”

Acceptance Criteria: To avoid bias in low level results, the absolute value of the y-intercept must be significantly less than the reporting limit, and preferably less than the MDL.

Also examine the residuals, paying particular attention to the residuals at the low end of the curve. If the intercept or the residuals are large, a second-order regression should be considered.

The linear regression must have a correlation coefficient (r) ≥ 0.990. Some programs (e.g., DoD) require a correlation coefficient ≥ 0.995.

Corrective Action: If the correlation coefficient falls below the acceptance limit, linear regression cannot be used and a second-order regression should be attempted.

10.6.5 Non-Linear Calibration

When the instrument response does not follow a linear model over a sufficiently wide working range, or when the previously described calibration approaches fail acceptance criteria, a non-linear, second-order calibration model may be employed. The second-order calibration uses the following equation:

$$y = ax^2 + bx + c \qquad \textit{Equation 10}$$

Where a, b, and c are coefficients determined using a statistical regression technique; y is the instrument response; and x is the concentration of the target analyte in the calibration standard.

10.6.6 Non-Linear Calibration Evaluation

A minimum of six points must be used for a second-order regression fit.

Acceptance Criteria: The coefficient of determination must be ≥ 0.990.

Second-order regressions should be the last option. **Note that some programs (e.g., South Carolina) do not allow the use of second-order regressions.**

Before selecting a second-order regression calibration model, it is important to ensure the following:

- The absolute value of the intercept is not large relative to the lowest concentrations being reported.
- The response increases significantly with increasing standard concentration (i.e., the instrument response does not plateau at high concentrations).
- The distribution of concentrations is adequate to characterize the curvature.

Corrective Action: If the coefficient of determination falls below the acceptance limit and the other calibration models are unacceptable, the source of the problem must be investigated and the instrument recalibrated. **Third-order regressions are <u>not</u> allowed at TestAmerica Pittsburgh.**

10.7 Initial Calibration Verification (ICV), 0.025 µg/mL for most compounds

A mid-level standard that is obtained from a source different from that of the calibration standards (second-source standard) is used to verify the initial calibration. The ICV standard is analyzed immediately following the initial calibration (ICAL).

Acceptance Criteria: The result for the target analyte(s) in the ICV standard must be within ± 20% of the expected value(s).

Corrective Action: If this is not achieved, the ICV standard, calibration standards, and instrument operating conditions should be checked. Correct any problems and rerun the ICV standard. If the ICV still fails to meet acceptance criteria, then repeat the ICAL.

10.8 Calibration Verification

10.8.1 12-Hour Calibration Verification

10.8.1.1 The 12-hour calibration verification sequence consists of, at a minimum, an instrument blank and the mid-level calibration standard. The 12-hour calibration verification sequence must be analyzed within 12 hours of the initial calibration and at least once every 12 hours thereafter when samples are being analyzed.

NOTE: It is not necessary to run a CCV standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.8.2 Continuing Calibration Verification (CCV), 0.020 µg/mL for most compounds

10.8.2.1 It may be appropriate to analyze a mid-level standard, Levels 3, 4 or 5, more frequently than every 12 hours. The mid-level calibration standard is analyzed as the continuing calibration verification (CCV) standard (see Section 7.6). At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCSs, and method blanks. A CCV is also analyzed at the end of each analytical sequence. Some programs require a CCV after every 10 samples to minimize the number of samples requiring re-injection when QC limits are exceeded. If 12 hours elapse, analyze the 12-hour standard sequence instead.

10.8.3 RL Standard

10.8.3.1 It may also be appropriate to analyze a standard prepared at or very near the

reporting limit (RL) for the method at the end of the analytical sequence, as a minimum (see Section 7.7). This standard can be used to rule out false negatives in client samples in cases where the %D for one or more of the analytes in a bracketing CCV falls below the lower acceptance limit. The results for the RL standard are not evaluated unless the previous CCV fails acceptance criteria.

10.8.4 Acceptance Criteria for Continuing Calibration Verification (CCV)

10.8.4.1 Detected Analytes (≥ RL)

For any analyte detected at or above the reporting limit (RL) in client samples, the percent difference (%D) for that analyte in the preceding and following CCVs (i.e., bracketing CCVs) or 12-hour calibration, on the column used for quantitation, must be within ± 20%.

In some cases, the nature of the samples being analyzed may be the cause of a failing %D. When the %D for an analyte falls outside of ± 20% in the CCV, and that analyte is detected in any or all of the associated samples, then those samples must be reanalyzed to prove a matrix effect. If the drift is repeated in the reanalysis, the analyst must generate an NCM for this occurrence to explain that the drift was most likely attributable to the sample matrix and that the samples may be diluted and reanalyzed to minimize the effect if so desired by the client.

10.8.4.2 Non-Detected Analytes (≤ RL)

However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >20%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, as the verification standard has demonstrated that the analyte would have been detected were it present. If an analyte was not detected in the sample and the standard response is more than 20% below the initial calibration response, then reinjection is necessary to ensure that the detector response has not deteriorated to the point that the analyte would not have been detected even though it was present (i.e., a false negative result).

Refer to Section 12 for which result to report.

The %D is calculated as follows:

$$\%D = \frac{\text{Measured Conc} - \text{Theoretical Conc}}{\text{Theoretical Conc}} \times 100 \qquad \textit{Equation 11}$$

10.9 Retention Time Windows

10.9.1 Retention time (RT) windows must be determined for all analytes.

10.9.2 Make an injection of all analytes of interest each day over a 72-hour period.

10.9.3 Calculate the mean and standard deviation for the three RTs for each analyte as follows:

$$\text{Mean RT} = \overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} \left(RT_i - \overline{RT}\right)^2}{n-1}}$$

Equations 12 & 13

Where:

RT_i = Retention time for the i^{th} injection.

n = Number of injections (typically 3).

SD = Standard deviation.

NOTE: For the multi-component analytes, Toxaphene and Technical Chlordane, the mean and standard deviation must be calculated for each of the 3 to 6 major peaks used for sample calculations.

10.9.4 Set the width of the RT window for each analyte at ± 3 standard deviations of the mean RT for that analyte.

10.9.5 The center of the RT window for an analyte is the RT for that analyte from the last of the three standards measured for the 72-hour study.

10.9.6 The center of the window for each analyte is updated with the RT from the Level 3 standard of the ICAL, or the CCV at the beginning of the analytical sequence. The width of each window remains the same until new windows are generated following the installation of a new column, or in response to an RT failure. The RT window width may be expanded if the RT drift observed in the ICAL is greater than the established window. The expanded window is noted on the ICAL checklist

10.10.6 If the RT window as calculated above is less than ± 0.01 minute, use ± 0.01 minute as the RT window. This allows for slight variations in retention times caused by sample matrix. Typically ± 0.05 minutes is used as the RT window.

10.10.7 TestAmerica Pittsburgh typically updates the retention time windows based on the previous CCV and would only determine a new RT window if a different phase column than those mentioned in Section 6 is used. The laboratory monitors the retention time for both surrogates throughout the analytical sequence.

11 Procedure

11.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP PT-QA-016. The NCM shall be filed in the project file and addressed in the case narrative.

11.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

11.3 Sample Preparation

11.3.1 Sample preparation for aqueous, soil, sediment, tissue, waste and oil samples is described in SOP PT-OP-001.

11.3.2 Cleanup and concentration of sample extracts is described in SOP PT-OP-001.

11.3.3 The final extract volume in hexane is dependent on matrix (see Table 8).

11.3.4 Use hexane to dilute sample extracts, if necessary.

11.4 Gas Chromatography

Chromatographic conditions for this method are presented in Table 2. Use the ChemStation interface to establish instrument operating conditions for the GC. Raw data obtained by the ChemStation software is transferred to the TARGET DB database for further processing. The data analysis method, including peak processing and integration parameters, calibration, RT windows, and compound identification parameters, is set up in the TARGET DB software.

11.5 Sample Introduction

All extracts and standards are allowed to warm to room temperature before injection. An autosampler is used to introduce samples into the chromatographic system by direct injection of 1 or 2 µL of the sample extract. Samples, standards, and QC samples must be introduced using the same procedure. Use the ChemStation interface to set up and run the analytical sequence. Sample injection and analysis are automated and may proceed unattended.

11.6 Analytical Sequence

An analytical sequence starts with a minimum five-level initial calibration (ICAL) or a daily calibration verification. Refer to Table 3 for the calibration levels used.

11.6.1 Prior to analyzing any calibration or calibration verification standards, the column

degradation evaluation standard is injected and the results are evaluated as described in Section 10.2.

11.6.2 The daily calibration verification includes analysis of the 12-hour calibration sequence (Section 10.8.1) and updating the retention time windows (see Section 10.9).

11.6.3 If there is a break in the analytical sequence of greater than 12 hours, a new analytical sequence must be started with a daily calibration verification.

11.6.4 The following is a typical analytical sequence:

- Solvent blank (optional)
- Eval B Std (column degradation evaluation)
- Toxaphene (Level 3[1])
- Technical Chlordane (Level 3[1])
- Pesticide Mix (All Levels)
- ICV (2nd source - all single component analytes)
- Eval B Std (column degradation evaluation)
- Solvent Blank (optional)
- Up to 20 samples (unless 12 hours comes first)[2]
- Pesticide Mix (CCV's - Level 3, 4 or 5[1])
- Eval B
- Up to 20 samples (unless 12 hours comes first)[2]
- Pesticide Mix (CCV's - Level 3, 4 or 5[1])
- Eval B

[1]A five-point curve for any of the multicomponent analytes may be included, if requested by the client.

[2]At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Pesticide Mix, and the breakdown mix must be run before the continuing calibration.

11.7 Daily Retention Time Windows

The center of the retention time (RT) windows determined in Section 10.9 are adjusted to the RT of each analyte as determined in the 12-hour calibration verification. The centers of the RT windows must be updated at the beginning of each analytical sequence and with each 12-hour calibration, but not for any other calibration verification standards.

11.8 Upon completion of the analytical sequence, transfer the raw chromatography data to the TARGET DB database for further processing.

11.8.1 Review chromatograms online and determine whether manual data manipulations are necessary.

11.8.2 All manual integrations must be justified and documented. See CA-Q-S-002 for requirements for manual integration.

11.8.3 Manual integrations may be processed using an automated macro, which prints the before and after chromatograms and the reason for the change, and attaches the analyst's electronic signature.

11.8.4 Alternatively, the manual integration may be processed manually. In the latter case, print both the both the before and after chromatograms and record the reason for the change and initial and date the after chromatogram. Before and after chromatograms must be of sufficient scale to allow an independent reviewer to evaluate the manual integration.

11.8.5 Case Narrative: For DoD the case narrative shall provide: identification of **samples and analytes** for which manual integration was necessary. DoD QSM, Version 3, Appendix DoD-A. For DoD V4.1 refer to SOP PT-QA-029.

11.9 Compile the raw data for all the samples and QC samples in a batch. The analytical batch is defined as containing no more than 20 samples, which include field samples and the MS and MSD.

11.9.1 Perform a level 1 data review and document the review on the data review checklist (GC and HPLC Data Review Checklist).

11.9.2 Submit the data package and review checklist to the peer reviewer for the Level 2 review process. The data review process is explained in SOP PT-QA-018.

12 Calculations / Data Reduction

12.1 Qualitative Identification

12.1.1 Tentative identification of an analyte occurs when a peak is found on the primary column within the RT window for that analyte, at a concentration above the reporting limit, or above the MDL if qualified data (J flags) are to be reported. Identification is confirmed if a peak is also present in the RT window for that analyte on the second (confirmatory) column and if the analyte concentration is greater than the MDL. When confirmation is

made using a second column, the analysis on the second column must meet all of the QC criteria for continuing calibration verification and RTs.

12.1.2 The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.2 Dual-Column Quantitation and Reporting

12.2.1 Each sample is analyzed on two different columns at the same time. The laboratory designates a primary column based on optimal separation of the compounds of interest and other desirable chromatographic characteristics. The higher of the two results is normally if the percent difference between the responses of the two columns or detectors is within 40%. **For DoD QSMV3.0, report the higher of the two confirmed results unless overlapping peaks are causing erroneously high results, then report the nonaffected result and document in the case narrative**. For DoD V4.1 refer to SOP PT-QA-029. The result from the secondary (confirmatory) column is reported if any of the following is true:

- There is obvious chromatographic interference on the primary column.
- The difference between the result for the primary column and the result for the secondary column is > 40% and chromatographic interference is evident.
- The continuing calibration verification, bracketing standard, or surrogate recovery fails on the primary column, but is acceptable on the secondary column. However, if the difference between the primary column result and the secondary column result is > 40% and the primary column calibration fails, then the sample must be evaluated for reanalysis.

12.2.2 Dual Column Results With > 40% RPD

12.2.2.1 If the Percent Difference (%D) between the response on the two columns or detectors is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. If the CCV % D is within ± 20% for one column and >20% for the other column and the %D between the two columns is within 40%, the data is reported from the column with the CCV within ± 20%.

12.2.2.2 The RPD between two results is calculated using the following equation:

$$\%RPD = \frac{\left|R_1 - R_2\right|}{\frac{1}{2}\left(R_1 + R_2\right)} \times 100\% \qquad \textit{Equation 14}$$

Where R_1 is the result for the first column and R_2 is the result for the second column.

12.3 Multi-Component Analytes (Toxaphene and Technical Chlordane)

12.3.1 Qualitative Identification

Retention time windows are also used for identification of multi-component analytes, but the “fingerprint” produced by major peaks of those compounds in the standard is used in tandem with the retention times to identify the compounds. The ratios of the areas of the major peaks are also taken into consideration. Identification of these compounds may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst’s judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

12.3.2 Quantitation of Toxaphene

12.3.2.1 While Toxaphene contains a large number of compounds that produce well resolved peaks in a GC/ECD chromatogram, it also contains many other components that are not chromatographically resolved. The unresolved complex mixture results in a "hump" in the chromatogram that is characteristic of the Toxaphene mixture of compounds. The resolved peaks are important for the identification of the mixture, and the area of the unresolved complex mixture contributes a significant portion of the area of the total response.

12.3.2.2 To measure total area, construct the baseline of Toxaphene in the sample chromatogram between the RTs of the first and last eluting Toxaphene components in the standard. In order to use the total area approach, the pattern in the sample chromatogram must be compared to that of the standard to ensure that all of the major components in the standard are present in the sample. Otherwise, the sample concentration may be significantly underestimated.

12.3.2.3 Toxaphene may also be quantitated on the basis of 4 to 6 major peaks. Using a subset of 4 to 6 peaks for quantitation provides results that agree well with the total peak approach and may avoid difficulties when interferences with Toxaphene peaks are present in the early portion of the chromatogram from compounds such as DDT.

12.3.2.4 When Toxaphene is determined using the 4 to 6 peaks approach, care must be taken to evaluate the relative areas of the peaks chosen in the sample and standard chromatograms.

12.3.2.5 The chosen peaks must be within the established retention time. If there is an interference that affects the accuracy of results, the analyst may use as few as 4 major peaks. The same peaks that are used for sample quantitation must be used for calibration.

12.3.2.6 The heights or areas of the chosen peaks should be summed together to determine the Toxaphene concentration.

12.3.2.7 Second column confirmation of multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

NOTE: USACE projects require the use of second-column confirmation of multi-component analytes unless the project work plans (SOW, SAP, QAPP, etc.) specify single-column analysis.

12.3.3 Quantitation of Technical Chlordane

12.3.3.1 Technical Chlordane is a mixture of at least 11 major components and 30 or more minor components that is used to prepare specific pesticide formulations. Cis-Chlordane (or α-Chlordane) and trans-Chlordane (or γ-Chlordane) are the two most prevalent major components of Technical Chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.

12.3.3.2 When the GC pattern of the sample resembles that of Technical Chlordane, Chlordane may be quantitated by comparing the total area of the Chlordane chromatogram using 3 to 5 major peaks or the total area. If the Heptachlor epoxide peak is relatively small, include it as part of the total Chlordane area for calculation. If Heptachlor and/or Heptachlor epoxide are much out of proportion, calculate these separately and subtract their areas from the total area to give a corrected Chlordane area.

NOTE: Octachlor epoxide, a metabolite of Chlordane, can easily be mistaken for Heptachlor epoxide on a nonpolar GC column.

12.3.3.3 To measure the total area of the Chlordane chromatogram, construct the baseline of Technical Chlordane in each calibration chromatogram between the RTs of the first and last eluting Technical Chlordane components. Use this area and the mass or concentration of Technical Chlordane in each calibration standard to establish the calibration function (Section 10.6). Construct a similar baseline in the sample chromatogram, measure the area, and use the calibration function to calculate the concentration in the sample extract.

12.3.3.4 When the GC pattern of Chlordane in a sample differs considerably from that of the Technical Chlordane standard, it may not be practical to relate a sample chromatogram back to the Technical Chlordane standard chromatogram. In these cases, all identifiable Chlordane components may be summed and reported as "Chlordane (not otherwise specified, CAS number 57-74-9)."

12.3.3.5 A third option for quantitating Technical Chlordane is to quantitate the peaks for α-Chlordane, γ-Chlordane, and Heptachlor separately against the appropriate reference materials, and report these individual components under their respective CAS numbers.

12.3.4 Second column confirmation of multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence. **NOTE: All South Carolina samples will be analyzed on a confirmation column.**

NOTE: USACE projects require the use of second-column confirmation of multi-component analytes unless the project work plans (SOW, SAP, QAPP, etc.) specify single-column analysis.

12.4 Surrogate recovery results are calculated and reported for tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) in all samples and QC. Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.

12.5 Calibration Range and Sample Dilutions

12.5.1 If the concentration of any analyte exceeds the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. Samples that were analyzed immediately following the high sample must be evaluated for carryover. If the samples have results at or above the RL for the analyte(s) that were found to be over the calibration range in the high sample, they must be reanalyzed to rule out carryover. It may also be necessary to dilute samples because of matrix interferences.

12.5.2 If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12.5.3 Guidance for Dilutions Due to Matrix Interference
If the sample is initially run at a dilution and only minor matrix peaks are present, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination. Ideally, the dilution chosen will make the response of the matrix interferences equal to approximately half the response of the mid-level calibration standard. Dilutions that are between 3X and 5X, report the data and narrate the dilution. Dilutions that are greater than 5X are reported as diluted out.

12.5.4 Reporting Dilutions

Some programs (e.g., South Carolina) and some projects require reporting of multiple dilutions (check special requirements in LIMS). In other cases, the most concentrated dilution with no target compounds above the calibration range will be reported.

12.6 Interferences Observed in Samples

12.6.1 Dual column analysis does not entirely eliminate interfering compounds. Complex samples with high background levels of interfering organic compounds can produce false positive and/or false negative results. The analyst must use appropriate judgment to take action as the situation warrants. If peak detection is prevented by interferences, further cleanup should be attempted (see SOP PT-OP-001). If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.7 Calculations

12.7.1 LCS and Surrogate Spike Recovery Calculation

LCS and surrogate spike recoveries are calculated using the following equation:

$$\%\text{Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100\% \qquad \textit{Equation 15}$$

12.7.2 MS and MSD Recovery Calculation

Matrix spike recoveries are calculated as follows:

$$\text{MS or MSD } \%\text{Recovery} = \left(\frac{SSR - SR}{SA}\right) \times 100\% \qquad \textit{Equation 16}$$

Where:

SSR = Measured concentration in spiked sample.

SR = Measured concentration in unspiked sample.

SA = Concentration of spike added to sample.

12.7.3 MS/MSD RPD Calculation

The relative percent difference between the MS and MSD is calculated as follows:

$$\%RPD = \frac{\left|R_1 - R_2\right|}{\frac{1}{2}\left(R_1 + R_2\right)} \times 100\% \qquad \textit{Equation 17}$$

Where *R1* is the result for the MS and *R2* is the result for the MSD.

12.7.4 Concentration of Analyte in the Sample Extract

Depending on the calibration function used, the concentration of the analyte in the sample extract is calculated as follows (see Section 10.6 for details on establishing the calibration function):

Average Calibration Factor: $C_e = \frac{A_s}{CF}$ *Equation 18*

Linear Regression: $C_e = \frac{\left[A_s - b\right]}{a}$ *Equation 19*

Non-Linear Regression: $C_e = f\left(A_s\right)$ *Equation 20*

Where:

C_e = Concentration of the analyte in the sample extract (ng/mL).

A_s = Peak area for the analyte in the sample extract injection.

B = y-intercept of the calibration fit.

A = Slope of the calibration fit.

$f(A_s)$ = Mathematical function established by the non-linear regression.

12.7.5 Concentration of Analyte in Original Sample

$$C_{sample} = \frac{C_e}{1000\frac{ng}{\mu g}} \times \frac{V_e}{V_s} \times DF \qquad \textit{Equation 21}$$

Where:

C_{sample} = Concentration of analyte in original sample (µg/L or µg/kg).

C_e = Concentration of analyte in sample extract injected in GC (ng/mL).

$1000\frac{ng}{\mu g}$ = Factor to convert ng/mL to µg/mL.

V_e = Volume of sample extract (mL).

V_s = Volume (or weight) of original sample (L or kg).

DF = Dilution Factor (post extraction dilutions)

12.8 All data are subject to two levels of review, which is documented on a checklist, as described in SOP DEN-QA-0020.

13.0 Method Performance

13.1 Initial Demonstration of Capability

An initial demonstration of capability for each method must be performed prior to analyzing samples.

13.1.1 For the standard analyte list, the initial demonstration consists of the preparation and analysis of a QC check sample (e.g., LCS) containing all of the standard analytes for the

method, as well as a method detection limit (MDL) study (described in Section 13.2 below).

13.1.2 Four aliquots of the LCS sample are analyzed with the same procedures used to analyze samples, including sample preparation.

13.1.3 The mean recovery and standard deviation are calculated for each analyte of interest. These results are compared with the established or project-specific acceptance criteria (e.g., LCS control limits). All four results must meet acceptance criteria before the method can be used to analyze samples.

13.1.4 For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is successful analysis of an extracted standard at the reporting limit and a single point calibration.

13.2 Method Detection Limit (MDL)

An initial method detection limit study is performed for each analyte and each sample matrix type in accordance with Policy PT-QA-007. An MDL verification is performed once a year to satisfy NELAC 2003 requirement. For DoD projects, an MDL verification is performed quarterly. MDLs are stored in the LIMS.

13.3 Analyst Training and Qualification

13.3.1 The Group/Team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP PT-QA-021.

13.3.2 Each analyst performing the method must complete an initial demonstration of capability (IDOC) by successfully preparing and/or analyzing four consecutive LCSs or other acceptable QC samples. The results of the IDOC study are summarized in the NELAC format, as described in SOP PT-QA-021. IDOCs are approved by the Quality Assurance Manager and the Technical Director. IDOC records are maintained by the QA staff in the central training files. Analysts who continue to perform the method must successfully complete a demonstration of capability annually.

14.0 Pollution Control

14.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.0 Waste Management

15.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Corporate Safety Manual, and PT-HS-001, "Waste Management Program."

15.2 The following waste streams are produced when this method is carried out:

15.2.1 Methylene Chloride in vials. This waste is placed in waste container identified as "Vials & Extracts", Waste #7.

15.2.2 Flammable solvents in vials. This waste is placed in waste container identified as "Vials & Extracts", Waste #7.

15.2.3 Waste flammable solvents. This waste is collected in a waste container identified as "Mixed Flammable Solvent Waste", Waste #3.

NOTE: Radioactive and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

16 References / Cross- References

16.1 Method 8082A, Polychlorinated Biphenyls (PCBs) by Gas Chromatograph, Revision 1, February, 2007, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

16.2 Method 8000B, Determinative Chromatographic Separations, Revision 2, December, 1996, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

16.3 SOP PT-OP-001, Extraction and Cleanup of Organic Compounds from Waters and Solids, Based on SW-846 3500 Series, 3600 Series, 8151A and 600 Series Methods, current version.

16.4 SOP PT-QA-001, Employee Orientation and Training, current version.

16.5 SOP CA-Q-S-002, Manual Integration, current version.

16.6 SOP PT-QA-007, Determination of Method Detection Limits (MDLs), current version.

16.7 SOP PT-QA-016, Nonconformance & Corrective Action System, current version.

16.8 SOP PT-QA-018, Technical Data Review Requirements, current version.

16.9 SOP PT-QA-021, Quality Control Program, current version.

16.10 SOP PT-QA-025, Implementation of the DoD QSM Version 3, January 2006, current version.

16.11 SOP PT-QA-029, DoD Version 4.1 Requirements, current version.

16.12 PT-LQAM, Pittsburgh Laboratory Quality Assurance Manual, current version.

17 Method Modifications:

Item	Method	Modification
1	8081B	Method 8081B includes an internal standardization option. Because of the high probability of interferences affecting internal standards, this SOP allows only external standards.
2	8081B	Section 11.4.1.1, allows the use of a single-point calibration for the multi-component pesticides. In this SOP an initial single-point calibration is used, but a five-point calibration followed by reanalysis of associated samples is required when one of the multi-component pesticides is detected.
3	8081B	Method 8081B references 8000B, which allows the use of third-order calibration curves. TestAmerica Pittsburgh does not allow third-order curves.

18 Tables

Table 1: Analyte List and Standard Reporting Limits

Table 2: Typical Instrument Conditions

Table 3: Calibration Levels ((µg/mL)

Table 4: Column Degradation Evaluation Mix

Table 5: LCS/Matrix Spike and Surrogate Spike Levels

Table 6: Evaluation Criteria and Corrective Actions for Continuing Calibration Verification

Table 7: LCS and MS/MSD Control Limits

Table 8: Initial Volumes/Weights/Exchange Solvents and Final Volumes for Pesticides

19 Revision History

19.1 Revision 1.

19.1.3 Added Section 9.5.1: Use of marginal exceedances is not permitted for South Carolina work for LCS. For SC work the LCS limits must be 70-130% at a maximum. Same limits or lab calculated limits can be used for MS/MSD. If limits are calculated for LCS, they must be within 70-130% range. Section 9.6 for updated for SC requirements. LCS and MS control limits corrected in Table 7.

19.2 Revision 2:

19.2.3 Updated section 9.5 to include use of control analytes. ME limit will only be used if required by a project. For DoD QSM 4.1 follow SOP PT-QA-029.

19.3 Revision 3

19.3.3 Section 9.5 was corrected to show that sodium sulfate not sodium thiosulfate is used for the LCS for soil analysis.

19.3.4 In Section 10.8.2.1 a statement was added to indicate that a CCV is analyzed at the end of each analytical sequence.

19.3.5 In Section 12.3.4 a statement was added to indicate that South Carolina samples will be analyzed on a confirmation column.

Table 1. Analyte List and Standard Reporting Limits µg/L, µg/wipe or µg/kg						
Compound	**CAS#**	**Water or Wipe/TCLP**	**Soil/ Low Level Soil**	**Tissue**	**Waste**	**Low Level Water**
Aldrin	309-00-2	0.05	1.7/0.0833	1.7	50	0.0013
α-BHC	319-84-6	0.05	1.7/0.0833	1.7	50	0.0013
β-BHC	319-85-7	0.05	1.7/0.0833	1.7	50	0.0013
δ-BHC	319-86-8	0.05	1.7/0.0833	1.7	50	0.0013
γ-BHC (Lindane)	58-89-9	0.05/0.5	1.7/0.0833	1.7	50	0.0013
α-Chlordane	5103-71-9	0.05	1.7/0.0833	1.7	50	0.0013
γ-Chlordane	5103-74-2	0.05	1.7/0.0833	1.7	50	0.0013
Chlordane (tech.)	57-74-9	0.5/5.0	17/0.0833	17	500	0.0125
4,4'-DDD	72-54-8	0.05	1.7/0.0833	1.7	50	0.0013
4,4'-DDE	72-55-9	0.05	1.7/0.0833	1.7	50	0.0013
4,4'-DDT	50-29-3	0.05	1.7/0.0833	1.7	50	0.0013
Dieldrin	60-57-1	0.05	1.7/0.0833	1.7	50	0.0013
Endosulfan I	959-98-8	0.05	1.7/0.0833	1.7	50	0.0013
Endosulfan II	33213-65-9	0.05	1.7/0.0833	1.7	50	0.0013
Endosulfan Sulfate	1031-07-8	0.05	1.7/0.0833	1.7	50	0.0013
Endrin	72-20-8	0.05/0.5	1.7/0.0833	1.7	50	0.0013
Endrin Aldehyde	7421-93-4	0.05	1.7/0.0833	1.7	50	0.0013
Endrin ketone	53494-70-5	0.05	1.7/0.0833	1.7	50	0.0013
Heptachlor	76-44-8	0.05/0.5	1.7/0.0833	1.7	50	0.0013
Heptachlor Epoxide	1024-57-3	0.05/0.5	1.7/0.0833	1.7	50	0.0013
Methoxychlor	72-43-5	0.1/1.0	3.3/0.1666	3.3	100	0.0025
Toxaphene	8001-35-2	2.0/20	67/3.333	67	2000	0.0500
NON ROUTINE STANDARDS*						
2,4'-DDE	3424-82-6	0.05	1.7	--	50	0.0013
2,4'-DDD	53-19-0	0.05	1.7	--	50	0.0013
Cis-Nonachlor	5103-73-1	--	1.7	--	--	0.0013
Trans-Nonachlor	39765-80-5	--	1.7	--	--	0.0013
Hexachlorobutadiene	87-68-3	--	1.7	--	--	--
2,4'-DDT	789—02-6	0.05	1.7	--	50	0.0030
Chlorbenside	103-17-3	0.1	3.3	3.3	100	0.0032
Dacthal (DCPA)	1861-32-1	0.1	3.3	3.3	100	0.0025
Hexachlorobenzene	118-74-1	0.05	1.7	--	50	0.0013
Hexachlorocyclopentadiene	77-47-4	0.1	3.3	--	100	--
Mirex	2385-85-5	0.05	1.7	1.7	50	0.0013
Diallate	2303-16-4	1.0	33	--	990	0.025

Table 1. Analyte List and Standard Reporting Limits µg/L, µg/wipe or µg/kg						
Compound	**CAS#**	**Water or Wipe/TCLP**	**Soil/ Low Level Soil**	**Tissue**	**Waste**	**Low Level Water**
Isodrin	465-73-6	0.05	1.7	--	50	0.0013
Chlorobenzillate	510-15-6	0.5	17	--	500	0.0373

* These are non-routine compounds that require a separate calibration, and are analyzed only upon request.

The following concentration factors are used when calculating the Reporting Limits:

	Extraction Vol.	**Final Vol.**
Groundwater	1000 mL	40 mL (1 mL for low-level)
TCLP Leachate	100 mL	40 mL
Soil	15 g	20 mL (1 mL for low-level)
Wipe	1 wipe	40 mL
High-Level Solid Waste	1 g	40 mL
Tissue	5 g	1 mL (with GPC clean-up)

Table 2.
Typical Instrument Conditions

Parameter	Recommended Conditions*
Injection port temperature	220 °C
Detector temperature	325 °C
Column 1 (HP6890 GC)	MR1: 30 m X 0.53 mm id, 0.5 µm
Column 2 (HP6890 GC)	MR2: 30 m X 0.53 mm id, 0.5 µm
Temperature program	120 °C for 1 minute 8.5 °C/min to 285 °C and hold for 6 minute
Injection	2 µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table 3. Calibration Levels (ng/mL)						
	Level 1	**Level 2**	**Level 3**	**Level 4**	**Level 5**	**Level 6[2]**
Individual Mix A and B						
Aldrin	1	5	25	50	100	200
g-BHC (Lindane)	1	5	25	50	100	200
Heptachlor	1	5	25	50	100	200
Methoxychlor	2	10	50	100	200	400
Dieldrin	1	5	25	50	100	200
Endosulfan I	1	5	25	50	100	200
Endosulfan II	1	5	25	50	100	200
4,4'-DDT	1	5	25	50	100	200
Endrin Aldehyde	1	5	25	50	100	200
Endrin ketone	1	5	25	50	100	200
β-BHC	1	5	25	50	100	200
δ-BHC	1	5	25	50	100	200
α-BHC	1	5	25	50	100	200
4,4'-DDD	1	5	25	50	100	200
4,4'-DDE	1	5	25	50	100	200
Endosulfan Sulfate	1	5	25	50	100	200
Endrin	1	5	25	50	100	200
α-Chlordane [3]	1	5	25	50	100	200
γ-Chlordane [3]	1	5	25	50	100	200
Heptachlor Epoxide	1	5	25	50	100	200
Appendix IX Standards						
Chlorobenside	2	10	250	100	200	400
Dacthal	2	10	250	100	200	400
Hexachlorobenzene	1	5	125	50	100	200
Hexachlorocyclopentadiene	2	10	250	100	200	400
Isodrin	0.4	2	50	20	40	20
Mirex	0.8	4	100	40	80	40
Oxychlordane isomer	0.4	2	50	20	40	20
Multicomponent Standards						
Chlordane (Technical)			250[4]			
Toxaphene			1000[5]			
Surrogates are included the AB Mix calibration mix at the following levels:						
Tetrachloro-m-xylene	1	5	25	50	100	200

Table 3. Calibration Levels (ng/mL)						
	Level 1	**Level 2**	**Level 3**	**Level 4**	**Level 5**	**Level 6[2]**
Decachlorobiphenyl	1	5	25	50	100	200

[1] Standards may be split into an A and B mix if resolution of all compounds on both columns is not obtained.

[2] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.

[3] Compounds may be used in lieu of running a daily technical Chlordane standard for samples that are non-detect for technical Chlordane.

[4] This standard may be used for quantitation of technical chlordane between 50 and 1000 ng/mL. If the chlordane is more concentrated, the extract must be diluted and reanalyzed.

[5] This standard may be used for quantitation of toxaphene between 200 and 4000 ng/mL. If the toxaphene is more concentrated, the extract must be diluted and reanalyzed

Table 4. Column Degradation Evaluation Mix	
Component	**Concentration (ng/mL)**
4,4'-DDT	50
Endrin	25
TCMX (surrogate)	20
DCB (surrogate)	20

Table 5. LCS/Matrix Spike and Surrogate Spike Levels µg/L, µg/wipe or µg/kg		
Compound	**Aqueous/Wipe**	**Soil/Tissue**
Aldrin	0.25	8.33
g-BHC (Lindane)	0.25	8.33
Heptachlor	0.25	8.33
Methoxychlor	0.25	8.33
Dieldrin	0.25	8.33
Endosulfan I	0.25	8.33
Endosulfan II	0.25	8.33
4,4'-DDT	0.25	8.33
Endrin Aldehyde	0.25	8.33
Endrin ketone	0.25	8.33
β-BHC	0.25	8.33
δ-BHC	0.25	8.33
α-BHC	0.25	8.33
4,4'-DDD	0.25	8.33
4,4'-DDE	0.25	8.33
Endosulfan Sulfate	0.25	8.33
Endrin	0.25	8.33
α-Chlordane [3]	0.25	8.33
γ-Chlordane [3]	0.25	8.33
Heptachlor Epoxide	0.25	8.33
Surrogates		
Decachlorobiphenyl	0.2	6.67
Tetrachlor-m-xylene (TCMX)	0.2	6.67

Table 6. LCS/Matrix Spike and Surrogate Spike Levels for TCLP (µg/L)	
Heptachlor	2.5
Heptachlor epoxide	2.5
g-BHC (Lindane)	2.5
Endrin	2.5
Methoxychlor	2.5
TCMX (surrogate)	2.0
DCB (surrogate)	2.0

Table 7.
LCS and MS/MSD Control Limits[1]

	Water			Solid		
	LCS and MS/MSD			LCS and MS/MSD		
Compound	**LCL**	**UCL**	**RPD**	**LCL**	**UCL**	**RPD**
Aldrin ©	69	121	22	70	123	22
α-BHC	55	133	20	59	127	20
β-BHC	71	129	24	70	128	20
δ-BHC	30	137	26	40	124	20
g-BHC (Lindane) ©	63	123	20	66	124	20
α-Chlordane	67	127	21	71	130	20
γ-Chlordane	65	121	21	68	123	24
Chlordane (technical)	47	143	41	33	150	40
4,4'-DDD	76	128	24	70	135	20
2,4'-DDD	50	150	20	50	150	20
4,4'-DDE	74	125	20	70	133	20
2,4'-DDE	50	150	20	50	150	20
4,4'-DDT ©	62	160	24	61	126	37

Table 7. LCS and MS/MSD Control Limits[1]						
	Water			Solid		
	LCS and MS/MSD			LCS and MS/MSD		
2,4'-DDT	50	150	20	50	150	20
Dieldrin ©	70	123	20	70	123	20
Endosulfan I	72	123	22	70	126	23
Endosulfan II	72	122	21	70	128	33
Endosulfan Sulfate	58	129	21	55	129	26
Endrin ©	70	125	24	70	127	20
Endrin Aldehyde	61	116	25	65	122	20
Endrin ketone	73	123	20	70	132	20
Heptachlor ©	65	127	25	70	128	20
Heptachlor Epoxide	71	122	20	69	131	20
Hexachlorobenzene	50	150	20	50	150	20
Methoxychlor	59	143	27	70	143	26
Mirex	40	135	30	40	135	30
trans-Nonachlor	50	150	20	50	150	20
Toxaphene	30	150	30	30	150	30
Decachlorobiphenyl (surrogate)	45	130	--	45	130	--
TCMX (surrogate)	45	130	--	45	130	--

[1]The Control Limits are subject to change as in-house limits are evaluated and updated by the QAM.

© Denotes control compounds. For DoD see SOP PT-QA-029.

Table 8.
Initial Volumes/ Weights, Exchange Solvents and Final Volumes[1] for Pesticides

Matrix	Initial Volume/Weight	Exchange Solvent for Analysis	Final Volume for Analysis (mL)
Water	1000 mL	Hexane	40.0
Soil/Sediment	15 g	Hexane	20.0
Tissue	6 g	Hexane	8.0
Low Level Analyses	1000 mL/ 15 g	Hexane	1.0

[1] Final Volumes will be ½ of the volume specified under Final Volume for Analysis if GPC Cleanup is performed (¼ if both Soxtherm® and GPC performed). GPC is required for all tissue analyses except PCBs, where it is recommended but optional if acid cleanup is performed.

POLYCHLORINATED BIPHENYLS (PCB) AS AROCLORS BY GAS CHROMATOGRAPHY (GC)

1 SCOPE AND APPLICATION

1.1 This method is used for the determination of PCBs as Aroclors in aqueous matrices, solid matrices, and wipes. The following compounds can be determined by this method:

Target Mixture	CAS Registry No.
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5

1.2 Instrumentation: HP 5890 Gas Chromatograph (GC) equipped with an electron capture detector (ECD) and a LEAP Technologies CTC A200S autosampler and Agilent Chemstation Data Acquisition software

1.3 Compound Target Mixtures are all part of a class of compounds known as Aroclors. The presence of an Aroclor will result in a specific GC-ECD chromatogram pattern with multiple peaks.

1.4 When the method is used to analyze unknown samples, Aroclor identification is done by retention time and pattern recognition. This method describes identification of specific Aroclors by pattern recognition.

1.5 Due to the complex nature of the multi-response Aroclor patterns, this method is restricted to the use by or under the supervision of analysts experienced in the use of a gas chromatograph and skilled in the interpretation of chromatograms.

2 SUMMARY OF METHOD

2.1 The method provides for the extraction and GC conditions for the analysis of PCB Aroclors in aqueous and solid matrices, and on wipes.

2.2 Soil samples are dried with sodium sulfate and extracted with a mixture of iso-octane/acetone. Water samples are saturated with sodium chloride and extracted with iso-octane or by using separatory funnel extraction with dichloromethane. Wipe samples are extracted with a mixture of iso-octane/acetone.

2.3 Extracts are transferred to injection vials and analyzed by GC-ECD.

2.4 The sensitivity and identification issues associated with this method depend on level of matrix interferences in addition to instrumental limitations. If interferences are

present, the resulting report limit may have to be elevated. Table 1 lists LODs that can be obtained in water, sand, and wipes in the absence of interferences.

2.5 A standard curve is generated for one of the Aroclors from a minimum six point standard curve using power regression as the regression analysis equation. The other Aroclor mixtures are quantitated using a single point calibration. Quantitation for each target mixture is done using reverse extrapolation.

3 DEFINITIONS AND ACRONYMS

3.1 There are many terms and acronyms used throughout this document. Check the definitions and acronyms sections of the Quality Manual for complete explanations.

4 INTERFERENCES

4.1 Sources of interference in this method can be grouped into three broad categories: contaminated solvents, reagents or sample processing hardware; contaminated GC carrier gas, parts, column surfaces or detector surfaces; and the presence of co-eluting compounds in the sample. Interferences co-extracted from the samples will vary considerably from sample to sample. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

4.2 Interferences by phthalates introduced during sample preparation can pose a major problem in PCB determinations. Common flexible plastics contain varying amounts of phthalates, which are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination can best minimize interferences from phthalate esters. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate ester contamination.

4.3 Glassware must be scrupulously cleaned if other than disposable glassware is used. Clean all glassware as soon as possible after use by detergent washing with hot water, three rinses with hot tap water, and three rinses with organic-free reagent water. Immediately prior to use, all non-disposable glassware/apparatus is rinsed with dichloromethane or another appropriate solvent.

4.4 Colored sample extracts should be cleaned with sulfuric acid prior to instrument analysis in accordance with PRE-004, Sulfuric Acid Clean-up.

4.5 The presence of elemental sulfur will result in a broad peak that interferes with the detection of and quantitation of PCB's. Sulfur contamination should be expected with sediment samples. Mercury cleanup is suggested for removal of sulfur in accordance with PRE-005, Mercury Clean-up.

5 SAFETY

5.1 Employees must abide by the policies and procedures in the ECCS Chemical Hygiene Plan (CHP), and this document. Refer to the CHP for more detailed safety information or for information not listed in this document.

5.2 Eye protection that protects against splash and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled during this procedure. Lab coats are recommended.

5.3 Employees must handle glassware and equipment carefully in order to prevent injury and accidents. Any damaged or broken glassware is to be discarded or moved to the glass repair box.

5.4 ECCS maintains a Material Safety Data Sheet (MSDS) for every chemical used in the laboratory. The MSDS file is kept in the main laboratory.

6 APPARATUS AND MATERIALS

6.1 Gas Chromatograph (GC)

6.1.1 Gas Chromatograph: HP5890
Autosampler: LEAP Technologies A200S
Detector: HP Electron Capture
Injector: Split/splitless Injector
Data system: Agilent Chemstation chromatography data system using HPIB capable of presenting chromatograms, retention time, peak integration data and calculating standard curves using regression analysis.

6.1.2 Columns

6.1.2.1 Column 1: RTX-35, 30 m x 0.53 mm ID, 0.5 µm film thickness or equivalent

NOTE: Primary column: Most Aroclor quantitation and identification is done utilizing this column.

6.1.2.2 Column 2: RTX-1701, 30 m x 0.53 mm ID, 0.25 µm film thickness or equivalent

NOTE: Backup column in the rare case where further identification is required.

6.1.3 GC supplies

6.1.3.1 High temperature septa, Restek part #27106

6.1.3.2 Injection port liners: Gooseneck 4 mm ID deactivated, Restek part # 20800

6.1.3.3 Gold seals, Restek part # 20476

6.2 Balances:

6.2.1 Top loader balance capable of weighting to 0.01 g

6.2.2 Analytical balance capable of weighting to 0.0001 g

6.3 Vials:

6.3.1 2 mL amber injection vials with Teflon lined crimp seals

6.3.2 200 µl inserts for 2 mL injection vials

6.3.3 20 mL scintillation vials

6.4 Syringes: Gas-tight, various sizes

6.5 Disposable glass transfer pipettes and 2 mL rubber bulbs

6.6 Glass funnel, 60-90 mm

6.7 Graduated glass cylinders, various sizes

6.8 Compressed Gas

6.8.1 Helium, Grade 5

6.8.2 Nitrogen, Grade 5

6.8.3 Hydrogen, Grade 5

6.9 Refrigerator capable of maintaining 4 °C

6.10 Freezer capable of maintaining temperatures below -15 °C

6.11 Repipetter – solvent delivery Optifix

6.12 Repeater digital – Eppendorf with appropriate size Combitips

7 REAGENTS

7.1 Solvents

7.1.1 Acetone – pesticide quality or equivalent

7.1.2 Iso-octane -pesticide quality or equivalent

7.1.3 80% Iso-octane/20% acetone: Combine 3200 mL of iso-octane with 800 mL of acetone in a 4 L solvent bottle. Measure the volumes independently. Label appropriately and assign a 6 month expiration date.

7.2 Solid Reagents – not used in this method.

7.3 Acids and Bases – not used in this method.

7.4 Stock Standards

7.4.1 Primary Aroclor stock standards are purchased from vendors as certified solutions at concentrations of 1000 or 100 µg/ml (Table 4). Alternative concentrations of Aroclor stock standards can be utilized to accommodate specific project objectives.

7.4.2 Primary chlorinated pesticide stock standards purchased for utilization in ECCS SOP LAM-003, OC Pesticides by 8081A, may be used in this method if needed as a chromatographic reference standard. This method is not applicable for the analysis of the chlorinated pesticides.

7.5 Intermediate Standards - This section is not applicable to this method.

7.6 Calibration Standards

7.6.1 Calibration standards are prepared at ten concentrations by dilution of the primary stock standards (Section 7.4.1) in 80% iso-octane/20% acetone to create a calibration curve (Table 6-1). A set of calibration standards is created for each individual Aroclor as needed. After the individual calibration standards are prepared, the solutions are entered into LIMS and transferred to LIMS labeled 40 mL VOA vials for storage. An example of how a standard solution is prepared is provided below.

7.6.1.1 Level 10, (2.0/0.24 µg/mL) Using a 250 µl gas tight syringe aliquot 200 µL of Aroclor stock at 1000 µg/mL (Section 7.4.1) and using a 4.0 mL volumetric pipette, aliquot 4.0 mL of the Surrogate Spike Mix TCMX/DCBP 6.0 µg/ml (Section 7.7.) into a 100 mL volumetric flask. Dilute to volume with 80% iso-octane/20% acetone.

7.6.1.2 See Table 6-1 for instruction on creation of the calibration standards Level 1 through Level 10.

7.6.2 If soil samples undergo sulfuric acid cleanup, the calibration and continuing calibration standards must also be acid treated.

7.7 Surrogate Spike

7.7.1 The surrogate spike mix (DCBP and TCMX at 6.0 µg/mL) is purchased from Absolute Standards (Absolute Part # 95677) in 1000 mL or 2000 mL batches.

7.7.2 No further dilution is required.

7.8 Laboratory Control Sample (LCS) Spike

7.8.1 One of the four primarily detected Aroclors (1242, 1248, 1254, and 1260) is typically used for LCs and MS/MSD spiking, usually the dominant Aroclor expected to be detected and fully calibrated. The spiking solutions are purchased from Absolute Standards at 100 µg/mL in acetone. Absolute part numbers are as follows:

Aroclor	Absolute Part #.
Aroclor 1242	94034
Aroclor 1248	94033
Aroclor 1254	94032
Aroclor 1260	95894

7.8.2 The stock spiking standards require no further dilution.

7.9 Matrix Spike / Matrix Spike Duplicate (MS/MSD) Spike

7.9.1 The same spike solution used for the Laboratory Control Spike (Section 7.8.1) is used for the matrix spike / matrix spike duplicate. The concentrations of the MS/MSD spiking solutions are found in Table 7.

7.9.2 The stock spiking standards require no further dilution.

7.10 Second Source Calibration Standards

7.10.1 Second source Aroclor stock standards are purchased from Absolute Standards at 100 µg/mL and are the same as the LCS spike standards (Section 7.8.1). The vendor for the second source standards should be different than the vendor not used as the source of the primary stock standards.

7.10.2 Second source calibration check standard.

7.10.2.1 Second source standards are prepared at 0.50/0.06 µg/mL. Using a gas tight syringe, aliquot 1 mL of the second source Aroclor stock (100 µg/ml) and using a volumetric pipette, aliquot 2.0 mL of surrogate mix at 6.0 µg/mL (see Section 7.7.4) into a 200 mL volumetric flask. Dilute to volume with 80% iso-octane/20% acetone.

7.10.2.2 Enter the standard into LIMS and transfer the standard to a LIMS labeled 40 mL VOA vials, store in a freezer and assign a one year expiration date.

7.11 Internal Standard – Not applicable to this method.

8 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Water samples should be collected in 1 L amber glass bottles with Teflon lined caps. Water samples must be extracted within 7 days of collection.

8.2 Soil samples should be collected in 4 ounce or larger amber glass jars with Teflon lined caps. Soil samples must be extracted within 14 days of collection. Hold times may be increased for soils to 1 year as long as they are frozen within the 14 day hold time window.

8.3 Wipe samples should be collected in 4 ounce or larger amber glass jars with Teflon lined caps. Wipe samples must be extracted within 14 days of collection.

8.4 All samples should be stored on ice or refrigerated at 4 °C immediately after collection. In the laboratory, store samples at 4 °C and out of direct sunlight at all times.

8.5 Extracts are stored in the freezer and must be analyzed within 40 days of extraction.

9 PROCEDURE

9.1 Preparation of Samples – Choose the appropriate preparation method below.

9.1.1 Water samples

9.1.1.1 PRE-001, Separatory Funnel Extraction

9.1.1.2 PRE-002, Self-Contained Water Extraction

9.1.2 Soil/sediment samples

9.1.2.1 PRE-003, Micro-Scale Soil Extraction

9.1.3 Wipe Samples

9.1.3.1 PRE-006, Wipe Sample Extraction

9.1.4 Waste

9.1.4.1 PRE-007, Waste Dilution

9.2 Clean-up of Samples – Choose the appropriate clean-up method below.

9.2.1 PRE-004, Sulfuric Acid Clean-up

Note: If soil samples undergo sulfuric acid cleanup, the calibration and continuing calibration standards must also be acid treated.

9.2.2 PRE-005, Mercury Clean-up

9.3 Instrument Conditions

9.3.1 Gas Chromatograph #1: RTX 35 Column, 0.53mm X 30m, 0.5µm, or equivalent

Temperature Program	
Initial Temp:	110 °C
Initial Hold:	2.0 min
Initial Rate:	15 °C/min
Final Temp (1):	330 °C
Hold Time (1):	2.0 min
Injector Temp:	280 °C
Detector Temp:	300 °C
Carrier Gas:	Helium
Head Pressure:	~7 PSI
Make up Gas:	Nitrogen
Flow Rate:	~30 mL/min
Split Vent:	~30-35 mL/min (total flow after column flow rate is set).
Septum Purge:	< 1.0 mL/min
Equilibration Time	1.50 min
Oven Max	350° C
Splitless Valve	Splitless box not checked
On time	0.5 min
Off time	3.00 min

NOTE: Instrument conditions may be modified to achieve optimum chromatographic response or to meet project specific requirements.

9.3.2 Gas Chromatograph #2: RTX-1701 Column, 0.53mm X 30m, 0.5µm, or equivalent

Temperature Program	
Initial Temp:	140 °C
Initial Hold:	1.0 min
Initial Rate:	5 °C/min
Final Temp:	280 °C
Hold Time:	2 min
Injector Temp:	250 °C
Detector Temp:	300 °C
Carrier Gas:	Helium
Head Pressure:	~7 PSI
Make up Gas:	Nitrogen
Flow Rate:	~30 mL/min

Split Vent:	~28 mL/min
Septum Purge:	< 1.0 mL/min
Equilibration Time	1.50 min
Oven Max	285° C
Splitless Valve	Splitless box not checked
On time	0.5 min
Off time	3.00 min

NOTE: Final temp for RTX-1701 must not exceed 280 °C. Temperatures above 280 °C cause rapid column degradation.

NOTE: Instrument conditions may be modified to achieve optimum chromatographic response or to meet project specific requirements. All instrument conditions other than those listed in this SOP must be documented.

NOTE: The chromatograms in Figures 1 through 7 portray examples of acceptable peak shape, peak resolution, compound response, and compound response ratios that are desired for each Aroclor..

9.4 Preventive Maintenance

9.4.1 Routine maintenance consists of clipping the column, replacing the liner and seal, cleaning the hat and installing a new septum.

9.4.2 Changing only the septum is acceptable on a daily basis or if a limited number of injections had been made on the GC.

9.4.3 Carryover on the GC is usually caused by a worn out injection syringe. When replacing the syringe, use fine sandpaper to file off the sharp point and/or burr. Rinse with solvent from the top to remove any grit left in the syringe tip.

9.4.4 The need for preventive maintenance in improving chromatographic response can only be determined by sufficient training and experience in the analysis of Aroclors. As stated in section 1.7, this method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and skilled in the interpretation of chromatograms.

9.5 Calibration

9.5.1 If soil samples undergo sulfuric acid cleanup, the calibration and continuing calibration standards must also be acid treated.

9.5.2 For one of the primary Aroclors of interest, prepare an initial calibration curve with a minimum of 5 concentrations from the ten available (see Table 6). Aroclor 1242, 1248, 1254, or 1260 are usually used for the multipoint ICAL. One of the standards in the curve must be at or below the limit of quantitation. .

9.5.3 Appropriate single point calibration standards at 0.5 µg/mL must also be analyzed during the initial calibration that include at a minimum, 1016 and 1260 to encompass the full Aroclor retention time range.

9.5.4 The example chromatograms in Figures 1 through 7 provide target peaks that are typically used for calibration and quantitation. Other peaks may be selected based on the individual chromatogram, but the targets must be attempted first.

9.5.5 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph. Refer to Table 8 for a typical sequence. Plot the peak height responses against the concentration of the calibration standard using power regression. The coefficient of determination (r^2) must be ≥0.990, which corresponds to a correlation coefficient of (r) of ≥0.995.

NOTE: Peak heights are normally used for all calculations.

$$Regression:\ Y = AX^B\ or\ \ln Y = B \ln X + \ln A$$

Where: Y = Peak height
X = Concentration in µg/mL
A = Constant
B = Exponent

9.5.6 Continuing calibration verification (CCV) -The working calibration curve is verified on each working day by the injection of one or more continuing calibration verification standards. If the response for any Aroclor varies from theory by more than ± 20%, a new calibration curve must be injected, and/or data are qualified.

$$Percent\ Difference = \frac{R2 - R1}{R1} \times 100$$

Where: R1 = Theoretical concentration.
R2 = Concentration from CCV.

9.6 Retention Time Windows

9.6.1 Retention times obtained from the ICAL are used to update the calibration file.

9.6.2 The ICAL retention times once established may be adjusted as processing the data occurs using CCVs, LCSs and MS/MSDs for reference retention times. Normally windows are established for the surrogate TCMX/DCBP at approximately 0.10 minutes. The surrogates are set as reference peaks, and as such the rest of the retention times will shift with the surrogate on an injection-by-injection basis.

9.6.3 The retention windows for the Aroclor target peaks are usually set between 0.04 and 0.06 minutes.

9.7 Sample Analysis

9.7.1 Set up the GC system using the conditions described in Section 9.3.

9.7.2 Samples are analyzed in a set referred to as a LIMS run sequence. See Table 8 for an example of a typical sequence. CCVs must be injected every 10 samples or less and at the end of the run. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded. Raw data is collected and archived by the LIMS sequence number. .

9.7.3 Aliquots of the standards, samples and QC are transferred using disposable pipets into properly labeled injection vials.

NOTE: The use of 250 µL inserts in the injection vials to preserve standard or sample extract volume is recommended.

Note: If soil samples undergo sulfuric acid cleanup, the calibration and continuing calibration standards must also be acid treated.

9.7.4 Injection – Inject approximately 2 µL of the sample extract. The data system will record the resulting peak height for each peak of interest.

9.7.5 If the calculated value exceeds the theoretical value of the highest standard, dilute the extract and re-inject. Dilute the sample so that all peaks are on scale but in the upper half of the standard curve range.

9.7.6 If target peak detection is prevented by the presence of interferences, further cleanup may be required (Refer to cleanup SOPs PRE-004 and PRE-005). If an interference is present, a target peak(s) may be eliminated from the number of peaks used in the total for that particular Aroclor.

9.7.7 Qualitative identification of Aroclors in a sample is based on pattern recognition of the Aroclor standard versus the pattern in the sample, if present. This identification is based on professional judgment.

NOTE: If multiple Aroclors are present in a sample causing target peak co-elution, the analyst must use professional judgment whether to include or exclude specific target peaks from the calculation of each Aroclor.

9.7.8 Quantitation of unknown samples is done by summing the results of the regression analysis for each target peak. Each of the target peaks identified by retention time is calculated by the data system to obtain a µg/mL value. To determine the amount of Aroclor, in µg/mL, in each sample, the µg/mL values for each target peak are added together and then divided by the total number of target peaks used.

9.7.9 There are several possible interferences that may occur, which prevent accurate calculation of some peaks, (i.e. sulfur, DDT and metabolites, unknown interference not removed by concentrated H_2SO_4, technical chlordane, toxaphene, 8081 pesticides). Any of these may result in either a peak that is buried under a large peak or one or more peaks that have elevated results compared to the rest of the positive hits. If any of the above occur, the peaks that are interfered with are excluded from the total calculation resulting in the division number being smaller than 9. (i.e. if peaks 2 and 5 are elevated, these peak concentrations are not included in the total concentrations and the divisor would be 7.

9.7.10 Chromatography Data Assembly and Review - Chromatography data are to be assembled and reviewed in accordance with ECCS SOP GEN-016, Data Review.

9.8 Calculations

9.8.1 The concentration of each Aroclor in the sample extract is determined from the calibration curve in µg/ml through reverse extrapolation from the peak height response in the sample using power regression. The concentration in µg/L or µg/kg of each of the Aroclors in the sample is then calculated as follows:

9.8.1.1 Water Samples (µg/L)

$$Concentration\ (\mu g/L) = \frac{A_x \times D \times V_e}{V_s}$$

Where: A_x = Concentration of Aroclor in the extract in µg/mL
D = Dilution factor, if applicable
V_e = Volume of extract in mL
V_s = Volume of sample extracted in liters

9.8.1.2 Soil Samples (µg/kg)

$$Concentration\ (\mu g/g) = \frac{A_x \times D \times V_e}{W_s}$$

Where: A_x = Concentration of Aroclor in the extract in µg/mL
D = Dilution factor, if applicable
V_e = Volume of extract in mL
W_s = Volume of sample extracted in kilograms

9.8.1.3 Wipe Samples (µg)

9.8.1.3.1 Wipe samples are reported in total micrograms. The total microgram result can be converted into a weight/area result if the area is supplied by the client. The calculation is performed as follows:

$$\text{Concentration } (\mu g) = A_x \times D \times V_e$$

Where: A_x = Concentration of Aroclor in the extract in µg/mL
D = Dilution factor, if applicable
V_e = Volume of extract in mL

10 QUALITY CONTROL

10.1 Refer to Method 8000 for general quality control procedures for chromatography methods.

10.2 An analytical batch consists of 20 or fewer samples. Batch quality control samples should be analyzed with each set with the following frequency:

Blanks - One per 20 or fewer samples, minimum one per day
LCSs - One per 20 or fewer samples, minimum one per day
MS/MSDs - One MS/MSD per 20 or fewer samples, minimum one set per day

If an MS/MSD cannot be prepared because of limited sample volume, a second LCS must be prepared.

10.3 Method blanks consist of an aliquot of laboratory reagent water or silica sand that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedure. If target analytes or interferences are present at concentrations that impact the analytical results for samples, the samples (including quality control samples) should be re-extracted or appropriately qualified in accordance with GEN-015, Qualification of Data.

10.4 LCSs consist of an aliquot of laboratory reagent water or silica sand spiked with the target analytes, prepared and processed simultaneously with and under the same conditions as samples through all steps of the analytical procedure. LCS control limits for precision and accuracy are established on at least a yearly basis through the use of at least 20 data points. For Aroclors with insufficient data to calculate control limits, the control limit shall be 70-130%. If the recovery of any of the target Aroclor is outside control limits, the samples (including quality control samples) should be re-extracted or appropriately qualified in accordance with GEN-015, Qualification of Data.

10.5 MS/MSD samples consist of duplicate aliquots of sample spiked with the target analytes, prepared and processed simultaneously with and under the same conditions as samples through all steps of the analytical procedure. MS/MSD control limits for precision and accuracy are established on at least a yearly basis through the use of at least 20 data points. For Aroclors with insufficient data to calculate control limits, the control limit shall be 60-140% and 20% RPD. MS/MSD control limits are advisory. If the recovery or RPD of any of the target analytes is outside control limits, data should be appropriately qualified in accordance with GEN-015, Qualification of Data.

10.6 Initial calibration (ICAL) is performed using the external standard technique by injecting a minimum of 5 of the available calibration standards. The lowest

calibration standard must be at or below the limit of quantitation. The coefficient of determination (r^2) must be ≥0.990, which corresponds to a correlation coefficient of (r) of ≥0.995.

10.7 The working calibration curve must be verified on each working day by the injection of one or more CCV standards. If the response for any Aroclor varies from the theoretical concentration by more than 20%, a new calibration curve must be prepared or data appropriately qualified in accordance with GEN-015, Qualification of Data.

10.8 Surrogates are added to every sample and QC sample. Surrogate control limits are generated on at least a yearly basis. If a surrogate recovery is outside of control limits, the sample should be re-extracted and re-analyzed, if possible. If not, the data should be appropriately qualified in accordance with GEN-015, Qualification of Data.

10.9 A second source calibration verification standard must be analyzed with every initial calibration. The accepted limits are 70-130% for all Aroclors. If an SCV fails, immediate corrective action is required before proceeding with sample analysis. Affected data should be qualified according to GEN-015, Qualification of Data.

11 METHOD PERFORMANCE

11.1 Estimated limits of detection (LODs) for eight replicates of laboratory reagent water, silica sand, and wipes are listed in Table 1.

11.2 Typical demonstration of capability (DOC) data for laboratory reagent water and silica sand are summarized in Table 2.

12 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

12.1 Contingencies for out-of-control data should be evaluated on a case-by-case basis. A Corrective Action Form (CAF) must be completed for those times that acceptable QC results cannot be achieved. The CAF must be completed by the analyst and filed with the Quality Manager. Analytical results shall be qualified as necessary.

13 WASTE MANAGEMENT / POLLUTION PREVENTION

13.1 All waste will be disposed of in accordance with federal, state, and local regulations. This method has been prepared to minimize the waste produced and the potential for pollution of the environment. All ECCS employees shall follow this method and the guidance provided in the ECCS Health and Safety manual.

14 REFERENCES

14.1 This is an ECCS procedure. The technical elements and procedural requirements of the following methods were considered in preparation of this SOP.

14.1.1 SW 846, Method 8082, Revision 0, December 1996.

TABLE 1-1

LIMIT OF DETECTION
PCBS AS AROCLORS

Soil				
	Mean Conc. (µg/kg)	Avg. % Rec. (µg/kg)	% RSD	LOD (µg/kg)
Aroclor 1016[1]	85.0	84.9	3.1	7.8
Aroclor 1221[1]	0.0212	106	6.2	4.1
Aroclor 1232[1]	0.0221	111	11	7.0
Aroclor 1242[2]	0.0201	101	7.3	4.4
Aroclor 1248[2]	0.024	118	4.1	2.9
Aroclor 1254[2]	0.021	105	4.7	3.0
Aroclor 1260[2]	0.021	107	4.3	2.8

[1]Data Source: A0L1302 December 17, 2010
[2]Data Source: A1A0601 January 10, 2011

Water (Self-contained Extraction)				
	Mean Conc. (µg/L)	Avg. % Rec. (µg/L)	%RSD	LOD (µg/L)
Aroclor 1016	NA	NA	NA	NA
Aroclor 1221[1]	0.17	132	4.0	0.020
Aroclor 1232[1]	0.16	128	7.6	0.037
Aroclor 1242[2]	0.16	125	7.1	0.033
Aroclor 1248[2]	0.13	101	5.2	0.020
Aroclor 1254[2]	0.12	99.3	2.4	0.009
Aroclor 1260[2]	0.128	102	6.4	0.025

[1]DATA SOURCE: A0L1302 DECEMBER 17, 2010
[2]Data Source: A1A1301 January 13, 2011

Soil-Acid Treated				
	Mean Conc. (µg/kg)	Avg. % Rec. (µg/kg)	% RSD	LOD Treated (µg/kg)
Aroclor 1016[1]				
Aroclor 1221[1]	0.0218	109	9.6	6.3
Aroclor 1232[1]	0.0222	111	4.2	4.2
Aroclor 1242[2]	0.0228	114	6.5	4.4
Aroclor 1248[2]				
Aroclor 1254[2]				
Aroclor 1260[2]				

[1]Data Source: A0L1302 December 17, 2010
[2]Data Source: A1A0601 January 10, 2011

TABLE 2

TYPICAL DEMOSTRATION OF CAPABILITY DATA

WATER – SELF CONTAINED

Compound	Spike Level (µg/L)	Mean Recovery	Avg. % Recovery	%RSD
Aroclor 1254	12.5	13.8	110	3.1
DCBP	-	0.79	106	1.0
TCMX	-	0.66	88.0	5.0

Data Source: A1A1301 January 14, 2011

TABLE 3-1

TYPICAL RETENTION TIME (IN MINUTES) OF AROCLORS BY GC

The peaks selected as quantitation peaks for Aroclor 1260, Aroclor 1254, Aroclor1248 and Aroclor 1242 are listed in reports and chromatograms in Figures 1.1 through 4.2. These are used for the analysis of these Aroclors. If sample chromatogram and multiple Aroclor presence indicate that alternative peaks should be used as quantitation peaks, then peak substitution is allowable.

The peaks selected as quantitation peaks for Aroclor 1016, Aroclor 1221, and Aroclor 1232 are listed in reports and chromatograms in Figures 5.1 through 7.2. These peaks are not defined as the quantitation peaks but are listed merely as examples of peak selection and Aroclor chromatography patterns.

TYPICAL RETENTION TIME (IN MINUTES) OF CHLORINATED PESTICIDES BY GC
MIX 1

Compound	**RTX-35**	**RTX-1701**
TCMX (surrogate)	7.386	7.791
α-BHC	9.292	11.168
γ-BHC (Lindane)	10.365	12.561
β-BHC	10.596	15.538
Heptachlor	11.430	13.097
δ-BHC	11.558	16.051
Aldrin	12.314	13.888
Heptachlor epoxide	13.764	16.295
γ-Chlordane	14.267	17.404
α-Chlordane	14.687	17.612
Endosulfan I	15.254	17.051
4,4'-DDE	15.468	18.046
Dieldrin	16.331	18.834
Endrin	16.632	18.834
4,4'-DDD	16.790	20.574
Endosulfan II (1)	17.409	20.478
4,4'-DDT (1)	17.409	21.003
Endrin aldehyde	17.542	21.812
Endosulfan sulfate	17.944	22.825
Methoxychlor	19.357	23.080
Endrin ketone	19.681	23.837
DCBP (Surrogate)	22.687	26.528

(1) Co-elute on RTX-35

TABLE 3-2

TYPICAL RETENTION TIMES (IN MINUTES) OF CHLORINATED PESTICIDES BY GC
MIX 2

Compound	**RTX-35**	**RTX-1701**
Hexachlorobenzene	8.881	9.457
Pentachlorobenzene	10.077	11.594
2,4'-DDE	14.583	16.970
Trans – Nonachlor	14.422	17.732
2,4'-DDD	15.824	19.059
2,4'-DDT	16.614	19.395
Cis –Nonachlor	16.497	20.604
Mirex	19.863	21.880

TABLE 4

STOCK STANDARD CONCENTRATIONS

PRIMARY AROCLOR STOCK STANDARD CONCENTRATION

Target Mixture	**µg/mL**
Aroclor 1016	1000
Aroclor 1221	1000
Aroclor 1232	1000
Aroclor 1242	1000
Aroclor 1248	1000
Aroclor 1254	1000
Aroclor 1260	1000

SECOND SOURCE AROCLOR STOCK STANDARD CONCENTRATION

Target Mixture	**µg/mL**
Aroclor 1016	1000
Aroclor 1221	1000
Aroclor 1232	1000
Aroclor 1242	100
Aroclor 1248	100
Aroclor 1254	100
Aroclor 1260	100

TABLE 5

INTERMEDIATE STANDARD CONCENTRATIONS

Not applicable to this method.

TABLE 6-1

PREPARATION OF AROCLOR INITIAL CALIBRATION STANDARDS

CONCENTRATION (µg/mL)

Target Mixture / Compound	**L-1**	**L-2**	**L-3**	**L-4**	**L-5**	**L-6**	**L-7**	**L-8**	**L-9**	**L-10**
Aroclor Std.	0.002	0.005	0.01	0.02	0.05	0.10	0.20	0.5	1.0	2.0[1]
TCMX (surrogate)	0.00024	0.006	0.0012	0.0024	0.006	0.012	0.024	0.06	0.12	0.24
DCBP (Surrogate)	0.00024	0.006	0.0012	0.0024	0.006	0.012	0.024	0.06	0.12	0.24

DILUTION VOLUMES FOR AROCLOR CALIBRATION CURVES

	L-1	**L-2**	**L-3**	**L-4**	**L-5**	**L-6**	**L-7**	**L-8**	**L-9**	**L-10**
Aliquot (mL) [2]	10	10	10	10	10	10	10	0.10	0.10	0.20
Stock ID µg/mL	-	-	-	-	-	-	-	1000	1000	1000
Level ID	L-4	L-5	L-6	L-7	L-8	L-9	L-10	-	-	-
Aliquot (mL) [3]	10	10	10	10	10	10	10	2.0	2.0	4.0
Surrogate ID µg/mL	-	-	-	-	-	-	-	6.0	6.0	6.0
Surrogate ID	L-4	L-5	L-6	L-7	L-8	L-9	L-10	-	-	-
Final Volume mL[4]	100	100	100	100	100	100	100	200	100	100

NOTE:
[1] Calibration standards greater than 2.0 µg/mL may be prepared as long as acceptable standard curves are obtained.
[2] Primary Aroclor stock standard (Section 7.4.1)
[3] Surrogate spike mix (Section 7.7.4)
[4] Solvent: 80% iso-octane/20% acetone

TABLE 7

CONCENTRATION OF LCS AND MS/MSD SPIKE SOLUTION

Aroclor	**Concentration (µg/mL)**
All	100 µg/ml

Note: Aroclors 1242, 1248, 1254 and 1260 are usually used for LCS and MS/MSD.

TABLE 8

ICAL RUN SEQUENCE ORDER

Description	**Concentration (µg/mL)**
Aroclor 1221	0.05
Aroclor 1016	0.05
Aroclor 1232	0.05
Aroclor 1242	0.05
Aroclor 1248	0.05
Aroclor 1260	0.05
Aroclor 1254[1]	0.002
Aroclor 1254[1]	0.005
Aroclor 1254[1]	0.01
Aroclor 1254[1]	0.02
Aroclor 1254[1]	0.05
Aroclor 1254[1]	0.1
Aroclor 1254[1]	0.2
Aroclor 1254[1]	0.5
Aroclor 1254[1]	1.0
Aroclor 1254[1]	2.0
Blank 80/20	-
Second Source 1242	0.5
Second Source 1248	0.5
Second Source 1254	0.5
Second Source 1260	0.5
ICV 1242	0.5
ICV 1248	0.5
ICV 1254	0.5
ICV 1260	0.5

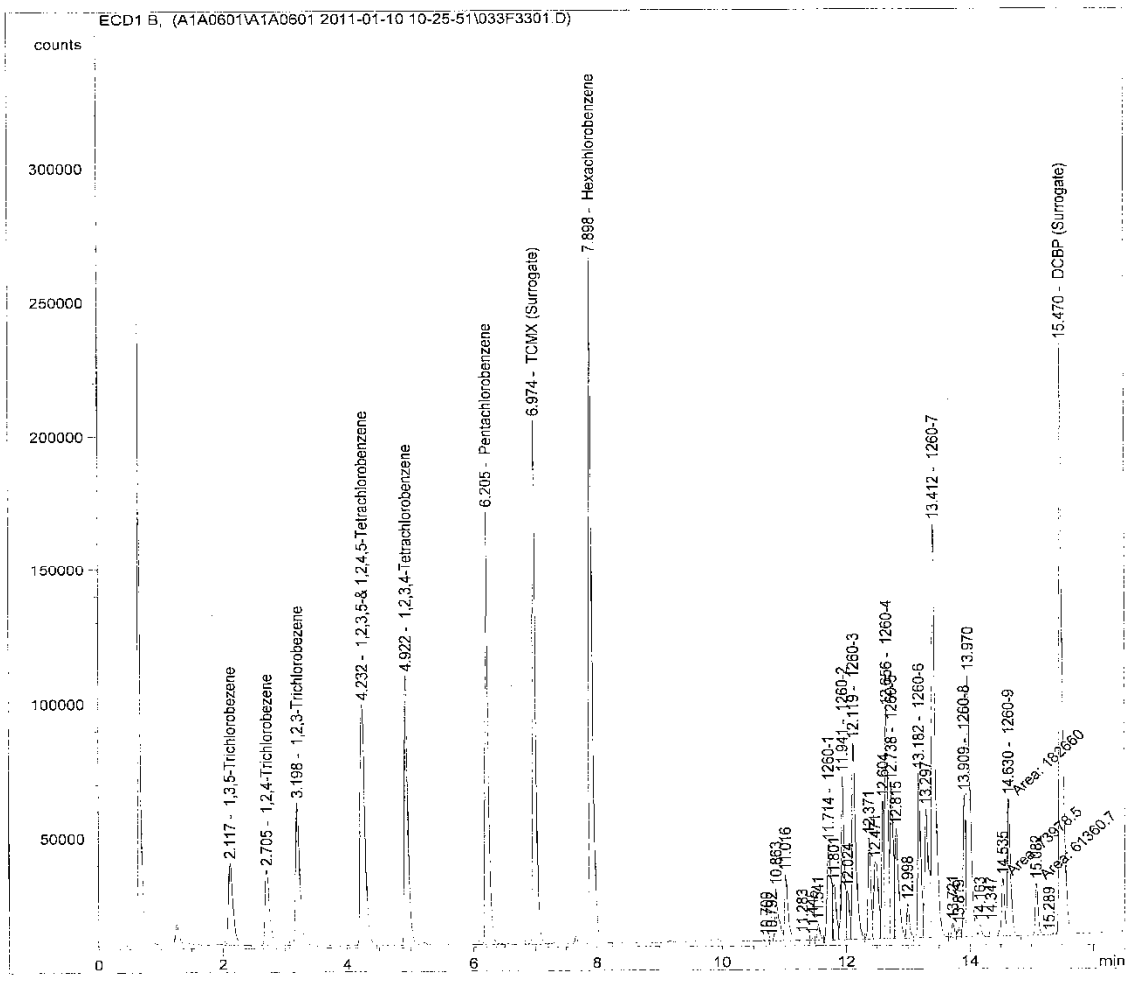
[1]Any of the Aroclors could be fully calibrated based on project specific needs.

FIGURE 1.1

CHROMATOGRAM OF AROCLOR 1260 & CHLORINATED BENZENES

```
Data File C:\CHEM32\4\DATA\A1A0601\A1A0601 2011-01-10 10-25-51\033F3301.D
Sample Name: A1A0601-CALS
    ==========================================================================
    Acq. Operator   : CJM                              Seq. Line :  33
    Acq. Instrument : 3310A49834                      Location : Vial 33
    Injection Date  : 1/10/2011 11:29:50 PM               Inj :  1
                                                    Inj Volume : Manually
    Acq. Method     : C:\CHEM32\4\DATA\A1A0601\A1A0601 2011-01-10 10-25-51\PCB.M
    Last changed    : 12/1/2010 3:51:50 PM by RBO
    Analysis Method : C:\CHEM32\4\METHODS\60CBA1A0601.M
    Last changed    : 6/28/2011 5:36:37 PM by cjm
                      (modified after loading)
    Method Info     : Method 8082.  Column Restek Rtx-35  30 M  X  0.53 mm  X  0.5 um Film  S/
                      N  976125.

    ==========================================================================
```




```
3310A49834 6/28/2011 5:38:28 PM cjm                    Page  1 of 3
```

FIGURE 1.2

REPORT OF AROCLOR 1260

Data File C:\CHEM32\4\DATA\A1A0601\A1A0601 2011-01-10 10-25-51\033F3301.D
Sample Name: A1A0601-CALS

Acq. Operator : CJM Seq. Line : 33
Acq. Instrument : 3310A49834 Location : Vial 33
Injection Date : 1/10/2011 11:29:50 PM Inj : 1
Inj Volume : Manually
Acq. Method : C:\CHEM32\4\DATA\A1A0601\A1A0601 2011-01-10 10-25-51\PCB.M
Last changed : 12/1/2010 3:51:50 PM by RBO
Analysis Method : C:\CHEM32\4\METHODS\60CBA1A0601.M
Last changed : 6/28/2011 5:36:37 PM by cjm
(modified after loading)
Method Info : Method 8082. Column Restek Rtx-35 30 M X 0.53 mm X 0.5 um Film S/N 976125.

External Standard Report

Sorted By : Retention Time
Calib. Data Modified : 1/12/2011 11:19:47 AM
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: ECD1 B,

RetTime [min]	Sig	Type		Height [counts]	Amt/Height	Amount [UG/ML]	Grp	Name
2.117	1	VV		3.07717e4	1.76044e-6	5.41718e-2		1,3,5-Trichlorobenzene
2.705	1	VV		2.82224e4	1.88967e-6	5.33312e-2		1,2,4-Trichlorobenzene
3.198	1	VV		5.34840e4	9.94810e-7	5.32064e-2		1,2,3-Trichlorobenzene
4.232	1	VV		8.99385e4	1.14566e-6	1.03039e-1		1,2,3,5-& 1,2,4,5-Tetrachlorobenzene
4.922	1	VV		1.00407e5	5.14202e-7	5.16297e-2		1,2,3,4-Tetrachlorobenzene
6.205	1	VV		1.61875e5	3.12441e-7	5.05764e-2		Pentachlorobenzene
6.974	1	VV	+	1.95757e5	3.15404e-7	6.17426e-2		TCMX (Surrogate)
7.898	1	BB		2.56468e5	1.98058e-7	5.07955e-2		Hexachlorobenzene
11.714	1	VV		3.56585e4	1.39917e-5	4.98923e-1	1	1260-1
11.941	1	VV		6.10714e4	8.18626e-6	4.99947e-1	1	1260-2
12.119	1	VV		7.34947e4	6.70686e-6	4.92919e-1	1	1260-3
12.656	1	VV		8.55216e4	5.98078e-6	5.11486e-1	1	1260-4
12.738	1	VV		5.76979e4	9.40089e-6	5.42412e-1	1	1260-5
13.182	1	VV		6.17043e4	8.22350e-6	5.07425e-1	1	1260-6
13.412	1	VV		1.54598e5	3.28203e-6	5.07395e-1	1	1260-7
13.909	1	VV		5.32726e4	9.55548e-6	5.09045e-1	1	1260-8
14.630	1	FM		5.14327e4	1.00382e-5	5.16291e-1	1	1260-9
15.470	1	BB	+	2.20580e5	2.68993e-7	5.93343e-2		DCBP (Surrogate)

Totals : 5.12367

Group summary :

Group ID	Use	Height [counts]	Amount [UG/ML]	Group Name
1		6.34452e5	4.58584	AROCLOR 1260

1 Warnings or Errors :

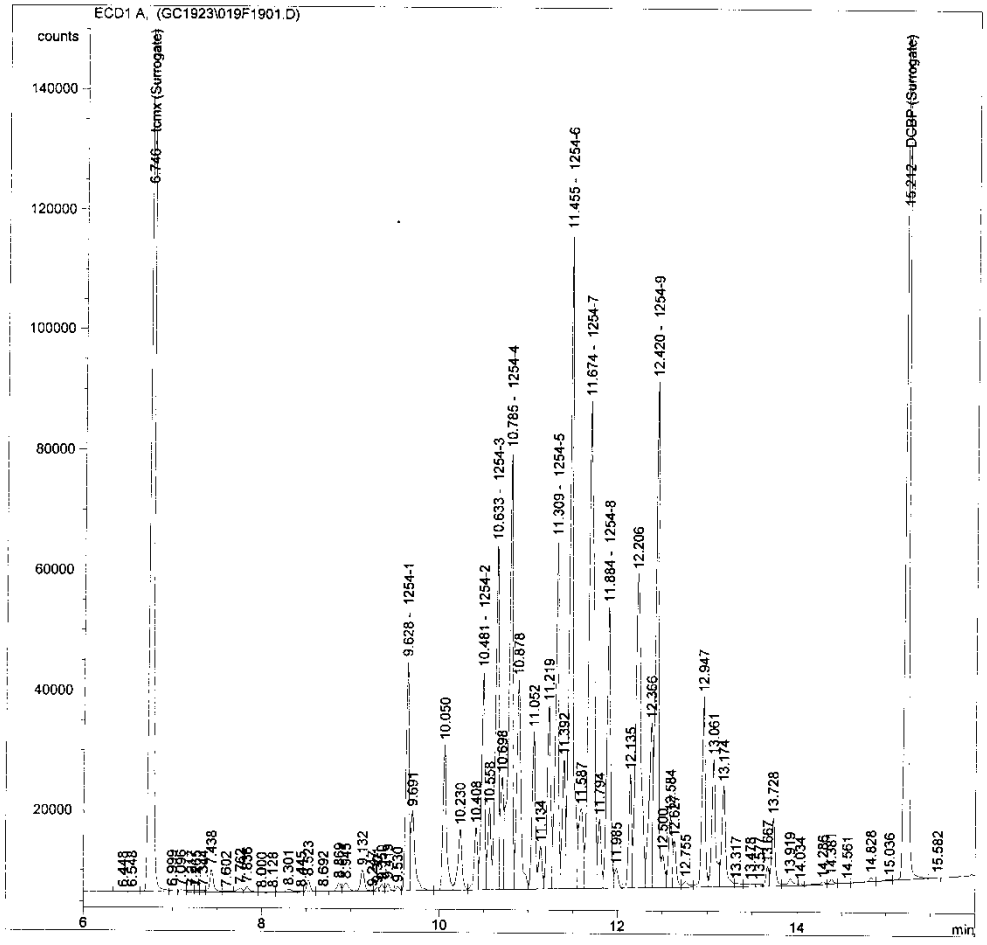
3310A49834 6/28/2011 5:38:28 PM cjm Page 2 of 3

FIGURE 2.1

CHROMATOGRAM OF AROCLOR 1254

Data File D:\HPCHEM\2\DATA\GC1923\019F1901.D Sample Name: CCV 1254 0.5
LOG 173 PAGE 85

```
==========================================================================
Injection Date  : 2/7/2008 10:19:25 PM          Seq. Line :  19
Sample Name     : CCV 1254 0.5                      Vial :  19
Acq. Operator   : FUZ                               Inj :   1
                                                Inj Volume : Manually
Acq. Method     : D:\HPCHEM\2\METHODS\PCB.M
Last changed    : 2/7/2008 2:46:21 PM by FUZ
Analysis Method : D:\HPCHEM\2\METHODS\54-1923.M
Last changed    : 3/24/2008 10:44:06 AM by RBO
                  (modified after loading)
FIELD PCB'S BY 8082. COLUMN RESTEK RTX-35 30M X 0.53 ID X 0.5 MICRON FILN S/
N (720902). 2uL injection splitless
==========================================================================
```



3203A41034 3/24/2008 10:44:06 AM RBO

FIGURE 2.2

REPORT OF AROCLOR 1254

```
Data File D:\HPCHEM\2\DATA\GC1923\019F1901.D              Sample Name: CCV 1254 0.5
    LOG 173 PAGE 85

    ================================================================================
    Injection Date  : 2/7/2008 10:19:25 PM           Seq. Line :  19
    Sample Name     : CCV 1254 0.5                        Vial :  19
    Acq. Operator   : FUZ                                  Inj :   1
                                                     Inj Volume : Manually
    Acq. Method     : D:\HPCHEM\2\METHODS\PCB.M
    Last changed    : 2/7/2008 2:46:21 PM by FUZ
    Analysis Method : D:\HPCHEM\2\METHODS\54-1923.M
    Last changed    : 3/24/2008 10:44:06 AM by RBO
                      (modified after loading)
    FIELD PCB'S BY 8082. COLUMN RESTEK RTX-35 30M X 0.53 ID X 0.5 MICRON FILN S/
    N (720902). 2uL injection splitless
    ================================================================================

    ================================================================================
                          External Standard Report
    ================================================================================

    Sorted By             :      Retention Time
    Calib. Data Modified  :      2/9/2008 2:35:06 PM
    Multiplier            :      1.0000
    Dilution              :      1.0000

    Signal 1: ECD1 A,

    RetTime Sig Type    Height   Amt/Height   Amount    Grp   Name
     [min]              [counts]              [ug/ml]
    -------|--|------|----------|----------|----------|--|---------------
      6.746  1 VV   +  2.23489e5  2.68469e-7 6.00000e-2  1 tcmx (Surrogate)
      9.628  1 VV     3.81552e4  1.31044e-5 5.00000e-1  2 1254-1
     10.481  1 VV     3.62775e4  1.37826e-5 5.00000e-1  2 1254-2
     10.633  1 VV     5.73636e4  8.71634e-6 5.00000e-1  2 1254-3
     10.785  1 VV     7.26741e4  6.88003e-6 5.00000e-1  2 1254-4
     11.309  1 VV     5.79228e4  8.63218e-6 5.00000e-1  2 1254-5
     11.455  1 VV     1.08978e5  4.58810e-6 5.00000e-1  2 1254-6
     11.674  1 VV     8.09502e4  6.17664e-6 5.00000e-1  2 1254-7
     11.884  1 VV     4.67519e4  1.06947e-5 5.00000e-1  2 1254-8
     12.420  1 VV     8.40903e4  5.94599e-6 5.00000e-1  2 1254-9
     15.212  1 VV   +  1.90063e5  3.15685e-7 6.00000e-2  1 DCBP (Surrogate)

    Totals :                                 4.71912e5

     Results obtained with standard integrator!
    Group summary :

     Group  Use   Height      Amount       Group Name
      ID          [counts]    [ug/ml]
    |------|---|----------|----------|--------------------------|
      1          4.13552e5  1.20000e-1  Surrogate
      2          5.83163e5     4.50000  Aroclor-1254

    1 Warnings or Errors :

    Warning : Calibration warnings (see calibration table listing)

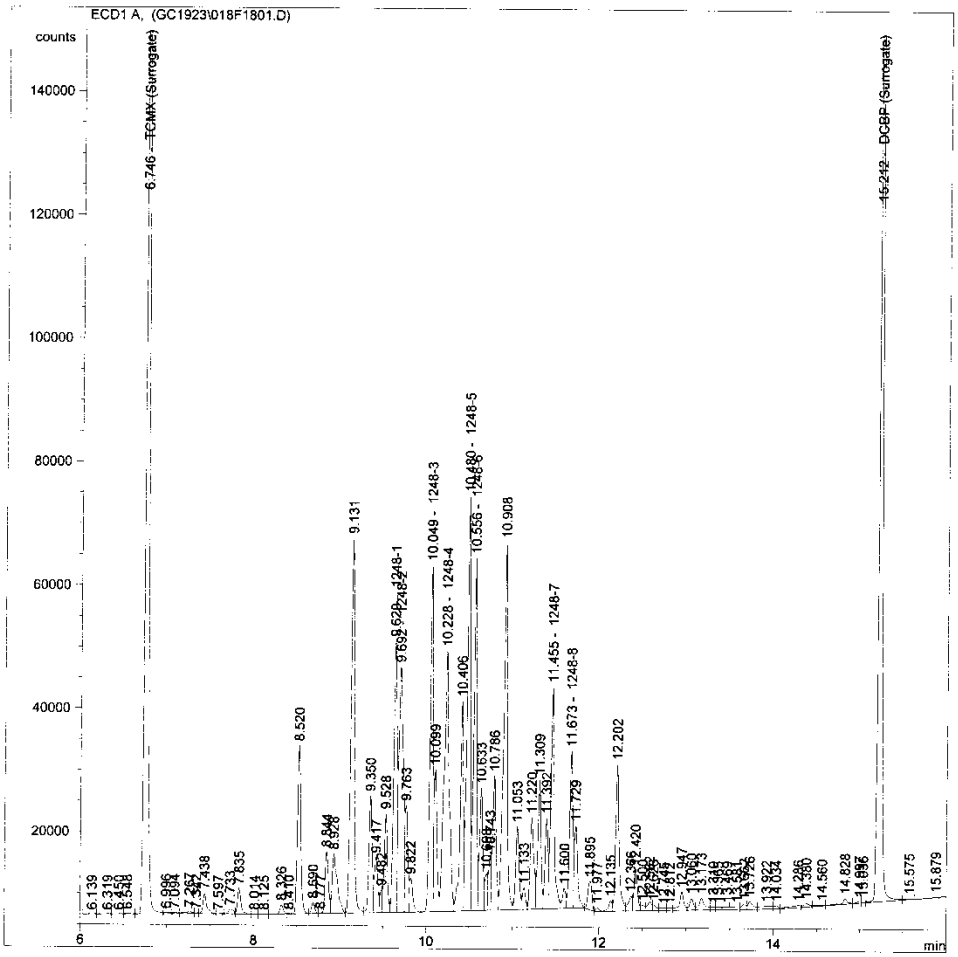
    ================================================================================
                              *** End of Report ***

3203A41034 3/24/2008 10:44:06 AM RBO                          Page 2 of 2
```

FIGURE 3.1

CHROMATOGRAM OF AROCLOR 1248

```
Data File D:\HPCHEM\2\DATA\GC1923\018F1801.D              Sample Name: CCV 1248 0.5
==========================================================================
Injection Date   : 2/7/2008 9:54:21 PM                 Seq. Line :  18
Sample Name      : CCV 1248 0.5                            Vial :  18
Acq. Operator    : FUZ                                      Inj :   1
                                                     Inj Volume : Manually
Acq. Method      : D:\HPCHEM\2\METHODS\PCB.M
Last changed     : 2/7/2008 2:46:21 PM by FUZ
Analysis Method  : D:\HPCHEM\2\METHODS\48-1923.M
Last changed     : 3/24/2008 10:23:08 AM by RBO
                   (modified after loading)
FIELD PCB'S BY 8082. COLUMN RESTEK RTX-35 30M X 0.53 ID X 0.5 MICRON FILN S/
N (482893). 2uL  injection
==========================================================================
```



3203A41034 3/24/2008 10:23:09 AM RBO

FIGURE 3.2

REPORT OF AROCLOR 1248

Data File D:\HPCHEM\2\DATA\GC1923\018F1801.D Sample Name: CCV 1248 0.5

Injection Date : 2/7/2008 9:54:21 PM Seq. Line : 18
Sample Name : CCV 1248 0.5 Vial : 18
Acq. Operator : FUZ Inj : 1
Inj Volume : Manually

Acq. Method : D:\HPCHEM\2\METHODS\PCB.M
Last changed : 2/7/2008 2:46:21 PM by FUZ
Analysis Method : D:\HPCHEM\2\METHODS\48-1923.M
Last changed : 3/24/2008 10:23:08 AM by RBO
(modified after loading)
FIELD PCB'S BY 8082. COLUMN RESTEK RTX-35 30M X 0.53 ID X 0.5 MICRON FILN S/N (482893). 2uL injection

External Standard Report

Sorted By : Retention Time
Calib. Data Modified : 2/8/2008 6:31:02 PM
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: ECD1 A,

RetTime [min]	Sig	Type		Height [counts]	Amt/Height	Amount [ug/ml]	Grp	Name
6.746	1	VV	+	2.06751e5	2.88197e-7	5.95850e-2	1	TCMX (Surrogate)
9.629	1	VV		4.40319e4	1.12558e-5	4.95616e-1	2	1248-1
9.692	1	VV		3.98310e4	1.23261e-5	4.90960e-1	2	1248-2
10.049	1	PV		5.62141e4	8.79145e-6	4.94203e-1	2	1248-3
10.228	1	VV		4.23060e4	1.18305e-5	5.00500e-1	2	1248-4
10.480	1	VV		6.72533e4	7.38270e-6	4.96510e-1	2	1248-5
10.556	1	VV		5.71933e4	8.72139e-6	4.98805e-1	2	1248-6
11.455	1	VV		3.59946e4	1.39880e-5	5.03493e-1	2	1248-7
11.673	1	VV		2.55046e4	1.98998e-5	5.07535e-1	2	1248-8
15.212	1	VV	+	1.91884e5	3.14773e-7	6.03998e-2	1	DCBP (Surrogate)

Totals : 5.06455e5

Results obtained with standard integrator!
Group summary :

Group ID	Use	Height [counts]	Amount [ug/ml]	Group Name
1		3.98635e5	1.19985e-1	Surrogate
2		3.68329e5	3.98762	Aroclor-1248

1 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)

*** End of Report ***

3203A41034 3/24/2008 10:23:09 AM RBO Page 2 of 2

FIGURE 4.1

CHROMATOGRAM OF AROCLOR 1242

```
Data File D:\HPCHEM\2\DATA\GC1923\017F1701.D              Sample Name: CCV 1242 0.5
    LOG 173 PAGE 89

    ========================================================================
    Injection Date  : 2/7/2008 9:29:19 PM            Seq. Line :  17
    Sample Name     : CCV 1242 0.5                        Vial :  17
    Acq. Operator   : FUZ                                  Inj :   1
                                                     Inj Volume : Manually
    Acq. Method     : D:\HPCHEM\2\METHODS\PCB.M
    Last changed    : 2/7/2008 2:46:21 PM by FUZ
    Analysis Method : D:\HPCHEM\2\METHODS\42-1923.M
    Last changed    : 3/24/2008 10:18:23 AM by RBO
                      (modified after loading)
    FIELD PCB'S BY 8081. COLUMN RESTEK RTX-35 30M X 0.35 ID X 0.50 MICRON FILM
    S/N 566535. 3ul injection with gooseneck liner.
    ========================================================================
```

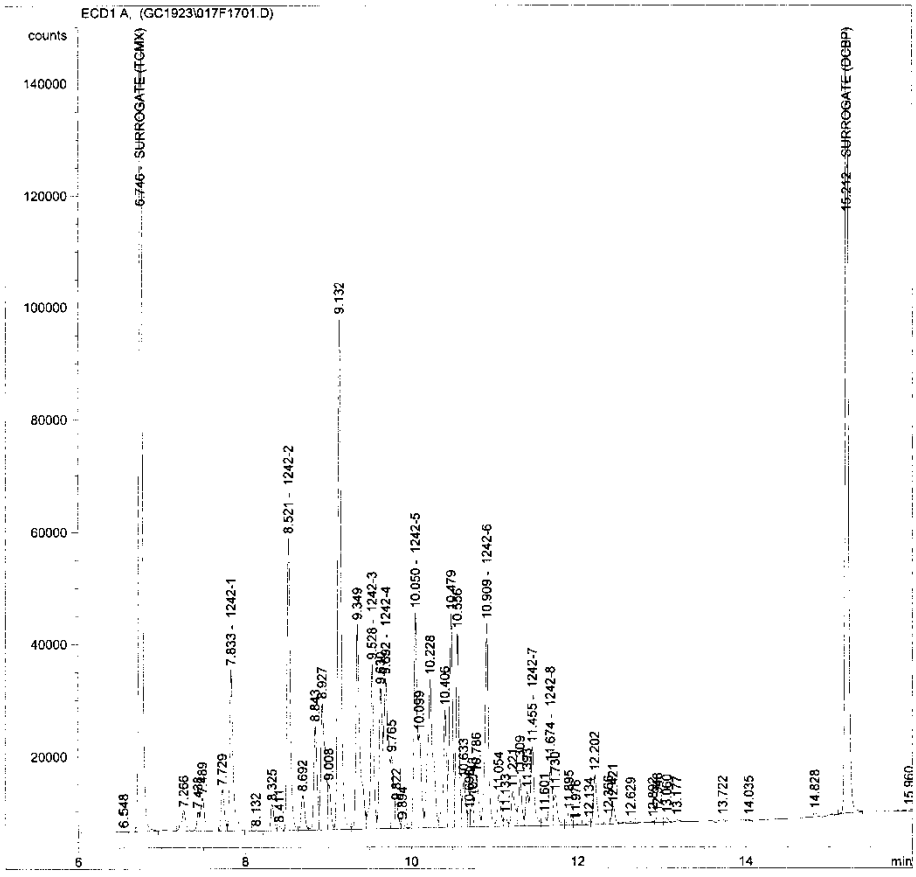


FIGURE 4.2

REPORT OF AROCLOR 1242

```
Data File D:\HPCHEM\2\DATA\GC1923\017F1701.D              Sample Name: CCV 1242 0.5
    LOG 173 PAGE 89

    ================================================================================
    Injection Date  : 2/7/2008 9:29:19 PM            Seq. Line :  17
    Sample Name     : CCV 1242 0.5                        Vial :  17
    Acq. Operator   : FUZ                                  Inj :   1
                                                     Inj Volume : Manually
    Acq. Method     : D:\HPCHEM\2\METHODS\PCB.M
    Last changed    : 2/7/2008 2:46:21 PM by FUZ
    Analysis Method : D:\HPCHEM\2\METHODS\42-1923.M
    Last changed    : 3/24/2008 10:18:23 AM by RBO
                      (modified after loading)
    FIELD PCB'S BY 8081. COLUMN RESTEK RTX-35 30M X 0.35 ID X 0.50 MICRON FILM
    S/N 566535. 3ul injection with gooseneck liner.
    ================================================================================

    ================================================================================
                           External Standard Report
    ================================================================================

    Sorted By             :      Retention Time
    Calib. Data Modified  :      2/9/2008 2:22:09 PM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Sample Amount         :      1.00000  [UG/ML]    (not used in calc.)

    Signal 1: ECD1 A,

    RetTime Sig Type    Height    Amt/Height   Amount    Grp   Name
     [min]              [counts]               [UG/ML]
    -------|--|------|----------|----------|----------|--|---------------
      6.746  1 BB   +  1.99248e5  3.01132e-7 6.00000e-2  1 SURROGATE (TCMX)
      7.833  1 VB      2.86529e4  1.74503e-5 5.00000e-1  2 1242-1
      8.521  1 VV      5.20885e4  9.59905e-6 5.00000e-1  2 1242-2
      9.528  1 VV      2.93145e4  1.70564e-5 5.00000e-1  2 1242-3
      9.692  1 VV      2.66815e4  1.87396e-5 5.00000e-1  2 1242-4
     10.050  1 VV      3.84080e4  1.30181e-5 5.00000e-1  2 1242-5
     10.909  1 VV      3.62073e4  1.38094e-5 5.00000e-1  2 1242-6
     11.455  1 VV      1.40142e4  3.56781e-5 5.00000e-1  2 1242-7
     11.674  1 VV      1.06554e4  4.69244e-5 5.00000e-1  2 1242-8
     15.212  1 BB   +  1.85437e5  3.23498e-7 5.99885e-2  1 SURROGATE (DCBP)

    Totals :                                 4.65145e5

     Results obtained with enhanced integrator!
    Group summary :

     Group  Use   Height     Amount      Group Name
      ID         [counts]    [UG/ML]
    |------|---|----------|----------|--------------------------|
      1         3.84685e5  1.19989e-1  SURROGATES
      2         2.36022e5     4.00000  AR 1242

    1 Warnings or Errors :

    Warning : Calibration warnings (see calibration table listing)

    ================================================================================
                              *** End of Report ***

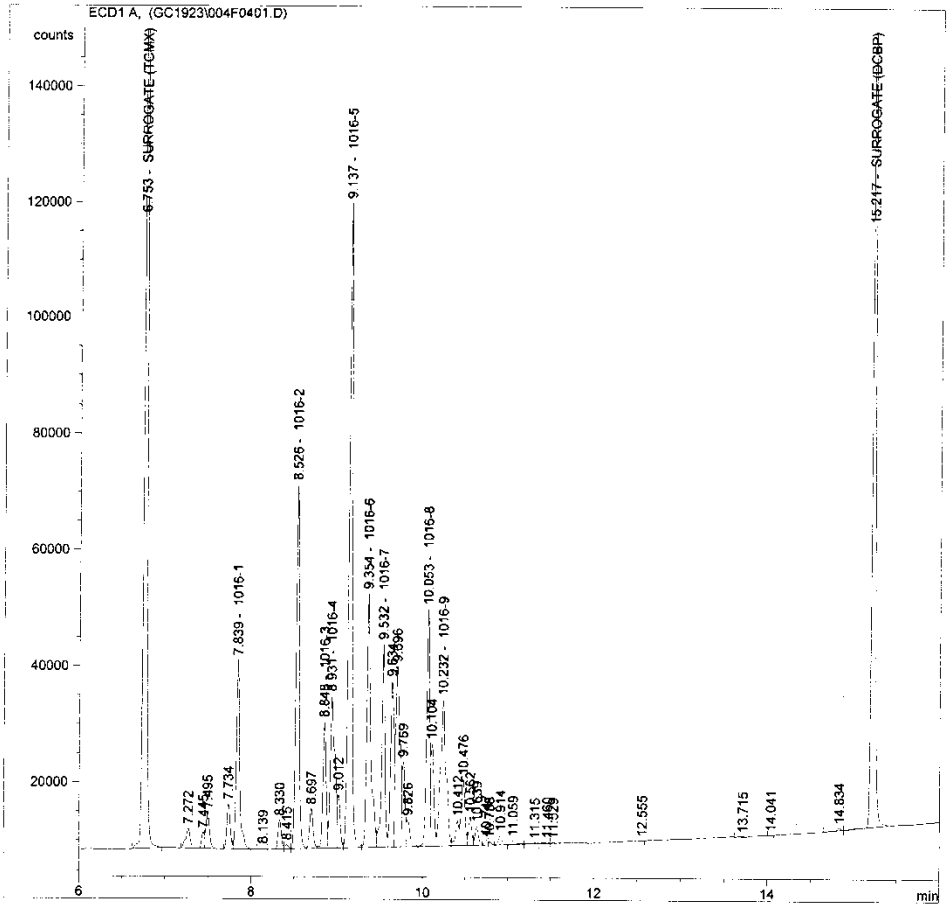
3203A41034 3/24/2008 10:18:23 AM RBO                          Page 2 of 2
```

FIGURE 5.1

CHROMATOGRAM OF AROCLOR 1016

Data File D:\HPCHEM\2\DATA\GC1923\004F0401.D Sample Name: 1016 0.5 UG/ML
LOG 173 PAGE 186

```
==========================================================================
Injection Date  : 2/7/2008 4:04:37 PM          Seq. Line :   4
Sample Name     : 1016 0.5 UG/ML                  Vial :   4
Acq. Operator   : FUZ                             Inj :   1
                                              Inj Volume : Manually
Acq. Method     : D:\HPCHEM\2\METHODS\PCB.M
Last changed    : 2/7/2008 2:46:21 PM by FUZ
Analysis Method : D:\HPCHEM\2\METHODS\16-1923.M
Last changed    : 3/24/2008 11:15:50 AM by RBO
                  (modified after loading)
FIELD PCB'S BY 8081. COLUMN RESTEK RTX-35 30M X 0.35 ID X 0.50 MICRON FILM
S/N 566535. 3ul injection with gooseneck liner.
==========================================================================
```



3203A41034 3/24/2008 11:15:50 AM RBO

FIGURE 5.2

REPORT OF AROCLOR 1016

Data File D:\HPCHEM\2\DATA\GC1923\004F0401.D Sample Name: 1016 0.5 UG/ML
LOG 173 PAGE 186

Injection Date : 2/7/2008 4:04:37 PM Seq. Line : 4
Sample Name : 1016 0.5 UG/ML Vial : 4
Acq. Operator : FUZ Inj : 1
Inj Volume : Manually

Acq. Method : D:\HPCHEM\2\METHODS\PCB.M
Last changed : 2/7/2008 2:46:21 PM by FUZ
Analysis Method : D:\HPCHEM\2\METHODS\16-1923.M
Last changed : 3/24/2008 11:15:50 AM by RBO
(modified after loading)
FIELD PCB'S BY 8081. COLUMN RESTEK RTX-35 30M X 0.35 ID X 0.50 MICRON FILM S/N 566535. 3ul injection with gooseneck liner.

External Standard Report

Sorted By : Retention Time
Calib. Data Modified : Monday, March 24, 2008 11:14:17 AM
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: ECD1 A,

RetTime [min]	Sig	Type		Height [counts]	Amt/Height	Amount [ug/mL]	Grp	Name
6.753	1	PB	+	1.89732e5	3.16236e-7	6.00000e-2	1	SURROGATE (TCMX)
7.839	1	VB		3.25294e4	1.53707e-5	5.00000e-1	2	1016-1
8.526	1	VV		6.26833e4	7.97661e-6	5.00000e-1	2	1016-2
8.848	1	VV		2.18030e4	2.29326e-5	5.00000e-1	2	1016-3
8.931	1	VV		2.62474e4	1.90495e-5	5.00000e-1	2	1016-4
9.137	1	VV		1.11093e5	4.50072e-6	5.00000e-1	2	1016-5
9.354	1	VV		4.36741e4	1.14484e-5	5.00000e-1	2	1016-6
9.532	1	VV		3.49813e4	1.42933e-5	5.00000e-1	2	1016-7
10.053	1	VV		4.08131e4	1.22510e-5	5.00000e-1	2	1016-8
10.232	1	VV		2.52372e4	1.98120e-5	5.00000e-1	2	1016-9
15.217	1	VB	+	1.61972e5	3.70434e-7	6.00000e-2	1	SURROGATE (DCBP)
Totals :						1.67113e5		

Results obtained with enhanced integrator!
Group summary :

Group ID	Use	Height [counts]	Amount [ug/mL]	Group Name
1		3.51704e5	1.20000e-1	SURROGATES
2		3.99062e5	4.50000	AR 1016

1 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)

*** End of Report ***

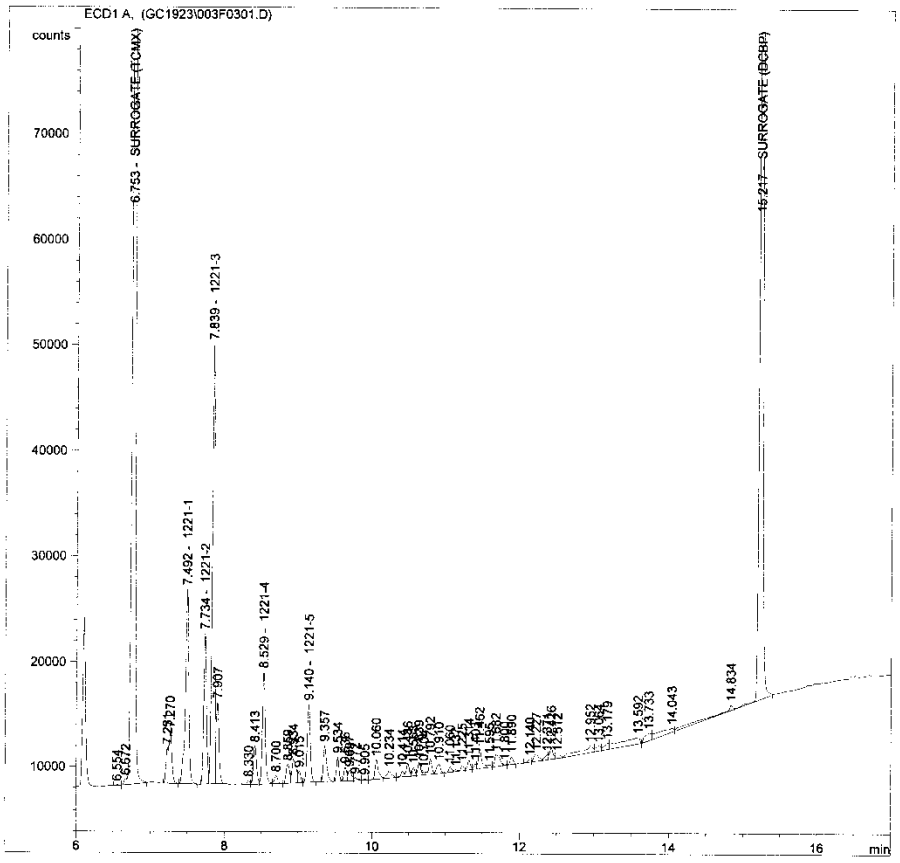
3203A41034 3/24/2008 11:15:50 AM RBO Page 2 of 2

FIGURE 6.1

CHROMATOGRAM OF AROCLOR 1221

Data File D:\HPCHEM\2\DATA\GC1923\003F0301.D Sample Name: 1221 0.5 UG/ML
LOG 173 PAGE 187

```
==========================================================================
Injection Date   : 2/7/2008 3:39:35 PM          Seq. Line :   3
Sample Name      : 1221 0.5 UG/ML                   Vial :   3
Acq. Operator    : FUZ                              Inj :   1
                                                Inj Volume : Manually
Acq. Method      : D:\HPCHEM\2\METHODS\PCB.M
Last changed     : 2/7/2008 2:46:21 PM by FUZ
Analysis Method  : D:\HPCHEM\2\METHODS\21-0917.M
Last changed     : 3/24/2008 11:07:47 AM by RBO
                   (modified after loading)
FIELD PCB'S BY 8081. COLUMN RESTEK RTX-35 30M X 0.35 ID X 0.50 MICRON FILM
S/N 566535. 3ul injection with gooseneck liner.
==========================================================================
```



3203A41034 3/24/2008 11:07:47 AM RBO Page 1 of 2

FIGURE 6.2

REPORT OF AROCLOR 1221

```
Data File D:\HPCHEM\2\DATA\GC1923\003F0301.D          Sample Name: 1221 0.5 UG/ML
    LOG 173 PAGE 187

    ================================================================================
    Injection Date  : 2/7/2008 3:39:35 PM              Seq. Line :   3
    Sample Name     : 1221 0.5 UG/ML                        Vial :   3
    Acq. Operator   : FUZ                                    Inj :   1
                                                      Inj Volume : Manually
    Acq. Method     : D:\HPCHEM\2\METHODS\PCB.M
    Last changed    : 2/7/2008 2:46:21 PM by FUZ
    Analysis Method : D:\HPCHEM\2\METHODS\21-0917.M
    Last changed    : 3/24/2008 11:07:44 AM by RBO
                      (modified after loading)
    FIELD PCB'S BY 8081. COLUMN RESTEK RTX-35 30M X 0.35 ID X 0.50 MICRON FILM
    S/N 566535. 3ul injection with gooseneck liner.
    ================================================================================

    ================================================================================
                            External Standard Report
    ================================================================================

    Sorted By             :      Retention Time
    Calib. Data Modified  :      Monday, March 24, 2008 11:05:19 AM
    Multiplier            :      1.0000
    Dilution              :      1.0000

    Signal 1: ECD1 A,

    RetTime Sig Type    Height    Amt/Height   Amount    Grp   Name
     [min]              [counts]               [ug/mL]
    -------|--|------|----------|----------|----------|--|---------------
      6.753  1 VB   +  1.86663e5  3.21435e-7 6.00000e-2  1 SURROGATE (TCMX)
      7.492  1 BB      1.85375e4  2.69723e-5 5.00000e-1  2 1221-1
      7.734  1 BV      1.43707e4  3.47930e-5 5.00000e-1  2 1221-2
      7.839  1 VV      4.17921e4  1.19640e-5 5.00000e-1  2 1221-3
      8.529  1 VB      1.07189e4  4.66467e-5 5.00000e-1  2 1221-4
      9.140  1 VB      7491.31885 6.67439e-5 5.00000e-1  2 1221-5
     15.217  1 VB   +  1.58031e5  3.79673e-7 6.00000e-2  1 SURROGATE (DCBP)

    Totals :                                  5.87054e4

     Results obtained with enhanced integrator!
    Group summary :

     Group  Use   Height      Amount       Group Name
      ID         [counts]    [ug/mL]
    |------|---|----------|----------|--------------------------|
      1         3.44694e5  1.20000e-1  SURROGATES
      2         9.29106e4     2.50000  AR 1221

    1 Warnings or Errors :

    Warning : Calibration warnings (see calibration table listing)

    ================================================================================
                              *** End of Report ***

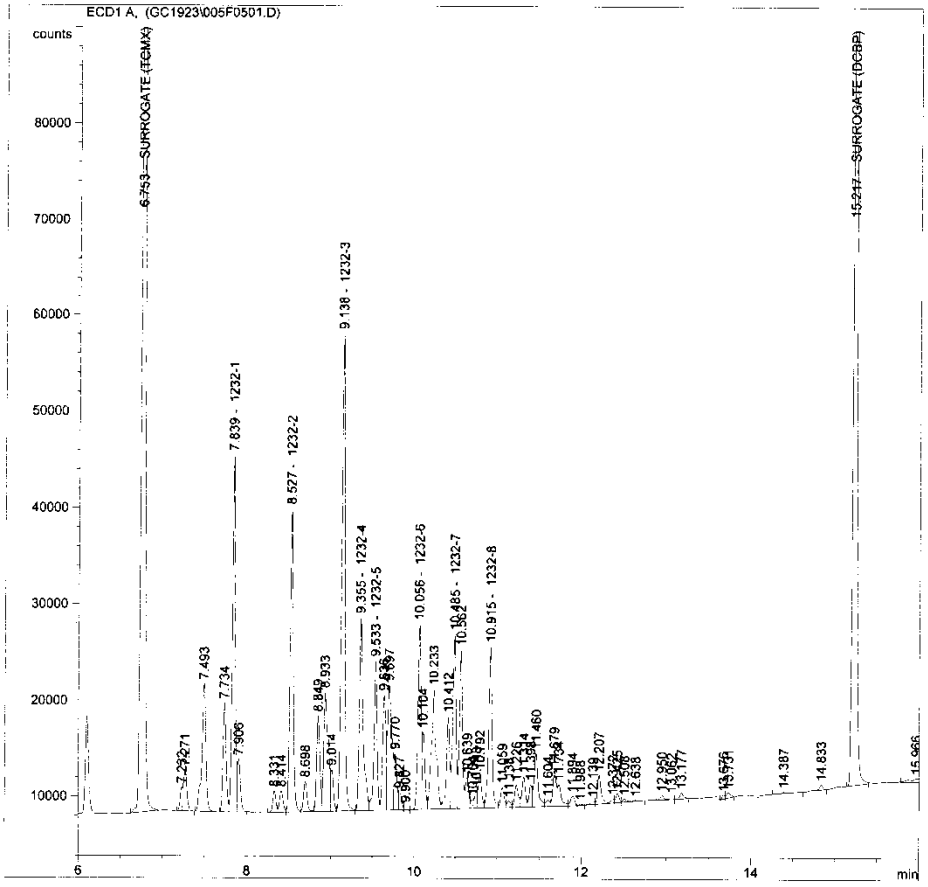
3203A41034 3/24/2008 11:07:44 AM RBO                          Page 2 of 2
```

FIGURE 7.1

CHROMATOGRAM OF AROCLOR 1232

Data File D:\HPCHEM\2\DATA\GC1923\005F0501.D Sample Name: 1232 0.5 UG/ML
LOG 173 PAGE 188

```
==========================================================================
Injection Date  : 2/7/2008 4:29:34 PM            Seq. Line :   5
Sample Name     : 1232 0.5 UG/ML                    Vial :   5
Acq. Operator   : FUZ                               Inj :   1
                                                 Inj Volume : Manually
Acq. Method     : D:\HPCHEM\2\METHODS\PCB.M
Last changed    : 2/7/2008 2:46:21 PM by FUZ
Analysis Method : D:\HPCHEM\2\METHODS\32-1923.M
Last changed    : 3/24/2008 11:22:29 AM by RBO
                  (modified after loading)
FIELD PCB'S BY 8081. COLUMN RESTEK RTX-35 30M X 0.35 ID X 0.50 MICRON FILM
S/N 566535. 3ul injection with gooseneck liner.
==========================================================================
```



3203A41034 3/24/2008 11:22:29 AM RBO Page 1 of 2

FIGURE 7.2

REPORT OF AROCLOR 1232

```
Data File D:\HPCHEM\2\DATA\GC1923\005F0501.D          Sample Name: 1232 0.5 UG/ML
    LOG 173 PAGE 188

    ================================================================================
    Injection Date  : 2/7/2008 4:29:34 PM            Seq. Line :   5
    Sample Name     : 1232 0.5 UG/ML                      Vial :   5
    Acq. Operator   : FUZ                                  Inj :   1
                                                     Inj Volume : Manually
    Acq. Method     : D:\HPCHEM\2\METHODS\PCB.M
    Last changed    : 2/7/2008 2:46:21 PM by FUZ
    Analysis Method : D:\HPCHEM\2\METHODS\32-1923.M
    Last changed    : 3/24/2008 11:22:29 AM by RBO
                      (modified after loading)
    FIELD PCB'S BY 8081. COLUMN RESTEK RTX-35 30M X 0.35 ID X 0.50 MICRON FILM
    S/N 566535. 3ul injection with gooseneck liner.
    ================================================================================

    ================================================================================
                            External Standard Report
    ================================================================================

    Sorted By             :      Retention Time
    Calib. Data Modified  :      Monday, March 24, 2008 11:21:02 AM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Sample Amount         :      1.00000  [UG/ML]    (not used in calc.)

    Signal 1: ECD1 A,

    RetTime Sig Type    Height    Amt/Height   Amount    Grp   Name
      [min]             [counts]               [UG/ML]
    -------|--|------|----------|----------|----------|--|---------------
      6.753  1 PB   +  1.91562e5  3.13215e-7 6.00000e-2  1 SURROGATE (TCMX)
      7.839  1 VV      3.71447e4  1.34609e-5 5.00000e-1  2 1232-1
      8.527  1 VV      3.15942e4  1.58257e-5 5.00000e-1  2 1232-2
      9.138  1 VB      4.96083e4  1.00790e-5 5.00000e-1  2 1232-3
      9.355  1 BV      2.01164e4  2.48553e-5 5.00000e-1  2 1232-4
      9.533  1 VV      1.56576e4  3.19334e-5 5.00000e-1  2 1232-5
     10.056  1 VV      1.93120e4  2.58907e-5 5.00000e-1  2 1232-6
     10.485  1 VV      1.81785e4  2.75050e-5 5.00000e-1  2 1232-7
     10.915  1 VV      1.68438e4  2.96845e-5 5.00000e-1  2 1232-8
     15.217  1 BB   +  1.65727e5  3.62042e-7 6.00000e-2  1 SURROGATE (DCBP)

    Totals :                                 1.94381e5

     Results obtained with enhanced integrator!
    Group summary :

     Group  Use   Height      Amount       Group Name
      ID          [counts]    [UG/ML]
    |------|---|----------|----------|--------------------------|
      1          3.57288e5  1.20000e-1  SURROGATES
      2          2.08455e5     4.00000  AR 1242

    1 Warnings or Errors :

    Warning : Calibration warnings (see calibration table listing)

    ================================================================================
                              *** End of Report ***

3203A41034 3/24/2008 11:22:29 AM RBO                          Page 2 of 2
```

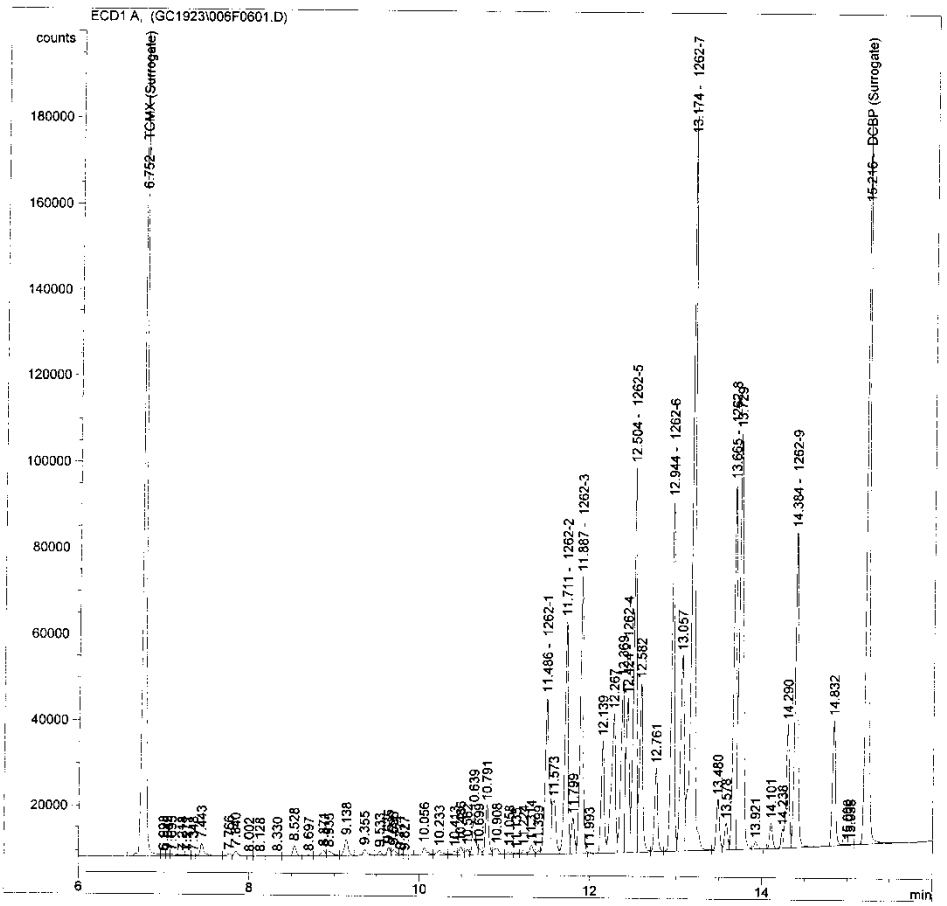
FIGURE 8.1

CHROMATOGRAM OF AROCLOR 1262

Data File D:\HPCHEM\2\DATA\GC1923\006F0601.D Sample Name: 1262 0.5 UG/ML
LOG 173 PAGE 189

Injection Date : 2/7/2008 4:55:26 PM Seq. Line : 6
Sample Name : 1262 0.5 UG/ML Vial : 6
Acq. Operator : FUZ Inj : 1
Inj Volume : Manually

Acq. Method : D:\HPCHEM\2\METHODS\PCB.M
Last changed : 2/7/2008 2:46:21 PM by FUZ
Analysis Method : D:\HPCHEM\2\METHODS\62-1923.M
Last changed : 3/24/2008 10:54:51 AM by RBO
(modified after loading)
FIELD PCB'S BY 8082. COLUMN RESTEK RTX-35 30M X 0.53 ID X 0.5 MICRON FILN S/N (482893). 2uL injection



3203A41034 3/24/2008 10:54:52 AM RBO

FIGURE 8.2

REPORT OF AROCLOR 1262

```
Data File D:\HPCHEM\2\DATA\GC1923\006F0601.D          Sample Name: 1262 0.5 UG/ML
    LOG 173 PAGE 189

    ================================================================================
    Injection Date   : 2/7/2008 4:55:26 PM              Seq. Line :   6
    Sample Name      : 1262 0.5 UG/ML                        Vial :   6
    Acq. Operator    : FUZ                                    Inj :   1
                                                      Inj Volume : Manually
    Acq. Method      : D:\HPCHEM\2\METHODS\PCB.M
    Last changed     : 2/7/2008 2:46:21 PM by FUZ
    Analysis Method  : D:\HPCHEM\2\METHODS\62-1923.M
    Last changed     : 3/24/2008 10:54:51 AM by RBO
                       (modified after loading)
    FIELD PCB'S BY 8082. COLUMN RESTEK RTX-35 30M X 0.53 ID X 0.5 MICRON FILN S/
    N (482893). 2uL  injection
    ================================================================================

    ================================================================================
                            External Standard Report
    ================================================================================

    Sorted By             :      Retention Time
    Calib. Data Modified  :      3/21/2008 10:00:12 AM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Sample Amount         :      1.00000  [UG/ML]    (not used in calc.)

    Signal 1: ECD1 A,

    RetTime Sig Type    Height    Amt/Height   Amount    Grp   Name
     [min]              [counts]               [UG/ML]
    -------|--|------|----------|----------|----------|--|---------------
      6.752  1 BV     1.92462e5  3.11750e-7 6.00000e-2  1 TCMX (Surrogate)
     11.486  1 VV     3.63862e4  1.37415e-5 5.00000e-1  2 1262-1
     11.711  1 VV     5.40776e4  9.24598e-6 5.00000e-1  2 1262-2
     11.887  1 VV     6.43538e4  7.76954e-6 5.00000e-1  2 1262-3
     12.424  1 VV     3.58817e4  1.39347e-5 5.00000e-1  2 1262-4
     12.504  1 VV     8.94137e4  5.59198e-6 5.00000e-1  2 1262-5
     12.944  1 VV     8.13914e4  6.14316e-6 5.00000e-1  2 1262-6
     13.174  1 VV     1.73569e5  2.88069e-6 5.00000e-1  2 1262-7
     13.665  1 VV     8.49494e4  5.88586e-6 5.00000e-1  2 1262-8
     14.384  1 VV     7.32312e4  6.82769e-6 5.00000e-1  2 1262-9
     15.216  1 VV  +  1.69059e5  3.54906e-7 6.00000e-2  1 DCBP (Surrogate)

    Totals :                                 4.64641e5

     Results obtained with standard integrator!
    Group summary :

     Group  Use    Height      Amount       Group Name
      ID          [counts]    [UG/ML]
    |------|---|----------|----------|--------------------------|
      1          3.61521e5  1.20000e-1  Surrogate
      2          6.93254e5     4.50000  Aroclor-1260

    1 Warnings or Errors :

    Warning : Calibration warnings (see calibration table listing)

    ================================================================================
                              *** End of Report ***

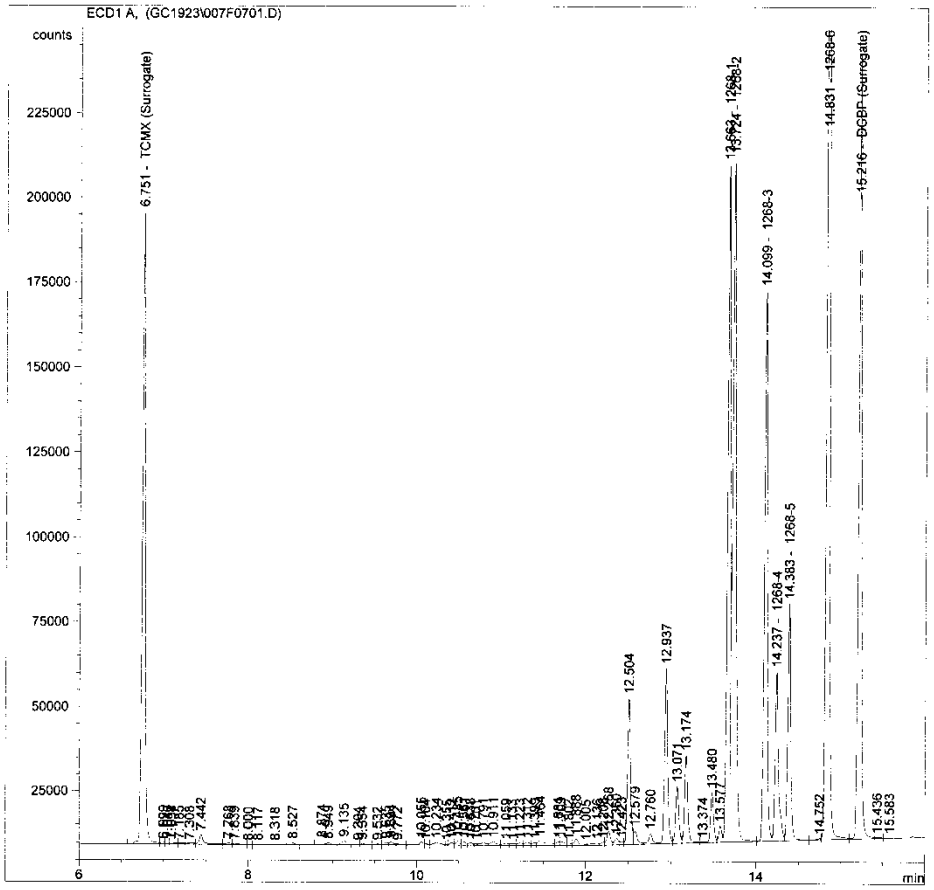
3203A41034 3/24/2008 10:54:52 AM RBO                          Page 2 of 2
```

FIGURE 9.1

CHROMATOGRAM OF AROCLOR 1268

```
Data File D:\HPCHEM\2\DATA\GC1923\007F0701.D          Sample Name: 1268 0.5 UG/ML
    LOG 173 PAGE 189

    ========================================================================
    Injection Date  : 2/7/2008 5:20:20 PM              Seq. Line :   7
    Sample Name     : 1268 0.5 UG/ML                       Vial :   7
    Acq. Operator   : FUZ                                   Inj :   1
                                                      Inj Volume : Manually
    Acq. Method     : D:\HPCHEM\2\METHODS\PCB.M
    Last changed    : 2/7/2008 2:46:21 PM by FUZ
    Analysis Method : D:\HPCHEM\2\METHODS\68-1923.M
    Last changed    : 3/24/2008 10:58:38 AM by RBO
                      (modified after loading)
    FIELD PCB'S BY 8082. COLUMN RESTEK RTX-35 30M X 0.53 ID X 0.5 MICRON FILN S/
    N (482893). 2uL  injection
    ========================================================================
```




```
3203A41034 3/24/2008 10:58:38 AM RBO                    Page 1 of 2
```

FIGURE 9.2

REPORT OF AROCLOR 1268

```
Data File D:\HPCHEM\2\DATA\GC1923\007F0701.D          Sample Name: 1268 0.5 UG/ML
    LOG 173 PAGE 189

    ================================================================================
    Injection Date  : 2/7/2008 5:20:20 PM            Seq. Line :   7
    Sample Name     : 1268 0.5 UG/ML                      Vial :   7
    Acq. Operator   : FUZ                                  Inj :   1
                                                    Inj Volume : Manually
    Acq. Method     : D:\HPCHEM\2\METHODS\PCB.M
    Last changed    : 2/7/2008 2:46:21 PM by FUZ
    Analysis Method : D:\HPCHEM\2\METHODS\68-1923.M
    Last changed    : 3/24/2008 10:58:38 AM by RBO
                      (modified after loading)
    FIELD PCB'S BY 8082. COLUMN RESTEK RTX-35 30M X 0.53 ID X 0.5 MICRON FILN S/
    N (482893). 2uL  injection
    ================================================================================

    ================================================================================
                           External Standard Report
    ================================================================================

    Sorted By             :      Retention Time
    Calib. Data Modified  :      3/21/2008 10:18:05 AM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Sample Amount         :      1.00000  [UG/ML]    (not used in calc.)

    Signal 1: ECD1 A,

    RetTime Sig Type    Height   Amt/Height   Amount   Grp   Name
     [min]              [counts]              [UG/ML]
    -------|--|------|----------|----------|----------|--|---------------
      6.751  1 BV     1.86554e5  3.21623e-7 6.00000e-2  1 TCMX (Surrogate)
     13.663  1 VV     1.99964e5  2.50045e-6 5.00000e-1  2 1268-1
     13.724  1 VV     2.01753e5  2.47828e-6 5.00000e-1  2 1268-2
     14.099  1 VV     1.62467e5  3.07754e-6 5.00000e-1  2 1268-3
     14.237  1 VV     5.00465e4  9.99071e-6 5.00000e-1  2 1268-4
     14.383  1 VV     6.99480e4  7.14816e-6 5.00000e-1  2 1268-5
     14.831  1 VV     4.39721e5  1.13708e-6 5.00000e-1  2 1268-6
     15.216  1 VV  +  2.31672e5  2.58986e-7 6.00000e-2  1 DCBP (Surrogate)

    Totals :                                2.06478e5

     Results obtained with standard integrator!
    Group summary :

     Group  Use    Height      Amount      Group Name
      ID          [counts]    [UG/ML]
    |------|---|----------|----------|--------------------------|
      1          4.18226e5  1.20000e-1  Surrogate
      2          1.12390e6     3.00000  Aroclor-1260

    1 Warnings or Errors :

    Warning : Calibration warnings (see calibration table listing)

    ================================================================================
                              *** End of Report ***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The signatures below indicate the following individuals have reviewed this document in its entirety and authorize its use to supersede prior revisions as of the effective date of this SOP.

Reviewed By:

Richard W Johnson

07/07/11

Richard Johnson, Senior Chemist — Date

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07/07/11

Michael Linskens, Quality Manager — Date

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07/07/11

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TESTAMERICA KNOXVILLE
SOP CHANGE FORM

SOP NUMBER: KNOX-ID-0013, Rev ~~10~~ 11 VMK 5/7/12
SOP TITLE: Analysis of Polychlorinated Biphenyl (PCB) Isomers by Isotope Dilution HRGC/HRMS
SOP SECTIONS AFFECTED BY CHANGE: Section 11.3.1
REASON FOR ADDITION OR CHANGE: To correct MID start time from 8 to 11 minutes
CHANGE EFFECTIVE FROM: 5/7/12
CHANGE OR ADDITION (SPECIFY SECTION; USE ADDITIONAL SHEETS IF NECESSARY) Section 11.3.1: Change MID start time form 8 to 11 minutes
SUBMITTED BY/DATE: Daniel [signature] 5-7-12
APPROVED BY:

[signature] **Technical Reviewer Signature**	5-7-12 **Date**
[signature] **Environmental Health & Safety Signature**	5-8-12 **Date**
[signature] **QA Signature**	5-8-12 **Date**
[signature] **Management Signature**	5/8/12 **Date**

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Analysis of Polychlorinated Biphenyl (PCB) Isomers by Isotope Dilution HRGC/HRMS

(SUPERSEDES: KNOX-ID-0013, Revision 10)

Prepared By: _____ 2-20-12

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1 Scope and Application

1.1 This procedure is designed to meet analytical program requirements where HRGC/HRMS analysis of polychlorinated biphenyl (PCB) isomers is specified. The procedure is used by TestAmerica Knoxville for the qualitative and quantitative measurement of all 209 PCB congeners in a variety of environmental matrices at part-per-trillion (ppt) to part-per-quadrillion (ppq) concentrations. This procedure is based on EPA method 1668A, 1668B and 1668C.

1.2 The compounds listed in Table 1 may be determined by this procedure. The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The estimated minimum levels (EMLs) in Table 4 are the levels at which the PCBs can be determined with only common laboratory interferences present. The actual limits of detection and quantitation will vary depending on the complexity of the matrix.

1.3 The Low Calibration Levels (LCLs) of the method are listed in Table 3 for individual congeners. Analysis of a one-tenth aliquot of the sample permits measurements of concentrations up to 10 times the upper calibration range. Samples containing concentrations of PCBs that are greater than ten times the upper calibration are analyzed by protocols designed for such concentration levels.

1.4 The GC/MS portions of this method are for use only by analysts experienced with HRGC/HRMS or under the close supervision of such qualified persons. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in section 9.1.

1.5 This procedure is a "performance-based" method. These reference methods allow modifications to overcome interferences or lower the cost of measurements, if all performance criteria in the methods are met and method equivalency is established. Deviations from the referenced methods have been incorporated into this procedure and are listed in section 17.1. Deviations to this procedure are only allowed as specified in section 11.1.

1.6 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCBs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2 Summary of Method

2.1 All solid, semi-solid and tissue samples are screened by GC/ECD prior to extraction. Aqueous samples may be screened if the potential for congener levels above 40 ng/L exists. Variations in sample size, spiking levels and final volume are established based on the screening result.

2.2 After sample extraction, cleanup, and concentration, recovery standards are added to each extract, and an aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high-resolution (≥10,000) mass spectrometer. Two exact masses are monitored for each analyte.

2.3 An individual PCB congener is identified by comparing the GC retention time and ion-abundance ratio of two exact masses with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact masses.

2.4 Quantitative analysis is performed using selected ion current profile (SICP) areas using the internal standard technique.

2.5 The quality of the analysis is assured through reproducible calibration and verification of the extraction, cleanup, and GC/MS systems.

3 Definitions

These definitions and purposes are specific to this method but conform to common usage as much as possible.

Note: Terminology differences existing in some isotope dilution reference methods regarding the functionality of the labeled analogs may lead to confusion. For example, EPA's Office of Solid Waste methods (8280, 8290) use the term "Internal Standards" to describe the labeled analogs which are added to the sample prior to extraction and used to quantitate the native targets. EPA's Office of Water methods (1613B, 1668) use the term "Labeled Analogs" to describe these same compounds while using the term "Internal Standards" to describe the labeled analogs which are added to the extract just prior to analysis and used to quantitate the recovery of the labeled analogs added before extraction. EPA's Office of Solid Waste methods (8280, 8290) uses the term "Recovery Standards" to describe these later labeled analogs.

The terminology conventions established by the EPA's Office of Solid Waste methods (8280, 8290) are used in the laboratory for all Standard Operating Procedures and internal communications as defined in this section.Analyte – A PCB tested for by this method. The analytes are listed in Table 1.

3.1 Calibration verification standard (VER) – The mid-point calibration standard (CS3) that is used to verify calibration. See Table 6a.

3.2 CB – Chlorinated biphenyl congener. One of the 209 individual chlorinated biphenyl congeners determined using this method. The 209 CBs are listed in Table 1.

3.3 Cleanup Standard – Isotopically labeled compounds that are added to samples, blanks, quality control samples, and calibration solutions. They are added to the samples after extraction but prior to extract cleanup, and are used to assess the efficiency of the cleanup procedures.

3.4 Congener – Any member of a particular homologous series, for example, 2,2'-DiCB.

3.5 CS0.5, CS1, CS2, CS3, CS4, CS5 – See Calibration standards and Table 6a.

3.6 Estimated Detection Limit (EDL) – The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level (noise level).

3.7 Estimated Maximum Possible Concentration (EMPC) – The calculated concentration of a signal having the same retention time as a PCB congener but which does not meet the other qualitative identification criteria defined in the method.

3.8 Estimated Minimum Level (EML) – The lowest concentration at which an analyte can be measured reliably with common laboratory interferences present. This is the reporting limit (RL)

3.9 Field blank – An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

3.10 GC – Gas chromatograph or gas chromatography.

3.11 Homologous Series – A series of compounds in which each member contains the same number of chlorine atoms. The members of the series are called homologs.

3.12 HRGC – High resolution GC.

3.13 HRMS – High resolution MS.

3.14 ICV – Initial Calibration Verification Standard. A calibration standard from a second source, traceable to a national standard if possible. The ICV is analyzed after the Initial calibration to verify the concentration of the initial calibration standards.

3.15 Internal Standards (IS) – Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the sample before extraction and are used to calculate the concentration of the target analytes or detection limits.

3.16 IPR (also known as IDOC)– Initial precision and recovery; four aliquots of the PAR standard analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed prior to the first time this method is used and any time the method or instrumentation undergoes significant modification.

3.17 Isomer – PCB congeners that contain the same number of chlorine atoms, but differ in the structural arrangement of the chlorine atoms. For example, PCB-4 and PCB-9 are isomers.

3.18 Laboratory blank – See Method blank.

3.19 Laboratory control sample (LCS) – See ongoing precision and recovery standard (OPR).

3.20 Laboratory reagent blank – See method blank.

3.21 Level of Chlorination (LOC) Congeners – The first and last eluting congeners in each homolog (or level of chlorination). (For the SPB-Octyl Column the LOC Congeners are 1, 3; 4, 15; 19, 37; 54, 77; 104, 126; 155, 169; 188, 189; 202, 205; 208, 206; 209)

3.22 Method blank – An aliquot of a clean test matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

3.23 Minimum Level (ML) – The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.24 Note: EML is the lowest concentration at which an analyte can be measured reliably with common laboratory interferences present

3.25 MS – Mass spectrometer or mass spectrometry.

3.26 OPR (also know as ODOC) – Ongoing precision and recovery standard (OPR); a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

3.27 PAR – Precision and recovery standard; secondary standard that is diluted and spiked to form the IPR and OPR.

3.28 PFK – Perfluorokerosene; the mixture of compounds used to calibrate the exact mass scale in the HRMS.

3.29 Primary dilution standard – A solution containing the specified analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

3.30 Quality control check sample (QCS) – A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

3.31 PCB – Polychlorinated biphenyl.

3.32 Reagent water – Water demonstrated to be free from the analytes of interest and potentially interfering substances at the method minimum level for the analyte.

3.33 Recovery Standard (RS) – Isotopically labeled compounds which are added to every sample, blank, and quality control spike sample extract prior to analysis. They are used to measure the recovery of the internal standards and the cleanup standards.

3.34 Relative Percent Difference (RPD) – A measure of the difference between two values normalized to one of the values. It is used to determine the accuracy of the concentration measurements of second source verification standards.

3.35 Relative standard deviation (RSD) – The standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

3.36 RF or RRF (Relative Response Factor) - The ratio of the response of the mass spectrometer to a known amount of a compound relative to that of a known amount of a reference standard as measured in the initial and continuing calibrations. It is used to determine instrument

performance and it is used to calculate the concentration of target analytes, internal standard recoveries, or detection limits in samples, blanks, and quality control samples. See Section 10.3.4.2.

3.37 SICP – Selected ion current profile.

3.38 SPE – Solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

3.39 Specificity – The ability to measure an analyte of interest in the presence of interferences and other analytes of interest encountered in a sample.

3.40 Stock solution - A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

3.41 Surrogate Standards (SS) - Isotopically labeled compounds that are added to XAD samples and calibration solution. They are added to XAD sampling tubes before sampling and are used to measure sampling and recovery efficiency.

3.42 Toxic Congeners (or Toxic Isomers) – PCBs determined by the World Health Organization and USEPA to have dioxin-like toxicity. (PCBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189)

3.43 Toxic/LOC Congeners – PCBs belonging to either the Toxic Congeners list or the LOC Congeners list.

3.44 VER – See Calibration verification standard.

3.45 Additional definitions can be found in the TestAmerica Knoxville Quality Assurance Manual (QAM), current revision.

4 Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. Where possible, glassware is cleaned by extraction or solvent rinse. The non-coplanar PCB congeners 105, 114, 118, 123, 156, 157, 167, and 180 have been shown to be very difficult to completely eliminate from the laboratory at the minimum levels in this method, and baking of glassware in a kiln or furnace at 450 - 500°C may be necessary to remove these and other contaminants.

4.2 All materials used in the analysis shall be demonstrated to be free from interferences by running laboratory method blanks (section 9.5) initially and with each sample batch.

4.3 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the PCBs. The most frequently encountered interferences are chlorinated dioxins and dibenzofurans, methoxy biphenyls, hydroxy-diphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides. Because

very low levels of PCBs are measured by this method, the elimination of interferences is essential. Cleanup steps can be used to reduce or eliminate these interferences and thereby permit reliable determination of the PCBs at the levels shown in Table 3.

5 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately.

5.3 The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.4 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them or use thermal protection when working on them while they are above room temperature.

5.5 The mass spectrometer is under high vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source. Alternatively, the source may be removed from the vacuum manifold through a vacuum interlock.

5.6 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power. If the work involved requires measurement of voltage supplies, the instrument may be left on.

5.7 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen, Irritant	25 ppm-TWA, 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Hexane	Flammable, Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable, Poison, Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Toluene	Flammable, Poison, Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Nonane	Flammable	None established	Harmful if inhaled/swallowed. Vapor/mist is irritating to eyes, mucous memebranes and upper respiratory tract. Causes skin irritiation.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.8 Chemicals that have been classified as **carcinogens**, **potential carcinogens**, or **mutagens include**: methylene chloride, polychlorinated biphenyls, and toluene. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.)

5.9 Chemicals known to be **flammable** are: acetone, hexane, nonane and toluene.

5.10 Exposure to chemicals will be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.11 The preparation of all standards will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.12 Personal Hygiene: Thorough washing of hands and forearms is recommended after each manipulation and before breaks (coffee, lunch, and shifts).

5.13 Confinement: Work areas should be isolated and posted with signs. Glassware and tools should be segregated. Bench tops should be covered with plastic backed absorbent paper.

5.14 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

5.15 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

5.16 All work must be stopped in the event of a known or potential compromise to the health or safety of laboratory personnel. The situation must be reported immediately to a laboratory supervisor.

6 Equipment and Supplies

6.1 Gas chromatograph - Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specifications in Section 10.

6.1.1 Column #1 – 30±5-m long x 0.25±0.02-mm ID; 0.25-µm film SPB-Octyl (Supelco 2-4218, or equivalent).

6.2 Mass spectrometer - Electron impact ionization, shall be capable of repetitively selectively monitoring 20 exact masses minimum at high resolution (≥10,000) during a period less than 1.0 second, and shall meet all of the performance specifications in Section 10.

6.3 GC/MS interface - The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams.

6.4 Data system - Capable of collecting, recording, and storing MS data.

7 Reagents and Standards

CAUTION: Refer to Material Safety Data Sheets (MSDS) for specific safety information on chemicals and reagents prior to use or as needed.

CAUTION: During preparation of reagents, associates shall wear lab coat, gloves, safety glasses with side shields, and laboratory approved shoes as a minimum. Reagents shall be prepared in a fume hood.

7.1 Solvents - Acetone, toluene, n-hexane, methanol, methylene chloride, and nonane; pesticide quality.

7.2 Perfluorokerosene (PFK) high boiling mass spectroscopy grade; bp 210-260°C; d^{20}_4 1.94; n^{20}_D 1.330; Fluka (Catalog No. - 77275).

7.3 $^{13}C_{12}$ Labeled PCB Congener Standards: Obtained as individual Certified Reference Standards from Cambridge Isotope Laboratories (CIL, Andover Massachusetts) and Wellington Laboratories (Guelph, Ontario, Canada). (Refer to Table 5b for a list of individual standards.) These standards are purchased at 40 µg/mL or 50 µg/mL in nonane. If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. Once a standard ampoule has been vortexed and opened, the solution is transferred to an amber glass vial with a Teflon®-lined screw cap. When not being used, standards are stored in a dark box at room temperature. These purchased standards are used to prepare the following mixed stock solutions and spiking solutions:

7.3.1 Internal Standard Stock Solution: Prepared by diluting the individual $^{13}C_{12}$ labeled internal standards listed in Table 5b, to a concentration of 1000 ng/mL in nonane. The concentration is verified by GC/MS before use.

7.3.2 Internal Standard Spiking Solution: Prepared by diluting the 1000 ng/mL internal standard stock solution to a concentration of 10 ng/mL in acetone. One to 4.0 mL of this solution is added to each solid/tissue sample prior to extraction. Refer to Table 12, "Assignment of Sample Preparation Protocols" to determine the exact volume to add. Twenty uL of the internal standard spiking solution is added to each aqueous sample prior to extraction.

7.3.3 Recovery Standard Stock Solution: Prepared by diluting the individual $^{13}C_{12}$ labeled recovery standards listed in Table 5b to a concentration of 1000 ng/mL in nonane. The concentration is verified by GC/MS before use.

7.3.4 Recovery Standard Spiking Solution: Prepared by diluting the 1000 ng/mL recovery standard stock solution to a concentration of 100 ng/mL in nonane. Fifty to 100 µL of this spiking solution is added to each solid/tissue sample extract prior to analysis (refer to Table 12), whereas, 20 µL is added to each aqueous sample extract.

7.3.5 Cleanup Standard Stock Solution: Prepared by diluting the individual $^{13}C_{12}$ labeled cleanup standards listed in Table 5b, to a concentration of 5000 ng/mL in

nonane. The concentration is verified by GC/MS before use.

7.3.6 Cleanup Standard Spiking Solution: Prepared by diluting the 5000 ng/mL cleanup standard stock solution to a concentration of 10 ng/mL in hexane. One half to 1.0 mL of this solution is added to each solid/tissue sample extract prior to cleanup (refer to Table 12), whereas, 0.20 mL is added to each aqueous sample extract.

7.3.7 Sampling Surrogate Standard Stock Solution: Prepared by diluting the individual $^{13}C_{12}$ labeled sampling surrogate standards listed in Table 5b to a concentration of 5000 ng/mL in nonane. The concentration is verified by GC/MS before use.

7.3.8 Sampling Surrogate Spiking Solution: Prepared by diluting the 5000 ng/mL sampling surrogate stock solution to a concentration of 50 ng/mL in nonane.

7.4 Native PCB Congener Standard Mix: Obtained as a Certified Reference Standard from Accustandard (New Haven, CT). This standard contains all 209 PCB congeners at 4000 ng/mL in nonane. If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. Once a standard ampoule has been vortexed and opened, the solution is transferred to an amber glass vial with a Teflon®-lined screw cap. When not being used, the standard is stored in a dark box at room temperature. This purchased standard is used to prepare the following native stock solution and spiking solution:

7.4.1 Native PCB Congener Stock Solution: Prepared by diluting the 4000 ng/mL native PCB congener standard mix to a concentration of 40 ng/mL in nonane. The concentration is verified by GC/MS before use.

7.4.2 LCS Spiking Solution: Prepared by diluting the 4000 ng/mL native PCB congener standard to a concentration of 5.0 ng/mL in acetone. One mL of this solution is added to each solid/tissue LCS prior to extraction, whereas, 0.20 mL is added to each aqueous LCS.

7.5 Calibration Standard Solutions (CS 0.5 through CS 5) are prepared by dilution of the native PCB congener standards in section 7.4 and 7.4.1 and the labeled standards in section 7.3 in nonane. Table 6a shows the calibration solution analytes and final concentrations. Table 6b provides details for preparation of these calibration solutions.

7.5.1 This series of solutions is used to establish linearity and relative response factors for all compounds in the initial calibration solutions. These RRFs are used to quantify PCB congeners in the calibration verification (VER) and all samples. The CS3 standard is used for calibration verification. The VER solution is also used to verify chromatographic performance.

7.6 PCB Congener Mix 1 through 5 standard solutions containing all 209 isomers are Certified Reference Standards (Accustandard Product No's. M-1668A-1, M-1668A-2, M-1668A-3, M-1668A-4, M-1668A-5). Stock solutions are purchased at 250-750 µg/mL in isooctane. Once the ampoule has been sonicated and opened, the solution is transferred to an amber glass vial with Teflon®-lined cap and is used as received. These five mixes are run in triplicate to determine the retention times for each of the congeners and which congeners will co-elute for each new SPB Octyl column used.

7.6.1 209 PCB ICAL Verification stock solution: Prepared by combining the five PCB Congener Mixes referred to in section 7.6 and diluting to a concentration of 5000-15000 ng/mL in nonane.

7.6.2 Initial Calibration Verification Standard. This is a single solution containing all 209 individual PCBs as well as internal standards and recovery standards at the following concentrations:

- mono, di, and tri CBs at 50 ng/mL
- tetra, penta, hexa and hepta CBs at 100 ng/mL
- octa, nona, and deca CBs at 150 ng/mL
- internal standards and recovery standards are at the same concentration as the calibration standards (CS 0.5 – CS 5).

This solution is always analyzed immediately after the initial calibration.

7.6.2.1 Combine 100 uL of 209 PCB ICAL verification stock solution (Section 7.6.1) (equivalent to 20 uL of each mix) with 100 uL of the 1000 ng/mL $^{13}C_{12}$ labeled internal standard stock solution, 100 uL of a 1/10 dilution of the 5000 ng/mL $^{13}C_{12}$ labeled cleanup standard stock solution, 100 uL of the 1000 ng/mL $^{13}C_{12}$ labeled recovery standard stock solution and 600 uL of nonane to produce the concentrations listed in section 7.6.2.

7.6.3 Retention Time Calibration Mixes: These are 5 solutions injected in triplicate to establish the retention time data referenced in section 10.2.3. Combine 20 uL of the Accustandard PCB Congener Mix 1 (Section 7.6) with 100 uL of the 1000 ng/mL $^{13}C_{12}$ labeled internal standard stock solution, 100 uL of a 1/10 dilution of the 5000 ng/mL $^{13}C_{12}$ labeled cleanup standard stock solution, 100 uL of the 1000 ng/mL $^{13}C_{12}$ labeled recovery standard stock solution and 600 uL of nonane to produce the concentrations listed in section 7.6.2. Repeat the process using the Accustandard PCB Congener Mixes 2 through 5.

7.7 QC Check Sample - A QC Check Sample should be obtained from a source independent of the calibration standards. This check sample is a certified standard reference material (SRM) containing the PCBs in known concentrations in a sample matrix similar to the matrix under test. The National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland has an SRM 1944 – New York/New Jersey Waterway Sediment that the NYSDEC recommends for use.

8 Sample Collection, Preservation and Storage

8.1 Sampling is not performed for this method by TestAmerica Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, “Sample Receipt and Login”, current revision.

8.2 Holding Times

8.2.1 Store sample extracts in a dark box at room temperature until analyzed. If stored in the dark at room temperature, sample extracts may be stored for up to one year.

9 Quality Control

9.1 Initial precision and recovery (IPR) or initial demonstration of capabilty (IDOC) samples are analyzed to demonstrate the ability to generate acceptable precision and accuracy.

9.1.1 For aqueous samples, extract, clean, concentrate, and analyze four 1-L aliquots of reagent water spiked with internal standards, cleanup standard, recovery standard and the LCS spiking solution, according to the procedures in section 11. For solid/tissue samples, extract, clean, concentrate, and analyze four aliquots of sodium sulfate/corn oil spiked with internal standards, cleanup standard, recovery standard and the LCS spiking solution, according to the procedures in section 11. All steps that are to be used for processing samples, including preparation, extraction and cleanup, shall be included in this test.

9.1.2 Using the results of the set of four analyses, compute the average percent recovery (%R) of the extracts and the relative standard deviation (%RSD) of the concentration in ng/L (aqueous) and ng/g (solid) for each compound.

9.1.3 For each PCB and labeled compound, compare the %RSD and %R with the corresponding limits for initial precision and recovery in the appropriate Table 10A or 10B. If the RSD and %R for all compounds meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, any individual %RSD exceeds the precision limit or any individual %R falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test.

9.2 Internal Standards

9.2.1 Every sample, blank, and QC sample is spiked with internal standards. Internal standard recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. When properly applied, results from isotope dilution techniques are independent of recovery. The recovery of each internal standard should be within the limits in Table 10A or 10B depending on the method revision being used. If the recovery is outside these limits the following corrective action should be taken:

- Check all calculations for error.
- Ensure that instrument performance is acceptable; if applicable, a daily CCV will be analyzed to confirm instrument performance.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- If the recovery of any internal standard is less than the limits indicated in Tables 10A and 10B, calculate the S/N ratio of the internal standard. If the S/N is > 10 and the estimated detection limits (EDLs) are less than the estimated minimum levels

(EMLs), report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the estimated detection limits (EDLs) are greater than the estimated minimum levels (EMLs), re-extract and reanalyze the sample. If the ion chromatogram of the PFK lock mass indicates ion suppression in the region where the internal standard elutes, reanalyzing the extract at up to a 1/10 dilution may improve the internal standard recovery. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample may be re-extracted or additional cleanups may be employed. The decision to reanalyze or flag the data should be made in consultation with the client.

9.2.2 Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.3 Cleanup Standards: Every sample, blank, and QC sample extract is spiked with $^{13}C_{12}$ labeled cleanup standards after extraction but prior to extract cleanup. They are used to assess the efficiency of the cleanup procedures.

9.4 Recovery Standards: Every sample, blank, and QC sample extract is spiked with $^{13}C_{12}$ labeled recovery standards prior to analysis. They are used to measure the recovery of the internal standards and the cleanup standards.

9.5 Method Blanks

9.5.1 A laboratory method blank must be run along with each analytical batch of 20 or fewer samples. The method blank consists of reagent water for aqueous samples, sodium sulfate for solid and tissue samples, processed in the same manner and at the same time as the associated samples. The method blank is used to identify any background interference or contamination of the analytical system that may lead to the reporting of elevated concentration levels or false positive data. Analyze the blank immediately after analysis of the LCS to demonstrate freedom from contamination. The method blank should not contain any of the compounds of interest at a concentration above the estimated minimum level (EML) shown in Table 4.

9.5.2 Corrective action is required when compounds of interest are detected in the method blank above the EML. Corrective action may include reanalysis of the method blank. Contact the Project Manager to determine further corrective action. At a minimum, all associated results are qualified with a B flag. Re-extraction and reanalysis of all samples associated with a contaminated method blank is required if requested by the client or Project Manager. Investigation of the source of the method blank contamination will be initiated before further samples are extracted.

9.5.3 The method blank must have acceptable internal standard recoveries. If internal standard recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If internal standard recoveries are low and there are reportable analytes in the associated samples, re-extraction of the blank and affected samples

will normally be required. Consultation with the client should take place.

9.5.4 Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.6 Instrument Blank

9.6.1 Instruments must be evaluated for contamination during each 12-hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed.

9.6.2 An instrument blank consists of solvent with the internal standards and recovery standards added. It is evaluated in the same way as the method blank.

9.7 Laboratory Control Sample – A laboratory control sample (LCS) is prepared and analyzed with every batch of 20 or fewer samples. All analytes must be within established control limits specified in the appropriate Table 10A or 10B. The LCS is spiked with the compounds listed in Table 5a.

9.7.1 If any analyte in the LCS is outside the control limits, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report.
- If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported and the failure is documented in the project narrative.

9.8 QC Check Sample - Analyze the QC Check Sample (section 7.7) periodically to assure the accuracy of calibration standards and the overall reliability of the analytical process. It is suggested that the QC Check Sample be analyzed at least annually.

10 Calibration and Standardization

10.1 Three types of calibration procedures are required. The first type establishes retention times, relative retention times and relative retention time windows to be used during the subsequent calibrations and analyses. The second type, initial calibration, is required to establish response factors and is required before any samples are analyzed. It may be required intermittently throughout sample analyses as dictated by the results of continuing calibration procedures described below. The third type, continuing calibration, consists of analyzing the continuing calibration verification solution (VER). No samples are to be analyzed until acceptable calibration as described in sections 10.2, 10.3 and 10.4 is demonstrated and documented.

10.2 Retention Time Calibration

Retention time calibration is required if the retention time criteria cannot be met.

10.2.1 The absolute retention time of CB 209 must exceed 55 minutes. Otherwise the GC temperature program must be adjusted and the test repeated until the requirement is met.

10.2.2 **NOTE**: When adjusting chromatographic conditions, the resolution requirements of sections 10.4.5.8 to 10.4.5.9 must be maintained.

10.2.3 Tune the instrument to meet the mass resolution and mass accuracy requirements of section 10.3.2. Document the resolution and accuracy.

10.2.4 Analyze 2µL of each of the five individual PCB mixtures (section 7.6.3). Repeat the series twice more in succession to provide 3 runs of each mix. It is not necessary to interrupt this analytical sequence to perform a 12-hour resolution check. Set the switch-points for the MID descriptors. The switch-points must be set to insure that the first and last eluting isomer of each homolog group and the labeled internal standards are acquired properly. Determine the average retention time of each PCB congener using the elution order information in Table 11.

NOTE 1: PCB Mixture 5 (M-1668A-5) contains the first and last eluting isomer in each homolog group for the SPB-Octyl column (see Table 7).

NOTE 2: Laboratory data has indicated that the SPB-Octyl column can exhibit significant differences in performance from column to column. It has also been indicated that the column's performance can change significantly due to oxidation with subsequent changes in congener retention times and elution order. The individual PCB mixtures should be analyzed whenever the column's performance or specific congeners retention times are in doubt.

10.2.5 Calculate the relative retention times for all native and labeled congeners, using their retention time references from Table 2 (RT Ref). Calculate the relative retention time for each run in which the congener and its retention time reference are present (i.e., three RRTs will be calculated for each native congener. Fifteen RRTs will be calculated for each internal standard.) Use the calculated average retention times for all native and labeled congeners as the RT calibration source in the calculation software.

10.2.6 Calculate the relative retention time window using the absolute retention time windows (RT Window) from Table 2.

$$\text{RRT Limit Low} = \frac{RT_A - (RT_{WIN}/2)}{RT_{IS}}$$

$$\text{RRT Limit High} = \frac{RT_A + (RT_{WIN}/2)}{RT_{IS}}$$

Where:

RT_A = Average retention time of analyte.

RT_{IS} = Average retention time of RT reference.

RT_{WIN} = Absolute RT window in seconds from Table 2.

10.2.7 A single pair of RRT limits is used for all congeners in coeluting set. Use the

RRT Limit Low that was calculated for the first eluting congener, and the RRT Limit High calculated for the last eluting congener (in the coelution set).

10.3 Initial Calibration

Initial calibration is required before any samples are analyzed for PCBs. Initial calibration is also required if any continuing calibration (section 10.4) does not meet the required criteria in section 10.4.5 after routine maintenance.

10.3.1 Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 6a. Calibration standards should be stored at room temperature and preferably in amber vials. Calibration standard solutions have an expiration date of ten (10) years from date of receipt based on stability of PCBs and history of vendor's recertification of standard lots.

10.3.2 Establish operating parameters for the GC/MS system (suggested operating conditions are displayed in Figure 1 and Figure 2). By using a PFK molecular leak, tune the instrument (see the appropriate instrument manufacturer's operating manual for tuning instructions) to meet the minimum resolving power of 10,000 (10 percent valley) at mass 342.97924 (PFK). For each MID descriptor group, monitor and record the mass resolution and exact masses of three reference peaks covering the mass range of the descriptor (see below). By using peak matching techniques, verify that the deviation between the exact mass and the theoretical mass for each mass monitored is less than 5 ppm. Iteratively adjust operating parameters and tuning values until the mass resolution and mass accuracy criteria are met for each ion. Document the mass resolution and mass accuracy for each of MID group ion sets. Because of the extensive mass range covered in each MID group, it may not be possible to maintain 10,000 resolution throughout the mass range of the MID group. Therefore, resolution must be greater than 8,000 throughout the mass range and must be greater than 10,000 in the center of the mass range for each MID group. The minimum resolution of 10,000 must be met for mass 342.97924.

MID Group 1 PFK ions - 192.9888, 230.98563, 280.98243
MID Group 2 PFK ions - 268.98243, 292.98243, 380.97605
MID Group 3 PFK ions - 342.97924, 380.97605, 430.97285
MID Group 4 PFK ions - 404.97604, 442.97285, 530.96646

10.3.3 Inject a 2 µL aliquot of the CS 0.5 calibration solution.

10.3.3.1 Ion abundance ratios, minimum levels, and signal-to-noise ratios.

10.3.3.1.1 Measure the SICP areas for each congener or congener group, and compute the ion abundance ratios at the exact masses specified in Table 8. Compare the computed ratio to the theoretical ratio given in Table 9.

10.3.3.1.2 All Toxic/LOC and labeled compounds in the CS-0.5 standard must be within the QC limits in Table 9 for their respective

ion abundance ratios; otherwise, the mass spectrometer must be adjusted and this test repeated until the mass ratios fall within the limits specified. If the adjustment alters the resolution of the mass spectrometer, resolution must be verified (Section 10.3.2) prior to repeat of the test.

10.3.3.1.3 The peaks representing the CBs and labeled compounds in the CS-0.5 calibration standard must have signal-to-noise ratios (S/N) ≥ 10; otherwise, the mass spectrometer must be adjusted and this test repeated until the signal to noise criteria are met.

10.3.3.1.4 An exception to the ion abundance ratio and signal to noise ratio requirements is the secondary ion for dichlorinated biphenyls (mass 223.9974). High background from PFK fragments at 223.9974 results in noise levels which exceed 10% of the signal height at levels that are reliably quantifiable.

10.3.4 Analyze 2 µL of each of the other calibration standards.

10.3.4.1 Isomer specificity

10.3.4.1.1 Use the CS-3 calibration standard to evaluate column performance. The toxic isomers must be uniquely resolved from all other congeners. Isomers may be unresolved so long as they have the same toxicity equivalency factor (TEF) and response factor and so long as these unresolved isomers are uniquely resolved from all other congeners. For example, the SPB-Octyl column achieves unique GC resolution of all Toxics except congeners with IUPAC numbers 156 and 157. This isomeric pair is uniquely resolved from all other congeners and these congeners have the same TEF and response factor.

10.3.4.1.2 Evaluate and document the percent valley between PCBs 34 and 23. The valley height must be less than 40 percent of the height of the shorter of the two peaks.

10.3.4.1.3 Evaluate and document the percent valley between PCBs 187 and 182. The valley height must be less than 40 percent of the height of the shorter of the two peaks.

10.3.4.1.4 Classify each congener as resolved or as a member of a coelution set. To be documented as resolved, the valleys between any two isomers must be less than 40 percent of the height of the shorter of the two adjacent peaks. Each member of a coelution set is designated with a qualifier in the format of CXXX, where XXX = the lowest numbered congener in the

set. For example, if PCB 156 and PCB 157 coelute, qualify PCB 157 with "C156".

10.3.4.2 Calculate the RRF of each compound of interest (target analytes, coelution sets, internal standards, cleanup standards, and surrogate standards) vs. the appropriate reference standard (as specified in Table 2) using the following equation:

$$RRF = \frac{As \times Cis}{Ais \times Cs}$$

Where:

As = sum of the areas of the quantitation ions of the compound of interest.
Ais = sum of the areas of the quantitation ions of the appropriate reference standard.
Cis = concentration of the appropriate reference standard.
Cs = concentration of the compound of interest.

NOTE: When calculating the RRF for a coelution set, sum the areas of all isomers in the set. Use the resulting RRF for all congeners within the set.

10.3.4.3 Calculate the mean relative response factor (mean RRF) and the percent relative standard deviation (%RSD) of the response factors for each compound of interest in the six calibration standard solutions using the following equations:

$$\overline{RRF}_{n=6} = \frac{1}{n} \times \sum_{i=1}^{n} RF_i$$

$$\%RSD_{n=6} = \sqrt{\frac{\sum_{i=1}^{n} \left(RF_i - \overline{RRF}\right)^2}{n-1}} \times \frac{100}{\overline{RRF}}$$

10.3.4.4 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met before sample analyses are performed. If acceptable initial calibration is not achieved, identify the root cause, perform corrective action, and repeat the initial calibration. If the root cause can be traced to problems with an individual analysis within the calibration series, repeat the individual analysis and recalculate the percent relative standard deviation. If the calibration is acceptable, document the problem and proceed, otherwise repeat the initial calibration.

10.3.4.5 The percent relative standard deviation (%RSD) for the mean relative response factors for the unlabeled native analytes calculated by isotope dilution must not exceed 20 percent. The percent RSD for the mean relative response factors for the unlabeled native analytes calculated by internal standard must not exceed 35 percent. The percent RSD for the mean relative response factors for the labeled standards must not exceed 35

percent.

10.3.5 Analyze 2µL of the Initial Calibration Verification (ICV) Standard in section 7.6.2 after completion of the ICAL prior to sample analysis. Calculate the concentration of the ICV using the RRFs from the CS-3 standard analyzed in section 10.3.4. Calculate the percent difference (%D) between the expected and the calculated ICV concentration using the following formula:

$$\%D = \frac{(C_{Exp} - C_{Calc})}{C_{Exp}} \times 100$$

Where:
C_{Exp} = The expected concentration of the ICV Standard.
C_{Calc} = The calculated concentration of the ICV Standard.

10.3.5.1 The criteria for acceptance of the ICV Standard are as follows:

- The %D may not exceed ±35% for more than 4 of the native and labeled compounds.
- The %D may not exceed ±50% for any native or labeled compound.

10.3.5.2 All data associated with compounds with percent differences exceeding ±35% must be reviewed before acceptance and shall be documented as a NCM. In addition, all data associated with these compounds require corrective action that may include the following:

- Reanalyze the ICV Standard.
- Replace and reanalyze the ICV Standard.
- Evaluate the instrument performance.
- Evaluate the Initial Calibration Standards.

10.4 Continuing Calibration

10.4.1 Continuing calibration is performed at the beginning of a 12-hour period after successful mass resolution check.

10.4.2 Document the mass resolution performance as specified in section 10.3.2 at both the beginning and end of the 12-hour period.

10.4.3 Analyze 2 µL of the Continuing Calibration Verification Standard (VER/CS3). Calculate the concentration (C) of the compounds of interest (target analytes, internal standards, cleanup standards, and surrogate standards) vs. the appropriate quantitation reference (as specified in Table 2) using the following equation:

$$C = \frac{As \times Cis}{Ais \times RRF}$$

Where:

As = sum of the areas of the quantitation ions of the compound of interest.
Ais = sum of the areas of the quantitation ions of the appropriate reference standard.
Cis = concentration of the appropriate reference standard.
RRF = mean relative response factor from section 10.3.4.2.

10.4.4 Calculate the concentrations as percentages of the test concentrations and compare them to the limits specified in the appropriate Table 10A or 10B using the following equation:

$$C_{ver}\% = \frac{C_{ver}}{C_{test}} \times 100$$

Where:

C_{ver} = the concentration of the VER standard calculated in section 10.4.3
C_{test} = the test concentration of the VER standard listed in Table 6a.

10.4.5 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met before sample analyses are performed. If the acceptance criteria are met, the calibration is deemed to be in control and the RRFs generated from the initial calibration are used to quantify samples. If acceptable calibration is not achieved, identify the root cause, perform corrective action, and repeat the continuing calibration. If a second consecutive attempt at a continuing calibration fails, two consecutive calibrations must meet the criteria, or an initial calibration must be run before proceeding with client samples.

10.4.5.1 The ion abundance ratios of the peaks representing the Toxics/LOCs and labeled standards must be within the control limits specified in Table 9.

10.4.5.2 The S/N for the GC signals present in every SICP (including those for labeled standards) must be ≥ 10.

10.4.5.3 For Toxic and LOC congeners, as listed in the first section of Table 10A or 10B, the percent of the calculated concentration relative to the test concentration must be within 70-130% for 1668A and 1668B and 75-125% for 1668C.

10.4.5.4 For non-Toxic congeners the calculated concentrations must be within 70-130% of the test concentrations for 1668A. 1668B and 1668C.

10.4.5.5 The absolute retention times (RT) of the labeled internal standards must be within ±15 seconds of the retention times obtained during initial calibration.

10.4.5.6 The relative retention times (RRT) of the Toxics/LOC congeners must be within their respective RRT limits generated in the retention time calibration in section 10.2.

10.4.5.6.1 If the RRTs or RTs are not within the limits above, the GC may not be performing properly. However, routine column maintenance may include removing short amounts of the

beginning of the column when active sites or non-volatile compounds in sample extracts cause poor chromatography and loss of specificity. Shortening of the column can cause the RRTs or RTs to fall outside the above limits.

10.4.5.6.2 When the RRT of any compound or the RT of any internal standard is not within the above limits, corrective action must be taken. If the GC is not performing properly, correct the problem and repeat the test. If the GC is performing properly but the RRTs or RTs have changed due to routine column maintenance, adjust the GC or replace the GC column, then repeat the test or repeat the retention time calibration.

10.4.5.7 Evaluate and document the percent valley between PCBs 34 and 23. The valley height must be less than 40 percent of the height of the shorter of the two peaks.

10.4.5.8 Evaluate and document the percent valley between PCBs 187 and 182. The valley height must be less than 40 percent of the height of the shorter of the two peaks.

10.4.6 Daily calibration must be performed every 12 hours of instrument operation. The 12-hour shift begins with the documentation of the mass resolution followed by the injection of the Continuing Calibration Standard (VER).

11 Procedure

11.1 One time procedural variations are allowed only if deemed necessary in the professional judgement of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variations in the procedure, except those specified by project specific instructions, shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager, and QA Manager. If contractually required, the client shall be notified.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.2 Sample Extraction and Cleanup

The extraction and cleanup procedures are described in SOP KNOX-OP-0021, "Extraction of Polychlorinated Biphenyl (PCB) Isomers for Analysis by Isotope Dilution HRGC/HRMS", current revision.

11.3 Sample Analysis

11.3.1 Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 2 µL into the GC/MS and acquire data beginning at 8 minutes and ending after decachlorobiphenyl has eluted from the column.

11.3.2 Record analysis information in the instrument logbook. The following

information is required:

- Date of analysis
- Time of analysis
- Instrument data system filename
- Analyst
- Lab sample identification

Additional information may be recorded in the logbook if necessary.

11.3.3 Generate integrated ion chromatograms for the masses listed in Table 8 that encompass the expected retention windows of the PCB homologous series.

11.3.4 Generate a reduced peak list file from the integrations shown in the ion chromatograms.

11.3.5 Load the reduced peak list file into the calculation software.

11.3.6 The RTs of the unambiguous labeled congeners (RT Markers) are used to calculate a least squares best fit regression for retention times compared to those of the retention time calibration.

11.3.7 The resulting regression is used to calculate predicted retention times for target analytes. These predicted retention times are used by the software to identify candidate peaks for targets.

11.3.8 The analyst reviews the peaks identified as targets and determines whether to accept the identification. This determination is made by evaluating the delta values (RT shift from predicted), knowledge of peak patterns and observations of localized shifting.

11.3.9 A RRT window is calculated by multiplying the RRT Limit High and the RRT Limit Low by the retention time of the designated RT reference. The software applies a qualitative flag to each peak identified as a target that has a RRT outside the RRT window.

11.4 HRGC/HRMS Troubleshooting Guide

11.4.1 Perform the instrument's leak check: Evaluate the air spectrum. Mass 28 should be less than 5 times mass 69. If the air spectrum is not acceptable, replace transfer line ferrule and/or pump out PFK reservoir.

11.4.2 Check the voltage on the 5V power supply: If voltage is not reading 5V, adjust voltage to read 5V.

11.4.3 Check daily calibration standard: Evaluate the signal to noise (S/N), examine peak shape/chromatography, and evaluate response factors. Refer to specific SOP's requirements and acceptance criteria for all natives and internal standards. If daily calibration is not acceptable , perform the following troubleshooting options as needed and reanalyze a daily CS-3 calibration standard:

- Replace the inlet seal and clean the injection port body with methanol to improve response factor.
- Perform column/injector port maintenance and/or retune the instrument to resolve chromatography/resolution, signal to noise issues.
- Perform a gain test on the electron multiplier.
- Adjust the tuning parameters of the instrumentation to achieve optimum sensitivity and peak shape.
- Evaluate carryover from sample analyses. If carryover or contamination is suspected, run solvent rinses (nonane) under MID to evaluate the contamination.
- When troubleshooting cannot resolve an instrument problem, a manufacture's service engineer may be consulted for possible solution, or called onsite for diagnosis/repair.

11.5 Refer to the TestAmerica Knoxville Quality Assurance Manual, KX-QAM, current revision for the HRGC/HRMS instrument equipment maintenance table.

11.6 Refer to TestAmerica Knoxville SOP KNOX-IT-0001, current revision for requirements for computer hardware and software.

12 Data Analysis and Calculations

12.1 Qualitative Identification Criteria for PCBs

For a gas chromatographic peak to be identified as a PCB, it must meet all of the following criteria:

12.1.1 The signals for the two exact masses in Table 8 must be present and must maximize within ±2 seconds.

12.1.2 The signal to noise ratio (S/N) for each GC peak at each exact mass must be greater than or equal to (≥) 2.5. (This requirement does not apply to the secondary ion for dichlorinated biphenyls [mass 223.9974]). High background from PFK fragments at 223.9974 results in noise levels which exceed 10% of the signal height at levels that are reliably quantifiable.

12.1.3 The ratio of the integrated areas of the two exact masses specified in Table 8 must be within the limits in Table 9 . Alternately, the ratios may be within ±15% of the ratio in the midpoint (CS-3) calibration or calibration verification (VER), whichever is most recent.

12.1.4 The relative retention time of the peak for a CB must be within the RRT QC limits calculated in section 10.2.5.

NOTE: For native CBs determined by internal standard quantitation, a given CB congener may fall within more than one RT window and be misidentified unless the

RRT windows are made very narrow, as in Table 2. Therefore, consistency of the RT and RRT with other congeners and the labeled compounds may be required for rigorous congener identification. Retention time regression analysis may be employed for this purpose.

12.1.5 If identification is ambiguous, (i.e., some, but not all of the identification criteria are met for a congener) an experienced analyst must determine the presence or absence of the congener.

12.2 Quantitation for PCBs

12.2.1 Calculate the Internal Standard Recoveries (Ris) relative to the Recovery Standard according to the following equation:

$$Ris = \frac{Ais \times Qrs}{Ars \times RRFis \times Qis} \times 100\%$$

Where:

Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Ars = sum of the areas of the quantitation ions of the recovery standard
Qrs = ng of recovery standard added to extract
Qis = ng of internal standard added to sample
RRFis = mean relative response factor of internal standard obtained during initial calibration

NOTE: In some situations, such as source testing, the extract is split for multiple analyses. In this case, Qrs must be correctly calculated to account for the splitting of extracts before the recovery standard was added.

$$Qrs = Qrss \times Split$$

Where:

Qrs = ng of recovery standard added to extract
Qrss= ng of recovery standard added to the split portion of the extract
Split= split ratio of the extract

12.2.2 Calculate the concentration of individual PCBs according to the following equation:

$$Concentration = \frac{As \times Qis}{Ais \times RRF \times W \times S}$$

Where:

As = sum of the areas of the quantitation ions of the compound of interest
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor of compound obtained during initial calibration
W = amount of sample extracted (grams or liters)

S = decimal expression of solids (optional, if results are requested to be reported on dry weight basis)

12.2.3 If reporting results for Total Homolog Groups, calculate the total concentration of all isomers within each homolog group by summing the concentrations of the individual PCB isomers within that homolog group.

12.2.4 If no peaks are present in the region of the ion chromatogram where the compounds of interest are expected to elute, calculate the estimated detection limit (EDL) for that compound according to the following equation:

$$EDL = \frac{N \times 2.5 \times Qis}{His \times RRF \times W \times S}$$

Where:

N = sum of peak to peak noise of quantitation ion signals in the region of the ion chromatogram where the compound of interest is expected to elute
His = sum of peak heights of quantitation ions for appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor of compound obtained during initial calibration
W = amount of sample extracted (grams or liters)
S = decimal expression of solids (optional, if results are requested to be reported on dry weight basis.

Note: do not use **S** if results are to be reported by QuantIMS since it performs all necessary moisture corrections.)

12.2.5 If peaks are present in the region of the ion chromatogram which do not meet the qualitative criteria listed in section 12.1, calculate an Estimated Maximum Possible Concentration (EMPC). Use the equation in section 12.2.2, except that "As" should represent the sum of the area under each mass peak calculated using the theoretical chlorine isotope ratio. The peak selected to calculate the theoretical area should be the one which gives the lower of the two possible results (i.e., the EMPC will always be lower than the result calculated from the uncorrected areas).

12.2.6 If the concentration in the final extract of any PCB isomer exceeds the upper method calibration limits, a dilution of the extract or a re-extraction of a smaller portion of the sample must be performed. Dilutions of up to 1/10 may be performed on the extract. If compound concentrations exceeding the calibration range cannot be brought within the calibration range by a 1/10 dilution, extraction of a smaller aliquot of sample may be performed or the sample may be analyzed by a more appropriate analytical technique such as HRGC/LRMS. Consultation with the client should occur before any re-extraction is performed. The lab may report the measured concentration and indicate that the value exceeds the calibration limit by flagging the results with "E". Consultation with the client should occur before compounds are reported which exceed the calibration range.

12.3 The estimated minimum level (EML) is defined as the lowest concentration at which an analyte can be measured reliably with common laboratory interferences present assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures. The EMLs for different matrices and extract volumes are listed in Table 4. Deviations from the extraction amounts or final volumes listed will result in corresponding changes in the actual sample EMLs.

12.4 Flag all compound results in the sample which are below the estimated minimum level with a "J" qualifier.

12.5 Flag all compound results in the sample which were detected in the method blank with a "B" qualifier.

12.6 Flag all compound results in the sample which are above the upper calibration limit with an "E" qualifier.

12.7 Flag all compound results in the sample which are "Estimated Maximum Possible Concentrations" with a "Q" qualifier.

12.8 Flag compound results in the sample that may contain co-eluting compounds with a "C" qualifier.

12.8.1 Flag congeners known to coelute with a higher numbered congener with a "C" qualifier.

12.8.2 Flag congeners that coelute with a lower numbered congener with a "Cx" qualifier where x is the CAS PCB number of the lowest numbered congener in the coeluting group.

12.9 If DOD QSM requirements are used, refer to SOP KNOX-QA-0021.

12.10 Flag compound results in the sample that may be affected by ion suppression with a "S" qualifier. When ion suppression of a PFK trace occurs at greater than or equal to 20% of full scale on both the lock mass and QC mass traces, and when the suppression is sustained for greater than 4 seconds, the suppression must be evaluated to determine which, if any, PCB congeners co-elute with the suppression. Samples may be diluted to decrease the effects of the ion suppression and rerun. Congeners that are determined to co-elute with the suppression are flagged with an "S" qualifier.

12.11 Data Review

12.11.1 Refer to Figure 3 for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data.

12.11.2 The analyst who performs the initial data calculations must initial and date the front chromatogram of the raw data package to document that they have performed the qualitative and quantitative analysis on the sample data.

12.11.3 A second analyst must verify all qualitative peak identifications. If discrepancies

are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.11.4 A second analyst must check all hand calculation and data entry into calculation programs, databases, or spreadsheets at a frequency of 100 percent. If discrepancies are found, the data must be returned to the analyst who performed the initial calculation for resolution.

12.11.5 The reviewing analyst must initial and date the front chromatogram of the raw data package to document that they have performed the second level review on the sample data.

12.11.6 All items listed on the data review checklist must be checked by both the analyst who performed the initial qualitative and quantitative analysis and the analyst who performed the second level review. An example data review checklist is shown in Figure 3.

13 Method Performance

13.1 Method Detection Limit (MDL) - An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in the SOP CA-Q-S006, current revision, based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit (ML).

13.2 Initial Demonstration of Capability – Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in TestAmerica Knoxville SOP KNOX-QA-0009.

13.3 Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. Refer to SOP KNOX-QA-0009 current revision for further requirements for performing and documenting initial and on-going demonstrations of capability**.**

14 Pollution Prevention

14.1 All attempts will be made to minimize the use of solvents and standard materials.

15 Waste Management

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 Waste Streams Produced by the Procedure: The following waste streams are produced when this method is carried out.

- Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar

materials shall be placed in the incinerable laboratory waste stream, contained in a steel or poly satellite accumulation container.

16 References

16.1 Knoxville Laboratory Quality Assurance Manual (QAM), current revision.

16.2 Method 1668, Revision A, B and C: Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS, EPA-821-R-00-002, December 1999.

16.3 Method 1613: Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS [Revision B], EPA#: 821/B-94-005a YEAR: 1994

16.4 Ballschmiter, K. and M. Zell, "Analysis of Polychlorinated Biphenyls (PCB) by Glass Capillary Gas Chromatography", *Fresenius Z. Anal. Chem*., 302:20-31 (1980).

16.5 Schulte, E. and R. Malisch, "Berechnung der Wahren PCB-Gehalte in Umweltproben I. Ermittlung der Zusammensetzung Zweier Technischer PCB-Gemische," *Fresenius Z. Anal. Chem*., 314:545-551 (1983).

16.6 Guitart, R., P. Puig and J. Gómez-Catalán, "Requirement for a Standardized Nomenclature Criterion for PCBs: Computer-Assisted Assignment of Correct Congener Denomination and Numbering," *Chemosphere*, 27(8):1451-1459 (1993).

16.7 Rigaudy, J. and Klesney, S.P., Nomenclature of Organic Chemistry, Pergamon, 1979.

16.8 Pretsch, Clerc, Seibl, Simon, Tables of Spectral Data for Structure Determination of Organic Compounds, Second Edition, Springer-Verlag, 1989.

16.9 CRC Handbook of Chemistry and Physics, 71st edition, CRC Press, 1990-1991.

16.10 Email dated 03/02/10 from Richard Reding Ph.D., Chief U.S. EPA, Engineering & Analytical Support Branch. Engineering & Analysis Division Office of Science and Technology, Office of Water – Subject: Use of QC Acceptance Limits."

17 Miscellaneous

17.1 Deviations from EPA Method 1668, Revisions A, B and C.

17.1.1 Additional recovery standards are used in this procedure. The additional standards are listed in Table 1.

17.1.2 Additional labeled standards are used in this procedure as field sampling surrogates. The additional standards are listed in Table 1

17.1.3 This procedure uses internal standards which are within the same MID group as the native congener that is being calculated. This improvement is used to reduce the effects of full verses reduced accelerating voltage tuning differences which can be exaggerated when crossing MID groups.

17.1.4 The calibration procedure in the method 1668A, revision B, and C call for a

single point standard for the non-Toxic/LOC congeners. This procedure uses a multi-point calibration for all 209 congeners.

17.1.5 This procedure uses MID groups that differ from the method. The procedure uses 4 groups, rather than 6, to improve instrument stability, by holding the magnet current steady for longer periods. Therefore alternate PFK lock masses are monitored, to reflect the mass ranges of the procedure's MID groups.

17.1.6 This procedure uses average retention times (and average relative retention times) produced by triplicate analyses of the 5 mixes specified, rather than single analyses of the diluted 209 standard.

17.1.7 The absolute retention times, relative retention times, and relative retention time limits used by the laboratory differ from those listed in all versions of Method 1668. Each SPC-Octyl column lot used by the laboratory has exhibited slightly different retention time characteristics resulting in different absolute retention times than those listed in the method or those observed with another SPB-Octyl column lot. To ensure that the correct peak assignments are made, a retention time study is performed for each new column lot to verify the original study. This study includes the triplicate analysis of the five retention time mixes listed in Method 1668A as described in Section 10.2.5 to 10.2.7. This procedure requires a minimum elution time of 55 minutes for PCB 209.

17.1.8 The calibration verification procedures in the method call for updating the retention times, relative retention times and response factors for non-Toxic compounds during daily calibration and use the retention times, relative retention times and response factors from the initial calibration for Toxic and LOC compounds. This laboratory uses the retention times and relative retention times from triplicate analyses of the 5-mix series, which contains all congeners, and uses response factors from the initial calibration for all 209 compounds. The practice of updating the relative retention times of only a subset of compounds causes significant error in the linear regression prediction formulas used by targeting software to identify the compounds. This procedure has provisions for updating all RTs and RRTs by analyzing a new retention time calibration series.

17.1.9 The EMLs listed in Table 4 differ from those listed in the reference method. The EMLs are set above the mean plus 2 standard deviations for the higher of detections or EDLs for method blanks. In no case is the EML lower than the low calibration limit. The survey period was approximately 14 months.

17.1.10 This procedure uses a 100uL final volume for solid samples, or a variation depending on the protocol assigned to the sample based on screen results prior to extraction.

17.1.11 Method 1668C requires recovery standards be added immediately prior to analysis. In this procedure recovery standards are added to sample extracts at the conclusion of the extraction / clean up process prior to analysis.

17.1.12 Method 1668C implies that all qualitative criteria must be met in order for a

positive hit to be reported. This procedure allows positive hits to be reported with "Q" qualifiers.

17.1.13 This procedure uses calculated concentrations for determining if a dilution is required not area counts as suggested by Method 1668C, section 17.5.

17.1.14 This procedure reports positive hits below the estimated minimum level (EML) which are determined to be greater than 2.5 signal to noise. These hits are qualified with a "J".

17.1.15 This procedure does not report blank corrected values.

17.1.16 When samples are diluted to bring a native analyte within the upper calibration range all 209 congeners are reported from this analysis. This procedure reports all congeners from one analytical analysis.

17.1.17 This procedure uses a daily calibration CCV consisting of all 209 congeners at the beginning of each 12 hour analytical shift.

17.1.18 Extracts are stored in a dark box at room temperature in the same manner as standards.

17.1.19 1668C EML limits are listed in Table 4. However, this laboratory currently uses the 1668A/B limits

17.1.20 The limits established in 1668B, Table 6 for the IPR and OPR performance evaluations have been observed by EPA reviewers to penalize an analyst who achieves better performance than those observed in the inter-laboratory study. Based on EPA's recommendations (section 16.10), TestAmerica Knoxville performs analysis by Method 1668B with the QC acceptance criteria in Table 6 of EPA Method 1668A. Table 10 "Acceptance Criteria for Performance Tests" of this SOP will be used for the IPR and OPR limits.

17.2 List of tables and figures referenced in the body of the SOP.

17.2.1 Table 1 – Polychlorinated Biphenyls Determined by High Resolution Gas Chromatography (HRGC)/High Resolution Mass Spectrometry (HRMS)

17.2.2 Table 2 – RT References, Quantitation References, Retention Times (RT), and Relative Retention Times (RRTs) for the 209 CB congeners on SPB-Octyl

17.2.3 Table 3 – Low Calibration Levels Based on Various Final Extract Volumes

17.2.4 Table 4 – Estimated Minimum Levels EPA 1668A, B & C– Matrix and Concentration

17.2.5 Table 5a – Concentration of Native PCB Congener Stock and Spiking Solutions

17.2.6 Table 5b – Concentration of $^{13}C_{12}$ Labeled PCB Congener Stock and Spiking Solutions

17.2.7 Table 6a – Concentration of PCBs in Calibration Solutions

17.2.8 Table 6b – Preparation of Calibration Solutions

17.2.9 Table 7 – Window Defining Mixture and SPB-Octyl Resolution Test Compounds

17.2.10 Table 8 – Ions Monitored for HRGC/HRMS Analysis of PCBs

17.2.11 Table 9 – Theoretical Ion Abundance Ratios and Control Limits for PCBs

17.2.12 Table 10A – Acceptance Criteria for Performance Tests (1668A & B)

17.2.13 Table 10B – Acceptance Criteria for Performance Tests (1668C)

17.2.14 Table 11 – Retention Times of Isomers on SPB-Octyl Column for PCB Standard Mixes

17.2.15 Table 12 – Assignment of Sample Preparation Protocols

17.2.16 Figure 1 – Recommended GC Operating Conditions

17.2.17 Figure 2 – Recommended MID Descriptors

17.2.18 Figure 3 – Example Data Review Checklist

17.2.19 Table 1 - Polychlorinated Biphenyls Determined by HRGC/HRMS

PCB Number[1]	BZ/IUPAC Number[2].	PCB Chemical Structure Name[3]	CAS Registry[4] Number	Labeled Analog	CAS Registry[4] Number	U
1	1	2-monochlorobiphenyl	2051-60-7	$^{13}C_{12}$-2-monochlorobiphenyl	234432-85-0	Inter
2	2	3-monochlorobiphenyl	2051-61-8			
3	3	4-monochlorobiphenyl	2051-62-9	$^{13}C_{12}$-4-monochlorobiphenyl	208263-77-8	Inter
4	4	2,2'-dichlorobiphenyl	13029-08-8	$^{13}C_{12}$-2,2'-dichlorobiphenyl	234432-86-1	Inter
5	5	2,3-dichlorobiphenyl	16605-91-7			
6	6	2,3'-dichlorobiphenyl	25569-80-6			
7	7	2,4-dichlorobiphenyl	33284-50-3			
8	8	2,4'-dichlorobiphenyl	34883-43-7	$^{13}C_{12}$-2,4'-dichlorobiphenyl		Surro
9	9	2,5-dichlorobiphenyl	34883-39-1	$^{13}C_{12}$-2,5-dichlorobiphenyl	250694-89-4	Reco
10	10	2,6-dichlorobiphenyl	33146-45-1			
11	11	3,3'-dichlorobiphenyl	2050-67-1			
12	12	3,4-dichlorobiphenyl	2974-92-7			
13	13	3,4'-dichlorobiphenyl	2974-90-5			
14	14	3,5-dichlorobiphenyl	34883-41-5			
15	15	4,4'-dichlorobiphenyl	2050-68-2	$^{13}C_{12}$-4,4'-dichlorobiphenyl	208263-67-6	Inter
16	16	2,2',3-trichlorobiphenyl	38444-78-9			
17	17	2,2',4-trichlorobiphenyl	37680-66-3			
18	18	2,2',5-trichlorobiphenyl	37680-65-2			
19	19	2,2',6-trichlorobiphenyl	38444-73-4	$^{13}C_{12}$-2,2',6-trichlorobiphenyl	234432-87-2	Inter
20	20	2,3,3'-trichlorobiphenyl	38444-84-7			
21	21	2,3,4-trichlorobiphenyl	55702-46-0			
22	22	2,3,4'-trichlorobiphenyl	38444-85-8			
23	23	2,3,5-trichlorobiphenyl	55720-44-0			
24	24	2,3,6-trichlorobiphenyl	55702-45-9			
25	25	2,3',4-trichlorobiphenyl	55712-37-3			
26	26	2,3',5-trichlorobiphenyl	38444-81-4			
27	27	2,3',6-trichlorobiphenyl	38444-76-7			
28	28	2,4,4'-trichlorobiphenyl	7012-37-5	$^{13}C_{12}$-2,4,4'-trichlorobiphenyl	208263-76-7	Clea
29	29	2,4,5-trichlorobiphenyl	15862-07-4			
30	30	2,4,6-trichlorobiphenyl	35693-92-6			
31	31	2,4',5-trichlorobiphenyl	16606-02-3	$^{13}C_{12}$-2,4',5-trichlorobiphenyl		Reco
32	32	2,4',6-trichlorobiphenyl	38444-77-8	$^{13}C_{12}$-2,4',6-trichlorobiphenyl		Reco
33	33	2',3,4-trichlorobiphenyl (2,3',4'-trichlorobiphenyl)	38444-86-9			
34	34	2',3,5-trichlorobiphenyl (2,3',5'-trichlorobiphenyl)	37680-68-5			
35	35	3,3',4-trichlorobiphenyl	37680-69-6			
36	36	3,3',5-trichlorobiphenyl	38444-87-0			
37	37	3,4,4'-trichlorobiphenyl	38444-90-5	$^{13}C_{12}$-3,4,4'-trichlorobiphenyl	208263-79-0	Inter
38	38	3,4,5-trichlorobiphenyl	53555-66-1			
39	39	3,4',5-trichlorobiphenyl	38444-88-1			
40	40	2,2',3,3'-tetrachlorobiphenyl	38444-93-8			
41	41	2,2',3,4-tetrachlorobiphenyl	52663-59-9			
42	42	2,2',3,4'-tetrachlorobiphenyl	36559-22-5			
43	43	2,2',3,5-tetrachlorobiphenyl	70362-46-8			
44	44	2,2',3,5'-tetrachlorobiphenyl	41464-39-5			
45	45	2,2',3,6-tetrachlorobiphenyl	70362-45-7			
46	46	2,2',3,6'-tetrachlorobiphenyl	41464-47-5			
47	47	2,2',4,4'-tetrachlorobiphenyl	2437-79-8			
48	48	2,2',4,5-tetrachlorobiphenyl	70362-47-9			
49	49	2,2',4,5'-tetrachlorobiphenyl	41464-40-8			
50	50	2,2',4,6-tetrachlorobiphenyl	62796-65-0			
51	51	2,2',4,6'-tetrachlorobiphenyl	68194-04-7			
52	52	2,2',5,5'-tetrachlorobiphenyl	35693-99-3	$^{13}C_{12}$-2,2',5,5'-tetrachlorobiphenyl	160901-66-6	Reco
53	53	2,2',5,6'-tetrachlorobiphenyl	41464-41-9			
54	54	2,2',6,6'-tetrachlorobiphenyl	15968-05-5	$^{13}C_{12}$-2,2',6,6'-tetrachlorobiphenyl	234432-88-3	Inter
55	55	2,3,3',4-tetrachlorobiphenyl	74338-24-2			
56	56	2,3,3',4'-tetrachlorobiphenyl	41464-43-1			
57	57	2,3,3',5-tetrachlorobiphenyl	70424-67-8			
58	58	2,3,3',5'-tetrachlorobiphenyl	41464-49-7			
59	59	2,3,3',6-tetrachlorobiphenyl	74472-33-6			
60	60	2,3,4,4'-tetrachlorobiphenyl	33025-41-1			

PCB Number[1]	BZ/IUPAC Number[2].	PCB Chemical Structure Name[3]	CAS Registry[4] Number	Labeled Analog	CAS Registry[4] Number	U
61	61	2,3,4,5-tetrachlorobiphenyl	33284-53-6			
62	62	2,3,4,6-tetrachlorobiphenyl	54230-22-7			
63	63	2,3,4',5-tetrachlorobiphenyl	74472-34-7			
64	64	2,3,4',6-tetrachlorobiphenyl	52663-58-8			
65	65	2,3,5,6-tetrachlorobiphenyl	33284-54-7			
66	66	2,3',4,4'-tetrachlorobiphenyl	32598-10-0			
67	67	2,3',4,5-tetrachlorobiphenyl	73575-53-8			
68	68	2,3',4,5'-tetrachlorobiphenyl	73575-52-7			
69	69	2,3',4,6-tetrachlorobiphenyl	60233-24-1			
70	70	2,3',4',5-tetrachlorobiphenyl	32598-11-1			
71	71	2,3',4',6-tetrachlorobiphenyl	41464-46-4			
72	72	2,3',5,5'-tetrachlorobiphenyl	41464-42-0			
73	73	2,3',5',6-tetrachlorobiphenyl	74338-23-1			
74	74	2,4,4',5-tetrachlorobiphenyl	32690-93-0			
75	75	2,4,4',6-tetrachlorobiphenyl	32598-12-2			
76	76	2',3,4,5-tetrachlorobiphenyl (2,3',4',5'-tetrachlorobiphenyl)	70362-48-0			
77	77	3,3',4,4'-tetrachlorobiphenyl	32598-13-3	$^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl	160901-67-7	Inter
78	78	3,3',4,5-tetrachlorobiphenyl	70362-49-1			
79	79	3,3',4,5'-tetrachlorobiphenyl	41464-48-6	$^{13}C_{12}$-3,3',4,5'-tetrachlorobiphenyl		Surro
80	80	3,3',5,5'-tetrachlorobiphenyl	33284-52-5			
81	81	3,4,4',5-tetrachlorobiphenyl	70362-50-4	$^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl	160901-68-8	Inter
82	82	2,2',3,3',4-pentachlorobiphenyl	52663-62-4			
83	83	2,2',3,3',5-pentachlorobiphenyl	60145-20-2			
84	84	2,2',3,3',6-pentachlorobiphenyl	52663-60-2			
85	85	2,2',3,4,4'-pentachlorobiphenyl	65510-45-4			
86	86	2,2',3,4,5-pentachlorobiphenyl	55312-69-1			
87	87	2,2',3,4,5'-pentachlorobiphenyl	38380-02-8			
88	88	2,2',3,4,6-pentachlorobiphenyl	55215-17-3			
89	89	2,2',3,4,6'-pentachlorobiphenyl	73575-57-2			
90	90	2,2',3,4',5-pentachlorobiphenyl	68194-07-0			
91	91	2,2',3,4',6-pentachlorobiphenyl	68194-05-8			
92	92	2,2',3,5,5'-pentachlorobiphenyl	52663-61-3			
93	93	2,2',3,5,6-pentachlorobiphenyl	73575-56-1			
94	94	2,2',3,5,6'-pentachlorobiphenyl	73575-55-0			
95	95	2,2',3,5',6-pentachlorobiphenyl	38379-99-6	$^{13}C_{12}$-2,2',3,5',6-pentachlorobiphenyl		Surro
96	96	2,2',3,6,6'-pentachlorobiphenyl	73575-54-9			
97	97	2,2',3',4,5-pentachlorobiphenyl (2,2',3,4',5'-pentachlorobiphenyl)	41464-51-1			
98	98	2,2',3',4,6-pentachlorobiphenyl (2,2',3,4',6'-pentachlorobiphenyl)	60233-25-2			
99	99	2,2',4,4',5-pentachlorobiphenyl	38380-01-7			
100	100	2,2',4,4',6-pentachlorobiphenyl	39485-83-1			
101	101	2,2',4,5,5'-pentachlorobiphenyl	37680-73-2	$^{13}C_{12}$-2,2',4,5,5'-pentachlorobiphenyl	160901-69-9	Reco
102	102	2,2',4,5,6'-pentachlorobiphenyl	68194-06-9			
103	103	2,2',4,5',6-pentachlorobiphenyl	60145-21-3			
104	104	2,2',4,6,6'-pentachlorobiphenyl	56558-16-8	$^{13}C_{12}$-2,2',4,6,6'-pentachlorobiphenyl	234432-89-4	Inter
105	105	2,3,3',4,4'-pentachlorobiphenyl	32598-14-4	$^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl	160901-70-2	Inter
106	106	2,3,3',4,5-pentachlorobiphenyl	70424-69-0			
107	107/109	2,3,3',4',5-pentachlorobiphenyl	70424-68-9			
108	108/107	2,3,3',4,5'-pentachlorobiphenyl	70362-41-3			
109	109/108	2,3,3',4,6-pentachlorobiphenyl	74472-35-8			
110	110	2,3,3',4',6-pentachlorobiphenyl	38380-03-9			
111	111	2,3,3',5,5'-pentachlorobiphenyl	39635-32-0	$^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl	160901-71-3	Clea
112	112	2,3,3',5,6-pentachlorobiphenyl	74472-36-9			
113	113	2,3,3',5',6-pentachlorobiphenyl	68194-10-5			
114	114	2,3,4,4',5-pentachlorobiphenyl	74472-37-0	$^{13}C_{12}$-2,3,4,4',5-pentachlorobiphenyl	160901-72-4	Inter
115	115	2,3,4,4',6-pentachlorobiphenyl	74472-38-1			
116	116	2,3,4,5,6-pentachlorobiphenyl	18259-05-7			
117	117	2,3,4',5,6-pentachlorobiphenyl	68194-11-6			
118	118	2,3',4,4',5-pentachlorobiphenyl	31508-00-6	$^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl	160901-73-5	Inter
119	119	2,3',4,4',6-pentachlorobiphenyl	56558-17-9			
120	120	2,3',4,5,5'-pentachlorobiphenyl	68194-12-7			
121	121	2,3',4,5',6-pentachlorobiphenyl	56558-18-0			

PCB Number[1]	BZ/IUPAC Number[2].	PCB Chemical Structure Name[3]	CAS Registry[4] Number	Labeled Analog	CAS Registry[4] Number	U
122	122	2',3,3',4,5-pentachlorobiphenyl (2,3,3',4',5'-pentachlorobiphenyl)	76842-07-4			
123	123	2',3,4,4',5-pentachlorobiphenyl (2,3',4,4',5'-pentachlorobiphenyl)	65510-44-3	$^{13}C_{12}$-2',3,4,4',5-pentachlorobiphenyl	160901-74-6	Inter
124	124	2',3,4,5,5'-pentachlorobiphenyl (2,3',4',5',5-pentachlorobiphenyl)	70424-70-3			
125	125	2',3,4,5,6'-pentachlorobiphenyl (2,3',4',5',6-pentachlorobiphenyl)	74472-39-2			
126	126	3,3',4,4',5-pentachlorobiphenyl	57465-28-8	$^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl	160901-75-7	Inter
127	127	3,3',4,5,5'-pentachlorobiphenyl	39635-33-1	$^{13}C_{12}$-3,3',4,5,5'-pentachlorobiphenyl		Reco
128	128	2,2',3,3',4,4'-hexachlorobiphenyl	38380-07-3			
129	129	2,2',3,3',4,5-hexachlorobiphenyl	55215-18-4			
130	130	2,2',3,3',4,5'-hexachlorobiphenyl	52663-66-8			
131	131	2,2',3,3',4,6-hexachlorobiphenyl	61798-70-7			
132	132	2,2',3,3',4,6'-hexachlorobiphenyl	38380-05-1			
133	133	2,2',3,3',5,5'-hexachlorobiphenyl	35694-04-3			
134	134	2,2',3,3',5,6-hexachlorobiphenyl	52704-70-8			
135	135	2,2',3,3',5,6'-hexachlorobiphenyl	52744-13-5			
136	136	2,2',3,3',6,6'-hexachlorobiphenyl	38411-22-2			
137	137	2,2',3,4,4',5-hexachlorobiphenyl	35694-06-5			
138	138	2,2',3,4,4',5'-hexachlorobiphenyl	35065-28-2	$^{13}C_{12}$-2,2',3,4,4',5'-hexachlorobiphenyl	160901-76-8	Reco
139	139	2,2',3,4,4',6-hexachlorobiphenyl	56030-56-9			
140	140	2,2',3,4,4',6'-hexachlorobiphenyl	59291-64-4			
141	141	2,2',3,4,5,5'-hexachlorobiphenyl	52712-04-6			
142	142	2,2',3,4,5,6-hexachlorobiphenyl	41411-61-4			
143	143	2,2',3,4,5,6'-hexachlorobiphenyl	68194-15-0			
144	144	2,2',3,4,5',6-hexachlorobiphenyl	68194-14-9			
145	145	2,2',3,4,6,6'-hexachlorobiphenyl	74472-40-5			
146	146	2,2',3,4',5,5'-hexachlorobiphenyl	51908-16-8			
147	147	2,2',3,4',5,6-hexachlorobiphenyl	68194-13-8			
148	148	2,2',3,4',5,6'-hexachlorobiphenyl	74472-41-6			
149	149	2,2',3,4',5',6-hexachlorobiphenyl	38380-04-0			
150	150	2,2',3,4',6,6'-hexachlorobiphenyl	68194-08-1			
151	151	2,2',3,5,5',6-hexachlorobiphenyl	52663-63-5			
152	152	2,2',3,5,6,6'-hexachlorobiphenyl	68194-09-2			
153	153	2,2',4,4',5,5'-hexachlorobiphenyl	35065-27-1	$^{13}C_{12}$-2,2',4,4',5,5'-hexachlorobiphenyl		Surro
154	154	2,2',4,4',5,6'-hexachlorobiphenyl	60145-22-4			
155	155	2,2',4,4',6,6'-hexachlorobiphenyl	33979-03-2	$^{13}C_{12}$-2,2',4,4',6,6'-hexachlorobiphenyl	234432-90-7	Inter
156	156	2,3,3',4,4',5-hexachlorobiphenyl	38380-08-4	$^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl	160901-77-9	Inter
157	157	2,3,3',4,4',5'-hexachlorobiphenyl	69782-90-7	$^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl	160901-78-0	Inter
158	158	2,3,3',4,4',6-hexachlorobiphenyl	74472-42-7			
159	159	2,3,3',4,5,5'-hexachlorobiphenyl	39635-35-3			
160	160	2,3,3',4,5,6-hexachlorobiphenyl	41411-62-5			
161	161	2,3,3',4,5',6-hexachlorobiphenyl	74472-43-8			
162	162	2,3,3',4',5,5'-hexachlorobiphenyl	39635-34-2			
163	163	2,3,3',4',5,6-hexachlorobiphenyl	74472-44-9			
164	164	2,3,3',4',5',6-hexachlorobiphenyl	74472-45-0			
165	165	2,3,3',5,5',6-hexachlorobiphenyl	74472-46-1			
166	166	2,3,4,4',5,6-hexachlorobiphenyl	41411-63-6			
167	167	2,3',4,4',5,5'-hexachlorobiphenyl	52663-72-6	$^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl	161627-18-5	Inter
168	168	2,3',4,4',5',6-hexachlorobiphenyl	59291-65-5			
169	169	3,3',4,4',5,5'-hexachlorobiphenyl	32774-16-6	$^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl	160901-79-1	Inter
170	170	2,2',3,3',4,4',5-heptachlorobiphenyl	35065-30-6	$^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl	160901-80-4	Inter
171	171	2,2',3,3',4,4',6-heptachlorobiphenyl	52663-71-5			
172	172	2,2',3,3',4,5,5'-heptachlorobiphenyl	52663-74-8			
173	173	2,2',3,3',4,5,6-heptachlorobiphenyl	68194-16-1			
174	174	2,2',3,3',4,5,6'-heptachlorobiphenyl	38411-25-5			
175	175	2,2',3,3',4,5',6-heptachlorobiphenyl	40186-70-7			
176	176	2,2',3,3',4,6,6'-heptachlorobiphenyl	52663-65-7			
177	177	2,2',3,3',4',5,6-heptachlorobiphenyl (2,2',3,3',4,5',6'-heptachlorobiphenyl)	52663-70-4			
178	178	2,2',3,3',5,5',6-heptachlorobiphenyl	52663-67-9	$^{13}C_{12}$-2,2',3,3',5,5',6-heptachlorobiphenyl	160901-81-5	Clea
179	179	2,2',3,3',5,6,6'-heptachlorobiphenyl	52663-64-6			
180	180	2,2',3,4,4',5,5'-heptachlorobiphenyl	35065-29-3	$^{13}C_{12}$-2,2',3,4,4',5,5'-heptachlorobiphenyl	160901-82-6	Reco

PCB Number[1]	BZ/IUPAC Number[2].	PCB Chemical Structure Name[3]	CAS Registry[4] Number	Labeled Analog	CAS Registry[4] Number	U
181	181	2,2',3,4,4',5,6-heptachlorobiphenyl	74472-47-2			
182	182	2,2',3,4,4',5,6'-heptachlorobiphenyl	60145-23-5			
183	183	2,2',3,4,4',5',6-heptachlorobiphenyl	52663-69-1			
184	184	2,2',3,4,4',6,6'-heptachlorobiphenyl	74472-48-3			
185	185	2,2',3,4,5,5',6-heptachlorobiphenyl	52712-05-7			
186	186	2,2',3,4,5,6,6'-heptachlorobiphenyl	74472-49-4			
187	187	2,2',3,4',5,5',6-heptachlorobiphenyl	52663-68-0			
188	188	2,2',3,4',5,6,6'-heptachlorobiphenyl	74487-85-7	$^{13}C_{12}$-2,2',3,4',5,6,6'-heptachlorobiphenyl	234432-91-8	Inter
189	189	2,3,3',4,4',5,5'-heptachlorobiphenyl	39635-31-9	$^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl	160901-83-7	Inter
190	190	2,3,3',4,4',5,6-heptachlorobiphenyl	41411-64-7			
191	191	2,3,3',4,4',5',6-heptachlorobiphenyl	74472-50-7			
192	192	2,3,3',4,5,5',6-heptachlorobiphenyl	74472-51-8			
193	193	2,3,3',4',5,5',6-heptachlorobiphenyl	69782-91-8			
194	194	2,2',3,3',4,4',5,5'-octachlorobiphenyl	35694-08-7	$^{13}C_{12}$-2,2',3,3',4,4',5,5'-octachlorobiphenyl	208263-74-5	Reco
195	195	2,2',3,3',4,4',5,6-octachlorobiphenyl	52663-78-2			
196	196	2,2',3,3',4,4',5,6'-octachlorobiphenyl	42740-50-1			
197	197	2,2',3,3',4,4',6,6'-octachlorobiphenyl	33091-17-7			
198	198	2,2',3,3',4,5,5',6-octachlorobiphenyl	68194-17-2			
199	201/199	2,2',3,3',4,5,5',6'-octachlorobiphenyl	52663-75-9			
200	199/200	2,2',3,3',4,5,6,6'-octachlorobiphenyl	52663-73-7			
201	200/201	2,2',3,3',4,5',6,6'-octachlorobiphenyl	40186-71-8			
202	202	2,2',3,3',5,5',6,6'-octachlorobiphenyl	2136-99-4	$^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl	105600-26-8	Inter
203	203	2,2',3,4,4',5,5',6-octachlorobiphenyl	52663-76-0			
204	204	2,2',3,4,4',5,6,6'-octachlorobiphenyl	74472-52-9			
205	205	2,3,3',4,4',5,5',6-octachlorobiphenyl	74472-53-0	$^{13}C_{12}$-2,3,3',4,4',5,5',6-octachlorobiphenyl	234446-64-1	Inter
206	206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	40186-72-9	$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	208263-75-6	Inter
207	207	2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl	52663-79-3			
208	208	2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	52663-77-1	$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	234432-92-9	Inter
209	209	2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	2051-24-3	$^{13}C_{12}$-decachlorobiphenyl	160901-84-8	Inter

1. The PCB congener number is from Method 1668C and Chemical Abstract Services.
2. The BZ number is from Ballschmiter and Zell (1980). The IUPAC number, when different from the BZ, follows the recommended changes to the BZ number per Schulte and Malisch (1983) and Guitart et al. (1993).
3. The chemical structure names are from Ballschmiter and Zell (1980). IUPAC nomenclature structure names are listed in parenthesis when different from the BZ name (source CAS Registry).
4. Chemical Abstract Service Registry number (source CAS Registry and 1668A Table 1).

Table 2 - RT References, Quantitation References, Retention Times (RTs), and Relative Retention Times (RRTs) for the 209 CB congeners on SPB-Octyl

Cl No[1]	IUPAC No[2,3]	RT Ref[4]	Quantitation Reference[5]	RT Win[6] (sec)
1	1L	9L	9L	30
1	3L	9L	9L	30
1	1	1L	1L	10
1	2	3L	1L/3L	6
1	3	3L	3L	6
2	4L	9L	9L	30
2	9L	9L	9L	25
2	8L	4L	4L/15L	6
2	15L	9L	9L	20
2	4	4L	4L	10
2	10	4L	4L/15L	6
2	9	4L	4L/15L	6
2	7	4L	4L/15L	6
2	6	4L	4L/15L	6
2	5	4L	4L/15L	6
2	8	4L	4L/15L	6
2	14	15L	4L/15L	6
2	11	15L	4L/15L	6
2	13	15L	4L/15L	6
2	12	15L	4L/15L	6
2	15	15L	15L	10
3	19L	32L	32L	30
3	32L	32L	32L	6
3	31L	31L	31L	6
3	28L	31L	31L	20
3	37L	31L	31L	30
3	19	19L	19L	10
3	30	19L	19L	6
3	18	19L	19L	6
3	17	19L	19L	6
3	27	19L	19L	6
3	24	19L	19L	6
3	16	19L	19L	6
3	32	19L	19L	6
3	34	19L	37L	6
3	23	19L	37L	6
3	29	19L	37L	10
3	26	19L	37L	10
3	25	37L	37L	6
3	31	37L	37L	6
3	28	37L	37L	10
3	20	37L	37L	10
3	21	37L	37L	10
3	33	37L	37L	10
3	22	37L	37L	6
3	36	37L	37L	6
3	39	37L	37L	6
3	38	37L	37L	6
3	35	37L	37L	6
3	37	37L	37L	6
4	54L	52L	32L	20
4	52L	52L	52L	25
4	79L	81L	81L/77L	6
4	81L	52L	52L	20
4	77L	52L	52L	20
4	54	54L	54L	10
4	50	54L	81L/77L	10
4	53	54L	81L/77L	10
4	45	54L	81L/77L	10
4	51	54L	81L/77L	10
4	46	54L	81L/77L	6
4	52	54L	81L/77L	6
4	73	54L	81L/77L	6
4	43	54L	81L/77L	6
4	69	54L	81L/77L	10
4	49	54L	81L/77L	10
4	48	54L	81L/77L	6
4	65	54L	81L/77L	10
4	47	54L	81L/77L	10
4	44	54L	81L/77L	10
4	62	54L	81L/77L	10
4	75	54L	81L/77L	10

Cl No[1]	IUPAC No[2,3]	RT Ref[4]	Quantitation Reference[5]	RT Win[6] (sec)
4	59	54L	81L/77L	10
4	42	54L	81L/77L	6
4	41	54L	81L/77L	10
4	71	54L	81L/77L	10
4	40	54L	81L/77L	10
4	64	54L	81L/77L	6
4	72	81L	81L/77L	6
4	68	81L	81L/77L	6
4	57	81L	81L/77L	6
4	58	81L	81L/77L	6
4	67	81L	81L/77L	6
4	63	81L	81L/77L	6
4	61	81L	81L/77L	12
4	70	81L	81L/77L	12
4	76	81L	81L/77L	12
4	74	81L	81L/77L	10
4	66	81L	81L/77L	6
4	55	81L	81L/77L	6
4	56	81L	81L/77L	6
4	60	81L	81L/77L	6
4	80	81L	81L/77L	6
4	79	81L	81L/77L	6
4	78	81L	81L/77L	6
4	81	81L	81L	6
4	77	77L	77L	6
5	104L	101L	101L	20
5	95L	104L	104L	10
5	101L	101L	101L	25
5	111L	101L	101L	20
5	123L	101L	127L	20
5	118L	101L	127L	20
5	114L	101L	127L	20
5	105L	101L	127L	20
5	127L	127L	127L	25
5	126L	101L	127L	20
5	104	104L	104L	10
5	96	104L	104L	10
5	103	104L	104L	6
5	94	104L	104L	6
5	95	104L	104L	10
5	100	104L	104L	10
5	93	104L	104L	10
5	102	104L	104L	10
5	98	104L	104L	10
5	88	104L	104L	12
5	91	104L	104L	10
5	84	104L	104L	6
5	89	104L	104L	6
5	121	104L	104L	6
5	92	123L	104L	6
5	113	104L	104L	10
5	90	104L	104L	10
5	101	104L	104L	10
5	83	104L	104L	12
5	99	104L	104L	10
5	112	104L	104L	6
5	119	104L	104L	16
5	108 (109)	104L	104L	16
5	86	104L	104L	16
5	97	104L	104L	16
5	125	104L	104L	16
5	87	104L	104L	10
5	117	104L	104L	12
5	116	104L	104L	12
5	85	104L	104L	10
5	110	104L	104L	10
5	115	104L	104L	10
5	82	104L	104L	6
5	111	104L	104L	6
5	120	104L	104L	6
5	107 (108)	104L	123L/114L/118L/105L/126L	10
5	124	104L	123L/114L/118L/105L/126L	10
5	109 (107)	104L	123L/114L/118L/105L/126L	6
5	123	123L	123L	6
5	106	123L	123L/114L/118L/105L/126L	6
5	118	118L	118L	6
5	122	118L	123L/114L/118L/105L/126L	6

Cl No[1]	IUPAC No[2,3]	RT Ref[4]	Quantitation Reference[5]	RT Win[6] (sec)
5	114	114L	114L	6
5	105	105L	105L	6
5	127	105L	123L/114L/118L/105L/126L	6
5	126	126L	126L	6
6	155L	138L	101L	20
6	153L	167L	156L/157L/167L/169L	10
6	138L	138L	138L	100
6	167L	138L	138L	20
6	156L	138L	138L	6
6	157L	138L	138L	20
6	169L	138L	138L	6
6	155	155L	155L	10
6	152	155L	155L	6
6	150	155L	155L	6
6	136	155L	155L	6
6	145	155L	155L	6
6	148	155L	155L	6
6	151	155L	155L	10
6	135	155L	155L	10
6	154	155L	155L	10
6	144	155L	155L	6
6	147	155L	156L/157L/167L/169L	10
6	149	155L	156L/157L/167L/169L	10
6	134	155L	156L/157L/167L/169L	10
6	143	155L	156L/157L/167L/169L	10
6	139	155L	156L/157L/167L/169L	10
6	140	155L	156L/157L/167L/169L	10
6	131	155L	156L/157L/167L/169L	6
6	142	155L	156L/157L/167L/169L	6
6	132	155L	156L/157L/167L/169L	10
6	133	155L	156L/157L/167L/169L	6
6	165	167L	156L/157L/167L/169L	6
6	146	167L	156L/157L/167L/169L	6
6	161	167L	156L/157L/167L/169L	6
6	153	167L	156L/157L/167L/169L	10
6	168	167L	156L/157L/167L/169L	10
6	141	167L	156L/157L/167L/169L	6
6	130	167L	156L/157L/167L/169L	6
6	137	167L	156L/157L/167L/169L	6
6	164	167L	156L/157L/167L/169L	6
6	138	167L	156L/157L/167L/169L	14
6	163	167L	156L/157L/167L/169L	14
6	129	167L	156L/157L/167L/169L	14
6	160	167L	156L/157L/167L/169L	10
6	158	167L	156L/157L/167L/169L	6
6	166	167L	156L/157L/167L/169L	10
6	128	167L	156L/157L/167L/169L	10
6	159	167L	156L/157L/167L/169L	6
6	162	167L	156L/157L/167L/169L	6
6	167	167L	167L	6
6	156	156L	156L/157L	6
6	157	157L	156L/157L	10
6	169	169L	169L	6
7	188L	180L	180L	20
7	178L	180L	180L	20
7	180L	180L	180L	100
7	170L	180L	180L	20
7	189L	180L	194L	20
7	188	188L	188L	6
7	179	188L	188L/170L	6
7	184	188L	188L/170L	6
7	176	188L	188L/170L	6
7	186	188L	188L/170L	6
7	178	188L	188L/170L	6
7	175	188L	188L/170L	6
7	187	188L	188L/170L	6
7	182	188L	188L/170L	6
7	183	188L	188L/170L	6
7	185	188L	188L/170L	6
7	174	188L	188L/170L	6
7	177	188L	188L/170L	6
7	181	188L	188L/170L	6
7	171	188L	188L/170L	10
7	173	188L	188L/170L	6
7	172	189L	188L/170L	6
7	192	189L	188L/170L	6
7	193	189L	188L/170L	6

Cl No[1]	IUPAC No[2,3]	RT Ref[4]	Quantitation Reference[5]	RT Win[6] (sec)
7	180	189L	188L/170L	6
7	191	189L	188L/170L	6
7	170	189L	170L	6
7	190	189L	188L/170L	6
7	189	189L	189L	6
8	202L	194L	180L	20
8	194L	194L	194L	25
8	205L	194L	194L	30
8	202	202L	202L	10
8	201	202L	202L	6
8	204	202L	202L	6
8	197	202L	202L	6
8	200	202L	202L	6
8	198	202L	202L	10
8	199	202L	202L	6
8	196	205L	202L	6
8	203	205L	202L	6
8	195	205L	205L	6
8	194	205L	205L	6
8	205	205L	205L	6
9	208L	194L	194L	20
9	206L	194L	194L	30
9	208	208L	208L	6
9	207	208L	208L/206L	6
9	206	206L	206L	6
10	209L	194L	194L	30
10	209	209L	209L	6

1. Number of chlorines on congener.
2. Suffix "L" indicates labeled compound.
3. IUPAC Number per Table 2 of Method 1668A. (Numbers in parentheses are PCB Numbers from 1668C)
4. Retention time reference that is used to locate target congener.
5. Quantitation reference that is used to calculate the concentration of the target congener or labeled standard.
6. RT window width for congener or group of two or more congeners.

Table 3 - Low Calibration Levels (LCLs) Based on Final Extract Volumes

		20 µL Extract Volume	100µL Extract Volume
Analyte	Minimum Cal. Level CS 0.5 (ng/mL)	Water 1L (ng/L)	Solids and Tissues 10g[2] (ng/g)
Monochlorobiphenyls	0.5	0.01[1]	0.005
Dichlorobiphenyls	0.5	0.01[1]	0.005
Trichlorobiphenyls	0.5	0.01	0.005
Tetrachlorobiphenyls	0.5	0.01	0.005
Pentachlorobiphenyls	0.5	0.01	0.005
Hexachlorobiphenyls	0.5	0.01	0.005
Heptachlorobiphenyls	0.5	0.01	0.005
Octachlorobiphenyls	0.5	0.01	0.005
Nonachlorobiphenyls	0.5	0.01	0.005
Decachlorobiphenyl	0.5	0.01	0.005

1. This value reflects the LCL. Reliable detection at this level may not be attained due to evaporative loss in adjusting the extract volume to 20 µL for these homolog groups.

2. The values for solids and tissues reflect the LCLs for Protocol 1 as described in Table 12. If the sample is prepared by another protocol described in that table, the LCLs shown in this table must be adjusted appropriately.

Table 4 - Estimated Minimum Levels EPA 1668A, B & C- Matrix and Concentration

	TestAmerica Knoxville EMLs [1] (1668A, B & C)			1668C Reference Method EMLs [2]		
Parameter	**Water ng/L**	**Other [3] ng/g**	**Extract ng/mL**	**Water ng/L**	**Other [3] ng/g**	**Extract ng/mL**
PCB 1	0.040	0.01	1.0	0.02	0.002	1
PCB 2	0.040	0.01	1.0	0.02	0.002	1
PCB 3	0.040	0.01	1.0	0.05	0.005	2.5
PCB 4	0.060	0.02	2.0	0.05	0.005	2.5
PCB 5	0.040	0.01	1.0	0.02	0.002	1
PCB 6	0.040	0.01	1.0	0.02	0.002	1
PCB 7	0.040	0.01	1.0	0.02	0.002	1
PCB 8	0.060	0.02	2.0	0.05	0.005	2.5
PCB 9	0.040	0.01	1.0	0.02	0.002	1
PCB 10	0.040	0.01	1.0	0.05	0.005	2.5
PCB 11	0.060	0.02	2.0	0.10	0.01	5
PCB 12	0.060	0.01	1.0	0.05	0.005	2.5
PCB 14	0.040	0.01	1.0	0.02	0.002	1
PCB 13	0.060	0.01	1.0	0.05	0.005	2.5
PCB 15	0.040	0.01	1.0	0.05	0.005	2.5
PCB 16	0.040	0.01	1.0	0.02	0.002	1
PCB 17	0.040	0.01	1.0	0.02	0.002	1
PCB 18	0.060	0.02	2.0	0.05	0.005	2.5
PCB 30	0.060	0.02	2.0	0.05	0.005	2.5
PCB 19	0.040	0.01	1.0	0.02	0.002	1
PCB 20	0.040	0.02	2.0	0.05	0.005	2.5
PCB 28	0.040	0.02	2.0	0.05	0.005	2.5
PCB 21	0.040	0.01	1.0	0.05	0.005	2.5
PCB33	0.040	0.01	1.0	0.05	0.005	2.5
PCB 22	0.040	0.01	1.0	0.02	0.002	1
PCB 23	0.040	0.01	1.0	0.02	0.002	1
PCB 24	0.040	0.01	1.0	0.02	0.002	1
PCB 25	0.040	0.01	1.0	0.02	0.002	1
PCB 26	0.040	0.01	1.0	0.05	0.005	2.5
PCB 29	0.040	0.01	1.0	0.05	0.005	2.5
PCB 27	0.040	0.01	1.0	0.02	0.002	1
PCB 31	0.040	0.02	2.0	0.05	0.005	2.5
PCB 32	0.040	0.01	1.0	0.02	0.002	1
PCB 34	0.040	0.01	1.0	0.02	0.002	1
PCB 35	0.040	0.01	1.0	0.02	0.002	1
PCB 36	0.040	0.01	1.0	0.02	0.002	1
PCB 37	0.040	0.01	1.0	0.02	0.002	1
PCB 38	0.040	0.01	1.0	0.02	0.002	1
PCB 39	0.040	0.01	1.0	0.02	0.002	1
PCB 40	0.040	0.01	1.0	0.1	0.01	5
PCB 41	0.040	0.01	1.0	0.1	0.01	5
PCB 71	0.040	0.01	1.0	0.1	0.01	5
PCB 42	0.040	0.01	1.0	0.05	0.005	2.5
PCB 43	0.040	0.01	1.0	0.05	0.005	2.5
PCB 73	0.040	0.01	1.0	0.05	0.005	2.5
PCB 44	0.040	0.01	1.0	0.1	0.01	5
PCB 47	0.040	0.01	1.0	0.1	0.01	5
PCB 65	0.040	0.01	1.0	0.1	0.01	5
PCB 45	0.040	0.01	1.0	0.05	0.005	2.5
PCB 51	0.040	0.01	1.0	0.05	0.005	2.5
PCB 46	0.040	0.01	1.0	0.02	0.002	1
PCB 48	0.040	0.01	1.0	0.05	0.005	2.5
PCB 49	0.040	0.01	1.0	0.1	0.01	5
PCB 69	0.040	0.01	1.0	0.1	0.01	5
PCB 50	0.040	0.01	1.0	0.1	0.01	5
PCB 53	0.040	0.01	1.0	0.1	0.01	5
PCB 52	0.040	0.01	1.0	0.05	0.005	2.5

Parameter	TestAmerica Knoxville EMLs [1] (1668A, B & C)			1668C Reference Method EMLs [2]		
	Water ng/L	Other [3] ng/g	Extract ng/mL	Water ng/L	Other [3] ng/g	Extract ng/mL
PCB 54	0.040	0.01	1.0	0.05	0.005	2.5
PCB 55	0.040	0.01	1.0	0.05	0.005	2.5
PCB 56	0.040	0.01	1.0	0.05	0.005	2.5
PCB 57	0.040	0.01	1.0	0.05	0.005	2.5
PCB 58	0.040	0.01	1.0	0.05	0.005	2.5
PCB 59	0.040	0.01	1.0	0.1	0.01	5
PCB 62	0.040	0.01	1.0	0.1	0.01	5
PCB 75	0.040	0.01	1.0	0.1	0.01	5
PCB 60	0.040	0.01	1.0	0.05	0.005	2.5
PCB 61	0.040	0.02	2.0	0.2	0.02	10
PCB 70	0.040	0.02	2.0	0.2	0.02	10
PCB 74	0.040	0.02	2.0	0.2	0.02	10
PCB 76	0.040	0.02	2.0	0.2	0.02	10
PCB 63	0.040	0.01	1.0	0.005	0.05	2.5
PCB 64	0.040	0.01	1.0	0.05	0.005	2.5
PCB 66	0.040	0.01	1.0	0.05	0.005	2.5
PCB 67	0.040	0.01	1.0	0.05	0.005	2.5
PCB 68	0.040	0.01	1.0	0.05	0.005	2.5
PCB 72	0.040	0.01	1.0	0.05	0.005	2.5
PCB 77	0.040	0.01	1.0	0.05	0.005	2.5
PCB 78	0.040	0.01	1.0	0.05	0.005	2.5
PCB 79	0.040	0.01	1.0	0.05	0.005	2.5
PCB 80	0.040	0.01	1.0	0.05	0.005	2.5
PCB 81	0.040	0.01	1.0	0.05	0.005	2.5
PCB 82	0.040	0.01	1.0	0.05	0.005	2.5
PCB 83	0.040	0.01	1.0	0.1	0.01	5
PCB 84	0.040	0.01	1.0	0.02	0.002	1
PCB 85	0.040	0.01	1.0	0.1	0.01	5
PCB 116	0.040	0.01	1.0	0.1	0.01	5
PCB 117	0.040	0.01	1.0	0.1	0.01	5
PCB 86	0.040	0.01	1.0	0.2	0.02	10
PCB 87	0.040	0.01	1.0	0.2	0.02	10
PCB 97	0.040	0.01	1.0	0.2	0.02	10
PCB 109	0.040	0.01	1.0	0.2	0.02	10
PCB 119	0.040	0.01	1.0	0.2	0.02	10
PCB 125	0.040	0.01	1.0	0.2	0.02	10
PCB 88	0.040	0.01	1.0	0.05	0.005	2.5
PCB 91	0.040	0.01	1.0	0.05	0.005	2.5
PCB 89	0.040	0.01	1.0	0.05	0.005	2.5
PCB 90	0.040	0.01	1.0	0.2	0.02	10
PCB 101	0.040	0.01	1.0	0.2	0.02	10
PCB 113	0.040	0.01	1.0	0.2	0.02	10
PCB 92	0.040	0.01	1.0	0.05	0.005	2.5
PCB 93	0.040	0.01	1.0	0.2	0.02	10
PCB 100	0.040	0.01	1.0	0.2	0.02	10
PCB 94	0.040	0.01	1.0	0.05	0.005	2.5
PCB 95	0.040	0.01	1.0	0.2	0.02	10
PCB 96	0.040	0.01	1.0	0.05	0.005	2.5
PCB 98	0.040	0.01	1.0	0.2	0.02	10
PCB 102	0.040	0.01	1.0	0.2	0.02	10
PCB 99	0.040	0.01	1.0	0.1	0.01	5
PCB 112	0.040	0.01	1.0	0.05	0.005	2.5
PCB 103	0.040	0.01	1.0	0.05	0.005	2.5
PCB 104	0.040	0.01	1.0	0.05	0.005	2.5
PCB 105	0.040	0.01	1.0	0.05	0.005	2.5
PCB 106	0.040	0.01	1.0	0.05	0.005	2.5
PCB 107	0.040	0.01	1.0	0.05	0.005	2.5
PCB 108	0.040	0.01	1.0	0.1	0.01	5
PCB 124	0.040	0.01	1.0	0.1	0.01	5
PCB 110	0.040	0.01	1.0	0.1	0.01	5

Parameter	TestAmerica Knoxville EMLs [1] (1668A, B & C)			1668C Reference Method EMLs [2]		
	Water ng/L	Other [3] ng/g	Extract ng/mL	Water ng/L	Other [3] ng/g	Extract ng/mL
PCB 115	0.040	0.01	1.0	0.1	0.01	5
PCB 111	0.040	0.01	1.0	0.05	0.005	2.5
PCB 114	0.040	0.01	1.0	0.05	0.005	2.5
PCB 118	0.040	0.01	1.0	0.1	0.01	5
PCB 120	0.040	0.01	1.0	0.05	0.005	2.5
PCB 121	0.040	0.01	1.0	0.05	0.005	2.5
PCB 122	0.040	0.01	1.0	0.05	0.005	2.5
PCB 123	0.040	0.01	1.0	0.05	0.005	2.5
PCB 126	0.040	0.01	1.0	0.05	0.005	2.5
PCB 127	0.040	0.01	1.0	0.05	0.005	2.5
PCB 128	0.040	0.01	1.0	0.1	0.01	5
PCB 166	0.040	0.01	1.0	0.1	0.01	5
PCB 129	0.040	0.01	1.0	0.2	0.02	10
PCB 138	0.040	0.01	1.0	0.2	0.02	10
PCB 163	0.040	0.01	1.0	0.2	0.02	10
PCB 130	0.040	0.01	1.0	0.05	0.005	2.5
PCB 131	0.040	0.01	1.0	0.05	0.005	2.5
PCB 132	0.040	0.01	1.0	0.05	0.005	2.5
PCB 133	0.040	0.01	1.0	0.05	0.005	2.5
PCB 134	0.040	0.01	1.0	0.1	0.01	5
PCB 143	0.040	0.01	1.0	0.1	0.01	5
PCB 135	0.040	0.01	1.0	0.1	0.01	5
PCB 151	0.040	0.01	1.0	0.1	0.01	5
PCB 136	0.040	0.01	1.0	0.05	0.005	2.5
PCB 137	0.040	0.01	1.0	0.05	0.005	2.5
PCB 164	0.040	0.01	1.0	0.05	0.005	2.5
PCB 139	0.040	0.01	1.0	0.1	0.01	5
PCB 140	0.040	0.01	1.0	0.1	0.01	5
PCB 141	0.040	0.01	1.0	0.05	0.005	2.5
PCB 142	0.040	0.01	1.0	0.05	0.005	2.5
PCB 144	0.040	0.01	1.0	0.05	0.005	2.5
PCB 145	0.040	0.01	1.0	0.05	0.005	2.5
PCB 146	0.040	0.01	1.0	0.05	0.005	2.5
PCB 147	0.040	0.01	1.0	0.1	0.01	5
PCB 149	0.040	0.01	1.0	0.1	0.01	5
PCB 148	0.040	0.01	1.0	0.05	0.005	2.5
PCB 150	0.040	0.01	1.0	0.05	0.005	2.5
PCB 152	0.040	0.01	1.0	0.05	0.005	2.5
PCB 153	0.040	0.01	1.0	0.1	0.01	5
PCB 168	0.040	0.01	1.0	0.1	0.01	5
PCB 154	0.040	0.01	1.0	0.1	0.01	5
PCB 155	0.040	0.01	1.0	0.05	0.005	2.5
PCB 156	0.040	0.01	1.0	0.1	0.01	5
PCB 157	0.040	0.01	1.0	0.1	0.01	5
PCB 158	0.040	0.01	1.0	0.05	0.005	2.5
PCB 159	0.040	0.01	1.0	0.05	0.005	2.5
PCB 160	0.040	0.01	1.0	0.2	0.02	10
PCB 161	0.040	0.01	1.0	0.05	0.005	2.5
PCB 162	0.040	0.01	1.0	0.05	0.005	2.5
PCB 165	0.040	0.01	1.0	0.05	0.005	2.5
PCB 167	0.040	0.01	1.0	0.05	0.005	2.5
PCB 169	0.040	0.01	1.0	0.05	0.005	2.5
PCB 170	0.040	0.01	1.0	0.05	0.005	2.5
PCB 171	0.040	0.01	1.0	0.1	0.01	5
PCB 173	0.040	0.01	1.0	0.1	0.01	5
PCB 172	0.040	0.01	1.0	0.05	0.005	2.5
PCB 174	0.040	0.01	1.0	0.05	0.005	2.5
PCB 175	0.040	0.01	1.0	0.05	0.005	2.5
PCB 176	0.040	0.01	1.0	0.05	0.005	2.5
PCB 177	0.040	0.01	1.0	0.05	0.005	2.5

Parameter	TestAmerica Knoxville EMLs [1] (1668A, B & C)			1668C Reference Method EMLs [2]		
	Water ng/L	Other [3] ng/g	Extract ng/mL	Water ng/L	Other [3] ng/g	Extract ng/mL
PCB 178	0.040	0.01	1.0	0.05	0.005	2.5
PCB 179	0.040	0.01	1.0	0.05	0.005	2.5
PCB 180	0.040	0.01	1.0	0.1	0.01	5
PCB 193	0.040	0.01	1.0	0.1	0.01	5
PCB 181	0.040	0.01	1.0	0.05	0.005	2.5
PCB 182	0.040	0.01	1.0	0.05	0.005	2.5
PCB 183	0.040	0.01	1.0	0.1	0.01	5
PCB 185	0.040	0.01	1.0	0.1	0.01	5
PCB 184	0.040	0.01	1.0	0.05	0.005	2.5
PCB 186	0.040	0.01	1.0	0.05	0.005	2.5
PCB 187	0.040	0.01	1.0	0.05	0.005	2.5
PCB 188	0.040	0.01	1.0	0.05	0.005	2.5
PCB 189	0.040	0.01	1.0	0.05	0.005	2.5
PCB 190	0.040	0.01	1.0	0.05	0.005	2.5
PCB 191	0.040	0.01	1.0	0.05	0.005	2.5
PCB 192	0.040	0.01	1.0	0.05	0.005	2.5
PCB 194	0.040	0.01	1.0	0.05	0.005	2.5
PCB 195	0.040	0.01	1.0	0.05	0.005	2.5
PCB 196	0.040	0.01	1.0	0.05	0.005	2.5
PCB 197	0.040	0.01	1.0	0.1	0.01	5
PCB 200	0.040	0.01	1.0	0.1	0.01	5
PCB 198	0.040	0.01	1.0	0.1	0.01	5
PCB 199	0.040	0.01	1.0	0.1	0.01	5
PCB 201	0.040	0.01	1.0	0.05	0.005	2.5
PCB 202	0.040	0.01	1.0	0.1	0.01	5
PCB 203	0.040	0.01	1.0	0.05	0.005	2.5
PCB 204	0.040	0.01	1.0	0.05	0.005	2.5
PCB 205	0.040	0.01	1.0	0.05	0.005	2.5
PCB 206	0.040	0.01	1.0	0.05	0.005	2.5
PCB 207	0.040	0.01	1.0	0.05	0.005	2.5
PCB 208	0.040	0.01	1.0	0.05	0.005	2.5
PCB 209	0.040	0.01	1.0	0.05	0.005	2.5

[1] The estimated minimum level (EML) is defined as the lowest concentration at which an analyte can be measured reliably with common laboratory interferences present assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures The values for other matrices (solids, tissues and solid wastes) reflect the EMLs for Protocol 1 as described in Table 12. If the sample is prepared by another protocol described in that section, the EMLs shown in this table must be adjusted appropriately. The EMLs are based on the mean plus 2 standard deviations for matrix-pooled historical blank data and calibration data obtained while performing EPA 1668A. The survey period was fourteen months, ending in February 2004. Individual EMLs may be adjusted to reflect more recent data.

[2] For reference purposes only, not currently used by TestAmerica Knoxville

[3] Other matrices include solids, tissues and solid wastes

Table 5a- Concentration of Native PCB Congener Stock and Spiking Solutions

Native PCB Congener	PCB	Standard Source	Catalog Number	Vendor Conc (ng/mL)	LCS Spiking Solution Conc (ng/mL)
2-MoCB	1	AccuStd	S-99994-4x	4000	5.0
4-MoCB	3	AccuStd	S-99994-4x	4000	5.0
2,2'-DiCB	4	AccuStd	S-99994-4x	4000	5.0
4,4'-DiCB	15	AccuStd	S-99994-4x	4000	5.0
2,2',6-TrCB	19	AccuStd	S-99994-4x	4000	5.0
3,4,4'-TrCB	37	AccuStd	S-99994-4x	4000	5.0
2,2',6,6'-TeCB	54	AccuStd	S-99994-4x	4000	5.0
3,3',4,4'-TeCB	77	AccuStd	S-99994-4x	4000	5.0
3,4,4',5-TeCB	81	AccuStd	S-99994-4x	4000	5.0
2,2',4,6,6'-PeCB	104	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4'-PeCB	105	AccuStd	S-99994-4x	4000	5.0
2,3,4,4',5-PeCB	114	AccuStd	S-99994-4x	4000	5.0
2,3',4,4',5-PeCB	118	AccuStd	S-99994-4x	4000	5.0
2',3,4,4',5-PeCB	123	AccuStd	S-99994-4x	4000	5.0
3,3',4,4',5-PeCB	126	AccuStd	S-99994-4x	4000	5.0
2,2',4,4',6,6'-HxCB	155	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4',5-HxCB	156	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4',5'-HxCB	157	AccuStd	S-99994-4x	4000	5.0
2,3',4,4',5,5'-HxCB	167	AccuStd	S-99994-4x	4000	5.0
3,3',4,4',5,5'-HxCB	169	AccuStd	S-99994-4x	4000	5.0
2,2',3,3',4,4',5-HpCB	170	AccuStd	S-99994-4x	4000	5.0
2,2',3,4,4',5,5'-HpCB	180	AccuStd	S-99994-4x	4000	5.0
2,2',3,4',5,6,6'-HpCB	188	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4',5,5'-HpCB	189	AccuStd	S-99994-4x	4000	5.0
2,2',3,3',5,5',6,6'-OcCB	202	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4',5,5',6-OcCB	205	AccuStd	S-99994-4x	4000	5.0
2,2',3,3',4,4',5,5',6-NoCB	206	AccuStd	S-99994-4x	4000	5.0
2,2',3,3',4',5,5',6,6'-NoCB	208	AccuStd	S-99994-4x	4000	5.0
DeCB	209	AccuStd	S-99994-4x	4000	5.0
All other CB congeners	NA	AccuStd	S-99994-4x	4000	5.0

Table 5b: Concentration of $^{13}C_{12}$ Labeled PCB Congener Stock and Spiking Solutions

Labeled PCB Congener	**PCB**	**Standard Source**	**Catalog Number**	**Vendor Conc (ng/mL)**	Stock Conc (ng/mL)	Spiking Solution Conc (ng/mL)
Internal Standards						
$^{13}C_{12}$-2-chlorobiphenyl	1L	Cambridge	EC-4908	40,000	1000	10
$^{13}C_{12}$-4-chlorobiphenyl	3L	Cambridge	EC-4990	40,000	1000	10
$^{13}C_{12}$-2,2'-dichlorobiphenyl	4L	Cambridge	EC-4911	40,000	1000	10
$^{13}C_{12}$-4,4'-dichlorobiphenyl	15L	Cambridge	EC-1402	40,000	1000	10
$^{13}C_{12}$-2,2',6-trichlorobiphenyl	19L	Cambridge	EC-4909	40,000	1000	10
$^{13}C_{12}$-3,4,4'-trichlorobiphenyl	37L	Cambridge	EC-4901	40,000	1000	10
$^{13}C_{12}$-2,2',6,6'-tetrachlorobiphenyl	54L	Cambridge	EC-4912	40,000	1000	10
$^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl	77L	Cambridge	EC-1404	40,000	1000	10
$^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl	81L	Cambridge	EC-1412	40,000	1000	10
$^{13}C_{12}$-2,2',4,6,6'-pentachlorobiphenyl	104L	Cambridge	EC-4910	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl	105L	Cambridge	EC-1420	40,000	1000	10
$^{13}C_{12}$2,3,4,4',5-pentachlorobiphenyl -	114L	Cambridge	EC-4902	40,000	1000	10
$^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl	118L	Cambridge	EC-1435	40,000	1000	10
$^{13}C_{12}$-2',3,4,4',5-pentachlorobiphenyl	123L	Cambridge	EC-4904	40,000	1000	10
$^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl	126L	Cambridge	EC-1425	40,000	1000	10
$^{13}C_{12}$-2,2',4,4',6,6'-hexachlorobiphenyl	155L	Cambridge	EC-4167	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl	156L	Cambridge	EC-1422	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl	157L	Cambridge	EC-4051	40,000	1000	10
$^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl	167L	Cambridge	EC-4050	40,000	1000	10
$^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl	169L	Cambridge	EC-1416	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl	170L	Cambridge	EC-4905	40,000	1000	10
$^{13}C_{12}$-2,2',3,4',5,6,6'-heptachlorobiphenyl	188L	Cambridge	EC-4913	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl	189L	Cambridge	EC-1409	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl	202L	Cambridge	EC-1408	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4',5,5',6-octachlorobiphenyl	205L	Cambridge	EC-4199	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206L	Cambridge	EC-4900	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	208L	Cambridge	EC-1419	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	209L	Cambridge	EC-1410	40,000	1000	10
Recovery Standards						
$^{13}C_{12}$-2,5-dichlorobiphenyl	9L	Cambridge	EC-4165	40,000	1000	100
$^{13}C_{12}$-2,4',5-trichlorobiphenyl	31L	Wellington	MBP-31	50,000	1000	100
$^{13}C_{12}$-2,4',6-trichlorobiphenyl	32L	Cambridge	EC-4163	40,000	1000	100
$^{13}C_{12}$-2,2',5,5'-tetrachlorobiphenyl	52L	Cambridge	EC-1424	40,000	1000	100
$^{13}C_{12}$-2,2',4,5,5'-pentachlorobiphenyl	101L	Cambridge	EC-1405	40,000	1000	100
$^{13}C_{12}$-3,3',4,5,5'-pentachlorobiphenyl	127L	Cambridge	EC-1421	40,000	1000	100
$^{13}C_{12}$-2,2',3,4,4',5'-hexachlorobiphenyl	138L	Cambridge	EC-1436	40,000	1000	100
$^{13}C_{12}$-2,2',3,4,4',5,5'-heptachlorobiphenyl	180L	Cambridge	EC-1407	40,000	1000	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-octachlorobiphenyl	194L	Cambridge	EC-1418	40,000	1000	100
Cleanup Standards						
$^{13}C_{12}$-2,4,4'-trichlorobiphenyl	28L	Cambridge	EC-1413	40,000	5000	10
$^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl	111L	Cambridge	EC-1415	40,000	5000	10
$^{13}C_{12}$-2,2',3,3',5,5',6-heptachlorobiphenyl	178L	Cambridge	EC-1417	40,000	5000	10
Sampling Surrogate Standards						
$^{13}C_{12}$-2,4'-dichlorobiphenyl	8L	Cambridge	EC-5095	40,000	5000	50
$^{13}C_{12}$-3,3',4,5'-tetrachlorobiphenyl	79L	Cambridge	EC-5048	40,000	5000	50
$^{13}C_{12}$-2,2',3,5',6-pentachlorobiphenyl	95L	Wellington	MBP-95	50,000	5000	50
$^{13}C_{12}$-2,2',4,4',5,5'-hexachlorobiphenyl	153L	Cambridge	EC-1406	40,000	5000	50

Table 6a - Concentration of PCBs in Calibration Solutions

Analyte Type	PCB[1]	CS 0.5 ng/mL	CS 1 ng/mL	CS 2 ng/mL	CS 3[2] ng/mL	CS 4 ng/mL	CS 5 ng/mL
Congeners							
2-MoCB	1	0.5	1.0	5.0	50	400	2000
4-MoCB	3	0.5	1.0	5.0	50	400	2000
2,2'-DiCB	4	0.5	1.0	5.0	50	400	2000
4,4'-DiCB	15	0.5	1.0	5.0	50	400	2000
2,2',6'-TrCB	19	0.5	1.0	5.0	50	400	2000
3,4,4'-TrCB	37	0.5	1.0	5.0	50	400	2000
2,2',6,6'-TeCB	54	0.5	1.0	5.0	50	400	2000
3,3',4,4'-TeCB	77	0.5	1.0	5.0	50	400	2000
3,4,4',5-TeCB	81	0.5	1.0	5.0	50	400	2000
2,2',4,6,6'-PeCB	104	0.5	1.0	5.0	50	400	2000
2,3,3',4,4'-PeCB	105	0.5	1.0	5.0	50	400	2000
2,3,4,4',5-PeCB	114	0.5	1.0	5.0	50	400	2000
2,3',4,4',5-PeCB	118	0.5	1.0	5.0	50	400	2000
2',3,4,4',5-PeCB	123	0.5	1.0	5.0	50	400	2000
3,3',4,4',5-PeCB	126	0.5	1.0	5.0	50	400	2000
2,2',4,4',6,6'-HxCB	155	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5-HxCB	156	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5'-HxCB	157	0.5	1.0	5.0	50	400	2000
2,3',4,4',5,5'-HxCB	167	0.5	1.0	5.0	50	400	2000
3,3',4,4',5,5'-HxCB	169	0.5	1.0	5.0	50	400	2000
2,2',3,4',5,6,6'-HpCB	188	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5,5'-HpCB	189	0.5	1.0	5.0	50	400	2000
2,2',3,3',5,5',6,6'-OcCB	202	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5,5',6-OcCB	205	0.5	1.0	5.0	50	400	2000
2,2',3,3',4,4',5,5',6-NoCB	206	0.5	1.0	5.0	50	400	2000
2,2',3,3',4',5,5',6,6'-NoCB	208	0.5	1.0	5.0	50	400	2000
DeCB	209	0.5	1.0	5.0	50	400	2000
All other CB congeners		0.5	1.0	5.0	50	400	2000
Labeled Congeners							
$^{13}C_{12}$-2-MoCB	1L	100	100	100	100	100	100
$^{13}C_{12}$-4-MoCB	3L	100	100	100	100	100	100
$^{13}C_{12}$-2,2'-DiCB	4L	100	100	100	100	100	100
$^{13}C_{12}$-4,4'-DiCB	15L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',6-TrCB	19L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4'-TrCB	37L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4'-TeCB	77L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	100	100	100	100	100
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5-HxCB	156L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB	157L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5-HpCB	170L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB	189L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	100	100	100	100	100

Analyte Type	PCB[1]	CS 0.5 ng/mL	CS 1 ng/mL	CS 2 ng/mL	CS 3[2] ng/mL	CS 4 ng/mL	CS 5 ng/mL
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4',5,5',6,6'-NoCB	208L	100	100	100	100	100	100
$^{13}C_{12}$-DeCB	209L	100	100	100	100	100	100
Cleanup Standards							
$^{13}C_{12}$-2,4,4'-TriCB	28L			5.0	50	400	--
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L			5.0	50	400	--
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L			5.0	50	400	--
Recovery Standards							
$^{13}C_{12}$-2,5-DiCB	9L	100	100	100	100	100	100
$^{13}C_{12}$-2,4',5-TriCB	31L	100	100	100	100	100	100
$^{13}C_{12}$-2,4',6-TriCB	32L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',5,5'-TeCB	52L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4',5,5'-PeCB	101L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,5,5'-PeCB	127L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3',4,4',5'-HxCB	138L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,4,4',5,5'-HpCB	180L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB	194L	100	100	100	100	100	100
Labeled Sampling Surrogates							
$^{13}C_{12}$-2,4'-DiCB	8L			5.0	50	400	--
$^{13}C_{12}$-3,3',4,5'-TeCB	79L			5.0	50	400	--
$^{13}C_{12}$-2,2',3,5',6-PeCB	95L			5.0	50	400	--
$^{13}C_{12}$-2,2',4,4',5,5'-HxCB	153L			5.0	50	400	--

Notes:

1. Suffix “L” indicates labeled compound.

2. The CS 3 standard is also used as the calibration verification solution.

Table 6b – Preparation of Calibration Solutions

Calibration Standard ID	Parent Standards	Parent Conc. (ng/mL)	Volume Added (mL)	Final Volume (mL)	Final Conc (ng/mL)
CS 0.5	Native PCB Congener Stock Solution	40	0.0125	1.0	0.50
	Internal Standard Stock Solution	1000	0.1000		100
	Recovery Standard Stock Solution	1000	0.1000		100
CS 1	Native PCB Congener Stock Solution	40	0.0250	1.0	1.0
	Internal Standard Stock Solution	1000	0.1000		100
	Recovery Standard Stock Solution	1000	0.1000		100
CS 2	Native PCB Congener Stock Solution	40	0.1250	1.0	5.0
	Internal Standard Stock Solution	1000	0.1000		100
	Recovery Standard Stock Solution	1000	0.1000		100
	Cleanup Standard Stock Solution	5000	0.0010		5.0
	Sampling Surrogate Stock Solution	5000	0.0010		5.0
CS 3	Native PCB Congener Standard Mix	4000	0.0375	3.0	50
	Internal Standard Stock Solution	1000	0.3000		100
	Recovery Standard Stock Solution	1000	0.3000		100
	Cleanup Standard Stock Solution	5000	0.0300		50
	Sampling Surrogate Stock Solution	5000	0.0300		50
CS 4	Native PCB Congener Standard Mix	4000	0.1000	1.0	400
	Internal Standard Stock Solution	1000	0.1000		100
	Recovery Standard Stock Solution	1000	0.1000		100
	Cleanup Standard Stock Solution	5000	0.0800		400
	Sampling Surrogate Stock Solution	5000	0.0800		400
CS 5	Native PCB Congener Standard Mix	4000	0.5000	1.0	2000
	Internal Standard Stock Solution	1000	0.1000		100
	Recovery Standard Stock Solution	1000	0.1000		100

Table 7 - GC Window Defining Mixture and SPB –Octyl Resolution Test Compounds

SPB-Octyl

Congener Group	First Eluted		Last Eluted	
Mono	1	2-	3	4-
Di	4	2,2'-	15	4,4'-
Tri	19	2,2',6-	37	3,4,4'-
Tetra	54	2,2',6,6'-	77	3,3',4,4'-
Penta	104	2,2',4,6,6'-	126	3,3',4,4',5-
Hexa	155	2,2',4,4',6,6'-	169	3,3',4,4',5,5'-
Hepta	188	2,2',3,4',5,6,6'-	189	2,3,3',4,4',5,5'-
Octa	202	2,2',3,3',5,5',6,6'-	205	2,3,3',4,4',5,5',6-
Nona	208	2,2',3,3',4,5,5',6,6'-	206	2,2',3,3',4,4',5,5',6-
Deca	209	2,2',3,3',4,4',5,5',6,6'-	209	2,2',3,3',4,4',5,5',6,6'-

SPB-Octyl Resolution Test Compounds

23	2,3,5-trichlorobiphenyl
34	2',3,5-trichlorobiphenyl (2,3',5'-trichlorobiphenyl)
182	2,2',3,4,4',5,6'-heptachlorobiphenyl
187	2,2',3,4',5,5',6-heptachlorobiphenyl

Table 8 - Ions Monitored for HRGC/HRMS Analysis of PCBs

Descriptor	Accurate Mass	Ion ID	Elemental Composition	Analyte
1	180.9888	Lock	C_4F_7	PFK
	188.0393	M	$C_{12}H_9{}^{35}Cl$	Mono
	190.0363	M+2	$C_{12}H_9{}^{37}Cl$	Mono
	200.0795	M	$^{13}C_{12}H_9{}^{35}Cl$	Mono-13C12
	202.0766	M+2	$^{13}C_{12}H_9{}^{37}Cl$	Mono-13C12
	222.0003	M	$C_{12}H_8{}^{35}Cl_2$	Di
	223.9974	M+2	$C_{12}H_8{}^{35}Cl^{37}Cl$	Di
	234.0406	M	$^{13}C_{12}H_8{}^{35}Cl_2$	Di-13C
	236.0376	M+2	$^{13}C_{12}H_8{}^{35}Cl^{37}Cl$	Di-13C
	255.9613	M	$C_{12}H_7{}^{35}Cl_3$	Tri
	257.9584	M+2	$C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Tri
	268.0016	M	$^{13}C_{12}H_7{}^{35}Cl_3$	Tri-13C
	269.9986	M+2	$^{13}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Tri-13C
	280.9824	QC	C_6F_{11}	PFK
	289.9224	M	$C_{12}H_6{}^{35}Cl_4$	Tetra
	291.9194	M+2	$C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Tetra
	301.9626	M	$^{13}C_{12}H_6{}^{35}Cl_4$	Tetra-13C
	303.9597	M+2	$^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Tetra-13C
2	255.9613	M	$C_{12}H_7{}^{35}Cl_3$	Tri
	257.9584	M+2	$C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Tri
	268.0016	M	$^{13}C_{12}H_7{}^{35}Cl_3$	Tri-13C
	268.9824	Lock	C_5F_{11}	PFK
	269.9986	M+2	$^{13}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Tri-13C
	289.9224	M	$C_{12}H_6{}^{35}Cl_4$	Tetra
	291.9194	M+2	$C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Tetra
	301.9626	M	$^{13}C_{12}H_6{}^{35}Cl_4$	Tetra-13C
	303.9597	M+2	$^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Tetra-13C
	325.8804	M+2	$C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Penta
	327.8775	M+4	$C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Penta
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Penta-13C
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Penta-13C
	359.8415	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Hexa
	361.8385	M+4	$C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Hexa
	371.8817	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Hexa-13C
	373.8788	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Hexa-13C
	380.9760	QC	$C_{10}F_{14}$	PFK

Table 8 - Ions Monitored for HRGC/HRMS Analysis of PCBs (continued)

Descriptor	Accurate Mass	Ion ID	Elemental Composition	Analyte
3	325.8804	M+2	$C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Penta
	327.8775	M+4	$C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Penta
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Penta-13C
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Penta-13C
	342.9792	Lock	C_8F_{13}	PFK
	359.8415	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Hexa
	361.8385	M+4	$C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Hexa
	371.8817	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Hexa-13C
	373.8788	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Hexa-13C
	393.8025	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Hepta
	395.7995	M+4	$C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Hepta
	405.8428	M+2	$^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Hepta-13C
	407.8398	M+4	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Hepta-13C
	427.7635	M+2	$C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Octa
	429.7606	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Octa
	430.9728	QC	C_9F_{17}	PFK
	439.8038	M+2	$^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Octa-13C
	441.8008	M+4	$^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Octa-13C
4	393.8025	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Hepta
	395.7995	M+4	$C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Hepta
	404.9760	Lock	$C_{10}F_{15}$	PFK
	405.8428	M+2	$^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Hepta-13C
	407.8398	M+4	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Hepta-13C
	427.7635	M+2	$C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Octa
	429.7606	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Octa
	439.8038	M+2	$^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Octa-13C
	441.8008	M+4	$^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Octa-13C
	461.7246	M+2	$C_{12}H^{35}Cl_7{}^{37}Cl_2$	Nona
	463.7216	M+4	$C_{12}H^{35}Cl_6{}^{37}Cl_3$	Nona
	473.7648	M+2	$^{13}C_{12}H^{35}Cl_7{}^{37}Cl_2$	Nona-13C
	475.7619	M+4	$^{13}C_{12}H^{35}Cl_6{}^{37}Cl_3$	Nona-13C
	495.6856	M+2	$C_{12}{}^{35}Cl_8{}^{37}Cl_2$	Deca
	497.6826	M+4	$C_{12}{}^{35}Cl_7{}^{37}Cl_3$	Deca
	504.9697	QC	$C_{12}F_{19}$	PFK
	507.7258	M+2	$^{13}C_{12}{}^{35}Cl_8{}^{37}Cl_2$	Deca-13C
	509.7229	M+4	$^{13}C_{12}{}^{35}Cl_7{}^{37}Cl_3$	Deca-13C

1. Nuclidic masses used: H = 1.007825 C = 12.00000 ^{13}C = 13.003355 F = 18.9984

O = 15.994915 ^{35}Cl = 34.968853 ^{37}Cl = 36.965903

Table 9 - Theoretical Ion Abundance Ratios and Control Limits for PCBs

Chlorine Atoms	mass's Forming Ratios	Theoretical Ratio	Lower QC Limit	Upper QC Limit
1	m/m+2	3.13	2.66	3.60
2	m/m+2	1.56	1.33	1.79
3	m/m+2	1.04	0.88	1.20
4	m/m+2	0.77	0.65	0.89
5	m+2/m+4	1.55	1.32	1.78
6	m+2/m+4	1.24	1.05	1.43
7	m+2/m+4	1.05	0.89	1.21
8	m+2/m+4	0.89	0.76	1.02
9	m+2/m+4	0.77	0.65	0.89
10	m+2/m+4	0.69	0.59	0.79

Table 10A - Acceptance Criteria for Performance Tests (1668A & B)

			IPR (IDOC)			
Toxic & LOC Congeners	**PCB**	**Test Conc (ng/mL)** [1]	**%RSD**	**%R**	**VER %R**	**LCS %R**
2-chlorobiphenyl	1	50	40	60-140	70-130	50-150
4-chlorobiphenyl	3	50	40	60-140	70-130	50-150
2,2'-dichlorobiphenyl	4	50	40	60-140	70-130	50-150
4,4'-dichlorobiphenyl	15	50	40	60-140	70-130	50-150
2,2',6-trichlorobiphenyl	19	50	40	60-140	70-130	50-150
3,4,4'-trichlorobiphenyl	37	50	40	60-140	70-130	50-150
2,2',6,6'-tetrachlorobiphenyl	54	50	40	60-140	70-130	50-150
3,3',4,4'-tetrachlorobiphenyl	77	50	40	60-140	70-130	50-150
3,4,4',5-tetrachlorobiphenyl	81	50	40	60-140	70-130	50-150
2,2'4,6,6'-pentachlorobiphenyl	104	50	40	60-140	70-130	50-150
2,3,3',4,4'-pentachlorobiphenyl	105	50	40	60-140	70-130	50-150
2,3,4,4',5-pentachlorobiphenyl	114	50	40	60-140	70-130	50-150
2,3',4,4',5-pentachlorobiphenyl	118	50	40	60-140	70-130	50-150
2',3',4,4',5-pentachlorobiphenyl	123	50	40	60-140	70-130	50-150
3,3',4,4',5-pentachlorobiphenyl	126	50	40	60-140	70-130	50-150
2,2',4,4',6,6'-hexachlorobiphenyl	155	50	40	60-140	70-130	50-150
2,3,3',4,4',5-hexachlorobiphenyl	156	50	40	60-140	70-130	50-150
2,3',4,4',5,5'-hexachlorobiphenyl	157	50	40	60-140	70-130	50-150
2,3,3',4,4',5'-hexachlorobiphenyl	167	50	40	60-140	70-130	50-150
3,3',4,4',5,5'-hexachlorobiphenyl	169	50	40	60-140	70-130	50-150
2,2',3,4'5,6,6'-heptachlorobiphenyl	188	50	40	60-140	70-130	50-150
2,3,3',4,4',5,5'-heptachlorobiphenyl	189	50	40	60-140	70-130	50-150
2,2',3,3',5,5',6,6'-octachlorobiphenyl	202	50	40	60-140	70-130	50-150
2,3,3',4,4',5,5',6-octachlorobiphenyl	205	50	40	60-140	70-130	50-150
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206	50	40	60-140	70-130	50-150
2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	208	50	40	60-140	70-130	50-150
2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	209	50	40	60-140	70-130	50-150
Internal Standards						
$^{13}C_{12}$-2-chlorobiphenyl	1L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-4-chlorobiphenyl	3L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,2'-dichlorobiphenyl	4L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-4,4'-dichlorobiphenyl	15L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,2',6-trichlorobiphenyl	19L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-3,4,4'-trichlorobiphenyl	37L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,2',6,6'-tetrachlorobiphenyl	54L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl	77L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl	81L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,2',4,6,6'-pentachlorobiphenyl	104L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl	105L	100	50	35-135	50-150	30-140
$^{13}C_{12}$2,3,4,4',5-pentachlorobiphenyl -	114L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl	118L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2',3,4,4',5-pentachlorobiphenyl	123L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl	126L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,2',4,4',6,6'-hexachlorobiphenyl	155L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl	156L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl	157L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl	167L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl	169L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl	170L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,2',3,4',5,6,6'-heptachlorobiphenyl	188L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl	189L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl	202L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,3,3',4,4',5,5',6-octachlorobiphenyl	205L	100	50	35-135	50-150	30-140

			IPR (IDOC)			
Toxic & LOC Congeners	**PCB**	**Test Conc (ng/mL)** [1]	**%RSD**	**%R**	**VER %R**	**LCS %R**
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	208L	100	50	35-135	50-150	30-140
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	209L	100	50	35-135	50-150	30-140
Cleanup Standards						
$^{13}C_{12}$-2,4,4'-trichlorobiphenyl	28L	50	45	45-120	60-130	40-125
$^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl	111L	50	45	45-120	60-130	40-125
$^{13}C_{12}$-2,2',3,3',5,5',6-heptachlorobiphenyl	178L	50	45	45-120	60-130	40-125
Sampling Surrogate Standards						
$^{13}C_{12}$-2,4'-dichlorobiphenyl	8L	50			50-150	50-150
$^{13}C_{12}$-3,3',4,5'-tetrachlorobiphenyl	79L	50			50-150	50-150
$^{13}C_{12}$-2,2',3,5',6-pentachlorobiphenyl	95L	50			50-150	50-150
$^{13}C_{12}$-2,2',4,4',5,5'-hexachlorobiphenyl	153L	50			50-150	50-150

[1] - Test concentrations are based on ng/mL in the sample extract or standard solution.

Table 10B - Acceptance Criteria for Performance Tests (1668C)

			IPR (IDOC)				
Toxic & LOC Congeners	**PCB**	**Test Conc (ng/mL)** [1]	**%RSD**	**Mean %R**	**VER %R**	**OPR (LCS) %R**	**Labeled Compound %R in Samples**
2-chlorobiphenyl	1	50	25	70-130	75-125	60-135	
4-chlorobiphenyl	3	50	25	70-130	75-125	60-135	
2,2'-dichlorobiphenyl	4	50	25	70-130	75-125	60-135	
4,4'-dichlorobiphenyl	15	50	25	70-130	75-125	60-135	
2,2',6-trichlorobiphenyl	19	50	25	70-130	75-125	60-135	
3,4,4'-trichlorobiphenyl	37	50	25	70-130	75-125	60-135	
2,2',6,6'-tetrachlorobiphenyl	54	50	25	70-130	75-125	60-135	
3,3',4,4'-tetrachlorobiphenyl	77	50	25	70-130	75-125	60-135	
3,4,4',5-tetrachlorobiphenyl	81	50	25	70-130	75-125	60-135	
2,2'4,6,6'-pentachlorobiphenyl	104	50	25	70-130	75-125	60-135	
2,3,3',4,4'-pentachlorobiphenyl	105	50	25	70-130	75-125	60-135	
2,3,4,4',5-pentachlorobiphenyl	114	50	25	70-130	75-125	60-135	
2,3',4,4',5-pentachlorobiphenyl	118	50	25	70-130	75-125	60-135	
2',3',4,4',5-pentachlorobiphenyl	123	50	25	70-130	75-125	60-135	
3,3',4,4',5-pentachlorobiphenyl	126	50	25	70-130	75-125	60-135	
2,2',4,4',6,6'-hexachlorobiphenyl	155	50	25	70-130	75-125	60-135	
2,3,3',4,4',5-hexachlorobiphenyl	156	50	25	70-130	75-125	60-135	
2,3',4,4',5,5'-hexachlorobiphenyl	157	50	25	70-130	75-125	60-135	
2,3,3',4,4',5'-hexachlorobiphenyl	167	50	25	70-130	75-125	60-135	
3,3',4,4',5,5'-hexachlorobiphenyl	169	50	25	70-130	75-125	60-135	
2,2',3,4'5,6,6'-heptachlorobiphenyl	188	50	25	70-130	75-125	60-135	
2,3,3',4,4',5,5'-heptachlorobiphenyl	189	50	25	70-130	75-125	60-135	
2,2',3,3',5,5',6,6'-octachlorobiphenyl	202	50	25	70-130	75-125	60-135	
2,3,3',4,4',5,5',6-octachlorobiphenyl	205	50	25	70-130	75-125	60-135	
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206	50	25	70-130	75-125	60-135	
2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	208	50	25	70-130	75-125	60-135	
2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	209	50	25	70-130	75-125	60-135	
Internal Standards							
$^{13}C_{12}$-2-chlorobiphenyl	1L	100	70	20-135	50-145	15-145	5-145
$^{13}C_{12}$-4-chlorobiphenyl	3L	100	70	20-135	50-145	15-145	5-145
$^{13}C_{12}$-2,2'-dichlorobiphenyl	4L	100	70	20-135	50-145	15-145	5-145
$^{13}C_{12}$-4,4'-dichlorobiphenyl	15L	100	70	20-135	50-145	15-145	5-145
$^{13}C_{12}$-2,2',6-trichlorobiphenyl	19L	100	70	20-135	50-145	15-145	5-145
$^{13}C_{12}$-3,4,4'-trichlorobiphenyl	37L	100	70	20-135	50-145	15-145	5-145
$^{13}C_{12}$-2,2',6,6'-tetrachlorobiphenyl	54L	100	70	20-135	50-145	15-145	5-145
$^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl	77L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl	81L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-2,2',4,6,6'-pentachlorobiphenyl	104L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl	105L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$2,3,4,4',5-pentachlorobiphenyl -	114L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl	118L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-2',3,4,4',5-pentachlorobiphenyl	123L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl	126L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-2,2',4,4',6,6'-hexachlorobiphenyl	155L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl	156L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl	157L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl	167L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl	169L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-2,2',3,4',5,6,6'-heptachlorobiphenyl	188L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl	189L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl	202L	100	50	45-135	50-145	40-145	10-145

			IPR (IDOC)				
Toxic & LOC Congeners	**PCB**	**Test Conc (ng/mL)** [1]	**%RSD**	**Mean %R**	**VER %R**	**OPR (LCS) %R**	**Labeled Compound %R in Samples**
$^{13}C_{12}$-2,3,3',4,4',5,5',6-octachlorobiphenyl	205L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	208L	100	50	45-135	50-145	40-145	10-145
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	209L	100	50	45-135	50-145	40-145	10-145
Cleanup Standards							
$^{13}C_{12}$-2,4,4'-trichlorobiphenyl	28L	50	70	20-135	65-135	15-145	5-145
$^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl	111L	50	50	45-135	75-125	40-145	10-145
$^{13}C_{12}$-2,2',3,3',5,5',6-heptachlorobiphenyl	178L	50	50	45-135	75-125	40-145	10-145
Sampling Surrogate Standards							
$^{13}C_{12}$-2,4'-dichlorobiphenyl	8L	50			50-150	50-150	50-150
$^{13}C_{12}$-3,3',4,5'-tetrachlorobiphenyl	79L	50			50-150	50-150	50-150
$^{13}C_{12}$-2,2',3,5',6-pentachlorobiphenyl	95L	50			50-150	50-150	50-150
$^{13}C_{12}$-2,2',4,4',5,5'-hexachlorobiphenyl	153L	50			50-150	50-150	50-150

[1] - Test concentrations are based on ng/mL in the sample extract or standard solution.

Table 11 - Retention Times of Isomers on the SPB-Octyl Column for the PCB Standard Mixes[1]

PCB Congener Mix 1 (AccustandardM-1668-1)

Cl Level	BZ No.[2]	Cl Level	BZ No.[2]	Cl Level	BZ No.[2]
1	2	4	78	6	161
2	10	4	81	6	153
2	9	5	96	6	130
2	6	5	103	6	129
2	8	5	95	6	166
2	14	5	88	6	159
2	11	5	89	6	167
3	30	5	92	6	156
3	27	5	113	7	179
3	32	5	83	7	176
3	34	5	119	7	178
3	26	5	87	7	175
3	31	5	85	7	183
3	33	5	82	7	177
3	36	5	120	7	171
3	38	5	124	7	172
3	35	5	106	7	191
4	50	5	122	7	170
4	45	5	105	7	190
4	52	5	127	8	200/201
4	49	6	152	8	204
4	75	6	136	8	199/200
4	41	6	148	8	198
4	72	6	151	8	196
4	57	6	144	8	195
4	63	6	143	8	194
4	66	6	142	9	207
4	79	6	133		

PCB Congener Mix 2 (Accustandard M-1668-2)

Cl Level	BZ No.[2]	Cl Level	BZ No.[2]	Cl Level	BZ No.[2]
2	7	4	55	6	139
2	5	4	60	6	132
2	12	5	94	6	165
3	18	5	100	6	168
3	24	5	91	6	137
3	23	5	121	6	160
3	28	5	90	6	128
3	22	5	99	6	162
3	39	5	109/108	6	157
4	53	5	117	7	184
4	51	5	111	7	186
4	73	5	108/107	7	187
4	48	5	118	7	185
4	62	5	114	7	181
4	71	6	150	7	192
4	68	6	145	8	197
4	58	6	135	8	201/199
4	61	6	149	8	203

Table 11 - Retention Times of Isomers on the SPB-Octyl Column for the PCB Standard Mixes[1] (Continued)

PCB Congener Mix 3 (Accustandard M-1668-3)

Cl Level	BZ No.[2]	Cl Level	BZ No.[2]	Cl Level	BZ No.[2]
2	13	4	80	6	140
3	17	5	93	6	146
3	29	5	84	6	141
3	20	5	101	6	164
4	46	5	112	6	158
4	65	5	86	7	182
4	59	5	116	7	174
4	40	5	107/109	7	173
4	67	6	154	7	193
4	76	6	147		

PCB Congener Mix 4 (Accustandard M-1668-4)

Cl Level	BZ No.[2]	Cl Level	BZ No.[2]	Cl Level	BZ No.[2]
3	25	4	64	5	123
3	21	4	70	6	134
4	69	5	102	6	131
4	47	5	97	6	163
4	42	5	115	7	180

PCB Congener Mix 5 (AccustandardM-1668-5)

Cl Level	BZ No.[2]	Cl Level	BZ No.[2]	Cl Level	BZ No.[2]
1	1	4	74	6	169
1	3	4	56	7	188
2	4	4	77	7	189
2	15	5	104	8	202
3	19	5	98	8	205
3	16	5	125	9	208
3	37	5	110	9	206
4	54	5	126	10	209
4	43	6	155		
4	44	6	138		

Notes:

[1] Each congener mix is analyzed in triplicate to establish the retention times of the PCB isomers in the absence of co-eluting isomers. The elution order listed here is used to assign peak identifications in the separate mixture analysis. The average retention time established in the analysis of the separate mixtures is then used to establish relative retention times. (See sections 10.2.3)

[2] BZ/IUPAC Number, if different.

Table 12: Assignment of Sample Preparation Protocols

1668 Protocol	Protocol Name	Sample Amount Extracted (g)	Fraction of Extract Cleaned	IS Added (mL)	Cleanup Std Added (mL)	Recovery Std Added (µL)	Extract Delivery Volume (µL)	Prep Split Factor	Prep Dilution Factor	QuantIMS Final Volume
P1	Clean	10	1/2	1	0.5 (added aftersplit)	50	50	2	1	100
P2	Low	2	1	1	1	100	100	1	1	100
P3	Medium	1.25	1/2	2	1 (added after split)	100	250	2	2.5	200
P4	High	1	1/4	4	1 (added after split)	100	500	4	5	400

Figure 1 - Recommended GC Operating Conditions

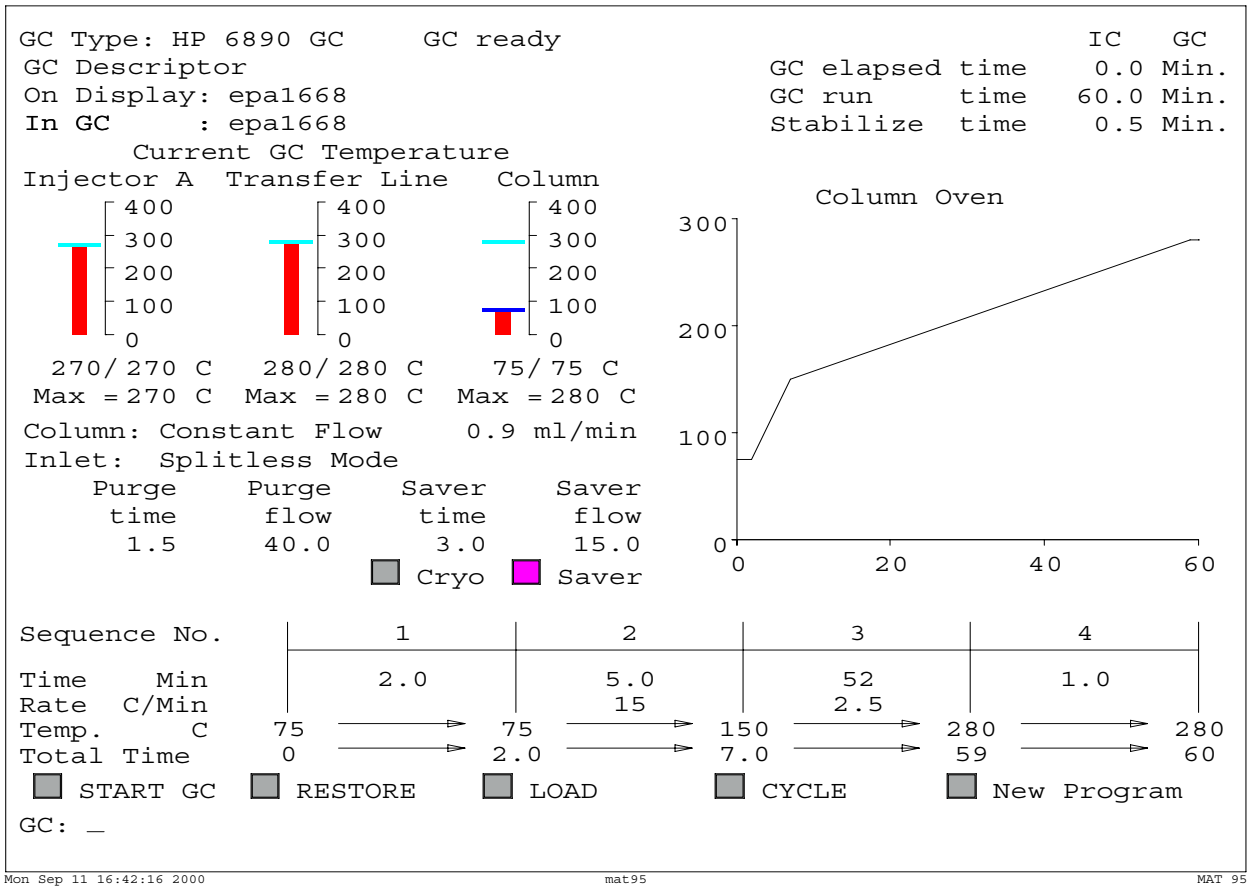
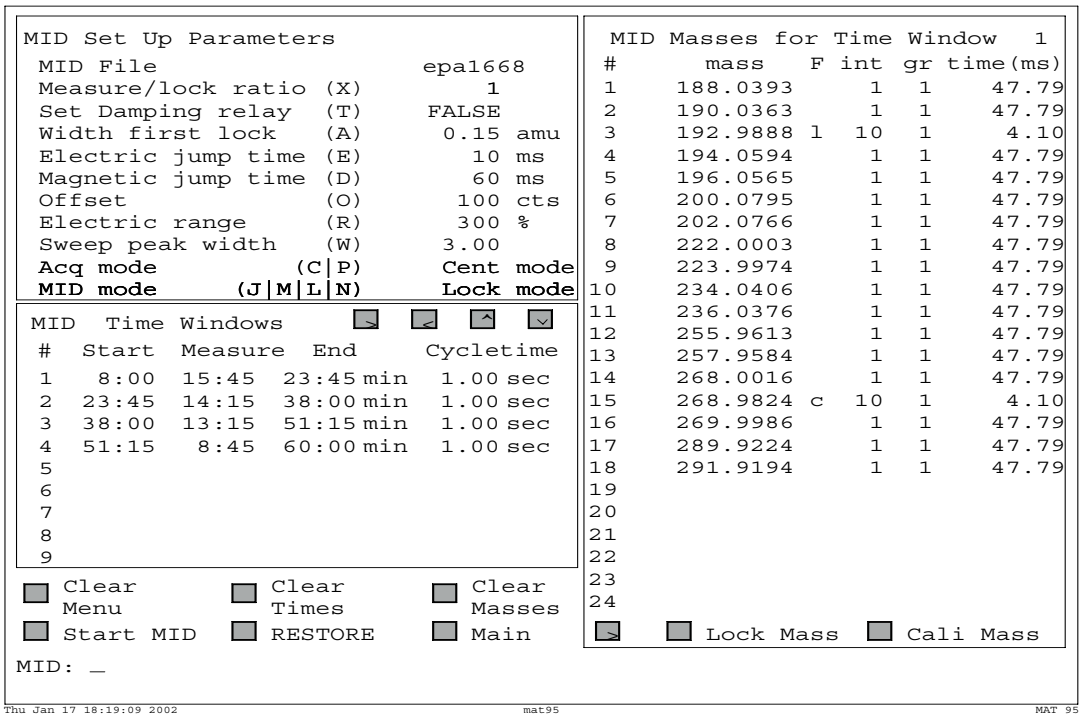


Figure 2 - Recommended MID Descriptors



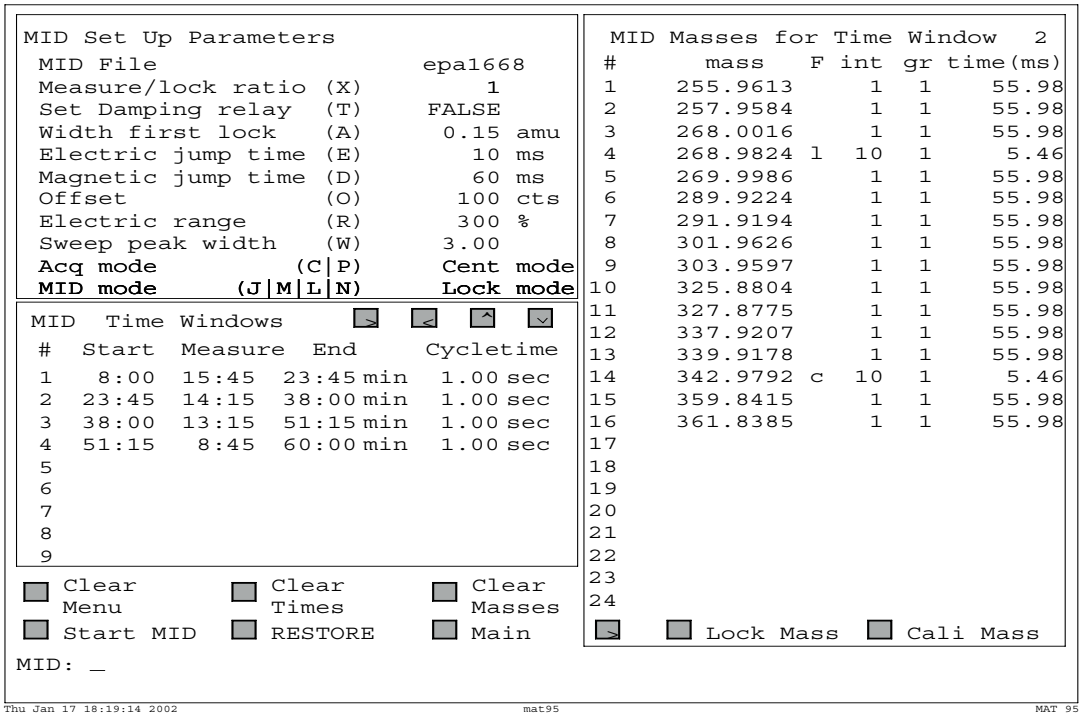
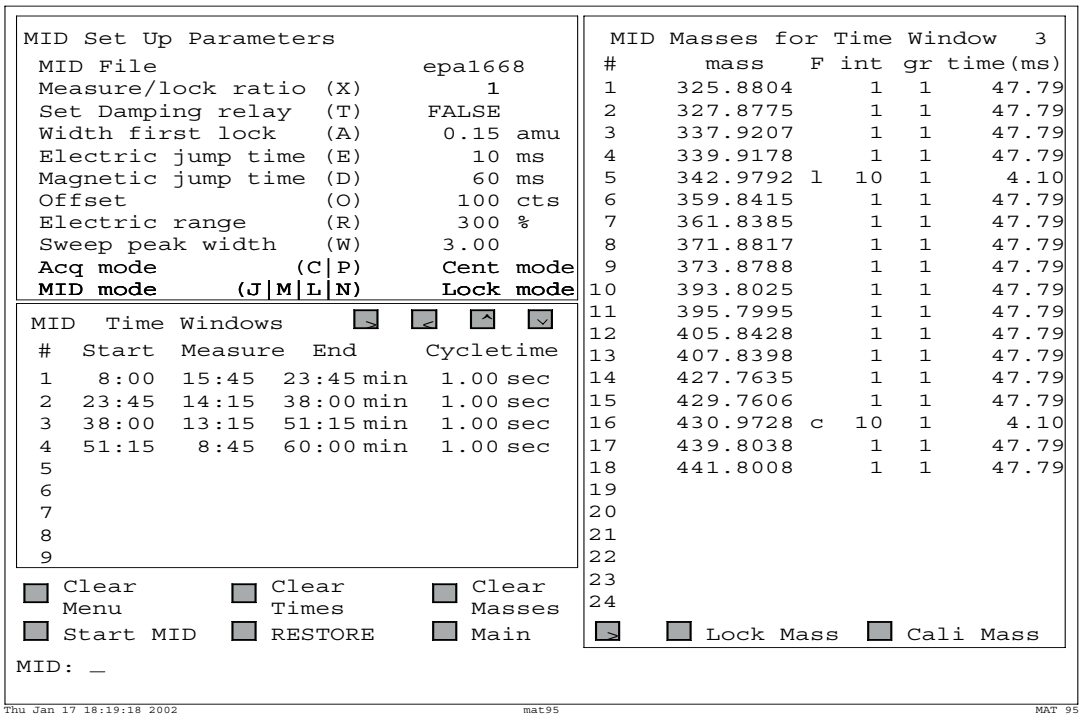


Figure 2 - Recommended MID Descriptors (Continued)



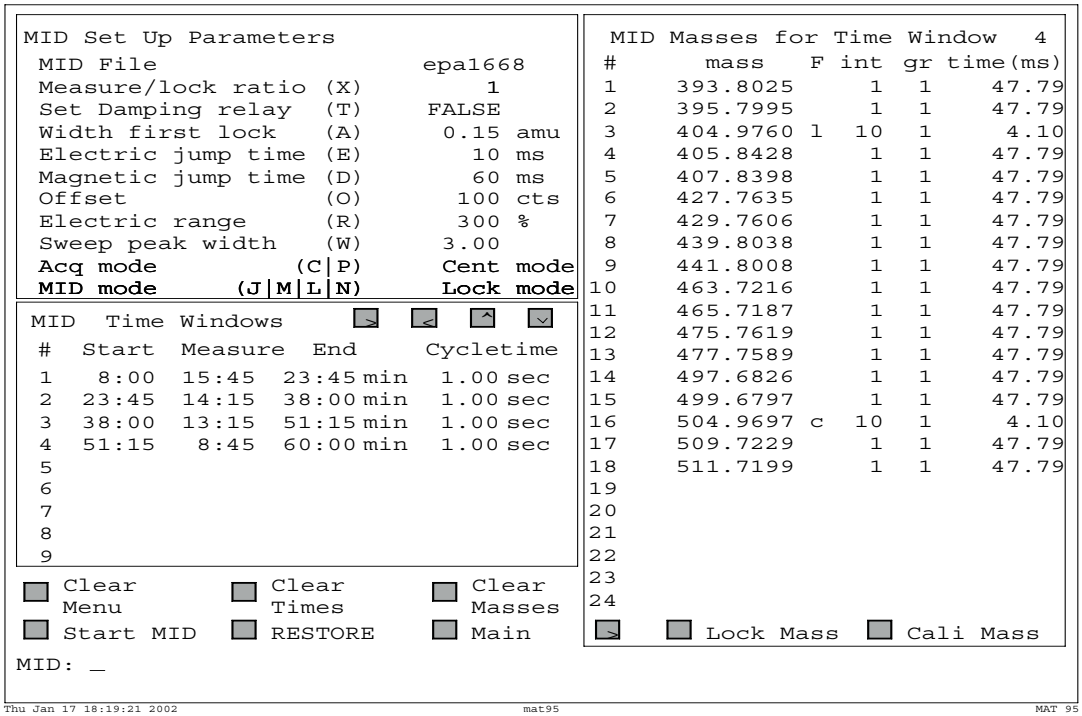


Figure 3 - Example Data Review Checklist

TestAmerica Knoxville Specialty Organics Group GC/MS Initial Calibration Data Review Checklist
Method or SOP Number: KNOX-ID-0013 Revision 11

PFK Date/Time:		Inst:		2nd Source Filename:	

CS0.5 Filename	CS1 Filename	CS2 Filename	CS3 Filename	CS4 Filename	CS5 Filename

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented before beginning the initial calibration?					
2. Was the instrument resolution ≥8,000 throughout (≥ 10,000 for m/z 342.9792) and ≥10,000 in the center of each m/z range. PFK m/z 192.9888, *230.9856, and *280.9824? PFK m/z 268.9824, *292.9824, and *380.9760? PFK m/z 342.9792, *380.9760, and *430.9728? PFK m/z 404.9760, *442.9728, and *530.9665?					
3. Were the measured exact masses listed above within 5 ppm at reduced accelerating voltage?					
4. Have PCB Mixes 1 - 5 been analyzed in triplicate using the installed column to assign congener retention times, method retention times, and MID switch points?					
5. Were the calibration standard solutions, at the number and concentrations specified in the Method/SOP, analyzed?					
6. Was date/time of analysis verified between analysis header and logbook as correct?					
7. Was the valley height less than 40% of the height of the shorter of the two peaks for the pair PCB 23 and PCB 34, and the pair PCB 182 and PCB 187 in the CS3 standard?					
8. Was the absolute retention time of PCB 209 greater than 55 minutes in the CS3 standard?					
9. Were the response factors calculated for each labeled standard and unlabeled native analyte using the Method/SOP specified reference compound, quantitation ions, and formula?					
10. Is the %RSD acceptable for all native analytes (within ± 20% calculated by isotope dilution, within ± 35% calculated by internal standard)?					
11. Is the %RSD acceptable (within ± 35%) for all labeled standards?					
12. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards (Exception: Secondary native dichloro biphenyl channel m/z 223.9974)?					
13. Are the ion abundance ratios for all native Toxics/LOCs and all labeled compounds within the control limits specified? (Exception: native dichlorobiphenyls)?					
14. Were all toxic congeners uniquely resolved from non-toxic congeners?					
15. Was an ICV analyzed, calculated using the CS3 RRFs, and the %D within ± 35%)?				< 5 outliers, none more than ±50% D.	
16. If manual integrations were performed, are they clearly identified, initialed and dated?					
17. If criteria were not met, was an NCM generated, approved by supervisor, and copy included in folder?					
18. Does the ICAL folder contain **complete** data in the following order? Data review checklist, a **complete** run log, Avg. %RSD summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation (HRMS only), and Total RIC, EICP's and manual integration - for window and all standards, in order from low to high standard.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

*At reduced accelerating voltage

Figure 3- Example Data Review Checklist (Continued)

TestAmerica Knoxville Specialty Organics Group GC/MS Continuing Calibration Data Review Checklist
Method or SOP Number: KNOX-ID-0013 Revision 11

Start PFK:		End PFK:		CS3 Filename:		Inst:		ICAL Date:	

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented at both the beginning and end of the 12 hour shift?					
2. Was the instrument resolution ≥8,000 throughout (≥ 10,000 for m/z 342.9792) and ≥10,000 in the center of each m/z range. PFK m/z 192.9888, *230.9856, and *280.9824? PFK m/z 268.9824, *292.9824, and *380.9760? PFK m/z 342.9792, *380.9760, and *430.9728? PFK m/z 404.9760, *442.9728, and *530.9665?					
3. Were the measured exact masses listed above within 5 ppm at reduced accelerating voltage?					
4. Was date/time of analysis verified between analysis header and logbook as correct?					
5. Were the MID switch points set to encompass the retention time windows of each congener group?					
6. Was the valley height less than 40% of the height of the shorter of the two peaks for the pair PCB 23 and PCB 34, and the pair PCB 182 and PCB 187					
7. Was the continuing calibration performed at the beginning of the 12 hour period after successful mass resolution and GC resolution performance check?					
8. Was the %D for all Toxic analytes within ± 30% for 1668A/B and ± 25% for 1668C? (PCB 81, 77, 123, 118, 114, 105, 126, 167, 156, 157, 169, 189) Was the %D for all LOC analytes within ± 30% for 1668A/B and ± 25% for 1668C? (PCB 1, 3, 4, 15, 19, 37, 54, 104, 155, 188, 202, 205, 206, 208, 209)					
9. Was the %D for all non-toxic/non-LOC analytes within ± 30% (for all versions of 1668)?					
10. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound, quantitation ions, and formula.					
11. Were the absolute retention times of all labeled internal standards within ± 15 seconds of the retention times obtained during initial calibration?					
12. Are %D within ± 50% for all labeled internal standards (for 1668A/B) or -50/+45% (for 1668C) in the calibration?					
13. Are the %D within ± 50% for all labeled surrogate standards (for all versions of 1668) in the calibration?					
14. Are the %D within -40/+30% (for 1668A/B) or ± 25% (for 1668C) for all labeled cleanup standards in the calibration? **Note: for 1668C, PCB28L's lower limit can extend to -35%D.**					
15. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
16. Are RRTs of all unlabled toxic/LOC analytes within their respective RRT limits?					
17. Are the ion abundance ratios for all labeled and unlabeled analytes within the specified control limits?					
18. If manual integrations were performed, are they clearly identified, initialed and dated?					
19. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
20. Does the CCAL folder contain **complete** data in the following order? Data review checklist, a **complete** run log, CCAL summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation (HRMS only), and Total RIC, EICP's and manual integration - for window and both standards.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

*At reduced accelerating voltag

Figure 3 - Example Data Review Checklist (Continued)

TestAmerica Knoxville SOG GC/MS Data Review/Narrative Checklist **Lot #**_____
SOP Number: KNOX-ID-0013 Revision 11 **Page 1 of 1** **Batch #**_____

Review Items **A. Initial Calibration**	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd**
1. Was the correct ICAL used for quantitation? (Check 1-2 compounds for batch by manually calculating concentration using the ICAL avg. RF.)					
B. Continuing Calibration	**N/A**	**Yes**	**No**		**2nd**
1. Has a Continuing Calibration Checklist been completed for each analytical batch?					
C. Client Sample AND QC Sample Results	**N/A**	**Yes**	**No**		**2nd**
1. Were all special project requirements met?				See narrative	
2. Were the header information, prep factors, and dilution factors verified?					
3. Is logbook date/time of analysis correct?					
4. Sample analyses done within preparation and analytical holding time (HT)? *If no, list samples:* _____				☐ HT expired upon receipt. ☐ Client requested analysis after HT expired. ☐ Re-extraction done after HT expired.	
5. Are internal standards within QC limits? *If no, list samples and reason (e.g.,* **sur1***):* Sample Reason Sample Reason _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____				☐ **[sup]** Ion suppression due to matrix. ☐ **[low]** Low recovery. S/N >10 and EDL<ML. ☐ **[sam]** Not enough sample to re-extract. ☐ **[dil]** Dilution showed acceptable %R. ☐ **[mtx]** Obvious matrix interference. Further cleanup not possible.	
6. Were peaks ≥2.5 S/N, which did not meet the following criteria, properly calculated and reported as EMPCs? • All analytes within Method/SOP retention time criteria and both ions maximized within ±2 seconds. • The ion abundance ratios for all labeled and unlabeled analytes within the specified control limits.					
7. Are all results < the upper calibration level? *If no, list samples:* _____				☐ Sample extracted at lowest possible volume	
8. If manual integrations were performed, are they clearly identified, initialed and dated?					
9. Final report acceptable? (Results correct, DLs calculated correctly, units correct, IS %R correct, appropriate flags used, dilution factor correct, and extraction/ analysis dates correct.)					
10. Was a narrative prepared and all deviations noted?					
D. Preparation/Matrix QC	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd**
1. LCS done per prep batch and all LCS/LCSD recoveries and RPDs within QC limits? *If no, list ID(s):*_____				☐ LCS/LCSD recoveries are high, no analytes detected above ML. ☐ Re-analysis not possible-insufficient sample ☐ See Comment/narrative	
2. Method blank done per prep batch and method blank or instrument blank analyzed with each sequence?					
3. Method blank internal standard recoveries within QC limits? *If no, list blank ID:* _____				☐ Internal standards are high and blank is free of contaminants. ☐ Internal standards are low, blank is free of contaminants, S/N>10 and EDL<EML.	
4. Are all analytes present in the method blank ≤ EML? *If no, list blank ID:* _____				☐ Sample results are > 20x higher than blank. ☐ No affected analytes > RL in the samples. ☐ Not enough sample for re-extraction.	
5. MS/MSD done per batch and are all recoveries and RPDs within laboratory generated QC limits? *If no, list MS/MSD ID:* _____				☐ LCS acceptable indicating sample matrix effects. ☐ LCS acceptable, high analyte concentration. ☐ LCS acceptable, lack of sample homogeneity.	
E. Other	**N/A**	**Yes**	**No**		**2nd**
1. Are all nonconformances documented appropriately and copy included with deliverable?					

Analyst:	**Date:**	**Analyst:**	**Date:**
Comments:		**Comments:**	

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Pittsburgh

Title: Analysis of Metals by Inductively Coupled Plasma/Mass Spectrometry (ICPMS)

Method(s): EPA 200.8, SW-846 6020, 6020A

Approvals (Signature/Date):			
	02/28/11		02/28/11
William Reinheimer Technical Manager	Date	Steve Jackson Health & Safety Manager	Date
	02/25/11		02/25/11
Nasreen K. DeRubeis Quality Assurance Manager	Date	Debbie Lowe Laboratory Director	Date

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of metals by inductively coupled plasma mass spectrometry (ICP-MS) by EPA Method 6020, 6020A and EPA Method 200.8.

1.2. This method is applicable to drinking, surface, and saline waters, soil, sediment, wipe, tissue and waste samples.

1.3. Reporting Limits

The standard reporting limits for metals analyzed by ICP-MS are listed in Table 1. Upon client request, results below the standard reporting limit but above the current method detection limit (MDL) may be reported and qualified as “estimated”.

1.4. Methods are based on the requirements of SW-846 methods 6020 and 6020A.

1.5. Elements that may be determined using this procedure include: Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Si, Ag, Sr, Tl, Sn, Ti, V, Zn, Ca, Mg, K, P, Cs and Na.

Note: successful Ag analysis may require all solutions to be prepared as described, but with the addition of hydrochloric acid to 1% (v/v). This may degrade performance for As, Se and V.

1.6. For DoD QSM Version 3 requirements, refer to SOP PT-QA-025. For DoD QSM current version refer to SOP PT-QA-029.

2. SUMMARY OF METHOD

2.1. The sample solution is introduced into a pneumatic nebulizer via a peristaltic pump. The nebulizer generates a fine aerosol by bringing the solution into contact with a high velocity flow of argon gas at its tip. The nebulized sample is sorted by droplet size in the spray chamber. Large droplets are rejected, whilst smaller particles are transported with the gas stream into the plasma.

2.2. The argon plasma operates with a continuously applied radio frequency (RF) field to give a high-energy discharge consisting of argon atoms, ions and electrons. The hottest part of the plasma can attain 6000-8000 K. In the plasma, aerosol droplets undergo evaporation, atomization and ionization. Ions are sampled through an aperture in a metal cone (sampler) at atmospheric pressure, into the expansion region at about 2 mbar and subsequently through an aperture in a second metal cone (skimmer) into the intermediate chamber.

2.3. An electrostatic ion lens system focuses the ion beam through a differential aperture into the analyser chamber, at about 10-7 mbar. The ions are filtered by mass-to-charge ratio in microsecond timescales by the quadrupole. The selected mass is detected by a discrete dynode electron multiplier. The multiplier has two simultaneous modes of operation: pulse count and analogue. The combination of these two modes allows seamless detection spanning 8 - 9 orders of magnitude. A detector “cross-calibration” is required for the analogue counts to be converted to equivalent pulse counts. The output from the detector is proportional to the concentration of the element in the aspirated solution, hence the concentration of unknown samples may be calculated when the instrument response is

calibrated with standards of known concentration.

2.4. The linear range may vary from instrument to instrument and is dependant upon the sensitivity determined by the optimization parameters. This should be determined by the individual laboratory. In the test study at TestAmerica Pittsburgh, the linear ranges listed in Table 1 (below) were obtained:

2.4.1. Table 1. Test study linear ranges for the X5 ICP-MS

Analytes	Linear Range (mg/L)
Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Ag, Tl, V, Zn	0.20 – 20.0
Al, Ca, Mg, K Na, Fe	100 - 1500

2.5. Calibration standard concentrations are listed in Table 2 below.

2.5.1. Table 2. Calibration standard concentrations for analysis of water and waste

Analytes	Calibration Range (mg/L)
Al, Mn	1.0
Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Ni, Se, Ag, Tl, V, Zn	0.20
Ca, Mg, K Na, Fe	100
Fe	50
B, Mo, Sn, Sr, Ti	0.20
Si	10

3. DEFINITIONS

3.1. See Pittsburgh Laboratory Quality Assurance Manual (PT–LQM) for definitions of general terms

3.2. See appendix for Glossary of Abbreviations

4. INTERFERENCES

4.1. Isobaric interferences. Elemental isobaric interferences occur when different elements have isotopes at the same nominal mass, e.g. ^{114}Cd and ^{114}Sn. Problematic elemental isobaric interferences for these methods are listed in Table 3. The correction factors given in Table 3 are based on theoretical isotopic abundance ratios and may require adjustment.

4.2.

4.3.

Table 3 Isobaric Interferences and Correction Equations

m/z	Analyte	Interferent	Correction
58	Ni	Fe	58Ni=58M-0.0040*56Fe
64	Zn	Ni	64Zn=64M-0.0440*60Ni
82	Se	Kr	82Se=82M-1.0010*83Kr
114	Cd	Sn	114Cd=114M-0.0270*118Sn
115	In	Sn	115In=115M-0.0140*118Sn
123	Sb	Te	123Sb=123M-0.1240*125Te
138	Ba	Ce	138Ba=138M-0.0030*140Ce

4.4. Abundance Sensitivity - Abundance sensitivity is the ability of the quadrupole to separate a low intensity peak from an adjacent high intensity peak. An example of the requirement of this is the detection of low concentrations of manganese (m/z 55) in the presence of high concentrations of iron (m/z 56). Quadrupole resolution and bias can be adjusted during set-up to resolve these signals.

4.5. Isobaric Polyatomic Ion Interferences - Polyatomic ions are produced by chemical reaction in the plasma and the interface region. If these polyatomic ions have the same nominal mass to charge (m/z) ratio as an analyte a polyatomic interference is observed. The principle polyatomic species for this method are listed in Table 4. Some of the correction factors given in Table 4 are based on theoretical isotopic abundance ratios and may require adjustment. Other factors were derived empirically. The stability of the empirical factors was determined during the test study at Thermo Electron. It was found that the factors require little or no adjustment and can be transferred between similarly configured X5 instruments.

Table 4. Isobaric Polyatomic Interferences and Correction Equations

m/z	Analyte	Interferent	Correction
51	V	ClO	51V = 51M-3.0460*53ClO 53ClO = M53-0.114*52Cr
52	Cr	ArC, ClOH	52Cr = 52M-0.0050*13C
56	Fe	CaO	56Fe = 56M-0.1500*43Ca
56	Co	CaO, CaOH	59Co = 59M-0.0046*43Ca
60	Ni	CaO	60Ni = 60M-0.0020*43Ca

m/z	Analyte	Interferent	Correction
75	As	ArCl	75As = 75M-3.000*77ArCl 77ArCl = 77M-0.8000*82Se 82Se = 82M-1.0010*83Kr
111	Cd	MoO	111Cd = 111M-0.9820*108MoO 108MoO = 108M-0.712*106Cd

4.6. Physical Interferences - Physical interferences include transport effects, ionization effects and deposition effects in the sample introduction system, plasma and interface, which result in signal suppression and signal drift. Transport effects arise from variations in solution properties, e.g. viscosity or surface tension, which affect nebulization efficiency and aerosol droplet size. The concentration of dissolved matter will affect the ionization efficiency of the analytes in the plasma and will cause a mass-dependant suppression effect and contribute to space-charge effects. Dissolved matter may also condense on the cones, altering the ion beam profile. This normally manifests itself as a time-dependant downward signal drift. To reduce the severity of these effects it is advised that the total dissolved solids concentration of solutions aspirated should be limited to <0.05%. Samples known to contain higher dissolved solids concentrations should be diluted. Signal suppression and drift can be corrected, to a degree, with the use of internal standardization techniques. Since these effects can be mass-dependant and may be related to the ionization potential of the element, a multiple-element internal standard approach should be used.

4.7. Memory Effects - Memory effects occur when the signal for an analyte from a sample contributes to the signal of a subsequent sample. This effect can be severe for certain elements due to their physico-chemical properties, e.g. mercury. This effect is minimised by aspirating a wash solution between samples. A monitored wash can be used in order to ensure that analyte signals recover to the background level.

4.8. Common molecular ion interferences for ICPMS are given in Table 6.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2. Specific Safety Concerns or Requirements

5.2.1. The ICP plasma emits strong UV light and is harmful to vision. All analysts must

avoid looking directly at the plasma.

5.3. Primary Materials Used

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

5.5. The following specific hazards are known

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.6. Eye protection that protects against splash, laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.7. The waste pumped from the spray chamber is corrosive and must be handled with care,

especially if large volume containers are used, as these may be heavy and awkward to carry. Empty the waste vessel daily to reduce the quantity that must be disposed each time and to keep weight to a minimum. Protective clothing, including hand and eye protection must be worn when handling this waste.

5.8. The wash solution is corrosive and must be handled with care. This solution must be prepared and stored in a vessel made of a robust acid-resistant material with a tight fitting lid that it is resistant to breakage if dropped. Large volumes of this solution will be heavy and may be awkward to carry. Ensure adequate provision for transporting the vessel, i.e. suitable handles on the vessel, minimum distance between the preparation area and the instrument. Use a cart to transport the vessel where necessary or ask for assistance in carrying.

5.9. Many of the concentrated metal standard solutions are toxic and must be handled with care. Skin and eye protection should be worn when handling and inhalation of vapours must be prevented.

5.10. Fumes generated by the plasma can be hazardous and must be removed from the laboratory with an extraction system as detailed in the X Series site planning guide. If the extraction system is faulty do not attempt to use the instrument. The extraction system should be inspected on a regular basis.

5.11. The plasma emits strong UV light and is harmful to vision.

5.11.1. ***WARNING***: AVOID looking directly at the plasma.

5.12. The plasma is a source of radio frequency (RF) radiation and intense, ultra-violet radiation that can damage the eyes. This radiation is normally contained by the system, but operators must be aware of the dangers. The instrument must be properly maintained by qualified service personnel. Never attempt to defeat hardware interlocks – they are there for your safety.

5.13. WARNING: People with pacemakers should not go near the instrument while in operation. DIAZOMETHANE is an extremely toxic gas with an explosion potential. Since the explosion potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free from etches, cracks, chips, and which does not have ground glass joints. Solutions of diazomethane will be kept at temperatures below 90°C. Diazomethane must be generated and handled in a fume hood.
Note: Diazomethane has not been classified as a carcinogen under the current OSHA definition.

5.14. Should the plasma need to be extinguished in an emergency, open the torch box door. This will immediately cut-off the power to the plasma RF generator, extinguishing the plasma. After extinguishing the plasma, the torch, torch box, cones and cone housing may remain very hot for some time. Operators must be aware of this fact and allow cooling time prior to handling these components.

5.15. There are high voltage components inside the instrument. Routine maintenance does not require access to any of the electronic components. If an electronic fault is suspected, a qualified service engineer must be called. Do not attempt to tamper with electronic components yourself.

5.16. Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.17. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.18. All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor and/or the EHSC.

6. EQUIPMENT AND SUPPLIES

6.1. Instrumentation

6.1.1. (2) X Series ICP-MSs fitted with Xi interface and Y-connector for on-line internal standard addition (supplied with this package).

6.1.2. (2) Cetac ASX-510 autosamplers.

6.2. Supplies

6.2.1. Ultrapure water system capable of delivering de-ionized, polished water of at least 18 MΩ cm

6.2.2. Yellow/orange tab peristaltic pump tubes (~0.5 mm ID)

6.2.3. White/white tab peristaltic pump tubes (~1 mm ID)

6.2.4. A range of adjustable pipettes, such as Rainin pipettes. Adjustable pipettes with a capacity of 0.1 mL, 1 mL, and 10 mL are recommended. These must be calibrated regularly to ensure accurate volumes are delivered.

6.3. Refer to Section 20 of PT-LQAM for instrument hardware/software specifications and routine instrument maintenance procedures

7. REAGENTS AND STANDARDS

7.1. General Reagents

7.1.1. **Laboratory Water** - All laboratory water used in these procedures must be of very high quality, purified with a reverse osmosis system and polished with an ion exchange system to give a final product of resistivity >18 MΩ cm.

7.1.2. **Hydrochloric Acid** (sp. gr. 1.18) - Hydrochloric acid must be at least Romil "SPA", J.T. Baker "Instra Analyzed", BDH/Merk "Analar", Fisher "Optima" - grade or equivalent. Hazards – corrosive, causes severe burns.

7.1.3. **Nitric Acid** (sp. gr. 1.42) - Nitric acid must be at least Romil "SPA", J.T. Baker "Instra Analyzed", BDH/Merk "Analar", Fisher "Optima" - grade or equivalent. Hazards – oxidising and corrosive, causes severe burns.

7.1.4. **2 % (m/v) Nitric Acid** - This reagent is used for the calibration blank, ICB, CCB, sample dilution and solution preparation. Add 5 mL of Conc of HNO3 to DI water and dilute to 250 mL.

7.1.5. For Standard preparation refer to standard log database. Composition of standards and concentration are given in Tables 2-5.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Samples are to be collected in plastic or glass containers.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2.

8.3. All soil and wipe samples must be refrigerated to $4^{o}C \pm 2^{o}C$.

8.4. Tissue samples are stored frozen until preparation.

8.5. The analytical holding time for metals by ICP-MS is 6 months.

8.6. Aqueous samples for total metals must be digested before analysis using an appropriate digestion procedure. Method 200.8 has its own digestion specifications that are followed by the laboratory. Method 3005A is used for total recoverable metals and dissolved and method 3010A is used for total metals by 6020 and 6020A. These are covered in the SOP PT-IP-003. Upon consultation with the client dissolved samples can forego digestion to help prevent contamination when very low detection limits are required.

8.7. Soil, wipe, tissue and waste samples should be digested before analysis using an appropriate digestion procedure. Method 3050B of SW846 is the appropriate digestion procedure. The SOP for 3050B is PT-IP-002.

8.8. Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

9. QUALITY CONTROL

9.1. Sample QC

9.1.1. Quality Control Batch

The batch is a set of up to 20 field samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, an LCS and a matrix spike/matrix spike duplicate. (In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD). If clients specify particular samples for MS/MSD, the batch may contain multiple MS/MSDs. See SOP PT-QA-021 for further definition of the batch. For QC abbreviations and criteria refer to Appendix 13.

9.1.2. Insufficient Sample

If insufficient sample is available to process a MS/MSD, then a second LCS may be processed, if precision data is required by the client. The LCS pair is then evaluated according to the MS/MSD RPD criteria.

9.1.3. Method Blank

One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 10% of the measured concentration of that analyte in the associated samples, whichever is higher. Certain programs, such as USACE, may require a more stringent evaluation of the method blank, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit. **Refer to PT-QA-025 for specific DoD requirements for the method blank.** For DoD QSM current version refer to SOP PT-QA-029.

- If the analyte is a common laboratory contaminant (copper, iron, zinc), the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than five times the RL. Such action must be documented in the NCM program.
- Re-preparation and reanalysis of any samples with reportable concentrations of analytes less that 10 times the value found in the method blank is required unless other actions are agreed with the client.
- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported. This must be documented in the NCM program.
- If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all positive results in associated samples are flagged with a "J", and appropriate comments may be made in a narrative to provide further documentation.

9.1.3.1. Refer to the QC Program document (PT-QA-021) for further details of the corrective actions.

9.1.3.2. For samples that have not been digested or matrix matched, a CCB result is reported as the method blank. The CCB analyzed immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB.

9.1.4. Laboratory Control Sample (LCS)

9.1.4.1. A laboratory control sample (LCS) is prepared and analyzed with every batch of 20 samples. All analytes must be within established control

limits. The LCS is spiked with the compounds listed in Tables 9 and 10 unless otherwise requested by the client.

9.1.4.2. If any analyte in the LCS is outside the laboratory established historical control limits, corrective action must occur:

- Check calculations,
- Check instrument performance,
- Reanalyze the LCS, and if still outside of control limits,
- Evaluate the data, and/or
- Re-prepare and reanalyze all samples in the QC batch.

9.1.4.3. Data may be reported with an anomaly in the following cases:

- The LCS recoveries are high and the analyte of concern is not detected in field samples,
- All target requested analytes are within control, but other LCS compounds are out of control,
- If no sample preparation is performed (eg., dissolved metals), the LCS may be reprepared and reanalyzed within the same sequence.

9.1.4.4. The analyst should evaluate the anomalous analyte recovery for possible trends.

9.1.4.5. If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report.

9.1.4.6. If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.1.4.7. For samples that have not been digested or matrix matched, a CCV result is reported as the LCS. The CCV run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCV.

9.1.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every batch of 20 samples for methods 6020 and 6020A. For method 200.8 matrix spike is prepared and analyzed per batch of 10 samples. The MS/MSD is spiked with the same analytes as the LCS (For spiking levels see Appendix 11). **Refer to PT-QA- 025 for specific DoD requirements for the MS/MSD.** For DoD QSM current version refer to SOP PT-QA-029. Matrix spike/matrix spike duplicate recovery for methods 6020 and 6020A should be within 75-125% and the RPD ± 20%. For method 200.8 the matrix spike recovery must be within 70-130% recovery and the RPD within ± 20%.

Note: Some programs require a Matrix Spike and Matrix Replicate in lieu of an MS/MSD. When a matrix spike/matrix replicate is performed the matrix spike is evaluated for accuracy (% recovery) and the matrix replicate is evaluated for precision (RPD).

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.
- If the recovery for any component is outside QC limits for both the matrix spike/spike duplicate and the LCS, the process is out of control and corrective action must be taken. Corrective action will normally include re-preparation and reanalysis of the batch.
- If a MS/MSD or MS/Dup is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.
- The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.1.5.1. If the amount of an analyte found in the unspiked sample is greater than 4 times the amount of spiked analyte added, then routine control limits do not apply and recoveries are not evaluated. Other analytes in the MS and MSD must still be reported. File an NCM stating that the 4X rule was applied, and report the recovery in the LIMS as “ND MSB”. This NCM must be included in the final report.

9.1.5.2. For samples that have not been digested or matrix matched, a MS/MSD must be performed per batch of up to 20 samples by spiking two aliquots of the sample.

9.1.6. Post-Digestion Spike Samples (PDS)

9.1.6.1. For 6020, 6020A and DoD samples, a post digestion spike will be run on a sample if the if the MS/MSD for the sample falls outside of % recovery criteria. A post digestion spike is a matrix spike on a sample, which is added after the sample preparation is completed. For 6020, 6020A and DoD the default matrix spike protocol is a “post digestion spike”. However, TestAmerica Pittsburgh will perform a conventional matrix spike and spike duplicated as the default matrix QC. We will perform the “PDS” only where the conventional matrix spike fails. We believe that this approach will provide more complete matrix information than the default requirements. For methods 6020 and DoD, the spike recovery from the post digestion spiked sample should be within the range 75-125% where the spike value is greater than 25% of the indigenous analyte concentration. The post digestion spike recovery for Method 6020A

should be within 80-120%. If this spike fails, then the dilution test (Sec. 9.6 should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed. The software calculates this based on the following equation:

%Repeatability = 100 * (Spk-Orig)/Tru

where, Spk is the spiked sample result and Orig is the original sample result and Tru is the True spiked concentration value. If a result is outside the required range, the data should be assessed carefully and samples may require reanalysis. Post digestion spike is not required for method 200.8.

9.1.7. Serial Dilution Samples (SER) – CLP/20.8 or Dilution Test (6020/6020A) – CLP/200.8 - Some regulatory programs such as require a dilution test be performed for each matrix within an analytical batch determination. If the analyte concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should be performed. The results of the serial dilution sample(s) (SER) after dilution correction should be within the range 90-110% of the original sample, if the result for the original sample is greater than 50*IDL for CLP or greater than 50*MDL (200.8/6020/6020A) then a chemical or physical interference effect should be suspected.

9.1.7.1. The software calculates this based on the following equation:

%Repeatability = 100 * Ser/Orig

where, SER is the dilution corrected serial diluted sample result and Orig is the original sample result. If a result is outside the required range, the data should be assessed carefully and samples may require reanalysis.

9.1.8. Duplicate Samples (DUP); %RPD = ±20%: Results of the duplicate sample(s) (DUP) must be within ±20% of the results of the original sample, where the result is greater than or equal to 5*CRQL for CLP or greater than 5*RL for 200.8 or 6020/6020A. The software calculates this based on the following equation:

%RPD = (S-D) / [(S+D)/2] * 100%

where, D is the duplicate sample result and S is the original sample result.

If a result is outside the required range, the data should be assessed carefully and samples affected may need to be reanalyzed where the project requires it.

9.2. Instrument QC

9.2.1. Linear Range Verification (LR) - The linear range is determined semi-annually (2x/year) for each element on the standard list. See Section 12 for details of the linear range verification.

9.2.2. The internal standard intensities in samples must be within 60 to 125% of the IS intensities for the Calibration Blank for method 200.8, 30% to 120% for method 6020 and 70 to 120% for method 6020A. If this criterion is not met, the sample will

be diluted and reanalyzed until the IS recoveries are within the limits. If the upper control limit is exceeded, the analyst should review the data for the presence possible contribution from the native sample. Narrate any findings.

9.2.2.1. For method 6020 the internal standard intensity in the ICV, ICB, CCV and CCB should be within 20% of the IS intensity in the calibration blank of the initial calibration. If not, the analyst should check for any instrument anomalies and continue if none are noted. For method 200.8 the IS acceptance range does not vary from the 60 to 125% noted above. For method 6020A the IS acceptance range does not vary from the 70 to 120% noted above.

9.2.3. Interference Check Solutions (ICSAs) - The results of ICSA must be within ±3CRQL of the analytes "true" value or ±20% of the analytes "true" value, whichever is the greater. The "true" value will be taken as zero, unless otherwise indicated in the solution manufacturer's literature. The software automatically checks for compliance with the above, based on a "true" value of zero. If a result falls outside this range, the analysis must be terminated and the samples associated must be reanalyzed. **Refer to PT-QA-025 for specific DoD requirements for the ICSA.** For DoD QSM current version refer to SOP PT-QA-029.

9.2.4. Interference Check Solution Spike Recoveries (ICSABs) - Results of ICSAB must be within ±20% of the analytes "true" value. The software automatically checks for compliance with the above, based on the values indicated in (Tables 4 and 5). If a result falls outside this range, the analysis must be terminated and the samples associated must be reanalyzed.

9.2.5. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV must fall within ± 10% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within ± the reporting limit (RL) from zero. (Certain programs, may require a more stringent evaluation of ICB, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit.) **Refer to PT-QA-025 for specific DoD requirements for the ICB.** For DoD QSM current version refer to SOP PT-QA-029. If either the ICV or ICB fail to meet criteria, the analytical sequence should be terminated, the problem corrected, the instrument recalibrated and the calibration re-verified.

9.2.6. CRQL Check Standard (CRI)

ILMO5.2**:** For CLP the CRI is at 2 X RL. The results of the CRI must be within the range 70-130% recovery for all analytes, except CO, Mn and Zn, which must be in the range 50-150% recovery. This is checked by the software, based on the true values.

For method 6020, the CRI is at the RL. The method does not specify criteria, however the lab uses the range 50 – 150%.

For method 6020A the CRI is at the RL. The CRI/LLICV/LLCCV must be within the 70 – 130% recovery range and analyzed at the beginning and end of the analytical sequence. For method 6020A the CRI which is the low level quantitation check sample is prepared and analyzed quarterly or as needed. The control limit is 70-130%. Please note the CRI (undigested) is still analyzed at the beginning and end of the analytical run. **For DoD refer to PT-QA-025 for specific DoD requirements**. For DoD QSM current version refer to SOP PT-QA-029.

If any analyte is outside the range indicated, the sample may be re-run once. If the results fall within the required values upon re-run, no further corrective action need be taken. If still outside the acceptable range, the analysis shall be terminated, the problem corrected and the samples reanalyzed.

9.2.7. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. Results for the CCV must be within the range 90-110% recovery. This is checked by the software, based on the true values. If outside this range, the analysis must be terminated, the problem corrected and the samples since the last valid CCV must be re-analyzed. The CCB result must fall within ± RL from zero. (Certain programs, may require a more stringent evaluation of the CCB, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit. The analyst should refer to the project notes provided by the PM to identify when this is an issue and if so what the corrective actions to take for exceedances.) **Refer to PT-QA-025 for specific DoD requirements for the CCB.** For DoD QSM current version refer to SOP PT-QA-029. Sample results may only be reported when bracketed by valid CCV/CCB pairs. If a mid-run CCV or CCB fails, the CCV or CCB may be reanalyzed once and accepted if there is a reason for the initial out-of-control event such as carryover from a high concentration sample. Otherwise, if the CCV or CCB fails, the analysis for the affected element must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. (Refer to Section 10.9 for an illustration of the appropriate rerun sequence).

9.2.8. High Level Calibration Standard (HLCS) for DoD:

9.2.8.1. A high level calibration standard is analyzed after the ICSAB before any

client samples are analyzed. This standard is analyzed once for a run. The percent recovery must be within 90-110%. If not the instrument is recalibrated and instrument QC along with high level calibration standard is reanalyzed before any samples can be analyzed. Sample concentration greater than high level calibration standard for analytes listed in Table 11 will be diluted. For analytes not included in high level calibration standard, Table 11, dilutions will be determined based on instrument calibration standard, Table 2.

9.3. Nonconformance and Corrective Action:

Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the QA Manager.

9.4. Quality Assurance Summaries:

Certain clients may require specific project or program QC that may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.5. QC Program:

Further details of QC and corrective action guidelines are presented in the QC Program SOP PT-QA-021. For QC abbreviations and criteria refer to Appendix 13.

10. PROCEDURE

10.1. Sample Preparation

10.1.1. Refer to SOPs PT-IP-002, PT-IP-003 and PT-IP-005.

10.2. Calibration

10.2.1. Instrument start-up

Follow the instrument start-up procedure outlined in the Thermo X-Series ICP-MS Operator's Manual.

10.2.2. Instrument Tuning

10.2.2.1. Aspirate a 20 ppb tuning solution containing all of the tuning elements. The 6020/6020A tuning elements are Li, Co, In, and Tl. The instrument manufacturer monitors Mg, Ce, Be & Pb for instrument performance.

10.2.2.2. Mass calibration and resolution checks must be documented and included as part of the raw data package.

10.2.2.3. Resolution must be < 0.90 amu at 10% peak height for the 6 tuning (Be, Ce, Co, In, Mg, & Pb) for 6020/6020A. And the resolution must be ≤ 0.9 amu at 5% of the peak height for Method 200.8.

10.2.2.4. Mass calibration must be within ± 0.1 amu from the actual value for the

6 tuning elements (Be, Ce, Co, In, Mg, & Pb) or the mass calibration must be adjusted.

10.2.2.5. A "daily" performance check must be performed. This uses the same tuning solution as above. The 6 tuning elements must have RSDs below 5%. The oxides must be below 3.5%. If any of these conditions are not met repairs or optimization procedures must be performed until these specifications are met.

10.2.2.6. Recommended analytical isotopes and additional masses that maybe monitored are given in Table 7. Recommended isotopes and additional masses that may be monitored are given in Table 8.

10.2.3. Initial Calibration

10.2.3.1. Calibration consists of a blank and the following calibration standards (STD1, STD 2X, and STD 3X see Table 2 for concentrations) in accordance with the manufacturer's procedure. Use the average of three integrations for both calibration and sample analyses.

10.2.3.2. Following the STD, STD2X & STD3X, an ICV/ICB pair is analyzed. The ICV must be within ± 10% of the true value to be acceptable.

10.2.3.3. For 6020/6020A, following the ICV/ICB pair, the CRI/RLV is run before the ICSA is analyzed. The CRI/RLV is analyzed again at the end of the sequence.

10.2.3.4. For 6020, 6020A, following the ICSA, analyze the ICSAB. The ICSAB must be within ± 20% of the true value. For method 200.8 ICSA and ICSAB is also analyzed although not required by the method.

10.2.3.5. Internal standards are added to all standards and samples by the instrument automatically prior to analysis.

10.2.4. Continuing Calibration:

10.2.4.1. Following every 10 samples (including lab QC), analyze a CCV/CCB pair. These must be within ± 10% of the true value for analysis to continue. For methods 6020/6020A, a CCV/CCB pair should also be analyzed immediately after the ICSAB.

10.2.4.2. All samples must be bracketed by an acceptable CCV/CCB pair. Where a CCV/CCB fails the samples preceding it back to the last acceptable CCV/CCB must be reanalyzed.

10.2.5. Instrument Set-up

10.2.5.1. Configure the X Series with the standard sample introduction equipment, i.e. a glass concentric nebulizer, glass impact bead spray chamber and a one-piece torch with 1.5mm ID injector tube. A Peltier spray chamber cooling unit is optional. Ensure that the Xi interface cones are fitted. These are standard with the X5 instrument and an

option for the X7. They can be identified as follows:

Xi Sampler - 1.1 mm orifice, no nipple, no holes around the flat circumference

Xi Skimmer - Small pointed skimmer mounted in a copper adapter with two screws

Yellow/orange tab peristaltic pump tubes (6.2.2) should be used for sample and internal standard uptake. Connect the liquid output end of the peristaltic pump tubes to the 1.0 mm (OD) barbed fitting screwed into the Y connector. Note that the barbed fitting may require tightening with a pair of grips to ensure a good fluid-tight seal. The mixed output flow should be connected to the nebulizer. See diagram in Appendix 6 for plumbing schematic. A white/white tab peristaltic pump tube (6.2.3) should be connected to the spray chamber drain outlet at one end and to a tube running into a waste vessel at the other and wound on the pump to draw the waste liquid away from the spray chamber.

10.2.5.2. Perform the daily maintenance as outlined in Appendix 3.

10.2.5.3. Switch the instrument into the *Operate* state by clicking the *ON* button at the top of the screen. During the automated ignition sequence, the following processes occur:

i. Torch purge with argon gas

ii. RF power match

iii. Plasma ignition

iv. Slide valve open

v. Electronics on

This process takes about two minutes. Upon successful ignition, the software will display *Operate* in the *Instrument State* bar. If the event of unsuccessful ignition, the software will display an error message and/or place a message in the *Technician Event Log*. Upon unsuccessful ignition, inspect the sample introduction equipment and torch, ensuring a good gas-seal at each connection and ensuring the torch is not misaligned or damaged. If all appears satisfactory, the ignition may be attempted again. If the ignition process consistently fails, contact your local Thermo service agent for advice.

10.2.5.4. Once the instrument is in the *Operate* state, it should be left for 30 minutes to reach thermal equilibrium prior to starting analytical measurements. The optimization (tuning), performance testing and instrument set-up calibrations may be performed after 15 minutes. Ensure that the peristaltic pump is operated at a default analytical speed of 15%. This is done by clicking on *Instrument*, *Configurations*, *Configuration Editor*, *View Selected Accessories* (network icon),

Peristaltic Pump, *Connect* (chain icon). Set pump speed to 15% using the slider bar and adjust the *Settle Time* to 10 seconds and click on *Apply*. Click *OK* to close the dialogue box.

10.2.5.5. During the initial 15 minutes, the system can be "conditioned" by aspirating the system thoroughly with 2% nitric acid + 1% HCL solution prior to continuing.

10.2.5.6. Instrument tuning (optimization) is performed using a 20 µg/L Tune Solution, aspirated through the sample uptake tube. Optimization may not be necessary from day to day if the sample introduction system and cones have not been adjusted in any way and if the instrument fulfils the performance requirements given below. If the instrument gives performance exceeding the requirements shown below, proceed to 10.2.5.7. Otherwise, tune the instrument manually or using *Autotune* while aspirating 20 µg/L Tune Solution through both the sample and internal standard uptake tubes. *Autotune*, using an appropriately defined sequence is advised (see Appendix 4).

The final conditions must give the following:

^{9}Be	>2000cps
^{115}In	>50000cps
^{208}Pb	>25000cps
$^{156}CeO/^{140}Ce$	<0.02

If the above criteria are met, proceed to 10.2.5.7. If the above criteria are not met, do not proceed. Check that the tune solution was prepared properly and remake if necessary. If the sensitivity is below the minimum requirement, a new detector plateau may be required (see Appendix 6), the cones may require cleaning (see Appendix 8), or the nebulizer or sample uptake lines may have become blocked or may not be properly clamped on the peristaltic pump. If the CeO/Ce ratio is >0.025, the nebulizer gas flow can be reduced and/or the sampling depth increased, obtaining a corresponding reduction in oxide formation. Recheck the above parameters after taking any remedial action.

10.2.5.7. Save the satisfactory instrument settings by clicking on the disk icon on the Tune page. Note that this is not necessary if Autotune has been used, as the instrument settings are saved automatically (unless manual adjustments have been made after autotuning).

10.2.5.8. Set-up the resolution as described in Appendix 5.

10.2.5.9. Perform a cross-calibration (and mass-calibration and detector voltage setup if required) as explained in Appendix 6. Note that retuning may be

necessary after performing this routine.

10.2.5.10. Aspirate Tune solution and run a *Performance Report* (see Appendix 4) to confirm the mass-calibration, resolution, minimum sensitivity and maximum cerium oxide requirement and to verify instrument stability. The performance report acquires five consecutive one-minute runs and calculates the percentage relative standard deviation (RSD) of the five measurements for each isotope. The RSD of the elemental analytes in the performance report must be <5%. If the performance report passes, proceed to (10.3). If the performance report fails, check:

a. Liquid uptake tubes for kinks or other damage

b. Condition and position of the peristaltic pump tubing

c. Tightness of the peristaltic pump clamp screws (these should be just tight enough to draw liquid through the tube smoothly)

d. Joints of all sample introduction components, ensuring a good seal

e. Nebulizer for blockage

f. Salt deposition on cones

Remedy the above as necessary and repeat the test. Note that retuning may be required if any sample introduction components are adjusted or replaced.

Note: Resolution set-up may require adjustment if the resolution check fails (see Appendix 5). Note that the quadrupole and hexapole bias strongly influence abundance sensitivity (Pole Bias should be kept >+4V and Hexapole Bias <-3V).

If the measured mass position for each mass in the performance report is not within ±0.1 amu of the nominal mass position, a new mass-calibration must be performed (see Appendix 6).

10.3. Sample Analysis

10.3.1. Open the method template by clicking on *Templates* and then <TESTAMERICA PITTSBURGH ICPMS ANALYSIS>. The method template will be opened. This contains all the saved analytical parameters and only the sample list need be amended. For work flow chart refer to Appendix 12.

10.3.2. Go to *Sample List*. This grid contains all the information about calibration, QC and samples to be run. The calibration and QC concentration information is already stored. Enter all unknown samples into the list in the appropriate order below the existing calibration and QC samples by overwriting the sample label fields. Delete any QC samples that do not apply to the required method. (If sample list changes are to be made permanent to the method, save the method as a *Template*, by going to *File*, *Save as Template*. Enter a new name to create an amended method,

or use the same name to overwrite the current one.)

10.3.3. Once all the sample information is added, check the required autosampler positions have been correctly entered. Amend as necessary. To sequentially renumber positions, add the correct position required for the initiation of the sequence and right mouse click on the first correctly numbered cell. A pop-up menu will appear. Select *Renumber autosampler positions* from this. Ensure that all samples have one survey run and 3 main runs and a probe depth of 155mm.

10.3.4. Save the experiment run by clicking on the *File* menu, then *Save as*. Enter the required file name, e.g. *enviro090902* and click *Save*.

10.3.5. To print the sample list, go to *Reports* and check the *Sample List* box. Click the refresh icon. The sample list will be displayed in a printable format. Press the print icon. Note that this can only be done with PlasmaLab version 2.3 and above.

10.4. Loading the Autosampler

10.4.1. Pour the required samples into pre-cleaned 15ml polypropylene test tubes (5.1.4). To avoid contamination, a small amount of the solution to be analyzed can be poured into the tube and then discarded. This will rinse out any residual contamination.

10.4.2. Pour blanks, standards and QCs (positioned in rack 0) into pre-cleaned 50ml polypropylene tubes. To avoid contamination, a small amount of the solution to be analyzed can be poured into the tube and then discarded. This will rinse out any residual contamination. Note that **2% nitric acid** (7.1.4) is used as the calibration blank, ICB, and CCB.

10.4.3. For the **serial dilution** ("L") sample(s), dispense 2.00±0.02 mL of the original sample into a pre-cleaned 15 mL polypropylene test-tube and add 8.00±0.08 mL of 2% nitric acid (7.1.4). Mix well. This is a 5-fold dilution.

10.4.4. Place the tubes for each sample into the appropriate position in the rack according to the sample list. Note that the autosampler works on a two-dimensional grid position system by rack number (0-4). See Appendix 9 for autosampler position map.

10.5. Initiating Analysis

10.5.1. Place the sample probe into the autosampler arm and the internal standard probe into the internal standard solution.

10.5.2. Go to *Instrument*, *Tune* and click on the accessories dialog icon. Click on *Autosampler* and then on the chain icon to connect. The autosampler should initialize. Ensure that the probe is at the correct height by positioning it so that its tip just protrudes through the hole in the bottom of the arm. Click on the *Go to Wash* icon (faucet) to send the probe to the wash station. Ensure that the wash solution is being correctly delivered to the wash station via the peristaltic pump at the rear of the autosampler. Allow at least 2 minutes for the liquid to be delivered to the sample introduction system.

10.5.3. Click on the experiment to be run. Click the *Queue* icon and then *Append* and *OK*. The analysis has now been initiated.

10.5.4. To monitor the progress of the analysis, right-mouse click on the *MS* icon at the bottom-right of the screen and select *Open Service Window* from the pop-up menu. The Service Window hovers over the current application window until moved or closed and displays the current instrument activity. This window is also used **to stop an analysis** if required. This is done by clicking on the ***^{X}Q* icon**.

10.5.5. To view results as they are generated, click on the experiment icon and go to the *Results* tab. Click on the *Refresh* button or the refresh icon (green circular arrows on a page) to calculate the results from the data obtained.

10.5.6. To view calibration plots, click on the *Calibration Data* tab. The calibration for each analyte can be viewed by clicking on the required isotope in the *Analyte* box. Each subsequent set of calibrations (calibration block) can be displayed by selecting the required calibration block from the drop-down combo box, e.g. *FQ Block 1*, *FQ Block 2*, etc. FQ denotes a Fully-Quantitative calibration and SQ denotes a Semi-Quantitative calibration, i.e. a response curve generated from the *FQ* calibrations. The SQ response curve is used to calculate semi-quantitative concentrations if required.

10.5.7. To view data, click on the *Numerical Results* tab. The *Analyte Dilution Conc.* tab is a tabular display of the calculated corrected concentrations for each analyte. These values have been corrected for internal standardization, external drift correction (if used), and dilution (where entered). The *Mass Uncorrected ICPS* tab shows the uncorrected raw data for each measured mass in units of integrated counts per second (ICPS). The *Analyte ICPS* tab shows integrated counts per second data that has been mathematically corrected for blank deduction, internal standardization, drift correction (if used), and dilution (as appropriate). The *Survey* tabs show the data integrated from the survey scan for each sample. Any concentrations displayed in the survey page will be semi-quantitative only.

10.5.8. To edit the amount of data on screen (filter the results display), click on the filter icon (funnel and lightening). Alter the numerical values or the check boxes to select the required data to display and click on *OK*. To jump directly to a particular sample of interest, find the sample in the drop-down combo box at the top of the data display and click on it.

10.5.9. To display mass-spectra, click on the *Spectra* tab. Display the spectrum for a particular sample by double-clicking on the sample name in the selection box on the left of the screen. Note that several spectra may be overlaid by double-clicking on each sample to be displayed. To zoom into a particular area, click the zoom icon (magnifying glass) and click and drag on the spectral display to zoom into the required area. The dashed-lines represent data acquired in the analogue mode of the detector whilst the solid-lines represent pulse-count data. To remove the noise associated with analogue detection at low signal levels, point at the display and right-mouse click to bring up a menu. Go to *View Options* and then click on *Eliminate Analogue Noise*. To identify a peak, click on it and wait for the options for

that mass to be displayed in the box above the spectral display. To fingerprint a spectrum, double click on the species to fingerprint in the options box. This will overlay the isotopic pattern for the selected species, based on the lowest relative intensity signal for the pattern masses. The spectra may be navigated by using the arrow buttons above the display. Allow the arrow cursor to hover over each button for an on-screen explanation of its function.

10.6. Post-Analysis Data Processing

10.6.1. Internal Standards

10.6.1.1. Check the internal standard recovery percentage for each internal standard isotope used for every sample. The percentage for each isotope must be within the range 30-120% for method 6020, 70 – 120% for method 6020A and 60 – 125% for method 200.8.

10.6.1.2. If above 120%, check that the other internal standard isotopes show similar deviation. If not, this may be due to the presence of the internal standard element in the sample. This is particularly common with the isotopes of Li, Sc and Y in environmental materials. If this is the case, the affected internal standard isotope may be excluded for the sample affected, as follows. Go to the *Sample List*.

Find the sample affected and select it in the list by clicking on the box in the left-hand column. Click *Show Advanced* and go to *Internal Standards*. Click on *New Internal Standard Set*. Select the affected isotope(s) in the *Internal Standards* box on the right. Remove the affected isotope from the *Internal Standards* box by using the left hand arrow button (<<). Recalculate the results for this sample by going back to *Results* and clicking on *Refresh*.

10.6.1.3. If any internal standard isotope is outside the range 30-120% and all other internal standard isotopes show similar values for that sample, the instrument may have drifted, or the sample may be producing a suppression or enhancement effect. Find the nearest blank following the sample in question and check its internal standard results. If these are similarly reduced or elevated, the instrument has drifted and the samples must be reanalyzed from the last compliant blank. If the blank does not exhibit similar drift, the sample must be producing a suppression or enhancement effect due to its matrix. In this case the sample must be re-analyzed after a five-fold (1+4) for CLP or a ten-fold (1+9) dilution for 6020/6020A to reduce the matrix effect.

10.7. General protocols

10.7.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the

client shall be notified. The Nonconformance Memo shall be filed in the project file.

10.7.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.7.3. An analytical run will consist of all customer samples and quality control samples analyzed under a daily initial calibration. Each new initial calibration will begin a new analytical run.

10.7.4. Type in the QC and sample information into the autosampler table.

10.7.5. In order to use the ICP-MS data upload program into LIMS, the following naming conventions must be followed:

- Samples are identified by the 5-character work order number
- Matrix spikes, duplicates, and matrix spike duplicates are identified by the 5-character work order number followed by S (matrix spike), D (matrix spike duplicate) or X (sample duplicate).
- Prep Blanks are identified by the 5-character work order number followed by B.
- LCSs are identified by the 5-character work order number followed by C (LCS) or L (LCS Duplicate).

10.8. Initial Calibration

10.8.1. Open a new dataset using the date and instrument in the title. For instance the first run (A) on instrument 2 on JAN 1, 2003 would be X30101A.

10.8.2. Open the appropriate method if one already exists or create a new one for the analytes to be quantitated in the run. Solicit the assistance of a senior ICP-MS operator in creating a new method.

10.8.3. See Tables 7, 8, and 9 for recommended isotopes and interference equations for commonly analyzed elements.

10.8.4. If no recommended isotopes are given for the element to be analyzed, consult a senior ICP-MS operator or appropriate reference.

10.8.5. See Table 10 for commonly used internal standards.

10.8.6. All masses which could affect data quality should be monitored to determine potential interferences either simultaneously during an analytical run or in a separate scan.

10.8.7. Internal standards are added to all standards and samples by the instrument prior to analysis.

10.8.8. Use of an existing autosampler table is suggested. A read delay of 45 to 60 seconds is used between all analyses.

10.8.9. Calibration consists of a blank and a single calibration standard (STD1, see Table 2 for concentrations) in accordance with the manufacturer's procedure. Use the

average of three integrations for both calibration and sample analyses.

10.9. The order of analysis for the initial QC samples and calibration should be:

1. Rinse
2. Performance Report (Tune Check)
3. STD1 (Calibration Standard)
4. STD2 (2x Calibration Standard)
5. STD3 (3X Calibration Standard)
6. ICV (Second source, must be ± 10% of true value)
7. ICB
8. CRI / RLV/LLICV (Reporting Limit Verification Standard)
9. ICSA (Interference check solution.)
10. ICSAB (Interference check solution, ± 20% of true value)
11. CCV
12. CCB
13. Prep QC such as LCS or MB, followed by samples (up to 10 runs)
14. Rinse
15. CCV
16. CCB
17. CRI / RLV/LLCCV (Method 6020A only at the end of the analytical sequence)
18. CCV
19. CCB

10.9.1. To continue the analytical run, add an additional 10 runs followed by a rinse and CCV/CCB, and repeat for up to 24 hours.

10.9.2. Analysis sequence when out-of-control QC is observed: Recalibrate and rerun all affected samples (including initial QC)

11. CALCULATIONS / DATA REDUCTION

11.1. All pertinent calculations are performed by the Plasma LAB software. Elemental equations used to calculate results are given in Table 9.

11.2. Reporting Requirements

11.2.1. Units are ug/L or mg/L for aqueous samples and mg/kg for soil samples and ug/wipe for wipe samples.

11.2.2. If dilutions were required due to insufficient sample, interferences, or other problems, the laboratory reporting limits are multiplied by the dilution factor.

11.2.3. For results less than 10, two significant figures will be reported. For results greater than or equal to 10, three significant figures will be reported. Refer to SOP PT-QA-009 for additional information on significant figures and rounding.

11.2.4. Document any non-standard procedures or anomalies by using the anomaly program (Clouseau).

11.3. Data Package Requirements

11.3.1. A complete data package consists of: the daily tuning package, the method printout, run log, internal standard summary for 5.2 only, standards documentation, level 1 checklist, and all raw data.

11.3.2. Level I review will be completed by the analyst.

11.3.3. Level II review will be completed by a senior level laboratory analyst familiar with the technical aspects of ICP-MS and in accordance with the ICP-MS DATA REVIEW checklists. The instrument operator of an analytical run may not perform the Level II review for that run.

12. METHOD PERFORMANCE

Prior to analysis of any analyte using Method 6020/6020A, the following requirements must be met.

12.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. MDL's must be determined as detailed in SOP PT-QA-007 and in 40 CFR Part 136 Appendix B.

12.1.1. On occasion, a non-routine analyte is requested by the client. In lieu of a full MDL study, a standard containing the non-routine analyte must be analyzed. The concentration of the standard must correspond to the reporting limit or ½ the reporting limit. This is to verify that the method can satisfactorily quantify the element near the chosen reporting limit. The recovery of the standard must be between 50% and 150% of the expected value. The standard analysis should be kept with the analytical data.

12.1.2. For new analytes an MDL study should be performed and calibration curve generated before analyzing any samples.

12.2. Initial Demonstration of Capability

12.2.1. For the standard analyte list, the initial demonstration IDOC and method detection limit (MDL) studies described above must be acceptable before analysis of samples may begin.

12.2.2. For the standard analyte list, the initial demonstration consists of the preparation and analysis of four LCS samples containing all of the standard analytes for the

method, as well as a method detection limit (MDL) study (described below).

12.2.3. Four LCS samples are analyzed with the same procedures used to analyze samples, including sample preparation.

12.2.4. The mean recovery and standard deviation are calculated for each analyte of interest. These results are compared with the established or project-specific acceptance criteria. All four results must meet acceptance criteria before the method can be used to analyze samples. For further detail refer to SOP PT-QA-001. .

12.2.5. Control Limits

12.2.6. The following control limits are utilized for matrix spikes and laboratory control samples (LCS). These limits must be reviewed at least annually against current data.

QC Type	200.8	6020/6020A
LCS	85 – 115	80 – 120
MS	70 – 130	75 – 125
RPD	± 20	± 20

12.2.7. All LCS and MS recoveries must be entered into QuantIMS or other database so that accurate historical control charts can be generated. For tests without a separate extraction, matrix spikes will be reported for all dilutions.

12.2.8. Refer to the QC program document (PT-QA-021) for further details regarding control limits.

12.3. Training Qualification

12.3.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

12.4. Instrumentation Detection Limit (IDL) 6020 – IDL for each analyte must be determined for each analyte wavelength used on each instrument. The IDL must be determined quarterly for method 6020/6020A for the standard analytes listed in Appendix A. For method 200.8 IDLs will be determined annually. If the instrument is adjusted in any way that may affect the IDL, the IDL for that instrument must be redetermined.

12.4.1. For 6020 the IDLs shall be determined by performing a blank analysis on 3 non-consecutive days with 7 consecutive measurements per day. The IDL is calculated by summing the standard deviations of the measurements from each day. For 200.8 the IDL is determined by performing 10 replicate blank analysis and multiplying the resulting standard deviation by 3.

12.4.2. Each measurement must be performed as though it were a separate analytical sample.

12.4.3. Each measurement must be followed by a rinse and/or any other procedure normally performed between the analyses of separate samples.

12.4.4. The IDL measurement must consist of the same number of replicates used for analytical samples with the average result used for reporting.

12.4.5. **DoD samples cannot be analyzed without a valid IDL.**

12.4.6. **For DoD, the established IDL must be less than the MDL (see below) for each analyte.**

12.5. Instrument detection limits (IDLs) 6020A – IDLs are useful means to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with the lower limit of quantitation, nor should they be used in establishing this limit. It may be helpful to compare the calculated IDLs to the established lower limit of quantitation, however, it should be understood that the lower limit of quantitation needs to be verified according to the guidance in Section 9.2.6.

12.5.1. IDLs in µg/L can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs should be determined at least every three months.

12.6. Linear Range Verification (LR) - The linear range is determined semi annually (2x/year) for each element on the standard list. Some regulatory programs, such as AFCEE, may require more frequent determinations.

12.6.1. To determine the linear range, analyze 3 standards at increasing concentration up to 90% of the last concentration where the element was within 10% of true value is considered the upper linear range.

12.6.2. An alternative is to prepare a higher concentration standard and run this in the analytical run. If this standard is within 10% of the expected value this value can be used as the upper linear range. If this option is chosen, then note the action in an anomaly.

13. POLLUTION CONTROL

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention.""

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1. Acid waste consisting of sample and rinse solution. This waste is collected in waste containers identified as “Acid Waste”, Waste #33. It is neutralized to a pH between 6 and 9 and then discharged down a lab sink.

14.1.2. Expired Metals Standards. This waste is collected in waste containers identified as “Acid Waste with Metals”, Waste #6.

15. REFERENCES

15.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, Method 6020, Inductively Coupled Plasma – Mass Spectrometry, Revision 0, September, 1994.

15.2. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update IV, Method 6020A, Inductively Coupled Plasma – Mass Spectrometry, Revision 1, February, 2007.

15.3. Thermo Electron X Series Users Manual

15.4. EPA Method 6020 CLP M, Version 8.

15.5. Methods for the Determination of Metals in Environmental Samples, Supplement 1 (EPA/600/R-94/111), Method 200.8, Determination of Trace Elements in Waters by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, 1994

15.6. EPA Method 200.8 EMSL Office of Research & Development, Cincinnati, OH (Draft Method, Revision 4.3, August 1990).

15.7. SOP PT-QA-001, Employee Orientation and Training, current version.

15.8. SOP PT-HS-001, Waste Collection, Accumulation and Storage, current version.

15.9. SOP PT-QA-006, Procurement of Standards and Materials; Labelling and Traceability, current version.

15.10. SOP PT-QA-007, Method Detection Limits.

15.11. SOP PT-QA-009, Rounding and Significant Figures.

15.12. SOP PT-QA-011, Data Recording Requirements, current version.

15.13. SOP PT-QA-015, Maintaining Time Integrity, current version.

15.14. SOP PT-QA-016, Nonconformance & Corrective Action System, current version.
15.15. SOP PT-QA-018, Technical Data Review Requirements, current version.
15.16. SOP PT-QA-021, TestAmerica Pittsburgh QC Program, current version.
15.17. SOP PT-QA-022, Equipment Maintenance, current version.
15.18. SOP PT-QA-024, Subsampling, current version.
15.19. SOP PT-QA-025, Implementation of the DoD QSM Version 3.
15.20. SOP PT-QA-027, Sample Receiving and Chain of Custody, current version.
15.21. SOP PT-QA-029, DoD QSM Version 4.1/4.2 Requirements, current version.
15.22. PT-LQAM, Pittsburgh Laboratory Quality Assurance Manual, current version.

16. METHOD MODIFICATIONS

16.1. Not applicable.

17. ATTACHMENTS

Table 1 – Standard Analyte List and Reporting Limits
Table 2 – Composition of the CAL Standard
Table 3 – Composition of the ICV Standard
Table 4 – Composition of the ICSA Standard
Table 5 – Composition of the ICSAB Standard
Table 6 – Common Molecular Ion Interferences in ICP-MS
Table 7 – Recommended Analytical Isotopes And Additional Masses That May Be Monitored
Table 8 – Recommended Isotopes And Additional Masses That May Be Monitored
Table 9 – Elemental Equations Used To Calculate Results
Table 10 – Internal Standards And Limitations Of Use
Table 11 – High Level Calibration Standard
Appendix 1 Cleaning Procedure for Glass- and Plastic-ware
Appendix 2 Wash Solution Preparation Instructions
Appendix 3 Daily Instrument Maintenance
Appendix 4 Autotune and Performance Reports
Appendix 5 Resolution Setup
Appendix 6 Instrument Calibrations

Appendix 7 Sample Introduction Plumbing Diagram
Appendix 8 Procedure for Cleaning Sample Introduction Equipment and Cones
Appendix 9 Autosampler Position Map
Appendix 11 Spiking Levels
Appendix 12 Work Flow Chart
Appendix 13 QC Abbreviations and Criteria

18. REVISION HISTORY

18.1. Revision 5, 5/19/08:

18.1.1. Renamed SOP as PT-MT-002.

18.1.2. Changed SOP format to correspond to corporate SOP format.

18.1.3. Corrected several typographical errors and incorrect Section references.

18.1.4. All changes have been highlighted throughout the document.

18.1.5. Updated SOP References

18.1.6. Corrected As and Ni RLs for water and soil.

18.2. Revision 6:

18.2.1. Updated to method 6020A requirements. Changes are highlighted.

18.2.2. Added to section 8: Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

18.2.3. Revised Appendix 13. Corrected typos and added QC criteria for applicable method requirements. Added cross references to tables and appendices.

18.3. Revision 7:

18.3.1. Added to Section 9.2.6: For method 6020A the CRI which is the low level quantitation check sample is prepared and analyzed quarterly or as needed. The control limit is 70-130%. Please note the CRI (undigested) is still analyzed at the beginning and end of the analytical run. Updated Appendix 13.

18.3.2. Added reference to SOP PT-QA-029.

18.4. Revision 9:

18.4.1.1. Added to section 6.3. Refer to Section 20 of PT-LQAM for instrument hardware/software specifications and routine instrument maintenance procedures

18.4.1.2. Added high level CCV requirements for DoD in section 9.2.8: A high level calibration standard is analyzed after the ICSAB before any client

samples are analyzed. This standard is analyzed once for a run. The percent recovery must be within 90-110%. If not the instrument is recalibrated and instrument QC along with high level calibration standard is reanalyzed before any samples can be analyzed. Sample concentration greater than high level calibration standard for analytes listed in Table 11 will be diluted. For analytes not included in high level calibration standard, Table 11, dilutions will be determined based on instrument calibration standard, Table 2. This was also added to Appendix 13.

18.4.1.3. Added Table VIII, high level CCV for DoD.

18.4.1.4. Replaced DoD V4.1 with DoD QSM 4.1/4.2 or current version.

18.4.1.5. Removed references to CLP ILM05.2.

18.4.1.6. Deleted from section 9.2.1: The Linear Range study must be performed quarterly if doing ILM05.2.

18.4.1.7. Deleted from section 10.2.2.3: Resolution must be ≤ 0.75 amu at 5% of the peak height for ILM05.2.

18.4.1.8. Deleted ILMO5.2 requirement from the table in section 12.2.6:

QC Type	ILM05.2
LCS	80 – 120
MS	75 – 125
RPD	± 20

18.4.1.9. Removed Appendix 10 ILM05.2D Contract Required Quantitation Limits (CRQLs).

Tables:

TABLE 1

STANDARD ANALYTE LIST AND REPORTING LIMITS*

Element	Symbol	CAS #	Aqueous RL mg/L	Aqueous QC SPIKE mg/L	Soil/Tissue RL mg/Kg	Soil/Tissue QC SPIKE mg/kg	Wipe RL ug/wipe	Wipe QC SPIKE ug/wipe
Aluminum	Al	7429-90-5	0.03	2.0	3.0	200	1.5	100
Antimony	Sb	7440-36-0	0.002	0.50	0.2	50	0.1	25
Arsenic	As	7440-38-2	0.001	0.04	0.1	4	0.05	100
Barium	Ba	7440-39-3	0.010	2.0	1.0	200	0.5	100
Beryllium	Be	7440-41-7	0.001	0.05	0.1	5	0.05	2.5
Boron	B	7440-42-8	0.005	1.0	0.5	100	0.25	50
Cadmium	Cd	7440-43-9	0.001	0.05	0.1	5	0.05	2.5
Calcium	Ca	7440-70-2	0.10	50	10.0	5000	5.0	2500
Chromium	Cr	7440-47-3	0.002	0.2	0.2	20	0.1	10
Cobalt	Co	7440-48-4	0.0005	0.5	0.05	50	0.025	25
Copper	Cu	7440-50-8	0.002	0.25	0.2	25	0.1	12.5
Iron	Fe	7439-89-6	0.05	1.0	5.0	100	2.5	50
Lead	Pb	7439-92-1	0.001	0.02	0.1	2	0.05	25
Magnesium	Mg	7439-95-4	0.10	50	10.0	5000	5.0	2500
Manganese	Mn	7439-96-5	0.0005	0.5	0.05	50	0.025	25
Molybdenum	Mo	7439-98-7	0.005	1.0	0.5	100	0.25	50
Nickel	Ni	7440-02-0	0.001	0.5	0.1	50	0.05	25
Potassium	K	7440-09-7	0.100	50	10.0	5000	5.0	2500
Selenium	Se	7782-49-2	0.005	0.01	0.5	1	0.25	100
Silver	Ag	7440-22-4	0.001	0.05	0.1	5	0.05	2.5
Sodium	Na	7440-23-5	0.10	50	10.0	5000	5.0	2500
Strontium	Sr	7440-24-6	0.005	1.0	0.5	100	0.25	50

TABLE 1

STANDARD ANALYTE LIST AND REPORTING LIMITS*

Element	Symbol	CAS #	Aqueous RL mg/L	Aqueous QC SPIKE mg/L	Soil/Tissue RL mg/Kg	Soil/Tissue QC SPIKE mg/kg	Wipe RL ug/wipe	Wipe QC SPIKE ug/wipe
Tin	Sn	7440-31-5	0.005	2.0	0.5	200	0.25	100
Titanium	Ti	7440-03-26	0.005	1.0	0.5	100	0.25	50
Thallium	Tl	7440-28-0	0.001	0.05	0.1	5	0.05	100
Vanadium	V	7440-62-2	0.001	0.5	0.1	50	0.05	25
Zinc	Zn	7440-66-6	0.005	0.5	0.5	50	0.25	25

** Note: These are the routine reporting limits for most sample types. Lower reporting limits may be achievable for special projects. Difficult sample matrices may cause reporting limits to be raised.*

TABLE 2

Composition of the Calibration Standards

Element	Concentration ug/mL	Element	Concentration ug/mL
Ag	0.200	Mn	1.0
Al	1.00	Mo	0.200
As	0.200	Na	100
B	0.200	Ni	0.200
Ba	0.200	Pb	0.200
Be	0.200	Sb	0.200
Ca	100	Se	0.200
Cd	0.200	Si	10
Co	0.200	Sn	0.200
Cr	0.200	Sr	0.200
Cu	0.200	Ti	0.200
Fe	50	Tl	0.200
K	100	V	0.200
Mg	100	Zn	0.200

TABLE 3
Composition of the ICV Standard

Element	Concentration ug/mL	Element	Concentration ug/mL
Ag	0.08	Mn	0.4
Al	0.4	Mo	0.08
As	0.08	Na	40
B	0.08	Ni	0.08
Ba	0.08	Pb	0.08
Be	0.08	Sb	0.08
Ca	40	Se	0.08
Cd	0.08	Si	4.0
Co	0.08	Sn	0.08
Cr	0.08	Sr	0.08
Cu	0.08	Ti	0.08
Fe	20	Tl	0.08
K	40	V	0.08
Mg	40	Zn	0.08

TABLE 4
Composition of the ICSA Standard

Element	Concentration ug/mL	Element	Concentration ug/mL
Al	100	P	100
Ca	100	S	100
Fe	100	C	200
K	100	Cl^-	1000
Mg	100	Mo	2.0
Na	100	Ti	2.0

TABLE 5
Composition of the ICSAB Standard

Element	Concentration ug/mL	Element	Concentration ug/mL
Ag	0.02	Na	100
Al	100	Ni	0.02
As	0.02	Pb	0.02
B	0.05	Sb	0.02
Ba	0.02	Se	0.05
Be	0.02	Si	0.50
Ca	100	Sn	0.10
Cd	0.02	Sr	0.02
Co	0.02	Ti	2.0
Cr	0.02	Tl	0.02
Cu	0.02	V	0.02
Fe	100	Zn	0.025
K	100	P	100
Mg	100.0	S	100
Mn	0.0225	C	200
Mo	2.00	Cl-	1000

TABLE 6[1]

COMMON MOLECULAR ION INTERFERENCES IN ICP-MS

Molecular Ion	Mass	Element	Molecular Ion	Mass	Element
BACKGROUND MOLECULAR IONS					
NH^+	15		$^{38}ArH^+$	39	
OH^+	17		$^{40}ArH^+$	41	
OH_2^+	18		CO_2^+	44	
C_2^+	24		CO_2H^+	45	Sc
CN^+	26		ArC^+, ArO^+	52	Cr
CO^+	28		ArN^+	54	Cr
N_2^+	28		$ArNH^+$	55	Mn
N_2H^+	29		ArO^+	56	
NO^+	30		$ArOH^+$	57	
NOH^+	31		$^{40}Ar^{36}Ar^+$	76	Se
O_2^+	32		$^{40}Ar^{38}Ar^+$	78	Se
O_2H_+	33		$^{40}Ar_2^+$	80	Se
$^{36}ArH^+$	37				
MATRIX MOLECULAR IONS – Chloride					
$^{35}Cl0^+$	51	V	$^{37}Cl0H^+$	54	Cr
$^{35}Cl0H^+$	52	Cr	$^{35}Cl0^+$	51	V
$^{37}Cl0^+$	53	Cr	$^{35}Cl0H^+$	52	Cr
$Ar^{35}Cl^+$	75	As	$Ar^{37}Cl^+$	77	Se
MATRIX MOLECULAR IONS – Sulfate					
$^{32}SO^+$	48		$^{34}SOH^+$	51	V
$^{32}SOH^+$	49		SO_2^+, S_2^+	64	Zn
$^{34}SO^+$	50	V, Cr			
$Ar^{32}S^+$	72		$Ar^{34}S^+$	74	
MATRIX MOLECULAR IONS – Phosphate					
PO^+	47		PO_2^+	63	Cu
POH^+	48				
ArP^+	71				
MATRIX MOLECULAR IONS – Group I, II Metals					
$ArNa^+$	63	Cu	$ArCa^+$	80	
ArK^+	79				
MATRIX OXIDES[3]					
TiO	62-66	Ni. Cu. Zn	MoO	108-116	Cd
ZrO	106-112	Ag, Cd			

[1] *From Method 200.8, Section 13.2.6*
[2] *Method elements or internal standards affected by the molecular ions.*

[3]*Oxide interferences will normally be very small and will only impact the method elements when present at relatively high concentrations. Some examples of matrix oxides are listed of which the analyst should be aware. It is recommended that Ti and Zr isotopes be monitored in solid waste samples, which are likely to contain high levels of these elements. Mo is monitored as a method analyte.*

TABLE 7

RECOMMENDED ANALYTICAL ISOTOPES AND ADDITIONAL MASSES THAT MAY BE MONITORED [1]

Isotope	Element of Interest	Isotope	Element of Interest
27	Aluminum [2]	80,**78**,**82**,**76**,**77**,74	Selenium
121,123	Antimony [2]	**107**,**109**	Silver [2]
75	Arsenic [2]	**23**	Sodium [2]
138,**137**,136,**135**,134,132,130	Barium [2]	203, **205**	Thallium [2]
9	Beryllium [2]	**51**,**50**	Vanadium [2]
114,112,**111**,110,113,116,106,**108**	Cadmium [2]	**66**, **68**	Zinc [2]
42,**43**,**44**,46,48	Calcium [2]	83	Krypton
52,**53**,**50**,54	Chromium [2]	72	Germanium
59	Cobalt [2]	139	Lanthanum
63,**65**	Copper [2]	140	Cerium
56,**54**,**57**,58	Iron [2]	129	Xenon
206,207,**208**	Lead [2]	**118**	Tin
24,**25**,**26**	Magnesium [2]	105	Palladium
55	Manganese [2]	47,**49**	Titanium
98,96,92,97,94,95	Molybdenum	125	Tellurium
58,**60**,62,**61**,64	Nickel [2]	69	Gallium
39	Potassium [2]	35,37	Chlorine

[1] *From Method 6020 CLP-M, Table 9*

[2] *Element approved for ICP-MS determination by SW846 Method 6020 CLP-M*

NOTE: Isotopes recommended for analytical determination are **bolded**.

TABLE 8			
RECOMMENDED ISOTOPES AND ADDITIONAL MASSES THAT MAY BE MONITORED			
Rare Earth Elements	**ICPMS Preferred Mass**	**Elemental Equations**	**Additional Masses**
Lanthanum	138.906		
Cerium	139.905		
Praseodymium	140.907		
Neodymium	141.908	-0.125266 * ^{140}Ce	142.910, 144.912
Samarium	151.920	-0.012780 * ^{157}Gd	144.912
Europium	152.929		
Gadolinium	157.924	-0.004016 * ^{163}Dy	156.934
Terbium	158.925		
Dysprosium	163.929	-0.047917 * ^{166}Er	
Holmium	164.930		
Erbium	165.930		
Thulium	168.934		
Ytterbium	173.939	-0.005935 * ^{178}Hf	171.937
Lutetium	174.941		

TABLE 8A			
RECOMMENDED ISOTOPES AND ADDITIONAL MASSES THAT MAY BE MONITORED			
Rare Earth Elements			
Other Elements			
Boron	11.009		
Calcium	43.956		
Cesium	132.905		
Galium	68.926		
Germanium	71.922		
Gold	196.967		
Hafnium	177.944		176.944
Holmium	164.930		
Iridium	192.963		
Lithium	7.016		
Tungsten	183.951	-0001242* ^{189}Os	
Uranium	238.050		
Yttrium	88.905		
Zirconium	238.050		
Niobium	92.906		
Palladium	104.905		
Phosphorus	30.994		
Platinum	194.965		
Rhenium	186.965	-0.099379 * ^{189}Os	
Rhodium	102.905		
Rubidium	84.912		
Ruthenium	101.904	-0.045678 * ^{105}Pd	
Scandium	44.956		
Strontium	87.906		
Tantalum	180.948		
Tellurium	127.905	-0.072348 * ^{129}Xe	
Thorium	232.03		

TABLE 9

ELEMENTAL EQUATIONS USED TO CALCULATE RESULTS

Element	Elemental Equation	Note
Al	(1.000) (^{27}C)	
Sb	(1.000) (^{121}C)	
As	(1.000) (^{75}C) - (3.1278)[^{77}C) - (1.0177)(^{78}C)]	Correction for chloride interference with adjustment for Se77. ArCl 75/77 ratio may be determined from the reagent blank.
Ba	(1.000) (^{137}C)	
Be	(1.000) (^{9}C)	
Cd	(1.000) (^{111}C) - (1.073) [(^{108}C) - (0.712) (^{106}C)]	Correction of MoO interference. An additional isobaric elemental correction should be made if palladium is present.
Cr	(1.000) (^{52}C)	In 0.4% v/v HCl, the background from ClOH will normally be small. However the contribution may be estimated from the reagent blank.
Co	(1.000) (^{59}C)	
Cu	(1.000) (^{63}C)	
Pb	(1.000) (^{206}C) + (1.000) (^{207}C) + (1.000) (^{208}C)	Allowance for isotopic variability of lead isotopes.
Mn	(1.000) (^{55}C)	
Mo	(1.000) (^{98}C) - (0.146) (^{99}C)	Isobaric elemental correction for ruthenium.
Ni	(1.000) (^{60}C)	
Se	(1.000) (^{82}C)	Some argon supplies contain krypton as an impurity. Selenium is corrected for Kr82 by background subtraction.
Ag	(1.000) (^{107}C)	
Tl	(1.000) (^{205}C)	
Th	(1.000) (^{232}C)	
U	(1.000) (^{238}C)	
V	(1.000) (^{51}C) - (3.127) [(^{53}C) - (0.113) (^{52}C)]	Correction of chloride inference with adjustment for Cr53. Cl0 51/53 ratio may be determined from the reagent blank.
Zn	(1.000) (^{66}C)	
Internal Standards		

TABLE 9 ELEMENTAL EQUATIONS USED TO CALCULATE RESULTS		
Bi	(1.000) (^{209}C)	
In	(1.000) (^{115}C) -(0.0149) (^{118}C)	Isobaric elemental correction for tin.
Ge	(1.000) (^{72}C)	
Sc	(1.000) (^{45}C)	
Tb	(1.000) (^{159}C)	
Tm	(1.000) (^{169}C)	
Y	(1.000) (^{89}C)	

* Method elements or internal standards affected by the molecular ions. C = Calibration blank subtracted counts at specified mass.

TABLE 10 INTERNAL STANDARDS AND LIMITATIONS OF USE		
Internal Standard	Mass	Possible Limitation
Lithium	6	a
Scandium	45	Polyatomic Ion Interference
Germanium	72	
Yttrium	89	a, b
Rhodium	103	
Indium	115	Isobaric Interference by Sn
Terbium	159	
Holmium	165	
Thulium	169	
Lutetium	175	
Bismuth	209	a

a May be present in environmental samples.

b In some instruments Yttrium may form measurable amounts of YO^+ (105 amu) and YOH^+ (106 amu). If this is the case, care should be taken in the use of the cadmium elemental correction equation.

Table 11	
High Level Calibration Standard for DoD	
Element	**Concentration Mg/L**
Al	500
Ba	15
Ca	1000
Cr	20
Cu	20
Fe	500
K	300
Mg	1000
Mn	20
Na	500
Pb	20
Zn	20

Appendices

Appendix 1

Cleaning Procedure for Glass- and Plastic-ware

All glassware and plastic-ware coming into contact with samples, reagents and standards must be cleaned in the following manner. Plastic pipette tips may be cleaned in the same manner by soaking them in a suitable plastic container.

1) Completely fill the container to be leached with 10% nitric acid solution (6.1.5) and fit the lid.
2) Leave soaking for at least 12 hours.
3) Empty the container of acid and rinse thoroughly with laboratory water (6.1.1). Note that the acid may be collected and re-used until it becomes too contaminated.
4) Allow the vessel to air-dry in a clean area (preferably Class-1000 or better). If no such clean area is available, the container should be allowed to dry in the cleanest possible environment, or may be emptied of residual water as much as is possible and re-capped.
5) Containers should be capped ready for use and stored in the cleanest area available.
6) If pre-cleaned containers are to be stored for long periods (weeks to months) prior to use, it is most effective to store them full of laboratory water (6.1.1). This must be discarded and the containers rinsed thoroughly with laboratory water (6.1.1) and dried before use.

Appendix 2

Wash Solution Preparation Instructions (2% Nitric Acid (v/v))

A large volume of this solution is required for supply to the autosampler rinse station in order to wash the probe between samples. These instructions detail the preparation procedure for 2.5 L of this solution that is normally sufficient for one day of analytical use. The procedure may be scaled up or down as required.

1) Into a 2.5 L container (pre-cleaned as per Appendix 1), add 500±450 mL of laboratory water (6.1.1)
2) Add 50±10 mL of concentrated nitric acid (6.1.3)
3) Make to 2.50±0.25 L with laboratory water (6.1.1)
4) Mix well

Notes:

If preparing larger quantities simply scale-up quantities proportionally.

If analyzing for Ag, add hydrochloric acid at 1% by adding 50±10 mL of concentrated hydrochloric acid (6.1.2) after step 2.

Appendix 3

Daily Instrument Maintenance

1) Wipe all instrument, autosampler and surrounding bench surfaces with a damp wipe – continual cleanliness is important for the minimization of contamination
2) Check Wash Solution volume and remake if necessary (see Appendix 2)
3) Empty Waste Vessel according to laboratory disposal policy
4) Check the condition of all peristaltic pump tubes and replace if required (it is recommended to replace these daily although this may not be necessary with lower sample loads)
5) Check condition of sample introduction system and cones and clean and/or replace as necessary (see Appendix 8)
6) Ensure instrument fume-extraction system is operational

Appendix 4

Autotune and Performance Reports

Description

Autotune is a *PlasmaLab* software tool that allows the X Series to be optimized in a consistent, routine manner, giving reproducible levels of performance and saving the operator time and effort. It works by following a pre-defined sequence, optimizing individual instrument parameters in turn. Default sequences are provided with the software upon installation and a further customized sequence is provided on the CD accompanying this productivity pack.

Performance Reports are a *PlasmaLab* software tool that allows the X Series performance to be checked on a daily basis. The *Performance Report* can be set-up to give information about instrument sensitivity, stability, background, oxide species, doubly charged species, mass-calibration validity and peak resolution. Like *Autotune*, the *Performance Report* is user definable but defaults are provided with the software. Customized *Performance Reports* are provided on the CD accompanying this package.

The philosophy of use of these tools is as follows. After the sample introduction system or the cones have been removed and replaced or upon using the instrument for the first time or following major adjustments, the full *Autotune* sequence should be used to properly optimize the system. This takes about 15 minutes. From this, an *Autotune Update* sequence can be automatically created. This is a shortened version of the optimization sequence and will take about 5 minutes to run. The performance of the X Series is, in general, very stable from day-to-day, meaning that large amounts of optimization are not normally needed on a daily basis. To check whether optimization is needed, a *Performance Report* can be run initially. The results of this tell the operator if the system requires resolution adjustment, re-mass-calibration, or re-optimization. If the required sensitivity, background, stability or oxide performance is not satisfied, an *Autotune* should be run (the faster *Autotune Update* is normally sufficient). The *Performance Report* should then be repeated to ensure that the problem has been resolved.

Installing the EPA Autotune Sequence

To install the custom Autotune sequence, follow the instructions below:

1) Insert the CD in the CD ROM drive of the instrument operating PC. Wait for it to autorun and install the Productivity Pack by following the prompts after clicking on *Install*.
2) Ensure that PlasmaLab version 2.2 (or higher) has been installed
3) In PlasmaLab, go to *Instrument*, *Tune* and click on the down arrow button next to the *Autotune* icon (musical note).
4) Point to *Tools* in the menu and then select *Import Autotune Sequences*

5) Click *Next* in the Autotune Wizard
6) Click on *Browse* and find the path

C:/Program Files/ThermoElemental/PlasmaLab/Data

7) Select *EPA Autotune Sequence* and click on *Open*
8) Click on *Next*
9) Select *EPA – Xi Interface* and click on *Next*
10) Click on *Finish*

Installing the EPA Performance Reports

To install the custom Performance Reports, follow the instructions below:

1) Ensure the Pack is installed from the CD as described above
2) Ensure that PlasmaLab version 2.2 (or higher) has been installed
3) In PlasmaLab, go to *Instrument*, *Tune* and click on the down arrow button next to the *Performance Report* icon (musical note on page).
4) Point to *Tools* in the menu and then select *Import Performance Report*
5) Click *Next* in the Performance Report Wizard
6) Click on *Browse* and find the path for the CD ROM drive

   C:/Program Files/ThermoElemental/PlasmaLab/Data
7) Select *EPA 6020 Report* and click on *Open*
8) Click on *Next*
9) Select *EPA 6020 2.1* and click on *Next*
10) Click on *Finish*

To install the second Performance Report, follow instructions 1) to 10) above, selecting the alternative Performance Report name, i.e. *EPA ILM05_2D Report*.

Running Autotune from the Tune Page

To run an Autotune Sequence, follow the instructions below:

1) In PlasmaLab go to *Instrument*, *Tune* and click on the *Autotune* icon (musical note)
2) Select *Run an Existing Autotune Sequence* and click on *Next*
3) Select the required sequence, e.g. *EPA Xi Interface*, or *EPA Xi Interface – Update* and click on *Next*

4) Ensure that the indicated solution is being aspirated (through both probes if on-line internal standard addition is being used) and allow sufficient time for the solution to be transported into the nebulizer

5) Click on *Finish*

The selected Autotune sequence will now be run. To monitor its progress, observe the processes indicated at the bottom left of the PlasmaLab screen and open the Service Window (double-click on *MS* icon at the bottom right of the screen). A printable *Autotune Report* is generated at the end of the sequence. To continue, this report must be closed. To access this report upon closure, go to *Instrument*, *Configurations*, *Configuration Editor* and point to the appropriate *Instrument Settings* line. Open a pop-up menu by right-clicking and use the *View Tune Report* selection.

Running a Performance Report from the Tune Page

To run a Performance Report, follow the instructions below:

1) In PlasmaLab go to *Instrument*, *Tune* and click on the *Performance Report* icon (musical note on a page)

2) Select *Run an Existing Performance Report* and click on *Next*

3) Select the required sequence, e.g. *EPA ILM05 / 6020*, or *EPA 6020* and click on *Next*

4) Ensure that the indicated solution is being aspirated (through both probes if on-line internal standard addition is being used) and allow sufficient time for the solution to be transported into the nebulizer

5) Click on *Finish*

The selected *Performance Report* will now be run. To monitor its progress, open the Service Window (double-click on *MS* icon at the bottom right of the screen). A printable *Performance Report* is generated at the end of the sequence. To access this report upon closure, go to *Instrument*, *Tune*, and click on the down arrow to the right of the Performance Report icon. Point at *Tools* and then select *View Performance Report Results*. Select the required Performance Report to view and click *OK*.

Running Performance Reports and Autotune in an Experiment

It is also possible to automate the running of these procedures using an instrument setup sample within an experiment. To do this, insert an *Instrument Setup Sample* at the beginning of the Sample List by selecting the first sample and using a right-mouse-click menu to *Insert New Before*. Define the *Sample Type* for this new sample as *Instrument Setup* and click on *Show Advanced*. Click on the *Instrument Performance Tests* tab and setup the Performance Report and Autotune functions following the logic and using the drop-down combo boxes to select the next action. An example would be as follows:

Acquire Performance Report	*EPA ILM05.2 / 6020*
If mass calibration verification fails then	*Abort the Queue*

If the Performance Report fails then	*Autotune using EPA – Xi Interface*
If the Autotune fails then	*Abort the experiment*
If the Autotune passes then	*re-run the Performance Report*
If the Performance Report fails again then	*Abort the Queue*

When Performance Reports and Autotunes are acquired in this way, the results are stored as part of the experiment report. Note that since this method of acquiring the report is done using the autosampler, the solution concentration should be adjusted if on-line internal standard addition is to be used, e.g. if the addition dilutes the samples 1:1, the solution concentration should be doubled to get an accurate measure of sensitivity.

Appendix 5

Resolution Set up

With the instrument in *Operate* mode, aspirate 10-µg/L Tune solution (6.4.1) (through both probes if using on-line internal standard addition). Go to *Instrument*, *Tune* and stop the real time display (RTD) using the square stop icon. Change the display mode from *Time vs ICPS* to *ICPS on the full mass range*. Insert Be as the mass to monitor and change the spacing to 10, the dwell to 1 ms and the channels to 200. Disable all other masses in the grid. Restart the RTD by clicking on the triangular play icon. The software will display the scanned peak for mass 9, Be. To adjust the resolution, go to the *Global* tab and use the slider bar marked *Standard resolution*. This must be set up to give a peak width of less than 0.75 amu at 5% peak height. This is typically reached at a setting of between 100 and 200. If high-resolution mode is to be used, this can be setup by changing the resolution setting on the RTD to *High*. The High Resolution peak width is typically set at about 0.4 amu at 5% peak height, again with values typically between 100 and 200. Note that this method does not use High-resolution mode. Each resolution mode should be checked with several other masses across the mass range, typically 55Mn, 115In, 203Tl and 238U are used. Special attention should be paid to the resolution setup for Mn. This is measured at m/z 55, which is adjacent to both iron and argon oxide at mass 56. These high signals must be properly resolved from the low Mn signal in standard resolution mode. When the correct resolution settings are achieved, save the setting using the disk icon. **Note that a new mass-calibration must always be performed after adjustment of the resolution.**

Appendix 6

Instrument Calibrations

There are three instrument calibrations that are fundamental for obtaining good quality data on the X Series. These are:

1) Mass-calibration
2) Detector Plateau and Analogue voltage set routines
3) Detector cross-calibration.

Mass calibration sets the quadrupole scan parameters to give the correct measured mass positions. The detector plateau sets the optimum voltage on the ion or pulse counting section of the discrete dynode detector. The analogue voltage set routine applies an appropriate voltage on the analogue part of the detector to obtain a cross-calibration factor of approximately 20,000 for a mid-mass isotope. The detector calibration, or cross-calibration, calculates the correction factor, for each measured mass, between the two detector modes, pulse counting and analogue. All three calibrations may be performed in a single routine, or may be performed separately.

Mass Calibration

A mass-calibration must be performed whenever the resolution settings are adjusted, as this will affect the apparent mass position. Mass-calibration must be performed when the Performance Report shows that measured peak positions are >0.1 amu from their nominal position. Mass-calibrations are best performed using a solution containing as many elements as possible or with every analyte required for analysis at the very least. The solution should contain Li and U as these are used as low and high mass datum points. An appropriate concentration solution be used (one that gives between **100,000-1,500,000 cps** for each mass to be calibrated is appropriate). To perform a mass calibration, follow the instructions below.

1) Click *Experiment*
2) Select *Create New Experiment*
3) Click *OK*
4) Select the *Default* database
5) Click *Open*
6) Go to *Sample List*
7) Click the *Report* check box in the sample list grid
8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*
9) Click on the *Show Advanced* button

10) Click on the *Instrument Calibrations* tab

11) Check the *Mass-Calibration* box

12) There is an option to *Update current mass-calibration* or form a *New mass-calibration*. Unless a major hardware change has been performed, the *Update current mass-calibration* option should be selected.

13) Click *Queue*

14) Save the experiment with an appropriate name, e.g. *masscal 090902* and click *Save*

15) Click *Append*

16) Click *OK*

Mass-calibration will now be performed.

To view the mass-calibration results, go to *Instrument*, *Calibrations*, *Mass-Calibration*. A mass-calibration for each of the two resolution modes is displayed in the graph of Peak Width and Error (y) versus Mass (x). The current mass-calibration is indicated by the row(s) displayed in green. To display alternative mass-calibrations, click on the appropriate date/time-stamped line in the top grid. The Performance Report function can be used to check mass-calibration accuracy (see Appendix 4).

Detector Plateau and Analogue Voltage Set

These routines can be performed separately, but it is advised to run them simultaneously as described here. The necessary frequency of these calibrations depends upon the amount of signal the detector is exposed to, i.e. how many samples are analyzed, which analytes and what concentrations. For most laboratories running a moderate sample load, this procedure may be run weekly. Up to three masses may be used in this procedure, however here, the use of a single mass is described. A solution that gives a countrate of between **100,000-1,500,000 cps** is appropriate. The default mass used here is indium (m/z 115), so this must be present in the solution for the routine to work. For an X5 instrument, an appropriate concentration would typically be between 10 and 100 µg/L, depending upon the sensitivity of the system. To perform this routine, follow the instructions below.

1) Click *Experiment*

2) Select *Create New Experiment*

3) Click *OK*

4) Select the *Default* database

5) Click *Open*

6) Go to *Sample List*

7) Click in the *Report* check box in the sample list grid

8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*

9) Click on the *Show Advanced* button

10) Click on the *Instrument Calibrations* tab

11) Check *the Set analogue voltage* box

12) Set the *Number of iterations* to *2*

13) Click *Queue*

14) Save the experiment with an appropriate name, e.g. *plateau 090902* and click *Save*

15) Click *Append*

16) Click *OK*

The voltage setup will now be performed. To view the plateau, go to *Instrument*, *Calibrations*, *Detector Plateau*. A graph of signal intensity (y) versus voltage (x) is displayed. The "knee" inflexion on this plot corresponds to the plateau voltage. This is automatically selected and applied to the detector by the software.

Detector Calibration (Cross-Calibration)

This routine must be performed whenever the detector voltages are altered and daily prior to analysis of samples. The solution used must contain all the analytes to be measured as an absolute minimum. The more analytes present, the better. All analytes should ideally be set at a concentration that gives between **500,000 and 1,500,000cps**. To perform the detector calibration, follow the instructions below:

1) Click *Experiment*

2) Select *Create New Experiment*

3) Click *OK*

4) Select the *Default* database

5) Click *Open*

6) Go to *Sample List*

7) Click in the *Report* check box in the sample list grid

8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*

9) Click on the *Show Advanced* button

10) Click on the *Instrument Calibrations* tab

11) Check the *Detector Calibrate* box

12) Click *Queue*

13) Save the experiment with an appropriate name, e.g. *xcal 090902* and click *Save*

14) Click *Append*

15) Click *OK*

The detector calibration will now be performed. To view the cross-calibration grap, go to *Instrument*, *Calibrations*, *Detector Cross-Calibration*. A graph of cross-calibration factor (y) versus mass (x) is displayed. **Use the data table to check that all analytical masses of interest have been used in the cross-calibration**. If not, the cross-calibration factor will be estimated from the equation of the graph. This may result in error.

All Routines in One

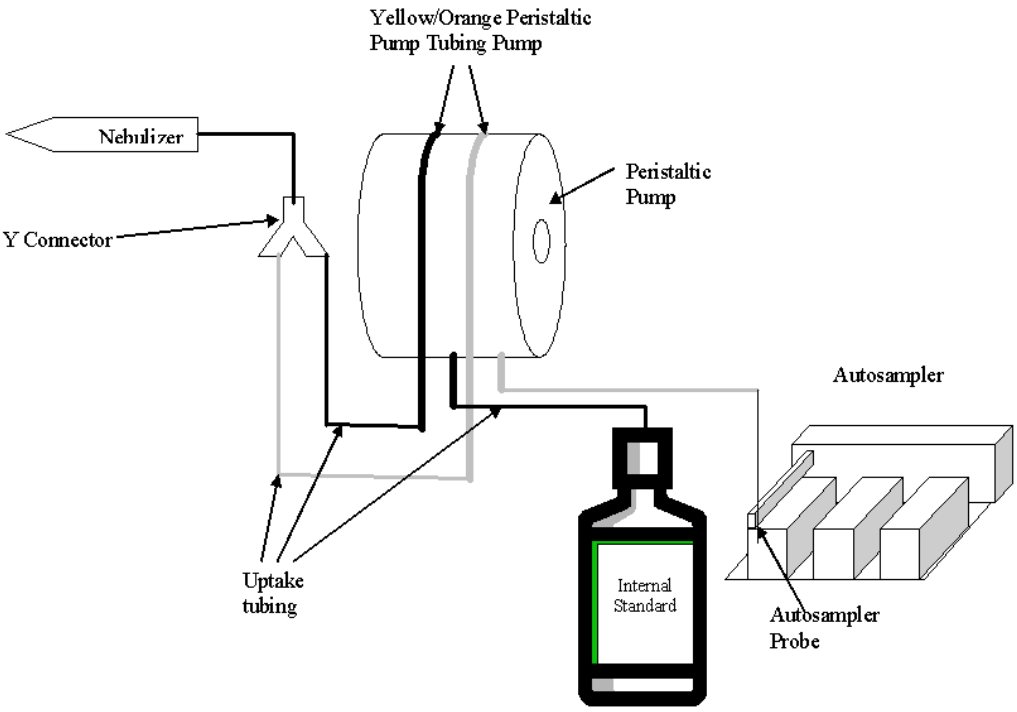
It is possible to run all three of the above routines on a single run if the solution used conforms to all of the criteria spelt out above. To do this, follow the instructions below.

1) Click *Experiment*
2) Select *Create New Experiment*
3) Click *OK*
4) Select the *Default* database
5) Click *Open*
6) Go to *Sample List*
7) Click in the *Report* check box in the sample list grid
8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*
9) Click on the *Show Advanced* button
10) Click on the *Instrument Calibrations* tab
11) Check the *Mass calibration*, *Detector Calibrate* and *Set analogue voltage* boxes
12) Set the *Number of iterations* to *2*
13) Click *Queue*
14) Save the experiment with an appropriate name, e.g. *instr cal 090902* and click *Save*
15) Click *Append*
16) Click *OK*

The instrument calibrations will now be performed. Each parameter can be viewed as described above.

Appendix 7

Sample Introduction Plumbing Diagram



Appendix 8

Procedure for Cleaning Sample Introduction Equipment and Cones

1) Ensure that the instrument is in the *vacuum* or *shutdown* state (i.e. the plasma is OFF and the slide valve is SHUT)
2) Dismantle the sample introduction system as follows:

a) Remove the gas connection from the nebulizer
b) Remove the sample input plug from the nebulizer
c) Remove the metal clip on the spray chamber to elbow joint
d) Remove the drain plug from the spray chamber
e) Slide the spray chamber and nebulizer away from the elbow
f) Carefully slide the nebulizer out of the spray chamber and set both pieces aside in a safe place
g) Open the torch box and the internal Faraday cage
h) Pull the gas connections away from the torch
i) Undo the torch catch
j) Remove the metal clip on the elbow to torch joint
k) Carefully remove the torch from the load coil and set aside in a safe place
l) Remove the elbow by sliding it out of the torch box bulkhead toward spray chamber end
m) Slide the torch box away from the mass spectrometer to reveal the interface
n) Use the flat metal cone tool to undo the locking ring over the sample cone
o) Carefully remove the sample cone and set aside in a safe place
p) Carefully unscrew and remove the skimmer cone from the interface using the cylindrical aluminium tool and set aside in a safe place

3) Clean the cones as follows.

a) Carefully place the cones into a large beaker and fill with sufficient 0.05% nitric acid to cover – CAUTION: Stronger acids will corrode the cone material and reduce lifetime
b) Place the beaker in an ultrasonic bath for about 10 minutes or until surface deposition has been removed
c) Carefully remove the cones from the solution and rinse thoroughly with deionised water
d) Allow the cones to air-dry prior to refitting

4) Clean the sample introduction equipment as follows.

e) Carefully place the glass sample introduction components into a large beaker and fill with sufficient 10% nitric acid to cover all components

f) Place in an ultrasonic bath for between 20 minutes and 1 hour

g) Carefully remove the glass components and rinse thoroughly with deionised water

h) Allow to air-dry prior to refitting

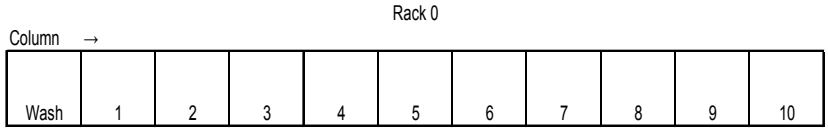
5) Reassemble the components in the reverse order to disassembly

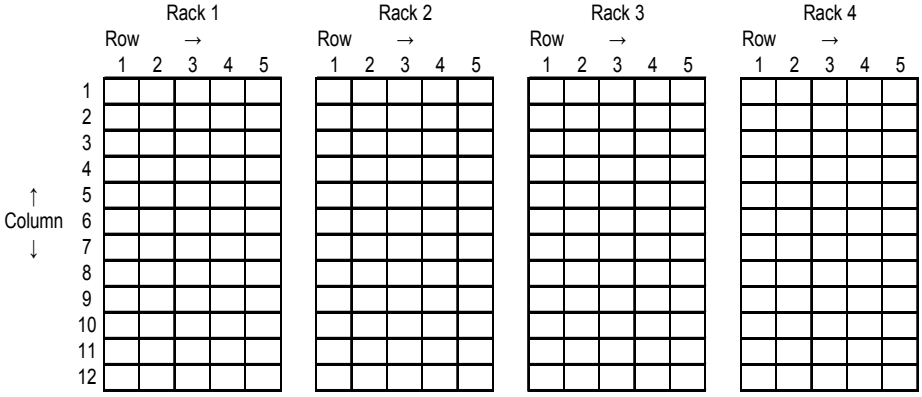
Note: Occasionally, glass sample introduction components crack when the ultrasonic cleaning procedure is used. To avoid this, the components may be soaked in acid, as above, for 12 hours, without ultrasonic treatment.

Thermo Electron cannot take any responsibility for any breakage that occurs during cleaning.

Appendix 9

Autosampler Position Map





NB: This map is only applicable for CETAC ASX-500/510 autosamplers fitted with 60 position racks.

Appendix 10

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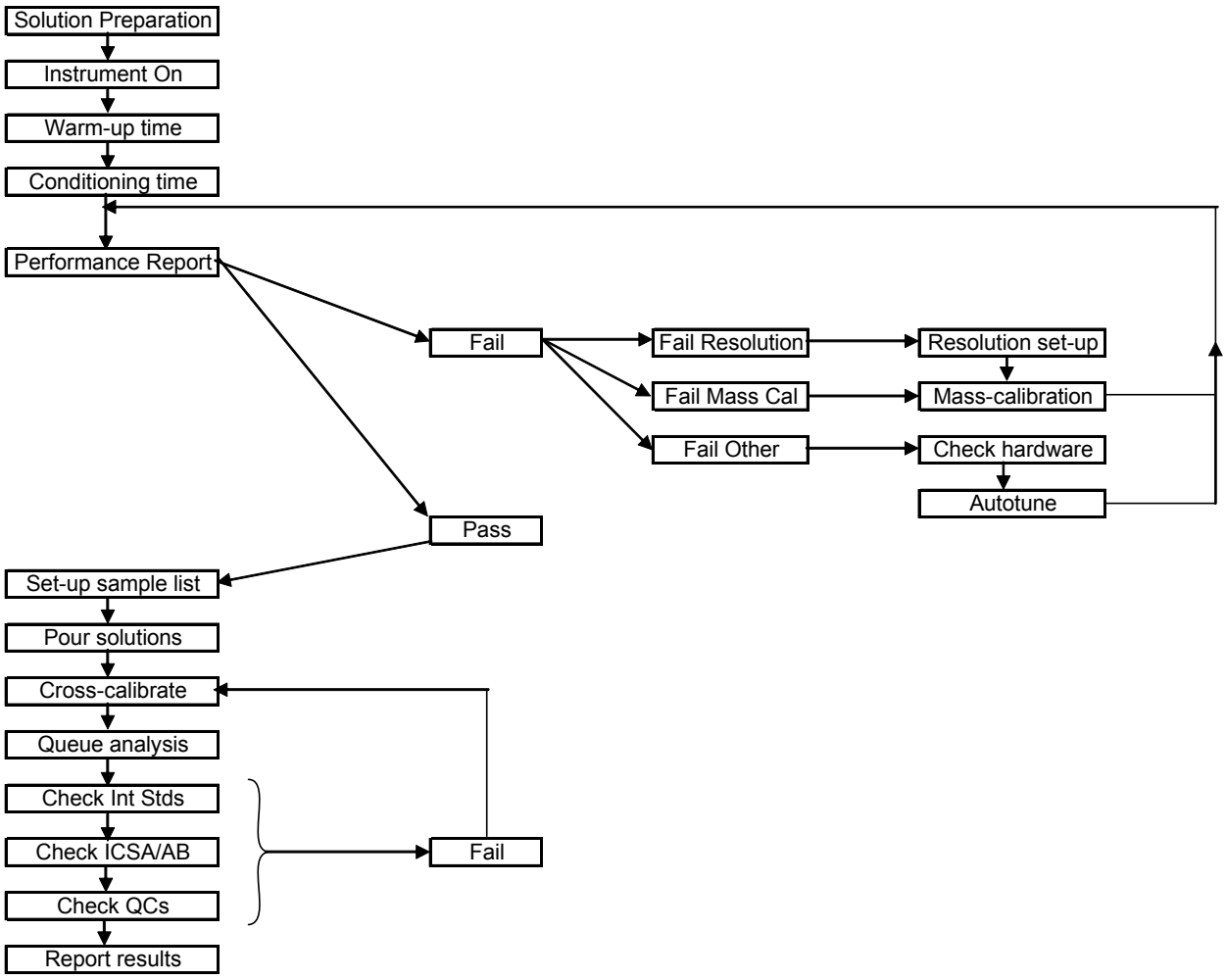
Appendix 11

Spiking Levels

(Concentration in Final Solution Based on Instructions Within this Document)

Analyte	Spike Value (µg/L)
Al	2000
Sb	500
As	40
Ba	2000
Be	50
Cd	50
Cr	200
Co	500
Cu	250
Pb	20
Mn	500
Ni	500
Se	10
Ag	50
Tl	50
V	500
Zn	500

Appendix 12
Work Flow-Chart



Appendix 13
QC Abbreviations and Criteria

QC Code	Method(s)	QC Name	Purpose	Frequency	Limits
ICV	CLP, 6020, 6020A, 200.8, DoD	Initial Calibration Verification	Checks the calibration against a second calibration source	After initial calibration	90-110%
ICB	CLP, 6020, 6020A, 200.8, DoD	Initial Calibration Blank	Initial check of read-back at blank level	After initial calibration	<CRQL (1)
CRI/ LLICV/LLCCV²	CLP, 6020, 6020A, 200.8, DoD	Contract Required Quantitation Limit Check	Checks accuracy at the required limit of quantitation	After each calibration. ²	50-150% (1) 70-130%(6020A)²
ICSA	CLP, 6020, 6020A, 200.8, DoD	Interference Check Solution A	Checks for freedom from interference	After initial calibration	For RL < 10 ±3 CRQL, RL > 10 ± RL or ±20% of the true value (whichever is the greater)
ICSAB	CLP, 6020, 6020A, 200.8, DoD	Interference Check Solution AB	Checks that analytes are accurately measured in an interference-producing matrix	After initial calibration	80-120% of true value
High Level Calibration Standard (DoD only)	6020 DoD	High level calibration check standard	Samples are diluted if results are above this standard and above the calibration standard, see section 9.2.8.1.	After ICSAB	90-110% of true value
CCV	CLP, 6020, 6020A, 200.8, DoD	Continuing Calibration Verification	A continuing periodic check on accuracy and drift	After each calibration and every 10 samples	90-110%
CCB	CLP, 6020, 6020A, 200.8,	Continuing Calibration Blank	A continuing periodic check	After each calibration and	<CRQL (1)

QC Code	Method(s)	QC Name	Purpose	Frequency	Limits
	DoD		on the read-back at blank levels	every 10 samples	
MB	CLP, 6020, 6020A, 200.8, DoD	Method Blank	Identify contamination	Once every 20 samples per matrix	< RL except for common lab contaminants at < 5 X RL. DoD < ½ RL, common lab contaminants < RL.
	CLP, 6020, 6020A, 200.8				
LCS	CLP, 6020, 6020A, 200.8, DoD	Laboratory Control Sample	Checks the accuracy of the entire analytical process	Once every 20 samples per matrix	80-120% 85-115% - 200.8
MS/MSD	CLP, 6020, 6020A, 200.8, DoD	Matrix Spike/Matrix Spike Duplicate	Accuracy and precision	Once every 20 samples – For 200.8 every 10 samples	75-125%, RPD ± 20%
DUP	CLP, 6020, 6020A, 200.8, DoD	Duplicate	Checks the reproducibility of results by analyzing an unknown sample in duplicate	Once every 20 samples per matrix	±20% Relative Percentage Difference (RPD)
PDS	6020, 6020A, DoD	Post Digestion Spike	Checks the recovery of analytes spiked into an unknown sample after preparation (digestion) – Performed if MS/MSD criteria not met.	Once every 20 samples per matrix	75-125% 80- 120% (6020A)
SER	CLP, 6020, 6020A, 200.8, DoD	Serial Dilution	Checks for matrix effects by assessing the variation of results for an unknown sample before and after dilution	Once every 20 samples per matrix	±10% of the original undiluted result after dilution correction for sample results ≥ 50 X MDL or IDL.

(1) For Method 6010A and 200.8, limit is 50-150%. For CLP see Section 9.2.6. For specific DoD requirements, refer to PT-QA-025. For DoD QSM current version refer to SOP PT-QA-029.

(2) For Methods 6020, 6020A & DoD requirements, the CRI is also analyzed at the end of the analytical sequence.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

TITLE: Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP)

METHODS: SW-846 6010B, 6010C AND EPA 200.7

Approvals (Signature/Date):

	07/17/09		07/20/09
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1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP-AES) using SW-846 Method 6010B, 6010C and EPA Method 200.7. Table I of Appendix A lists the elements appropriate for analysis by Methods 6010B/6010C and 200.7. Additional elements may be analyzed under Methods 6010B, 6010C and 200.7 provided that the method performance criteria presented in Section 13.0 are met. In addition to SOW ILMO4.0, this SOP is also compliant with the requirements of CLP SOWs 7/88, 3/90, ILMO1.0 and ILMO2.1.

1.2. ICP analysis provides for the determination of metal concentrations over several orders of magnitude. Detection limits, sensitivity and optimum concentration ranges of the metals will vary with the matrices and instrumentation used. For instance, in comparison to conventional ICP technique, ICP-Trace can achieve detection levels comparable to those determined using the graphite furnace atomic absorption spectroscopy (GFAAS) technique.

1.3. Method 6010B and 6010C are applicable to the determination of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, tissues, wipes and TCLP, EP and other leachates/extracts. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators may require digestion of dissolved samples and this must be clarified and documented before project initiation. Silver concentrations must be below 2.0 mg/L in aqueous samples and 100 mg/kg in solid matrix samples. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data.

1.4. Method 200.7 is applicable to the determination of dissolved, suspended, total recoverable, and total elements in water, waste water, and solid wastes. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples if the criteria in Section 11.1 are met. Silver concentrations must be below 0.1 mg/L in aqueous samples and 50 mg/kg in solid matrix samples.

1.5. For DoD QSM Version 3 requirements, refer to SOP PT-QA-025. For DoD V4.1 refer to SOP PT-QA-029.

1.6. On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.1 in the Quality Assurance Manual.

2. SUMMARY OF METHOD

2.1. This method describes a technique for the determination of multi elements in solution using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate actions taken. Alternatively, multivariate calibration methods may be chosen for which point selection for background correction is superfluous since whole spectral regions are processed. Consult the appropriate SOP's for details on sample preparation methods.

2.2. Refer to the appropriate SOPs for details on sample preparation methods.

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following vigorous digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

4. INTERFERENCES

4.1. Spectral, physical and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by:

- Overlap of a spectral line from another element.
- Unresolved overlap of molecular band spectra.
- Background contribution from continuous or recombination phenomena.
- Stray light from the line emission of high concentration elements.

4.1.1. Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not significant with the ICP technique but if observed can be minimized by buffering the sample, matrix matching or standard addition procedures.

4.1.2. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.1.3. Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte channel. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections IECs must be applied to the analyte to remove the effects of these unwanted emissions.

4.1.4. Physical interferences are generally considered to be effects associated with sample transport, nebulization and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension) or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If

physical interferences are present, dilution of the sample, use of a peristaltic pump, mass flow controller, use of an internal standard and/or use of a high solids nebulizer can reduce the effect.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

5.3 The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5 The RF generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.6 Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Metals digestates can be processed outside of a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.7 The preparation of standards and reagents will be conducted in a fume hood or well-ventilated area.

5.8 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor or EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Inductively Coupled Plasma Atomic Emission Spectrometer equipped with autosampler and background correction.

6.2. Radio Frequency Generator.

6.3. Nitrogen or argon gas supply, welding grade or equivalent.

6.4. Cool flow or appropriate water cooling device.

6.5. Peristaltic Pump.

6.6. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.7. Class A volumetric flasks.

6.8. Autosampler tubes.

7. REAGENTS AND STANDARDS

7.1. Intermediate standards are purchased as custom TestAmerica multielement mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Expiration dates can be extended provided that the acceptance criteria described in laboratory-specific SOPs are met.

7.2. Working calibration and calibration verification solutions may be used for up to 3 months and must be replaced sooner if verification from an independent source indicates a problem. Standards should be prepared in a matrix of 5% hydrochloric and 5% nitric acids. An exception to this is in the event the Trace ICP is utilized without the internal standard. In this case, the standard acid matrix must be matched to the final preparation matrix.

7.3. Refer to Tables III, IV, IVA, V and VI (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification, interference correction and spiking solutions.

7.4. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.5. Concentrated hydrochloric acid (HCl), trace metal grade or better.

7.6. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Sample holding times for metals are six months from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. Soil and wipe samples do not require preservation but must be stored at 4°C ± 2° until the time of preparation. Tissue samples are stored frozen until preparation.

8.4. Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

9. QUALITY CONTROL

9.1. Table VII (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action. See SOP PT-QA-021"TestAmerica Quality Control Program" for additional detail on criteria and corrective actions.

9.2. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 12.0.

9.3. Method Blank (MB) - One method blank must be processed with each preparation batch of up to 20 samples. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit (exception: common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 10X higher than the blank

contamination level). **Refer to PT-QA-025 for specific DoD requirements for the method blank. For DoD V4.1 refer to SOP PT-QA-029.**

- If the analyte is a common laboratory contaminant (copper, iron, lead (Trace only) or zinc) the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than two times the RL. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**
- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).
- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**
- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**
- For dissolved metals samples, which have not been digested, a CCB result is reported as the method blank. The CCB run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB.

9.4. Laboratory Control Sample (LCS) - One aqueous LCS (referred to as a Laboratory Fortified Blank in 200.7) must be processed with each preparation batch of up to 20 samples. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. Aqueous LCS spike levels are provided in Table III (Appendix A). The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

- If any analyte is outside established control limits the system is out of control and corrective action must occur. Control limits are established, for method 6010B/6010C, a control limit of 80 - 120% (85-115% for 200.7) recovery must be applied.
- In the event that an MS/MSD analysis is not possible a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- In the instance where the LCS recovery is greater than 120% (115% for 200.7) and the sample results are < RL, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the report narrative.**
- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.
- For dissolved metals samples, which have not been digested, a CCV result is reported as the LCS. The CCV run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCV.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch of up to 20 samples (6010B and 6010C) or one MS for every 10 or fewer samples (200.7). A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added (referred to as a Laboratory Fortified Matrix in 200.7). A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Tables III and VI (Appendix A).

- If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. For method 6010B and 6010C, control limits of 75 - 125% (70 – 130% for 200.7) recovery and 20% RPD or historical acceptance criteria must be applied to the MS/MSD. **Refer to PT-QA-025 for specific DoD requirements for the MS.** For DoD V4.1 refer to SOP PT-QA-029. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.
- If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits

do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level.".

- If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.
- For dissolved metals samples by 200.7, which have not been digested, a MS must be performed per every 10 or fewer samples by spiking an aliquot of the sample at the levels specified in Table III (Appendix A).
- For Methods **6010B/ 6010C/DoD** samples- If the MS/MSD recoveries are unacceptable, the same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. Otherwise, another sample from the same preparation batch should be used as an alternative. An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 80% to 120% (for Method 6010C) of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. The spike recovery from the post digestion spiked sample **for method 6010B/DoD** the spike recovery should be within the range 75-125%. If this spike fails, then the dilution test (Sec. 9.6 should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed.

9.6 Dilution test – A dilution test is performed to determine whether significant physical or chemical interferences exist due to the sample matrix. One sample per preparation batch must be processed as a dilution test. The test is performed by running a sample at a 5x (1:5) dilution. Samples identified as field blanks cannot be used for dilution tests. The results of the diluted sample, after correction for dilution, should agree within 10% of the original sample determination when the original sample concentration is greater than 50x the MDL. If the results are not within 10%, the possibility of chemical or physical interference exists.

9.7 Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). For analyses conducted under Method 200.7, the ICV result must fall within 5% of the true value for that solution with relative standard deviation <3% from replicate readings of four exposures of the ICV standard. For Method 6010B and 6010C, the ICV must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of three) exposures. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the RL from zero. **Refer to PT-QA-025 for specific DoD requirements for the ICB. For DoD V4.1 refer to SOP PT-QA-029.** If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated

and the calibration reverified. This standard is equivalent to the Quality Control Standard (QCS) and the first Instrument Performance Check (IPC) specified in 200.7.

9.8 Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV is a mid-range standard made from a dilution of the calibration standard. The CCV for both methods must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of three) exposures. A CCB is analyzed immediately following each CCV. The CCB result must fall within +/- RL from zero. **Refer to PT-QA-025 for specific DoD requirements for the CCB.** For DoD V4.1 refer to SOP PT-QA-029. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within 10% of the action limit, reanalysis and recalibration are not required before continuation of the run. If a mid-run CCV or CCB fails, the analytical run may be continued; however, the result(s) for the affected element(s) may only be reported when bracketed by valid CCV/CCB pairs. If analytical results for one or more elements are not bracketed by valid CCV/CCB pairs, the problem must be corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed for those elements only.

9.9 Reporting Limit Verification Standard (RLV)/CRA or LLICV/LLCCV (6010C) – Calibration accuracy at the laboratory reporting limit is verified after the analysis of the ICB by running the RLV, CRA or LLICV/LLCCV. For method 6010C it must be analyzed at beginning and end of the analytical run. This standard is at the reporting limit. For Methods 200.7 and 6010B the control limit is 50 – 150%. For Method 6010C LLICV/LLCCV the control limit is 70-130%. For method 6010C the RLV/CRA which is the low level quantitation check sample is prepared and analyzed quarterly or as needed. The control limit is 70-130%. Please note the RLV/CRA (undigested) is still analyzed at the beginning and end of the analytical run. **Refer to PT-QA-025 for specific DoD requirements for the RLV standard.** For DoD V4.1 refer to SOP PT-QA-029.

9.10. Interference Check Analysis (ICSA/ICSAB) - The validity of the interelement correction factors is demonstrated through the successful analysis of interference check solutions. The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Table V (Appendix A) for the details of ICSA and ICSAB composition. Custom TestAmerica multielement ICS solutions must be used. All analytes should be spiked into the ICSAB solution therefore, if a non-routine analyte is required then it should be manually spiked into the ICSAB using a certified ultra high purity single element solution or custom lab-specific mix. If the ICP will display over correction as a negative number then the non-routine elements can be controlled from the ICSA as described in section 9.10.3. Elements known to be

interferents on a required analyte must be included in the ICP run when that analyte is determined. Aluminum, iron, calcium and magnesium must always be included in all ICP runs.

9.10.1. The ICSA and ICSAB solutions must be run at the beginning of the run. (See Section 10.11 for required run sequence).

9.10.2. The ICSAB results for the interferents must fall within 80 - 120% of the true value. If any ICSAB interferent result fails criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the samples rerun.

9.10.3. ICSA results for the non-interfering elements with reporting limits ≤ 10 ug/L must fall within the TestAmerica guidelines of ± 2x RL from zero. ICSA results for the non-interfering elements with RLs > 10 µg/L must fall within the TestAmerica guidelines of ± 1x RL from zero. **Refer to PT-QA-025 for specific DoD requirements for the ICSA.** For DoD V4.1 refer to SOP PT-QA-029. If the ICSA results for the non-interfering elements do not fall within +/- 2x RL (RL ≤10) or ± 1xRL (RL>10) from zero the field sample data must be evaluated as follows:

- If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted.
- If the affected element was not required then the sample data can be accepted.
- If the interfering elements are not present in the field sample at a concentration, which would result in a false positive or negative result greater than +/- 2x RL from zero then the field sample data can be accepted.
- If the interfering element is present in the field sample at a level which would result in a false analyte signal greater than ± 2x RL from zero, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the analyte signal in the ICSA.
- If the data does not meet the above conditions then the IECs must be re-evaluated and corrected if necessary and the affected samples reanalyzed or the sample results manually corrected through application of the new IEC to the raw results. If the results are

recalculated manually the calculations must be clearly documented on the raw data.

9.12 Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences, which cause a baseline shift. Refer to Section 10.15 for additional information on when MSA is required as well as Appendix D for specific MSA requirements.

9.13 Quality Assurance/Project Summaries - Certain clients may require project- or program-specific QC, which may supersede this SOP's requirements. Quality Assurance Summaries (QASs) or equivalent documents providing project-specific requirements should be developed so that project staff clearly understands the special project requirements.

10. PROCEDURE

10.1. Calibration and Standardization

10.1.1. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.1.2. The instruments are profiled and calibrated according to the manufacturer's recommended procedures. Thermo has set up the ICP 61E to be profiled on Cu and the Trace ICPs are to be profiled on As. All other lines are preset by Thermo and should not be adjusted by the user. Flush the system with the calibration blank. The calibration curve must consist of a minimum of a blank and a standard. Refer to the facility-specific instrument SOP or ICP instrument manual for a detailed set up and operation protocols.

10.1.3. Calibration must be performed daily and each time the instrument is set up. Instrument runs may be continued over periods exceeding 24 hours as long as all calibration verification (CCV) and interference check QC criteria are met. The instrument standardization date and time must be included in the raw data.

10.1.4. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corresponding corrective actions. The NELAC requirement for verification of the initial calibration at varied concentrations is met daily since the ICVs, CCVs, and RLVs/CRA are all at different concentrations.

10.2. For 200.7 analyses, dissolved (preserved) samples must be digested unless it can be documented that the sample meets all of the following criteria:

A. Visibly transparent with a turbidity measurement of 1 NTU or less.

B. Is of one liquid phase and free of particulate or suspended matter following acidification.

C. Is NOT being analyzed for silver.

If the above criteria are met, the dissolved samples can be analyzed directly after an appropriate amount of 1:1 nitric acid is added to an aliquot of sample to adjust the acid concentration to approximately a 1% (v/v) nitric acid solution. Allowance for sample dilution should be made in the calculation.

10.3. A minimum of three exposures for each standard, field sample and QC sample is required. The average of the exposures is reported. For Trace ICP analyses, the results of the sum channel must be used for reporting.

10.4. Prior to calibration and between each sample/standard the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless following the protocol outlined in 10.1.2 it can be demonstrated that a shorter rinse time may be used. Triton-X can be added to the rinse solution to facilitate the rinse process.

10.5. The use of an autosampler for all runs is strongly recommended.

10.6. The use of automated QC checks through the instrument software is highly recommended for all calibration verification samples (ICV, CCV, RLV/CRA/LLICV/LLCCV), blanks (ICB, CCB, PB), interference checks (ICSA, ICSAB) and field samples (linear range) to improve the data review process.

10.7. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

10.8. To facilitate the data review and reporting processes it is strongly recommended that all necessary dilutions be performed before closing out the instrument run. If any digestate for Method 200.7 has silver detected above 100 mg/L, add 1.0 ml of concentrated HCl to the digestate, mix and reanalyze. If the second analysis yields a higher value for silver, the second analysis is reported and discussed in the report narrative.

10.9. The use of an internal standard is recommended on the conventional, non-Trace ICPs as an alternative to using the method of standard additions. This technique is useful in overcoming matrix interferences especially in high solids matrices.

However, for conventional ICP techniques, internal standards may not be necessary provided that one of the following is performed to minimize physical interferences: (1) peristaltic pump is used, (2) high solids nebulizer is used, or (3) high solids samples are diluted and reanalyzed.

10.10. The use of an internal standard is **required** on any axial ICP unless the calibration and QC standards are matrix matched to each digestion procedure. The following procedural guidelines must be followed when using an internal standard:

10.10.1. Typically used internal standards are: yttrium or scandium. (Note: Any element can be used that is not typically found in environmental samples at a high rate of occurrence.)

10.10.2. The internal standard (IS) must be added to every sample and standard at the same concentration. It is recommended that the IS be added to each analytical sample automatically through use of a third pump channel and mixing coil. Internal standards should be added to blanks, samples and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

10.10.3. The concentration of the internal standard should be sufficiently high to obtain good precision in the measurement of the IS analyte used for data correction and to minimize the possibility of correction errors if the IS analyte is naturally present in the sample.

10.10.4. The internal standard raw intensity counts must be printed on the raw data.

10.10.5. The analyst must monitor the response of the internal standard throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte).

10.10.5.1. If the internal standard counts fall within ±30% of the counts observed in the ICB then the data is acceptable.

10.10.5.2. If the internal standard counts in the field samples are more than ±30% higher than the expected level, the field samples must then be:

(1) Diluted and reanalyzed;

(2) The IS concentrations must be raised; or

(3) A different internal standard must be used.

10.11. The following analytical sequence must be used for Methods 6010B/6010C and 200.7:

Instrument Calibration

ICV

ICB

RLV/CRA/LLICV

ICSA

ICSAB

7 Samples

CCV

CCB

10 samples

CCV

CCB

Repeat sequence of up to 10 samples between CCV/CCB pairs as required to complete run

CCV

CCB

RLV/CRA/LLCCV

CCV

CCB

Refer to Quality Control Section 9.0 and Table VII (Appendix A) for Method 6010B/6010C and 200.7 quality control criteria.

10.12. Full method required QC must be available for each wavelength used in determining reported analyte results.

10.13. Guidelines are provided in the appendices on procedures to minimize contamination of samples and **standards, preventive maintenance and troubleshooting.**

10.14. All measurements must fall within the defined linear range where spectral interference correction factors are valid. Dilute and reanalyze all samples for required analytes that exceed the linear range or use an alternate wavelength for which QC data are established. If an interelement correction exists for an analyte, which exceeds the linear range, the IEC may be inaccurately applied. Therefore, even if an overrange analyte may not be required to be reported for a sample, if that analyte is a interferent for any requested analyte in that sample, the sample must be diluted. Acid strength must be maintained in the dilution of samples.

10.15. For TCLP samples, full four-point MSA will be required if all of the following conditions are met:

- recovery of the analyte in the matrix spike is not at least 50%,
- the concentration of the analyte does not exceed the regulatory level, and,
- the concentration of the analyte is within 20% of the regulatory level.

The reporting and regulatory limits for TCLP analyses as well as matrix spike levels are detailed in Table VI (Appendix A). Appendix D provides guidance on performing MSA analyses.

10.16. Any variation in procedure shall be completely documented using instrument run logs, maintenance logs, report narratives, a Nonconformance Memo, or an anomaly report and is approved by a Supervisor/Group Leader and QA Manager. If contractually required, the client shall be notified by the Project Manager.

10.17. Nonconformance documentation shall be filed in the project file.

10.18. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11. DATA ANALYSIS AND CALCULATIONS

11.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

11.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

11.3. RLV/CRA percent recoveries are calculated using the same equation as the ICV or CCV (replace ICV or CCV with RLV/CRA in the above equations).

11.4. Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:

SSR = Spike Sample Result

SR = Sample Result

SA = Spike Added

11.5. The relative percent difference (RPD) of matrix spike/matrix spike duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration

MSD = determined matrix spike duplicate concentration

11.6. The final concentration for a digested aqueous sample is calculated as follows:

$$mg/L = \frac{CxV1xD}{V2}$$

Where:

C = Concentration (mg/L) from instrument readout

D = Instrument dilution factor

V1 = Final volume in liters after sample preparation

V2 = Initial volume of sample digested in liters

11.7. The final concentration determined in digested solid samples when reported on a dry weight basis is calculated as follows:

$$mg/Kg, dryweight = \frac{CxVxD}{WxS}$$

Where:

C = Concentration (mg/L) from instrument readout

D = Instrument dilution factor

V = Final volume in liters after sample preparation

W = Weight in Kg of wet sample digested

S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on wet weight basis the "S" factor should be omitted from the above equation.

11.8. The final concentration determined in digested wipe samples is calculated as follows:

ug/wipe = (C x V x D x 1000)

Where:

C = Concentration (mg/L) from instrument readout

V = Volume of digestate (L)

D = Instrument dilution factor

11.9. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

11.10. The dilution test percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} x100$$

Where:

I = Sample result (Instrument reading)

S = Dilution test result (Instrument reading × 5)

11.11. Appropriate factors must be applied to sample values if dilutions are performed.

11.12. Sample results should be reported with up to three significant figures in accordance with the TestAmerica significant figure policy.

12. METHOD PERFORMANCE

12.1. Initial Demonstration of Capability

12.1.1. An initial demonstration of capability for each method must be performed prior to analyzing samples. For the standard analyte list, the initial demonstration consists of the preparation and analysis of an LCS sample containing all of the standard analytes for the method, as well as a method detection limit (MDL) study (described below).

12.1.2. Four LCS samples are analyzed with the same procedures used to analyze samples, including sample preparation.

12.1.3. The mean recovery and standard deviation are calculated for each analyte of interest. These results are compared with the established or project-specific acceptance criteria. All four results must meet acceptance criteria before the method can be used to analyze samples. For further detail refer to SOP PT-QA-001.

12.2. Prior to analysis of any analyte using either Method 200.7, Method 6010B or 6010C, the following requirements must be met.

12.2.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte prior to the analysis of any client samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be determined in accordance with 40 CFR Part 136 Appendix B requirements as

detailed in TestAmerica QA SOP PT-QA-007. The result of the MDL determination must be below the TestAmerica reporting limit (RL).

12.2.2. Instrument Detection Limit (IDL) 200.7/6010B - The IDL for each analyte must be determined for each analyte wavelength used on each instrument. The IDL will be determined quarterly (every 3 months). If the instrument is adjusted in any way that may affect the IDL, the IDL for that instrument must be redetermined. The IDL shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x - 5x the previously determined IDL, with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure performed between the analysis of separate samples). The IDL must be < MDL.

12.2.3. Instrument detection limits (IDLs) – Method 6010C – IDLs are useful means to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with the lower limit of quantitation, nor should they be used in establishing this limit. It may be helpful to compare the calculated IDLs to the established lower limit of quantitation, however, it should be understood that the lower limit of quantitation needs to be verified according to the guidance in Sec. 9.9.

12.2.4. IDLs in µg/L can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs should be determined at least every three months.

12.2.4.1. **DoD samples cannot be analyzed without a valid IDL**.

12.2.4.2. **For DoD, the established IDL must be less than the MDL for each analyte**.

12.2.5. Linear Range Verification (LR) - The linear range will be determined on a quarterly basis for each analyte wavelength used on each instrument as per CLP requirements. Method 6010B/6010C require that the linear range only be determined semiannually. Method 200.7 requires linear ranges to be determined annually. The standards used to define the linear range limit

must be analyzed during a routine analytical run. For the **initial** determination of the upper limit of the linear dynamic range (LDR) for each wavelength, determine the signal responses from a minimum of three to five different concentration standards across the estimated range. One standard should be near the upper limit of the estimated range. The determined concentration of the linear range standards must be within 5% of the true value. The linear range is the concentration above which results cannot be reported without dilution of the sample. If the instrument is adjusted in any way that may affect the LR's, the LR's must be redetermined. The LR data must be documented and kept on file.

12.2.6. Background Correction Points - To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Background correction points must be set prior to determining IECs. Refer to the facility-specific instrument operation SOP and ICP instrument manual for specific procedures to be used in setting background correction points.

12.2.7. Inter-element Corrections (IECs) - ICP interelement correction factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IECs, the IECs must be redetermined. When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC then the possibility of contamination should be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., GFAA or ICP-MS). Published wavelength tables (e.g. MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to evaluate the validity of the IECs. Refer to the facility specific instrument operation SOP and instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any interelement interference which results in a false analyte signal greater than ± the RL as defined in Tables I, IA or II. To determine IECs, run a single element standard at the established linear range. To

calculate an IEC, divide the observed concentration of the analyte by the observed concentration of the "interfering element."

Note: Trace ICP IECs are more sensitive to small changes in the plasma and instrument setup conditions. Adjustments in the IECs will be required on a more frequent basis for the Trace as reflected by the ICSA response.

12.2.8. Rinse Time Determination - Rinse times must be determined whenever a new instrument is set up. . To determine the appropriate rinse time for a particular ICP system, the linear range verification standard should be aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < RL will define the rinse time for a particular ICP system. For some analytes it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level). Until the required rinse time is established, the method recommends a rinse period of at least 60 seconds between samples and standards. If a memory effect is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file, if a concentration other than the linear range level is used to set the rinse time. The concentration levels used to establish the rinse time must be taken into consideration when reviewing the data. Linear Range Verifications are performed at a minimum of every six months. Whenever Linear Range Verifications are performed the suitability of the rinse time settings will be evaluated and the rinse time determination will be repeated when necessary.

12.3. Method performance is determined by the analysis of matrix spike and matrix duplicate samples as well as preparation blanks and laboratory control samples. The matrix spike recovery should fall within +/- 25 % and the matrix duplicates should compare within 20% RPD. Preparation blanks must meet the criteria specified in Section 9.3. The LCS should recover within 20% of the true value for aqueous LCS and within the control limits supplied by the manufacturer of the soil LCS.

12.4. Training Qualification:

12.4.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13. POLLUTION PREVENTION

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

13.2. This method does not contain any specific modifications that serve to minimize or prevent pollution.

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to CW-E-M-001. The following waste streams are produced when this method is carried out.

14.1.1. Acid waste consisting of sample and rinse solution, this waste is collected in waste containers identified as "Acid Waste", Waste #33.

14.1.2. Expired Metals Standards – This waste is collected in containers identified as "Acid Waste with Metals", Waste #6.

15. REFERENCES/CROSS REFERENCES

15.1. 40 CFR Part 136, Appendix B, 7-5-95, Determination of Method Detection Limits.

15.2. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Method 6010B,Revision 2, December 1996.

15.3. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update IV, Method 6010C, Revision 3, February, 2007.

15.4. Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, May 1994. Method 200.7.

15.5. Standard Methods 20th Edition 2340B; Hardness by Calculation.

15.6. SOP PT-QA-001, Employee Orientation and Training, current version.

15.7. SOP PT-HS-001, Waste Collection, Accumulation and Storage, current version.

15.8. SOP PT-QA-007, Determination of Method Detection Limits (MDLs), current version.

15.9. SOP PT-QA-009, Rounding and Significant Figures.

15.10. SOP PT-QA-016, Nonconformance & Corrective Action System, current version.

15.11. SOP PT-QA-018, Technical Data Review Requirements, current version.

15.12. SOP PT-QA-021, Quality Control Program, current version.

15.13. SOP PT-QA-025, Implementation of the DoD QSM Version 3, January 2006, current version.

15.14. SOP PT-QA-029, DoD QSM Version 4.1 Requirements, current version.

16. METHOD MODICATIONS

16.1. Modifications/Interpretations from reference method

16.1.1. Modifications/interpretations from both Methods 6010B and 200.7.

16.1.1.1. TestAmerica laboratories use mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in house as recommended by the subject methods.

16.1.1.2. Methods 200.7 and 6010B state that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. In determining IECs, because of lack of definition clarification for “concentration range around the calibration blank,” TestAmerica has adopted the procedure in EPA CLP ILM04.1.

16.1.1.3. Section 8.5 of Method 6010B and Section 9.5 of Method 200.7 recommend that whenever a new or unusual matrix is encountered, a series of tests be performed prior to reporting concentration data for that analyte. The dilution test helps determine if a chemical or physical interference exists. Because TestAmerica laboratories receive no prior information from clients regarding when to expect a new or unusual matrix, TestAmerica may select to perform a dilution test on one sample in each prep batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. At TestAmerica labs, matrix interference is determined by evaluating data for the LCS and MS/MSD. TestAmerica requires documented, clear guidance when a new or

unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample.

16.1.2. Modifications from Method 200.7.

16.1.2.1. The calibration blank is prepared in an acid matrix of 5% HNO_3/5% HCl instead of the specified 2% HNO_3/10% HCl matrix as the former matrix provides for improved performance relative to the wide variety of digestate acid matrices which result from the various EPA preparation protocols applied.

16.1.2.2. Section 7.12 of 200.7 indicates that the QCS (ICV) should be prepared at a concentration near 1 ppm. The ICV specified in this SOP accommodates the 1 ppm criteria for the majority of analytes. For the remaining analytes, this SOP specifies ICV concentrations, which are appropriate to the range of calibration. The intent of the ICV, verification of calibration standard accuracy, is independent of the ICV concentration used.

16.1.2.3. The ICS criteria applied by this SOP differ from those stated in the method. Method 200.7 section 10.4 states that results should fall within the established control limits of 3 times the standard deviation of the calibration blank for that analyte. TestAmerica Pittsburgh follows the CLP ICS procedures because it is applicable to a wider number of programs. Therefore, we feel it is a more conservative approach.

16.1.2.4. Method 200.7 section 9.3.4 states the CCB should be less than the IDL, but > the lower 3-sigma control limit of the calibration blank. The intent of this requirement is to ensure that the calibration is not drifting at the low end. TestAmerica has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. SOP section 9.8 provides the detailed corrective action criteria that must be followed. **Refer to PT-QA-025 for specific DoD requirements for the CCB.** For DoD V4.1 refer to SOP PT-QA-029.

16.1.3. Modifications from Method 6010B.

16.1.3.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client. **Refer to PT-QA-025 for specific DoD**

requirements for the method blank. For DoD V4.1 refer to SOP PT-QA-029.

16.1.3.2. Method 6010B section 8.6.1.3 states that the results of the calibration blank are to agree within 3x the IDL. If not, repeat the analysis two or more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. The intent of this requirement is to ensure that the calibration is not drifting at the low end. TestAmerica has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. See SOP Section 9.8 for a detailed description of the required corrective action procedures. **Refer to PT-QA-025 for specific DoD requirements for the calibration blanks.** For DoD V4.1 refer to SOP PT-QA-029.

17. ATTACHMENTS

17.1. Documentation and Record Management

- The following documentation comprises a complete ICP raw data package:
- Raw data (direct instrument printout).
- Relevant sample preparation benchsheets.
- Run log printout from instrument software where this option is available (TJA) or manually generated run log (i.e., Ward WSL printout).
- Data review checklist - See Appendix B.
- Standards documentation (including prep and expiration dates, source, and lot #).
- Nonconformance/anomaly documentation (if applicable).

17.2. FIGURE 1 – FLOW DIAGRAM

17.3. APPENDIX A - TABLES

17.4. APPENDIX B - TESTAMERICA ICP DATA REVIEW CHECKLIST

17.5. APPENDIX C - TROUBLESHOOTING GUIDE

17.6. APPENDIX D - CONTAMINATION CONTROL GUIDELINES

17.7. APPENDIX E - PREVENTIVE MAINTENANCE

18. REVISION HISTORY

18.1. Revision 10, 03/31/09

18.1.1. Updated into the new Corporate format; added the appropriate Corporate text to the Scope, Safety, Waste Management and Pollution Control sections; added text to section 9 concerning the Initial Demonstration of Capability being moved to section 12; changed STL to TestAmerica throughout the SOP; updated reference numbers and SOP references throughout the document; updated the Reference section SOP numbers; in section 9.3 changed 20X to 10X; in section 10.10 changed the Trace to any axial ICP.

18.1.2. 6010C method reference added. SOP references updated.

18.1.3. Updated SOP for requirement of Method 6010C, see SOP areas highlighted referring to 6010C.

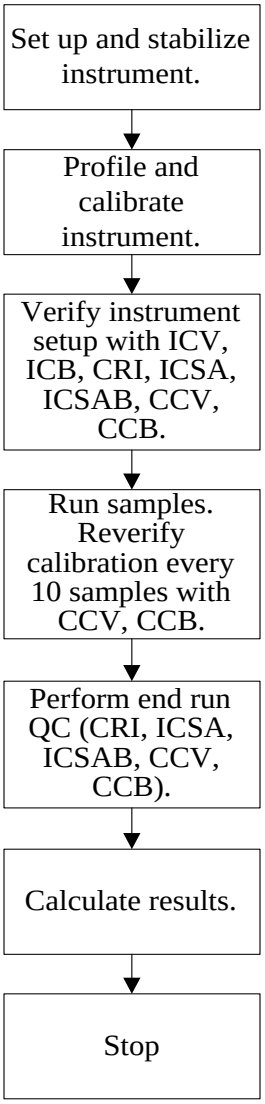
18.1.4. Added to section 8: Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

18.2. Revision 11:

18.2.1. Added to section 9.9: For method 6010C the RLV/CRA which is the low level quantitation check sample is prepared and analyzed quarterly or as needed. The control limit is 70-130%. Please note the RLV/CRA (undigested) is still analyzed at the beginning and end of the analytical run.

18.2.2. Added references to SOP PT-QA-029.

Figure 1. Flow Diagram



APPENDIX A

TABLES

TABLE I. Method 200.7, 6010B and 6010C Target Analyte List

ELEMENT	Symbol	CAS #	6010B/6010 C analyte	200.7 analyte	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil	Reporting Limit (ug/wipe) Wipe
Aluminum	Al	7429-90-5	X	X	200	20	10
Antimony	Sb	7440-36-0	X	X	60	6	3
Arsenic	As	7440-38-2	X	X	300	30	15
Barium	Ba	7440-39-3	X	X	200	20	10
Beryllium	Be	7440-41-7	X	X	4	0.4	0.25
Boron	B	7440-42-8	X	X	200	20	10
Cadmium	Cd	7440-43-9	X	X	5	0.5	0.25
Calcium	Ca	7440-70-2	X	X	5000	500	250
Chromium	Cr	7440-47-3	X	X	10	1	0.5
Cobalt	Co	7440-48-4	X	X	50	5	2.5
Copper	Cu	7440-50-8	X	X	25	2.5	1.25
Iron	Fe	7439-89-6	X	X	100	10	5
Lead	Pb	7439-92-1	X	X	100	10	5
Lithium	Li	7439-93-2	X	X	50	5	2.5
Magnesium	Mg	7439-95-4	X	X	5000	500	250
Manganese	Mn	7439-96-5	X	X	15	1.5	0.75
Molybdenum	Mo	7439-98-7	X	X	40	4	2
Nickel	Ni	7440-02-0	X	X	40	4	2
Phosphorus	P	7723-14-0	X	X	300	30	NA
Potassium	K	9/7/7440	X	X	5000	500	250
Selenium	Se	7782-49-2	X	X	250	25	12.5
Silicon	Si	7631-86-9	X	X	500	N/A	N/A
Silver	Ag	7440-22-4	X	X	10	1	0.5
Sodium	Na	7440-23-5	X	X	5000	500	250
Strontium	Sr	7440-24-6	X	X	50	5	2.5
Thallium	Tl	7440-28-0	X	X	2000	200	100
Vanadium	V	7440-62-2	X	X	50	5	2.5
Zinc	Zn	7440-66-6	X	X	20	2	1

Note: Where reporting “Hardness” by ICP use the following equations per SM20th ed. 2340B:

Calcium Hardness = 2.497 [Ca, mg/L]
Total Hardness = 2.497 [Ca, mg/L] + 4.118 [Mg, mg/L]
Where reporting "Silica" by ICP use the following equation:

Silica = Silicon * 2.14

TABLE IA. Method 200.7, 6010B and 6010C Trace ICP Target Analyte List

ELEMENT	Symbol	CAS #	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil	Reporting Limit (ug/wipe) Wipe
Arsenic	As	7440-38-2	10	1.0	0.5
Lead	Pb	7439-92-1	3.0	0.3	0.15
Selenium	Se	7782-49-2	5.0	0.5	0.25
Thallium	Tl	7440-28-0	10	1.0	0.5
Antimony	Sb	7440-36-0	10	1.0	0.5
Cadmium	Cd	7440-43-9	5.0	0.5	0.25
Silver	Ag	7440-22-4	5.0	0.5	0.25
Chromium	Cr	7440-47-3	5.0	0.5	0.25

TABLE II. Non-Routine Analyte List

			Reporting	Reporting	Reporting

ELEMENT	Symbol	CAS #	Limit (ug/L) Water	Limit (mg/kg) Soil	Limit (ug/wipe) Wipe
Tin	Sn	7440-31-5	100	10	5
Titanium	Ti	7440-32-6	50	5	2.5

TABLE III. Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	LCS Level (ug/L)	Matrix Spike Level (ug/L)
Aluminum	2000	2000
Antimony	500	500
Arsenic	2000	2000
Barium	2000	2000
Beryllium	50	50
Cadmium	50	50
Calcium	50000	50000
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1000	1000
Lead	500	500
Lithium	1000	1000
Magnesium	50000	50000
Manganese	500	500
Molybdenum	1000	1000
Nickel	500	500
Potassium	50000	50000
Selenium	2000	2000
Silver	50	50
Sodium	50000	50000
Strontium	1000	1000
Thallium	2000	2000
Vanadium	500	500
Zinc	500	500

ELEMENT	LCS Level (ug/L)	Matrix Spike Level (ug/L)
Boron	1000	1000
Silicon	10000	10000
Tin	2000	2000
Titanium	1000	1000

TABLE IV. ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	100000	200	25000	50000
Antimony	10000	60	1000	5000
Arsenic	10000	300	1000	5000
Barium	10000	200	1000	5000
Beryllium	10000	4	1000	5000
Cadmium	10000	5	1000	5000
Calcium	100000	5000	25000	50000
Chromium	10000	10	1000	5000
Cobalt	10000	50	1000	5000
Copper	10000	25	1000	5000
Iron	100000	100	25000	50000
Lead	10000	100	1000	5000
Lithium	10000	50	1000	5000
Magnesium	100000	5000	25000	50000
Manganese	10000	15	1000	5000
Molybdenum	10000	40	1000	5000
Nickel	10000	40	1000	5000
Potassium	100000	5000	25000	50000
Selenium	10000	250	1000	5000
Silver	2000	10	500	1000
Sodium	100000	5000	25000	50000
Strontium	10000	50	1000	5000
Thallium	20000	2000	5000	10000
Vanadium	10000	50	1000	5000
Zinc	10000	20	1000	5000

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Boron	10000	200	1000	5000
Silicon	10000	500	1000	5000
Tin	10000	100	1000	5000
Titanium	10000	50	1000	5000

TABLE IVA. Trace ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	50000	200	12500	25000
Antimony	1000	10	250	500
Arsenic	1000	10	250	500
Barium	4000	10	1000	2000
Beryllium	4000	4	1000	2000
Cadmium	1000	5	250	500
Calcium	100000	5000	25000	50000
Chromium	4000	5	1000	2000
Cobalt	4000	50	1000	2000
Copper	4000	25	1000	2000
Iron	50000	100	12500	25000
Lead	1000	3	250	500
Magnesium	100000	5000	25000	50000
Manganese	4000	15	1000	2000
Molybdenum	4000	40	1000	2000
Nickel	4000	40	1000	2000
Potassium	250000	5000	50000	125000
Selenium	1000	5	250	500
Silver	2000	5	500	1000
Sodium	250000	5000	50000	125000
Thallium	2000	10	500	1000
Vanadium	4000	50	1000	2000
Zinc	4000	20	1000	2000
Boron	4000	200	1000	2000

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Silicon	4000	500	1000	2000
Tin	4000	100	1000	2000
Titanium	4000	50	1000	2000

TABLE V. Interference Check Sample Concentrations*

Element	ICSA (ug/L)	ICSAB (ug/L)
Aluminum	500000	500000
Antimony	-	1000
Arsenic	-	1000
Barium	-	500
Beryllium	-	500
Cadmium	-	1000
Calcium	500000	500000
Chromium	-	500
Cobalt	-	500
Copper	-	500
Iron	200000	200000
Lead	-	1000
Magnesium	500000	500000
Manganese	-	500
Molybdenum	-	1000
Nickel	-	1000
Potassium	-	10000
Selenium	-	1000
Silver	-	1000
Sodium	-	10000
Thallium	-	10000**
Vanadium	-	500
Zinc	-	1000
Tin	-	1000

* Custom TestAmerica solutions contain common analytes. Non-routine elements not listed above should be spiked into the ICSAB at 1000 ug/L.
** Thallium level for Trace ICP should be at 1000 ug/L.

TABLE VI. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	Reporting Level (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

TABLE VII. Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Two-point Initial Calibration	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criterion is not met	RSD between duplicate exposures ≤5%	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
ICV	Beginning of every analytical run.	Method 200.7: 95 - 105 % recovery. Method 6010B & 6010C: 90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate.
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero. (1)	Terminate analysis; Correct the problem; Recalibrate.
RLV/CRA/LLICV/LLCCV	Beginning of every analytical run, immediately following the ICB. Method 6010C also requires analysis at the end of the analytical sequence.	50 – 150% recovery. (1) Method 6010C: 70 – 130% recovery	Terminate analysis; Correct the problem; Recalibrate.
CCV	Every 10 samples and at the end of the run.	Method 200.7, 6010B & 6010C: 90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
CCB	Immediately following each CCV.	The result must be within +/- RL from zero. (1)	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB.

TABLE VII. Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICSA	Beginning of every run	See Section 9.10.3 [(1)]	See Section 9.10.3.
ICSAB	Immediately following each ICSA.	Results must be within 80 - 120% recovery.	See Section 9.10.2.
Dilution Test	One per prep batch.	For samples > 50x MDL, dilutions must agree within 10%.	Narrate the possibility of physical or chemical interference per client request.
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. [(1)] Common lab contaminants may be accepted up to 2x the RL after consultation with the client (See 9.3). Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL may not require redigestion or reanalysis (see Section 9.3).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.3 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits. (85-115% for 200.7)	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS.

TABLE VII. Summary of Quality Control Requirements			
QC PARAMETER	**FREQUENCY**	**ACCEPTANCE CRITERIA**	**CORRECTIVE ACTION**
		Samples for which the contaminant is < RL and the LCS results are > 120% (115% for 200.7) may not require redigestion or reanalysis (see Section 9.4)	
Matrix Spike	One per sample preparation batch of up to 20 samples (6010B/6010C) or one per every 10 or fewer samples (200.7).	75 - 125 % (6010B & 6010C) or 70 – 130% (200.7) recovery or in-house control limits. (1) For TCLP See Section 10.15.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. For TCLP see Section 10.15.
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery; RPD ≤ 20%. (1)	See Corrective Action for Matrix Spike.

(1) For specific DoD requirements, refer to PT-QA-025. For DoD V4.1 refer to SOP PT-QA-029.

APPENDIX B

TESTAMERICA ICP DATA REVIEW CHECKLIST

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

TestAmerica Pittsburgh ICP Data Review Checklist

Run Date: _____ 3. _____ 10. _____ 17. _____ 24. _____ 31. _____
Analyst: _____ 4. _____ 11. _____ 18. _____ 25. _____ 32. _____
Inst: _____ 6. _____ 12. _____ 19. _____ 26. _____ 33. _____
Meth: _____ 8. _____ 13. _____ 20. _____ 27. _____ 34. _____
Lots Analyzed: 7. _____ 14. _____ 21. _____ 28. _____ 35. _____
1. _____ 8. _____ 15. _____ 22. _____ 29. _____ 36. _____
2. _____ 9. _____ 16. _____ 23. _____ 30. _____ 37. _____

Review Item	Yes (✓)	No (✓)	N/A (✓)	2nd Lv (✓)	Comments
A. Calibration/Instrument Run QC					
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels?					
2. ICV/CCV analyzed at appropriate frequency and within control limits? (6010B, CLP=90-110%, 200.7=95-105%[ICV])?					
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?					
4. CRA/RLV/CRI analyzed? (CRI for CLP only)					
5. ICSA/ICSAB run at required frequency and within SOP limits?					
B. Sample Results					
1. Were samples with concentrations > the linear range for any parameter diluted and reanalyzed?					
2. All reported results bracketed by in control QC?					
3. Sample analyses done within holding time?					
C. Preparation/Matrix QC					
1. LCS done per prep batch and within QC limits?					
2. Method blank done per prep batch and < RL or CRDL (CLP)?					
3. MS run at required frequency and within limits?					
4. MSD or DU run at required frequency and RPD within SOP limits?					
5. Dilution Test done per prep batch (or per SDG for CLP)?					
6. Post digestion spike analyzed if required (CLP only)?					
D. Other					
1. Are all nonconformances documented appropriately?					
2. Current IDL/LR/IEC data on file?					
3. Calculations checked for error?					
4. Transcriptions checked for error?					
5. All client/project specific requirements met?					
6. Date/Time of analysis verified as correct?					

General Comments: _____

Analyst & Date: _____ Second-Level Review & Date: _____

APPENDIX C

CROSS REFERENCE OF TERMS USED IN METHODS 6010B, 6010C, 200.7 AND BY TESTAMERICA

CROSS REFERENCE OF TERMS COMMONLY USED IN

METHODS EPA 200.7, SW846 6010B/6010C AND TESTAMERICA INC. SOP

EPA 200.7	SW6010B/6010C	TestAmerica Inc. SOP
Calibration blank (CB)	Calibration blank	Initial and continuing calibration blanks (ICB/CCB)
Dilution test	Dilution test	Dilution Test
Instrument detection limit (IDL)	Instrument detection limit (IDL)	Instrument detection limit (IDL)
Instrument performance check (IPC)	Continuing calibration verification (CCV)	Continuing calibration verification (CCV)
Internal standard	Internal standard	Internal standard (IS)
Laboratory duplicates	n/a	n/a
Laboratory fortified blank (LFB)	n/a	Laboratory control sample (LCS)
Laboratory fortified sample matrix (LFM)	Matrix spike and matrix spike duplicate (MS/MSD)	Matrix spike and matrix spike duplicate (MS/MSD)
Laboratory reagent blank (LRB)	Method blank	Method or Prep blank (MB)
Linear dynamic range (LDR)	Linear dynamic range (LDR)	Linear dynamic range (LDR)
Method detection limit (MDL)	Method detection limit (MDL)	Method detection limit (MDL)

EPA 200.7	SW6010B/6010C	TestAmerica Inc. SOP
Quality control sample (QCS)	Check standard or Initial calibration verification (ICV)	Initial calibration verification (ICV)
Spectral interference check solution (SIC)	Interference check solution (ICS)	Interference check solution (ICSA/ICSAB)

APPENDIX D

MSA GUIDANCE

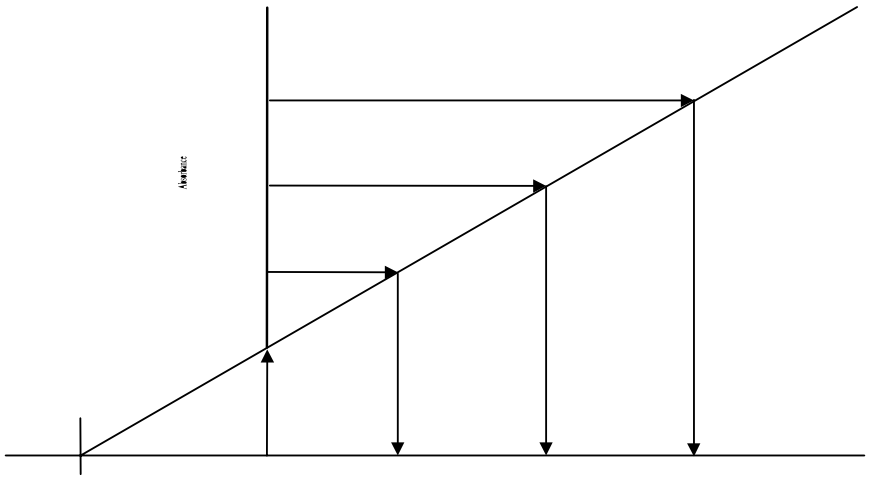
Appendix D. MSA Guidance

Controlled Source: Intranet

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked standard should be the same.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown.



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.

- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX E

TROUBLESHOOTING GUIDE

Problem	Possible Cause/Solution
High Blanks	Increase rinse time Clean or replace tip Clean or replace torch Clean or replace sample tubing Clean or replace nebulizer Clean or replace mixing chamber Lower Torch
Instrument Drift	RF not cooling properly Vacuum level is too low Replace torch (Crack) Clean or replace nebulizer (blockage) Check room temperature (changing) Replace pump tubing Room humidity too high Clean torch tip (salt buildup) Check for argon leaks Adjust sample carrier gas Reprofile Horizontal Mirror Replace PA tube
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks Adjust sample carrier gas Replace tubing (clogged) Check drainage(back pressure changing) Increase uptake time (too short) Increase flush time (too short) Clean nebulizer, torch or spray chamber Increase sample volume introduced Check that autosampler tubes are full Sample or dilution of sample not mixed Increase integration time (too short) Realign torch Reduce amount of tubing connectors
Cu/Mn Ratio Outside Limits or Low Sensitivity	Plasma conditions changed Clean nebulizer, torch or spray chamber Replace tubing (clogged)

Problem	Possible Cause/Solution
	Realign torch Check IECs
Standards reading twice normal absorbance or concentration	Incorrect standard used Incorrect dilution performed

APPENDIX F

CONTAMINATION CONTROL GUIDELINES

APPENDIX F. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 20% nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Yellow pipette tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The markings on glass beakers have been found to contain lead. If acid baths are in use for glassware cleaning, they should be periodically checked for contaminants since contaminant concentrations will increase over time.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

APPENDIX G

PREVENTATIVE MAINTENANCE

APPENDIX G. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Daily	Change sample pump tubing and pump windings Check argon gas supply level Check rinse solution and fill if needed Check waste containers and empty if needed Check sample capillary tubing is clean and in good condition Check droplet size to verify nebulizer is not clogged. Check sample flow for cross flow nebulizer Check Cu/Mn ratio-should be 30% of value at date that IECs were performed Check pressure for vacuum systems
As Needed	Clean plasma torch assembly to remove accumulated deposits Clean nebulizer and drain chamber; keep free-flowing to maintain optimum performance Replace peristaltic pump tubing, sample capillary tubing, and autosampler sipper probe
Weekly	Apply silicon spray on autosampler tracks Check water level in cool flow
Monthly	Clean air filters on back of power unit to remove dust Check D mirror for air instruments
Bi-yearly	Change oil for vacuum systems Replace coolant water filter (may require more or less frequently depending on quality of cooling water)

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN SOLID SAMPLES BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY

METHOD: SW846 7471A AND 7471B

Approvals (Signature/Date):			
	6/23/2010		6/17/2010
Larry Matko Technical Manager	Date	Steve Jackson Health & Safety Manager / Coordinator	Date
Nasreen K. DeRubeis	06/23/10		6/23/2010
Nasreen K. DeRubeis Quality Assurance Manager	Date	Larry Matko Laboratory Director	Date

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7471A and 7471B.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.3. Method 7471A and 7471B is applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits, sludge-type materials wipes, and tissue matrices. All matrices require sample preparation prior to analysis.

1.4. The TestAmerica reporting limit for mercury in solid matrices is 0.033 mg/kg based a 0.6 g sample aliquot (wet weight). The TestAmerica reporting limit for wipes is 0.02 ug/wipe.

1.5. For DoD QSM Version 3 requirements, refer to SOP PT-QA-025, current revision.

1.6. For DoD QSM Version 4.1 requirements, refer to SOP PT-QA-029, current revision.

1.7. On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.1 in the Quality Assurance Manual.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer.

Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate, which is used to breakdown organic mercury compounds, also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.2. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.3. Chlorides can cause a positive interference. Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely

encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE:** This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury (1,000 PPM in Reagent)	Oxidizer Corrosive Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 Mg/M3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Stannous Chloride	Irritant	2 Mg/M3 TWA as Tin	Causes irritation to the respiratory tract. Can irritate skin and eyes. Symptoms include coughing and shortness of breath. Contact with skin and/or eyes may cause redness, itching and pain.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of

getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.5.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.5.2. Iodine, 0.25%, in a 3% KI solution.

5.6. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.7. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.8. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

5.10. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor and/or the EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Hot blocks capable of maintaining temperature of 95 ± 5 °C.

6.2. Leeman HYDRA AA Automated Mercury Analysis System.

6.3. Disposable Sealable Sample Containers (Corning).

6.4. Argon gas supply (ultrahigh purity-grade).

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Top-loading balance, capable of reading up to two decimal places.

6.8. Thermometer (capable of accurate readings at 95 °C).

6.9. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (1000 ppm) mercury standards (in 10% HNO_3) are purchased as custom TestAmerica solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The intermediate standard must be made monthly and must be prepared in a matrix of 2% HNO_3. This acid (2 mL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. Working mercury standard (0.1 ppm): Take 1 mL of the intermediate mercury standard (7.3) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of

concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot. A second source working standard is prepared at 0.1 ppm for preparation of the ICV.

7.5. The calibration standards must be prepared fresh daily from the working standard (7.4) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into sample prep bottles and proceeding as specified in Section 11.1. The 0, .5, 1.0, 5.0 and 10 standards are recommended by Thermo Electron. The 0.2 standard level was selected to include a standard at the RL. See Table 1 (Appendix A) for the preparation of the ICV, CCV and RLV standards.

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard (ICV) must be made from a different stock solution than that of the calibration standards.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.9. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9.1. Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated H_2SO_4 to 1 liter with reagent water.

7.10. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.11. Stannous chloride solution: Add 200 g of stannous chloride to 2 L of 10% hydrochloric acid.

Note: Stannous sulfate may be used in place of stannous chloride. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

7.12. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.13. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.14. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of sample analysis.

8.2. Soil and wipe samples do not require preservation but must be stored at 4° C ± 2° C until the time of analysis. Tissue samples are stored frozen.

8.3. Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.2. Sample Count - Laboratory generated QC samples (method blanks, LCS and MS/MSDs) are not included in the sample count for determining the size of a preparation batch.

9.3. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20 times higher than the blank contamination level). **Refer to PT-QA-025 or PT-QA-029 for specific DoD requirements for method blank.**

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.4. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. The CCV results can be reported as the LCS results since all CCVs (as well as all other standards) are processed through the sample preparation step with the field samples. No more than 20 samples can be associated with one CCV used for the purpose of reporting LCS data.

- If the LCS is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, a control limit of 80 - 120% recovery must be applied.

- In the instance where the LCS recovery is > 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative.

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 75 - 125 % recovery and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative. **Refer to PT-QA-025 or PT-QA-029 for specific DoD requirements for the MS/MSD.**

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual

recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.6. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 10% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. **Refer to PT-QA-025 or PT-QA-029 for specific DoD requirements for the ICB.** If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.7. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples and at the end of the analytical sequence. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. The CCB result must fall within +/- RL from zero. **Refer to PT-QA-025 or PT-QA-029 for specific DoD requirements for the CCB.** Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV or CCB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.8. Reporting Limit Verification Standard (RLV) – Calibration accuracy at the laboratory reporting limit is verified after the analysis of the ICB. Until in-house control limits are established, a control limit of 50 - 150% recovery will be applied.

9.9. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences, which cause a baseline shift. Refer to Section 10.3.11 for

additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. PROCEDURE

10.1. Calibration and Standardization

10.1.1. Calibration standards must be processed through the preparation procedure as described in Section 10.2.

10.1.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.1.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.1.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the facility specific instrument SOP and CVAA instrument manual for detailed setup and operation protocols.

10.1.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the TestAmerica reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.1.6. The calibration curve must have a correlation coefficient of ≥ 0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient.

10.1.7. Refer to Section 9.0 and Table II for calibration verification procedures, acceptance criteria and corrective actions. The NELAC requirement for

verification of initial calibration at varied concentrations is met daily since the ICVs, CCVs, and RLVs are all at different concentrations.

10.2. Standard and Sample Preparation:

10.2.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB, RLV) are processed through the digestion procedure as well as the field samples.

10.2.2. Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (7.5) into a series of sample digestion bottles.

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

10.2.3. Add reagent water to each standard bottle to make a total volume of 10 mL. Continue preparation as described under 10.2.5 or 10.2.6 below.

10.2.4. Transfer triplicate, 0.2 g portions of a well mixed sample into a clean sample digestion bottle. Refer to PT-QA-024 for subsampling procedures. For wipes, add the entire contents of the sample jar into a clean sample digestion container. Continue preparation as described under 10.2.5 or 10.2.6 below.

10.2.5. Hot Block protocol (default procedure):

10.2.5.1. Add 5 mL concentrated of H_2SO_4 and 2 mL of concentrated HNO_3.

10.2.5.2. To the LCS, add 2.5 mL, and to the MS, and MSD, add 1.0 mL of 0.1 ppm working standard (7.4)

10.2.5.3. Add 5 mL of saturated potassium permanganate solution.

10.2.5.4. Add 8 mL of potassium persulfate solution.

10.2.5.5. Cover digestion bottle with aluminum foil or screw cap loosely applied.

10.2.5.6. Heat the samples at 95 $\pm$ 5 °C for 2 hours.

10.2.5.7. Cool.

10.2.5.8. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate.

Note: Alternate final volumes may be used as long as the standards and sample are treated the same way and reagents are adjusted proportionally.

10.2.5.9. Make up to volume of 100 mL with reagent water.

10.2.5.10. Continue as described under Section 10.3.

10.3. Sample Analysis:

10.3.1. Refer the instrument manual for detailed setup and operation protocols for the Hydra AA.

10.3.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

10.3.3. Automated determination: Follow instructions provided by instrument manufacturer.

10.3.4. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. ug of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

10.3.5. All measurements must fall within the defined calibration range to be valid. When sample concentrations exceed the upper limit of the calibration curve, the samples will be diluted and reanalyzed (if possible) to bring them within calibration curve. When reported sample concentrations either exceed the upper limit of the curve (i.e. cannot be rerun) or fall below the reporting limit, the data will be qualified as estimated.

10.3.6. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

10.3.7. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

10.3.8. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

10.3.9. The following analytical sequence must be used with 7471A and 7471B:

Instrument Calibration
ICV
ICB
RLV
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV

CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7471A and 7471B.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

10.3.10. The following run sequence is consistent with 7471A, 7471B and CLP and may be used as an alternate to the sequence in 10.3.9. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration
ICV
ICB

RLV or CRA*
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

Refer to the appropriate CLP SOP (CORP-MT-0008) for quality control requirements for QC samples.

* Refer to the CLP SOP for information on the CRA.

10.3.11. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

Appendix C provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

10.4. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

10.5. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and parts maintenance. For instrument troubleshooting, use the autodiagnostics software. If a the problem cannot be determined using the software, place a call to service personnel

10.6. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

10.7. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11. CALCULATIONS / DATA REDUCTION

11.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

11.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

11.3. RLV percent recoveries are calculated using the same equation as the ICV or CCV (replace ICV or CCV with RLV in the above equations).

11.4. Matrix spike recoveries are calculated according to the following equation:

$$\%\ R\ = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:

SSR = Spike Sample Result

SR = Sample Result

SA = Spike Added

11.5. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration

MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:

DU1 = Sample result

DU2 = Sample duplicate result

11.6. For automated determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

mg/kg, dry weight = (C x V x D)/(W x S)

Where:

C = Concentration (ug/L) from instrument readout

V = Volume of digestate (L)

D = Instrument dilution factor

W = Weight in g of wet sample digested

S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

11.7. For automated determinations, the final concentration determined in wipe samples is calculated as follows:

ug/wipe = (C x V x D)

Where:

C = Concentration (ug/L) from instrument readout

V = Volume of digestate (L)

D = Instrument dilution factor

11.8. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

11.9. Sample results should be reported with up to three significant figures in accordance with the TestAmerica significant figure policy.

12. METHOD PERFORMANCE

12.1. Prior to the analysis of Hg using 7471A or 7471B, the following requirements must be met:

12.2. Initial Demonstration of Capability

12.2.1. An initial demonstration of capability for each method must be performed prior to analyzing samples. For the standard analyte list, the initial demonstration consists of the preparation and analysis of four LCS samples containing all of the standard analytes for the method, as well as a method detection limit (MDL) study (described below).

12.2.2. Four LCS samples are analyzed with the same procedures used to analyze samples, including sample preparation.

12.2.3. The mean recovery and standard deviation are calculated for each analyte of interest. These results are compared with the established method acceptance criteria. All four results must meet acceptance criteria before the method can be used to analyze sample. The results of the initial demonstration study must be acceptable before analysis of samples may begin For further detail refer to SOP PT-QA-001.

12.2.4. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, and have been carried through the entire analytical procedure. MDLs are determined in accordance with 40 CFR Part 136 Appendix B requirements and SOP PT-QA-007. The result of the MDL determination must be below the TestAmerica reporting limit.

12.3. Method performance is determined by the analysis of method blank, laboratory control sample, matrix spike and matrix spike duplicate samples. The matrix spike recovery

should fall within +/- 25 % and the matrix spike duplicates should compare within 20% RPD. **Refer to PT-QA-025 or PT-QA-029 for specific DoD requirements for the MS.** The method blanks must meet the criteria in Section 9.3. **Refer to PT-QA-025 or PT-QA-029 for specific DoD requirements for the method blank.** The laboratory control sample should recover within 20% of the true value until in house limits are established.

12.4. Training Qualification:

12.4.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13. POLLUTION CONTROL

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

13.2. This method does not contain any specific modifications that serve to minimize or prevent pollution.

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1. Extracted sample containing less than 1 ppb Hg. This waste is collected in waste containers identified as “Acid Waste”, Waste #33. It is neutralized to a pH between 6 and 9 and is disposed down a lab sink.

14.1.2. Unused Standards. This waste collected in containers identified as “Mercury Standards Waste”, Waste #4.

14.1.3. Extracted sample containing greater than 1 ppb Hg. This waste collected in containers identified as “Mercury Standards Waste”, Waste #4.

14.1.4. Mercury Analyzer Waste. Waste discharged from mercury analyzer is collected in containers identified as “Mercury Standards Waste”, Waste #4.

15. REFERENCES / CROSS-REFERENCES

15.1. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A (Mercury).

15.2. Mercury In Solid Or Semisolid Waste (Manual Cold-Vapor Technique), Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update IV, Revision 2, February 2007, Method 7471B (Mercury).

15.3. U.S.EPA Statement of Work for Inorganics Analysis, ILM04.0.

15.4. SOP PT-QA-001, Employee Orientation and Training, current version.

15.5. SOP PT-HS-001, Waste Collection, Accumulation and Storage, current version.

15.6. SOP PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability, current version.

15.7. SOP PT-QA-007, Detection Limits, current version.

15.8. SOP PT-QA-009, Rounding and Significant Figures, current version.

15.9. SOP PT-QA-016, Nonconformance & Corrective Action System, current version.

15.10. SOP PT-QA-018, Technical Data Review Requirements, current version.

15.11. SOP PT-QA-021, Quality Assurance Program, current version.

15.12. SOP PT-QA-022, Equipment Maintenance, current version.

15.13. SOP PT-QA-024, Subsampling, current version.

15.14. SOP PT-QA-025, DoD QSM Version 3, current version.

15.15. SOP PT-QA-027, Sample Receiving and Chain of Custody, current version.

15.16. SOP PT-QA-029, QA/QC Requirements for DoD QSM Version 4.1, April 2009, current version.

16. METHOD MODIFICATIONS:

16.1. Modifications/Interpretations from reference method.

16.1.1. Modifications from 7471A.

16.1.1.1. A potassium persulfate oxidation step has been included to facilitate the breakdown of organic mercurials which are not completely oxidized by potassium permanganate. Use of potassium persulfate in combination with the permanganate improves the recovery of mercury from organo-mercury compounds. The use of persulfate has been incorporated in several recent EPA mercury protocols.

16.1.1.2. The alternate run sequence presented in Section 10.3.10 is consistent with method requirements.

16.1.1.3. Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

16.1.1.4. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

16.1.2. Modifications from Revision 4: Safety Section 5.0, Pollution Prevention Section 14.0 and Waste Management Section 15.0 updated. References to DoD criteria were added. Wipe samples were added to the SOP.

17. ATTACHMENTS

17.1. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

18. REVISION HISTORY

18.1. Revision 7, 01/15/09

18.1.1. Updated the Section headers to the new format; changed STL to TestAmerica throughout the SOP; updated section and SOP reference numbers; added text from the new template in the Safety, Pollution Control and Waste Management Sections; added Section 8.3 concerning lab filtered and preservation sample procedure; Updated the Reference Section.

18.1.2. Added references to Method 7471B.

18.1.3. Added: Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

18.2. Revision 8, 10/8/2009

18.2.1. Removed reference to the autoclave throughout the SOP and added reference to the hot block procedure.

18.2.2. Added the appropriate references to SOP PT-QA-029 where necessary throughout the SOP. Added reference to SOP PT-QA-022, Equipment Maintenance.

18.2.3. Updated Appendix F to be consistent with PT-QA-022.

18.3. Revision 9

18.3.1. Removed reference of the LEEMAN PS200II Mercury Analyzer from sections 6.2, 10.3.1 and Appendix F since this instrument has been removed from service.

18.3.2. Removed section 10.2.5 Water Bath Protocol since only Hot Blocks are used for soils.

18.3.3. Removed Figure 2 detailing the Water Bath Procedure since only Hot Blocks are used for soil digestion.

18.3.4. In section 6.1 removed the Water Bath Temperature requirement since only Hot Blocks are used for soil digestion.

18.3.5. Removed section 7.11 Aqua Regia since soils are digested by hotblock and not wath bath.

Figure 1. Solid Sample Preparation for Mercury - Hot Block Procedure (Default)

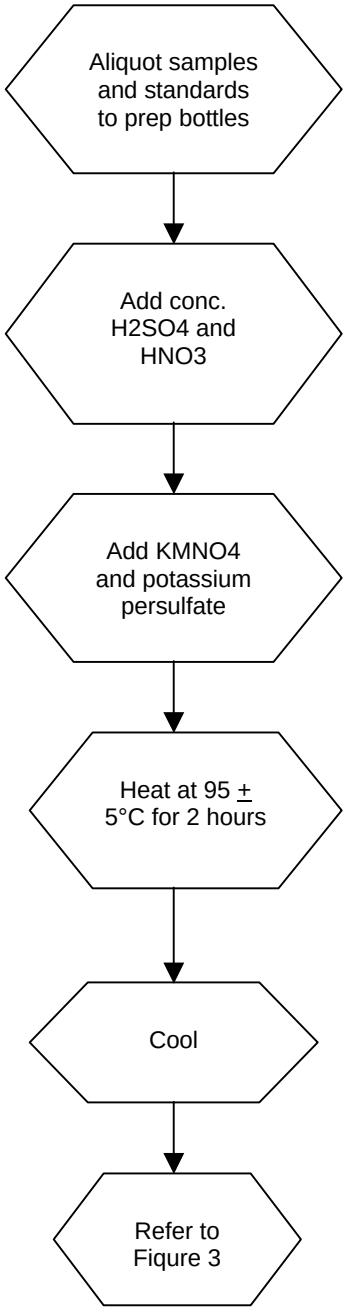
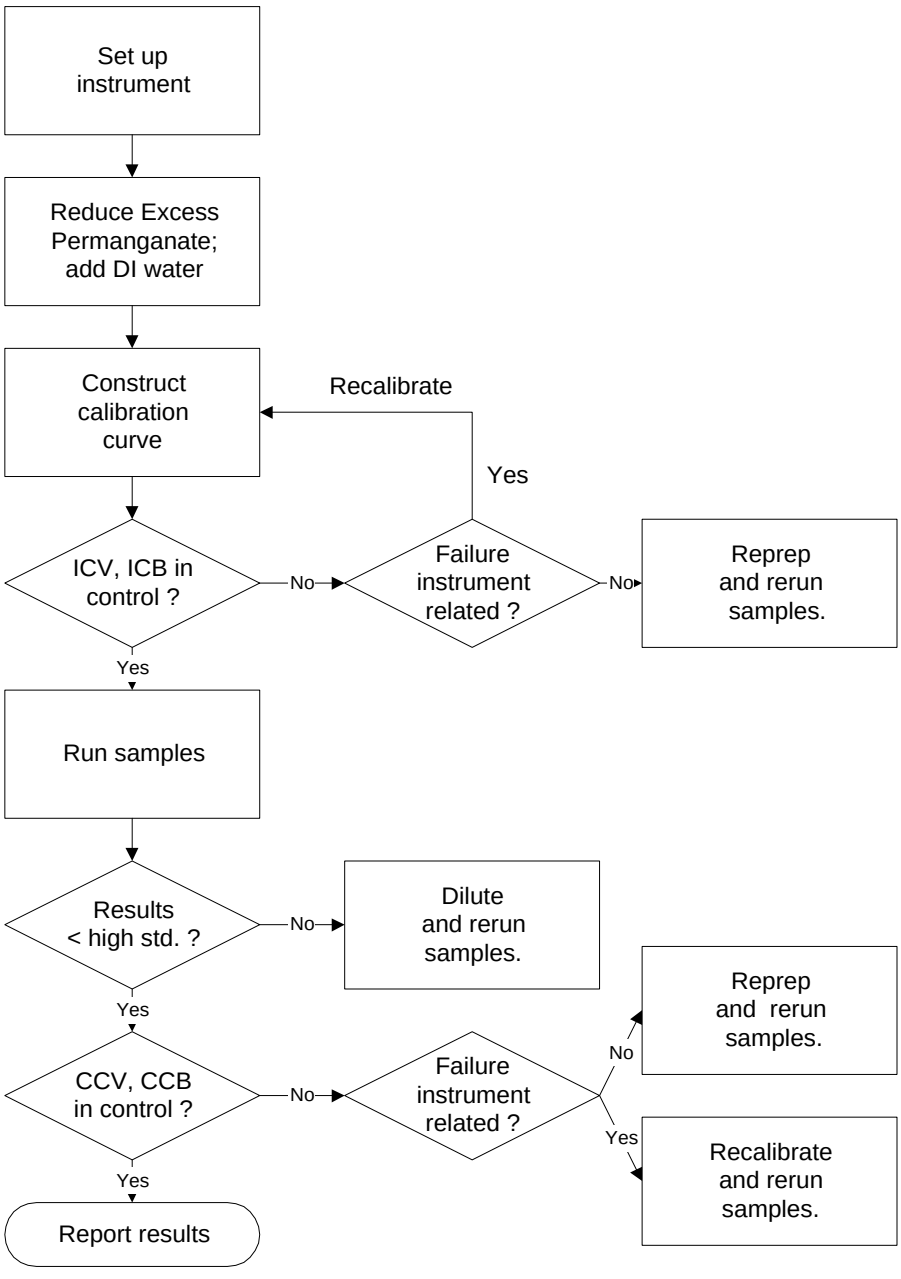


Figure 2. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS

Method	Reporting Limit	
SW846 7471A/7471B	0.033 mg/kg or 0.02 ug/wipe	
Standard or QC sample	**mLs of 0.1 ppm Working Standard**	**Concentration (mg/L) *** **
Std 0	0	0
Std 1	0.2	0.0002
Std 2	0.5	0.0005
Std 3	1.0	0.001
Std 4	5.0	0.005
Std 5	10.0	0.010
ICV	2.5 **	0.0025
CCV	5.0	0.005
RLV	0.2	0.0002
LCS	2.5	0.0025
MS	1.0	0.001

* SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be documented in the facility specific instrument operation SOP and must be approved by the facility technical manager and Quality Assurance Manager.

** Prepared from a second source 0.1 ppm working standard.

*** When brought to a 100 mL final volume.

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.(1)	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
RLV	Beginning of every analytical run, immediately following the ICB.	50 - 150 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.9).
CCV	Every 10 samples and at the end of the run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.8).
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.(1)	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.8).
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL.(1) Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.4)	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5).

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits.(1) If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 10.3.11
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery or in-house control limits; RPD ≤ 20%.(1) (See MS)	See Corrective Action for Matrix Spike.

(1) For specific DoD requirements, refer to PT-QA-025 or PT-QA-029.

THE LEADER IN ENVIRONMENTAL TESTING

APPENDIX B

TESTAMERICA PITTSBURGH Hg DATA REVIEW CHECKLIST

TestAmerica Pittsburgh Example Data Review Checklist – Mercury

Run Date: _____ Lots Analyzed: 4. _____ 8. _____ 12. _____

Analyst: _____ 1. _____ 5. _____ 9. _____ 13. _____

Instrument: _____ 2. _____ 6. _____ 10. _____ 14. _____

Methods: _____ 3. _____ 7. _____ 11. _____ 15. _____

Review Item	Yes ( )	No ( )	N/A ( )	2nd Level Review ( )	Comments
A. Calibration/Instrument Run QC 1. Instrument calibrated per manufacturer's instructions and at SOP specified levels?					
2. ICV/CCV analyzed at appropriate frequency and within control limits?					
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?					
4. CRA run? (CLP only)					
B. Sample Results 1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?					
2. All reported results bracketed by in control QC?					
3. Sample analyses done within holding time?					
C. Preparation/Matrix QC 1. LCS done per prep batch and within QC limits?					
2. Method blank done per prep batch and < RL or CRDL (CLP)?					
3. MS run at required frequency and within limits?					

Review Item	Yes ( )	No ( )	N/A ( )	2nd Level Review ( )	Comments
4. MSD or DU run at required frequency and RPD within SOP limits?					
D. Other 1. Are all nonconformances documented appropriately?					
2. Current IDL/MDL data on file?					
3. Calculations and transcriptions checked for error?					
4. All client/project specific requirements met?					
5. Date/Time of analysis verified as correct?					

General Comments:_____
_____

Analyst & Date: _____**Second-Level Review & Date:** _____

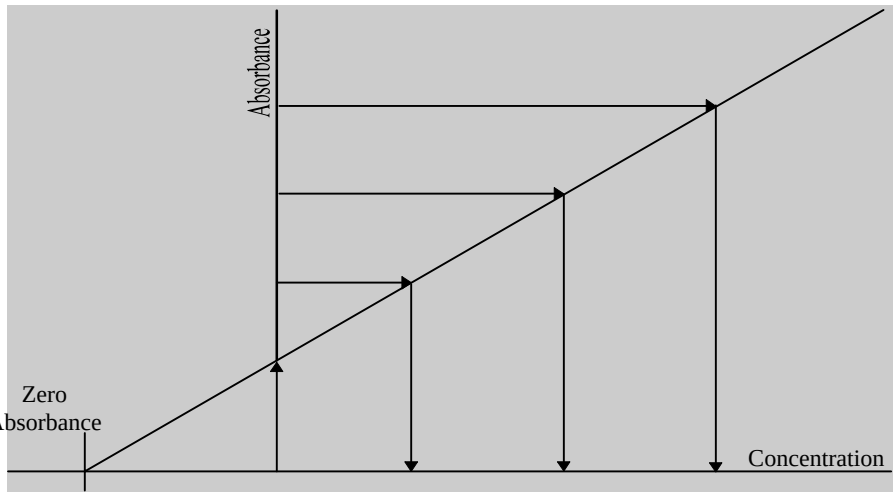
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



Conc. of Sample	Addn 0 No Addn	Addn 1 Addn of 50% of Expected Amount	Addn 2 Addn of 100% of Expected Amount	Addn 3 Addn of 150% of Expected Amount

- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

THE LEADER IN ENVIRONMENTAL TESTING

APPENDIX D. PARTS MAINTENANCE GUIDE

Maintenance Schedule

The software offers a simple to use online Scheduled Maintenance page. To view the page go to Instrument:Scheduled Maintenance (F1 Menu, I, S). A page displaying all items necessary to keep the instrument well maintained is shown (see figure 6.1A).

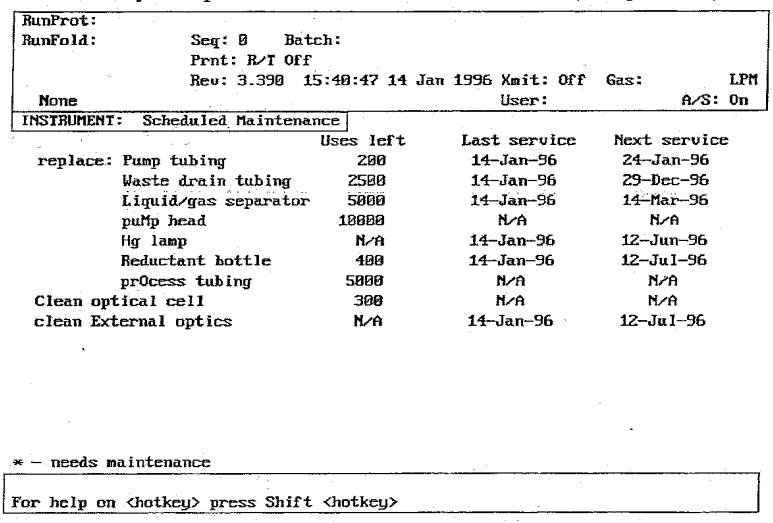


Figure 6.1a. Scheduled maintenance screen

Each scheduled maintenance item has a usage counter, timed usage, or both (N/A indicates that the usage counter or the timed usage is not applicable for that item). If either condition expires for a given item a maintenance message will alert the user at the top of the status box.

Maintenance Procedures

An asterisk(*) will appear next to the item requiring maintenance on the Scheduled Maintenance screen. To clear the message hit <Tab> or replace, clean, or replenish the item using the hot key for the item on the Scheduled Maintenance page. To perform the maintenance on a given item simply type the hot key (e.g. Type <P> for Pump tubing) and follow the directions. Once the directions are followed to completion, the usage counter and timed usage gets updated.

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 20% nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Hydra AA)

Daily	As Needed	Annually
Clean lens windows with methanol.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture reading.	Check pump tubing/drain tubing.	Check liquid/gas separator.
Check argon flow/pressure.	Clean optical cell	
Check tubing and replace, if needed.	Lubricate pump	
Check drain.		
Replace drying tube.		

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS SAMPLES BY COLD VAPOR ATOMIC ABSORPTION

METHODS: SW846 7470A AND MCAWW 245.1

Approvals (Signature/Date):

01/13/2012	12/6/2011
William T. Reinheimer Date	Steve Jackson Date
Technical Manager	Health & Safety Manager / Coordinator
01/05/12	12/8/2011
Nasreen DeRubeis Date	Deborah L. Lowe Date
Quality Assurance Manager	Laboratory Director

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7470A and MCAWW Method 245.1. Both the water bath digestion and the hot block digestion are available at the TestAmerica Pittsburgh facility, however the default practice is the hot block digestion for 7470A and 245.1. Both procedures are described in this SOP.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.3. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, wastes, wipes, TCLP, EP and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed, however Method 7471A/B (see PT-MT-007) is usually the method of choice. All matrices require sample preparation prior to analysis.

1.4. Method 245.1 is applicable to the determination of mercury in drinking, surface and saline waters, domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.5. The TestAmerica reporting limit for mercury in aqueous matrices is 0.0002 mg/L.

1.6. For DoD QSM Version 3 requirements, refer to SOP PT-QA-025 and for DoD QSM Version 4.1 requirements, refer to SOP PT-QA-029.

1.7. On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.1 in the Quality Assurance Manual.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate, which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.2. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.3. Chlorides can cause a positive interference. Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample head space before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE:** This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury (1,000 PPM in Reagent)	Oxidizer Corrosive Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 Mg/M3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Stannous Chloride	Irritant	2 Mg/M3 TWA as Tin	Causes irritation to the respiratory tract. Can irritate skin and eyes. Symptoms include coughing and shortness of breath. Contact with skin and/or eyes may cause redness, itching and pain.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.6. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.6.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.6.2. Iodine, 0.25%, in a 3% KI solution.

5.7. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.8. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.9. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor or EH&S coordinator.

5.10. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.11. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining a temperature of 90-95 °C) or hot block capable of maintaining a temperature of 95 ± 5°C for 2 hours.

6.2. Leeman HYDRA AA Automated Mercury Analysis System.

6.3. Disposable Sealable Sample Containers (Corning).

6.4. Argon gas supply (ultrahigh purity-grade).

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Thermometer (capable of accurate readings at 95 °C).

6.8. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (1000 ppm) mercury standards (in 10% HNO_3) are purchased as custom TestAmerica solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The intermediate standard must be made monthly and must be prepared in a matrix of 2% HNO_3. This acid (2 mL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. Working mercury standard (0.1 ppm): Take 1 mL of the intermediate mercury standard (7.3) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot. A second source working standard is prepared at 0.1 ppm for preparation of the ICV.

7.5. The calibration standards listed in Table I must be prepared fresh daily from the working standard (7.4) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into 100 mL flasks and diluting to volume with reagent water. The 0, .5, 1.0, 5.0 and 10 standards are recommended by Thermo Electron. The 0.2 standard level was selected to include a standard at the RL. See Table 1 (Appendix A) for the preparation of the ICV, CCV and RLV standards.

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, automated

mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard (ICV) must be made from a different stock solution than that of the calibration standards.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.9. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9.1. Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated H_2SO_4 to 1 liter with reagent water.

7.10. Stannous chloride solution: Add 200 g of stannous chloride to 2 L of 10% hydrochloric acid.

7.11. Stannous sulfate may be used in place of stannous chloride. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

7.12. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.13. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.14. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of analysis. For TCLP leachates, the holding time is 28 days from the time of TCLP extraction to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 12.0.

9.2. Preparation Batch - A group of up to 20 samples composed of the same matrix and processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate for 7470A or a matrix spike (one per 10 or fewer samples) for 245.1. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS, MSD) are not included in the sample count for determining the size of a preparation batch.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit, or above 10% of either the measured concentration of that analyte in associated samples or the regulatory limit. See SOP PT-QA-021 for more detail on criteria and corrective actions. In addition, blank contamination should always be evaluated against project specific requirements. **Refer to PT-QA-025 (QSM 3.0) or PT-QA-029 (QSM 4.1) for specific DoD requirements for the method blank.**

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the project narrative.

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative and the client must be notified.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS (referred to as a Laboratory Fortified Blank in 245.1) must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. The CCV results can be reported as LCS results since all CCVs (as well as all other standards) are processed through the sample preparation step with the field samples. No more than 20 samples can be associated with one CCV used for the purpose of reporting LCS data.

- If the LCS is outside established control limits the system is out of control and corrective action must occur. Corrective action will result in the batch being re-prepped and re-analyzed. In-house control limits are 80 - 120% for SW-846 method 7470A and 85 – 115% for EPA method 245.1.

- In the instance where the LCS recovery is > 120% (7470A) or > 115% (245.1) and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative.

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch of up to 20 samples for 7470A or a MS must be processed for every 10 or fewer samples for 245.1. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added (referred to as a Laboratory Fortified Matrix in 245.1). A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample

duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 75 - 125 % (7470A) or 70 – 130% (245.1) recovery and 20% RPD must be applied to the MS/MSD. **Refer to PT-QA-025 (QSM 3.0) or PT-QA-029 (QSM 4.1) for specific DoD requirements for the MS/MSD.** If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 10% (7470A) or 5% (245.1) of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. **Refer to PT-QA-025 (QSM 3.0) or PT-QA-029 (QSM 4.1) for specific DoD requirements for the ICB.** If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the associated samples. The ICV is equivalent to the Quality Control Sample (QCS) and the first Initial Performance Check (IPC) specified in 245.1.

9.8. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples and at the end of the analytical sequence. The CCV must be a mid-range

standard at a concentration other than that of the ICV. **The CCV result must fall within 10% (7470A and 245.1) of the true value for that solution.** If both methods are analyzed in the same sequence the tighter criteria of 10% is used for the CCV. A CCB is analyzed immediately following each CCV. The CCB result must fall within +/- RL from zero. **Refer to PT-QA-025 (QSM 3.0) or PT-QA-029 (QSM 4.1) for specific DoD requirements for the CCB.** Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV or CCB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.9. Reporting Limit Verification Standard (RLV) – Calibration accuracy at the laboratory reporting limit is verified after the analysis of the ICB. Until in-house control limits are established, a control limit of 50 – 150% recovery will be applied.

9.10. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 10.3.11 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. PROCEDURE

10.1. Calibration and Standardization

10.1.1. Calibration standards must be processed through the preparation procedure as described in Section 10.2.

10.1.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.1.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.1.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to CVAA instrument manual for detailed setup and operation protocols.

10.1.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the TestAmerica reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.1.6. The calibration curve must have a correlation coefficient of ≥0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient.

10.1.7. Refer to Section 9.0 and Table II for calibration verification procedures, acceptance criteria and corrective actions. The NELAC requirement for verification of the initial calibration at varied concentrations is met daily since the ICVs, CCVs, and RLVs are all at different concentrations.

10.2. Sample Preparation:

10.2.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB, RLV) are processed through the digestion procedure as well as the field samples. *An exception to this is for Method 245.1 samples. The calibration curve samples are* ***not*** *heated.*

10.2.2. Transfer 50 mL of well-mixed sample or standard to a clean sample digestion bottle. Refer to PT-QA-024 for subsampling procedures.

Note: Reduced sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the same sample to reagent ratio. All samples and standards must be processed similarly.

10.2.3. Add 2.5 mL of concentrated H_2SO_4 and 1.25 mL of concentrated HNO_3 mixing after each addition.

Note: All spiking (LCS, MS, MSD) should be done after the initial addition of acids (see Appendix A, Table 1).

10.2.4. Add 7.5 mL of potassium permanganate solution. For samples high in organic materials or chlorides, additional permanganate may be added. Shake and add additional portions of permanganate solution until a purple color persists for at least 15 minutes. If after the addition of up to 15 mL additional permanganate the color does not persist, sample dilution prior to reanalysis may be required.

Note: When performing analyses using automated vs. manual techniques the sample dilution resultant from the addition of more than the original aliquot of permanganate solution must be compensated for by the addition of the same volume of permanganate to all associated samples, standards, *and QC samples (e.g. LCS and blank)* in the run. In instances, where this is not feasible, the addition of excess reagent can be addressed through mathematical correction of the results to account for the resultant dilution effect.

10.2.5. Add 4 mL of potassium persulfate solution for a 50 mL sample and heat for two hours in a hot block at 95 ± 5°C . (**Note:** 8 mL of potassium persulfate solution would be used for a 100 mL sample, etc. for proportional volumes).

NOTE: Alternatively, for analyses using 7470A and 245.1, samples may be digested using a water bath capable of maintaining a temperature of 90 - 95 °C for 2 hours.

10.2.6. Cool samples.

10.2.7. Samples are adjusted to a final volume of 50 ml after digestion.

10.2.8. **NOTE:** All Safety Kleen Total and TCLP waters are prepared a 10 fold dilution, 5 mls of sample diluted to a final volume of 50 mls.

10.2.9. For the procedure in how to make a dilution, refer to work Instruction PT-QA-W-006.

10.3. Sample Analysis:

10.3.1. Refer to the SOP PT-MT-010 and the instrument manuals for detailed setup and operation protocols for the LEEMAN Hydra AA.

10.3.2. Refer to CVAA instrument manual for detailed setup and operation protocols.

10.3.3. When ready to begin analysis, add 6 mL of sodium chloride-hydroxylamine hydrochloride “clearing solution” to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains). Add this solution in 6 mL increments until the permanganate is completely reduced i.e. colorless.

10.3.4. Automated determination: Follow instructions provided by instrument manufacturer.

10.3.5. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. concentration of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

10.3.6. All measurements must fall within the defined calibration range to be valid. When sample concentrations exceed the upper limit of the calibration curve, the samples will be diluted and reanalyzed (if possible) to bring them within calibration curve. When reported sample concentrations either exceed the upper limit of the curve (i.e. cannot be rerun) or fall below the reporting limit, the data will be qualified as estimated. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

10.3.7. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

10.3.8. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

10.3.9. The following analytical sequence must be used with 7470A and 245.1:

Instrument Calibration

ICV

ICB

RLV

Maximum 10 samples

CCV

CCB

Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run

CCV

CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7470A and 245.1.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

10.3.10. The following run sequence is consistent with 7470A, CLP and 245.1 and may be used as an alternate to the sequence in 10.3.9. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration

ICV

ICB

RLV or CRA*

CCV

CCB

10 samples

CCV

CCB

Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.

CCV

CCB

Refer to the appropriate CLP SOPs (PT-MT-006) for quality control requirements for QC samples.

* Refer to the CLP SOPs for information on the CRA.

10.3.11. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and matrix spike levels for TCLP analyses are detailed in Table I (Appendix A). Appendix E provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

10.4. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

10.5. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and parts maintenance. For instrument troubleshooting, use the auto diagnostics software. If the problem cannot be determined using the software, place a call to service personnel.

10.6. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity,

chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

10.7. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11. DATA ANALYSIS AND CALCULATIONS

11.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

11.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

11.3. RLV percent recoveries are calculated using the same equation as the ICV or CCV (replace ICV or CCV with RLV in the above equations).

11.4. Matrix spike recoveries are calculated according to the following equation:

$$\%\ R\ = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:

SSR = Spike Sample Result

SR = Sample Result

SA = Spike Added

11.5. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration

MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:

DU1 = Sample result

DU2 = Sample duplicate result

11.6. The final concentration for an aqueous sample is calculated as follows:

$$mg/L = C \times D$$

Where:

C = Concentration (mg/L) from instrument readout

D = Instrument dilution factor

11.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

11.8. Appropriate factors must be applied to sample values if dilutions are performed.

11.9. Sample results should be reported with up to three significant figures in accordance with the TestAmerica significant figure policy.

12. METHOD PERFORMANCE

12.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7470A or the 245.1, the following requirements must be met.

12.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be determined in accordance with 40 CFR Part 136 Appendix B requirements and SOP PT-MT-007. The result of the MDL must be below the TestAmerica reporting limit.

12.1.2. Initial Demonstration Study - This requires the analysis of four LCS samples. The LCS sample is a well characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin. Refer to SOP PT-QA-001.

12.1.2.1. Four aliquots of the LCS are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

12.2. Method performance is determined by the analysis of method blanks, laboratory control samples, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 25 % (7470A) or +/- 30% (245.1) and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.4. **Refer to PT-QA-025 (QSM 3.0) or PT-QA-029 (QSM 4.1) for specific DoD requirements for the method blank and MS.** The laboratory control sample should

recover within 20% (7470A) or 15% (245.1) of the true value until in house limits are established.

12.3. Training Qualification:

12.3.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13. POLLUTION PREVENTION

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

13.2. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1. Extracted sample containing less than 1 ppb Hg. This waste is collected in waste containers identified as "Acid Waste", Waste #33. It is neutralized to a pH between 6 and 9 and is disposed down a lab sink.

14.1.2. Unused Standards. This waste collected in containers identified as "Mercury Standards Waste", Waste #4.

14.1.3. Extracted sample containing greater than 1 ppb Hg. This waste collected in containers identified as “Mercury Standards Waste”, Waste #4.

14.1.4. Mercury Analyzer Waste. Waste discharged from mercury analyzer is collected in containers identified as “Mercury Standards Waste”, Waste #4.

15. REFERENCES/CROSS-REFERENCES

15.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury).

15.2. “Methods for the Chemical Analysis of Water and Wastes”, EPA-600/4-79-020, U.S.EPA, 1994, Method 245.1, Revision 3.0.

15.3. U.S.EPA Statement of Work for Inorganics Analysis, ILM04.1.

15.4. PT-QA-001, Employee Orientation and Training.

15.5. PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability.

15.6. PT-QA-007, Method Detection Limits.

15.7. PT-QA-009, Rounding and Significant Figures.

15.8. PT-QA-016, Nonconformance & Corrective Action System.

15.9. PT-QA-018, Technical Data Review Requirements.

15.10. PT-QA-021, Quality Assurance Program.

15.11. PT-QA-022, Equipment Maintenance

15.12. PT-QA-024, Subsampling.

15.13. PT-QA-025, DoD QSM Version 3.

15.14. PT-QA-027, Sample Receiving and Chain of Custody.

15.15. PT-QA-029, QA/QC Requirements for DoD QSM Version 4.1.

15.16. PT-MT-010, Operation of Leeman PS200 (Automated) for Mercury Analysis.

15.17. PT-LQAM- Pittsburgh Laboratory Quality Assurance Manual.

15.18. PT-QA-W-006, Metals Dilution Calculation Table.

16. **METHOD MODIFICATIONS:**

16.1. Modifications/Interpretations from reference method.

16.1.1. Modifications from both 7470A and 245.1.

16.1.1.1. The 200 series methods and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

16.1.1.2. This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, "Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology."

16.1.1.3. The alternate run sequence presented in Section 10.3.10 is consistent with method requirements.

16.1.2. Modifications from Method 7470A

16.1.2.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. **Refer to PT-QA-025 (QSM 3.0) or PT-QA-029 (QSM 4.1) for specific DoD requirements for the method blank.**

16.1.2.2. Documentation is on file from EPA's Office of Solid Waste (Oliver Fordham 11/28/95) regarding the acceptance of the autoclave as an equivalent heating device to the water bath. In his letter, Mr. Fordham

cited the CLP water protocol 245.1 CLP-M and therefore the operating parameters from that method were adopted for 7470A (15 minutes at 120 °C and 15 lbs.).

16.1.3. Modifications from 245.1

16.1.3.1. Method 245.1, Section 9.3 states concentrations should be reported as follows: Between 1 and 10 ug/L, one decimal; above 10 ug/L, to the nearest whole number. TestAmerica reports all Hg results under this SOP to two significant figures.

17. ATTACHMENTS

17.1. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

17.2. APPENDIX A - TABLES

17.3. APPENDIX B - TestAmerica Hg DATA REVIEW CHECKLIST

17.4. APPENDIX C - MSA GUIDANCE

17.5. APPENDIX D – PARTS MAINTENANCE GUIDE

17.6. APPENDIX E- CONTAMINATION CONTROL GUIDELINES

17.7. APPENDIX F - PREVENTIVE MAINTENANCE

18. REVISION HISTORY

18.1. Revision 8, 9/2/2008

18.1.1. Updated the Headers to the new Corporate format; updated SOP and section references throughout the SOP; added Corporate text to the Scope, Safety, Pollution Control and Waste Management sections; changed STL to TestAmerica throughout the SOP; updated the Reference section.

18.1.2. Addedto Section 8.3: Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

18.2. Revision 9, 10/8/2009

18.2.1. Removed all reference to the autoclave and add the reference for the hot block digestion requirements throughout the SOP.

18.2.2. Added the SOP reference for DoD QSM 4.1, PT-QA-029 in the appropriate areas within the SOP. Added reference to SOP PT-QA-022, Equipment Maintenance.

18.2.3 In section 10.2.2 changed 100 mL to 50 mL.

18.2.4 In section 10.2.3 changed 5 mL to 2.5 mL and 2.5 mL to 1.25 mL.

18.2.5 In section 10.2.4 changed 15 mL to 7.5 mL.

18.2.6 In section 10.2.5 changed 8 mL to 4 mL.

18.2.7 Updated Figure 1/Figure 2 to remove the autoclave requirements and add the hot block requirements.

18.2.8 Updated Table 1 to separate out the Working Standard requirements for 7470A and 245.1.

18.3. Revision 10

18.3.1. Updated the SOP reference for 7471A/B to PT-MT-007 in section 1.3.

18.3.2. Removed reference to the LEEMAN PS200II Mercury Analyzer in sections 6.2 and 10.3.1 since this instrument has been taken out of service.

18.3.3. Added to section 9.8: If both methods are analyzed in the same sequence the tighter criteria of 10% is used for the CCV.

18.3.4. In section 10.2.5, corrected the potassium persulfate portion to 4 mL for a 50 mL sample.

18.4. Revision 11

18.4.1. Updated CCV criteria to ±10% for 7470A in section 9.8 and Table II.

18.5. Revision 12

18.5.1. Updated section 1.1, added method 245.1 to be prepared using hot block. Default prep for both method is hot block. Removed "the water bath procedure is always used for 245.1".

18.5.2. Updated section 10.2.5 and Figure 1 to indicate that digestion for both Method 7470A and 245.1 can be performed using a hot block. Indicated in a NOTE under this section that using a water bath for digestion is an alternative digestion procedure.

18.6. Revision 13

18.6.1. Added to section 10.2.7: Samples are adjusted to a final volume of 50 ml after digestion.

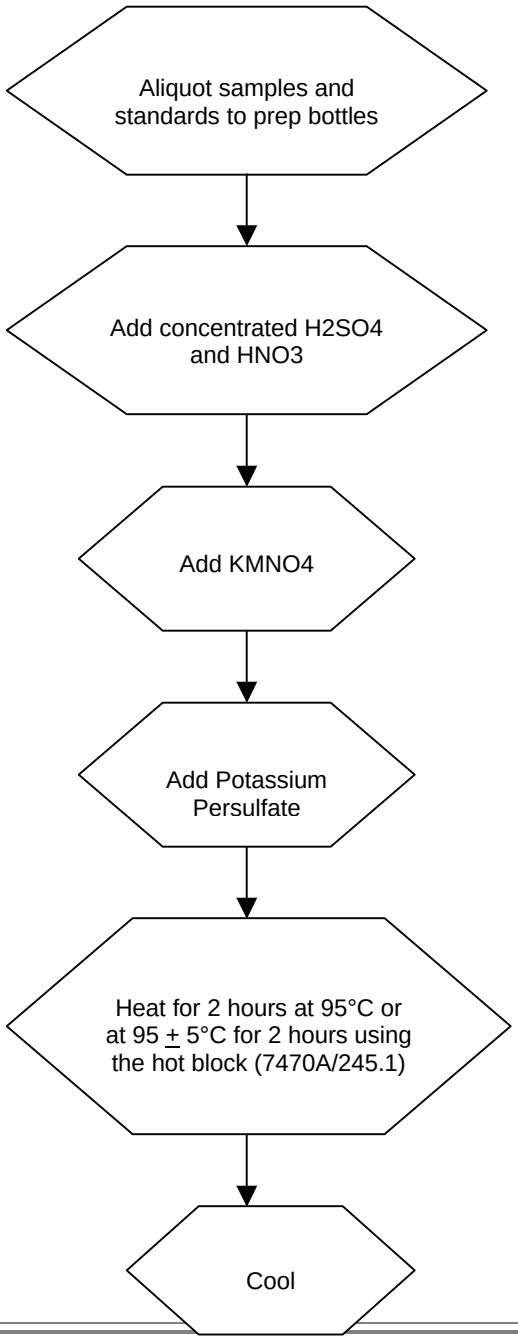
18.6.2. Added section 10.2.8 to note how Safety Kleen samples are handled for mercury preparation.

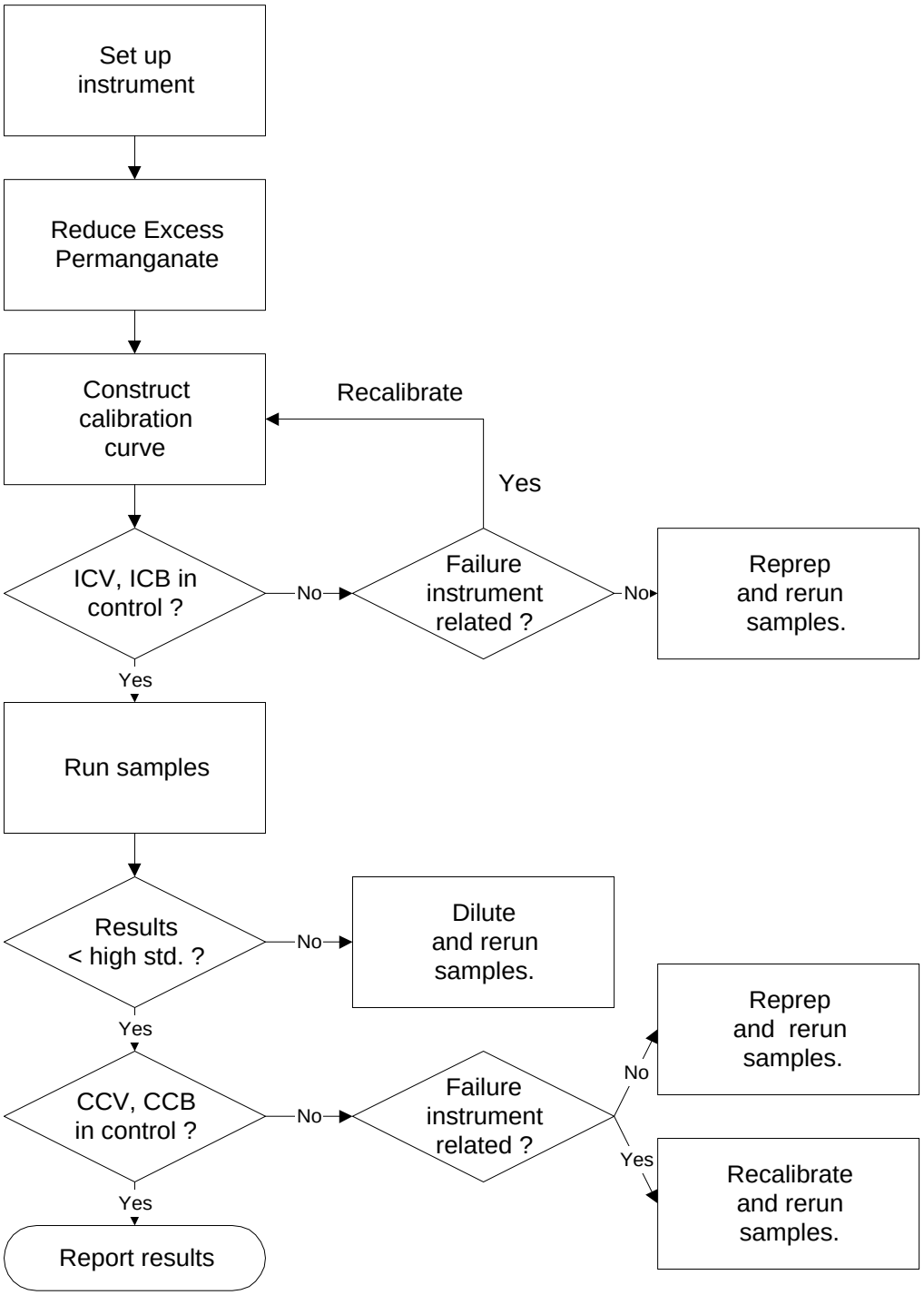
18.6.3. Added to section 10.2.9: For a procedure in how to make a dilution, refer to work Instruction PT-QA-W-006.

18.6.4. Added to section 15.18: PT-QA-W-006, Metals Dilution Calculation Table

18.6.5. Replaced Larry Matko with Bill Reinheimer as the Technical Manager.

18.6.6. **Figure 1**. Aqueous Sample Preparation – Mercury / **Figure 2**. CVAA Mercury Analysis




Set up instrument
Reduce Excess Permanganate
Construct calibration curve
Recalibrate
Yes
ICV, ICB in control ?
No
Failure instrument related ?
No
Reprep and rerun samples.
Yes
Run samples
Results < high std. ?
No
Dilute and rerun samples.
Yes
CCV, CCB in control ?
No
Failure instrument related ?
No
Reprep and rerun samples.
Yes
Recalibrate and rerun samples.
Yes
Report results

APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS (MG/L)

Method		Reporting Limit	
SW846 7470A		0.0002 mg/ L	
SW846 7470A (TCLP)		0.0002 mg/ L	
MCAWW 245.1		0.0002 mg/ L	
Standard or QC sample	**7470A mLs of 0.1 ppm Working Standard**	**245.1 mLs of 0.1 ppm Working Standard**	**Concentration (mg/L)*** **
Std 0	0	0	0
Std 1	0.1	0.2	0.0002
Std 2	0.25	0.5	0.0005
Std 3	0.5	1.0	0.001
Std 4	2.5	5.0	0.005
Std 5	5.0	10.0	0.010
ICV	1.25	2.5**	0.0025
CCV	2.5	5.0	0.005
RLV	0.1	0.2	0.0002
LCS	1.25	2.5	0.0025
Aqueous MS	0.5	1.0	0.001
TCLP MS	0.25	5.0	0.005

* SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements.

** Prepared from a second source 0.1 ppm working standard.

*** When brought to a 100 mL final volume.

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	7470A: 90 - 110 %. 245.1: 95 – 105%	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero. (1)	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
RLV	Beginning of every analytical run, immediately following the ICB.	50 – 150% recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.9).
CCV	Every 10 samples and at the end of the run.	7470A: 90 - 110%. 245.1: 90 – 110%	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.8).
CCB	Immediately following each CCV.	The result must be within +/- RL from zero. (1)	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.8).
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. (1) Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.4).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% (7470A) or 85 – 115% (245.1) recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5).
Matrix Spike	One per sample preparation batch of up to 20 samples (7470A) or one for every 10 or fewer samples (245.1).	75 - 125 % (7470A) or 70 – 130% (245.1) recovery or in-house control limits. [(1)] If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 10.3.11
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % (7470A) or 70 – 130% (245.1) recovery or in-house control limits; RPD ≤ 20%. [(1)] (See MS)	See Corrective Action for Matrix Spike.

[(1)] For specific DoD requirements, refer to PT-QA-025 (QSM 3.0) or PT-QA-029 (QSM 4.1).

APPENDIX B
Example Hg DATA REVIEW CHECKLIST

Run Date: _____ Lots Analyzed: 4. _____ 8. _____ 12. _____

Analyst: _____ 1. _____ 5. _____ 9. _____ 13. _____

Instrument: _____ 2. _____ 6. _____ 10. _____ 14. _____

Methods: _____ 3. _____ 7. _____ 11. _____ 15. _____

Review Item	Yes (✓)	No (✓)	N/A (✓)	2nd Level Review (✓)	Comments
A. Calibration/Instrument Run QC					
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels?					
2. ICV/CCV analyzed at appropriate frequency and within control limits?					
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?					
4. CRA run? (CLP only)					
B. Sample Results					
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?					
2. All reported results bracketed by in control QC?					
3. Sample analyses done within holding time?					
C. Preparation/Matrix QC					
1. LCS done per prep batch and within QC limits?					
2. Method blank done per prep batch and < RL or CRDL (CLP)?					
3. MS run at required frequency and within limits?					
4. MSD or DU run at required frequency and RPD within SOP limits?					
D. Other					
1. Are all nonconformances documented appropriately?					
2. Current IDL/MDL data on file?					

APPENDIX B - DATA REVIEW CHECKLIST

Review Item	Yes (✓)	No (✓)	N/A (✓)	2nd Level Review (✓)	Comments
3. Calculations and transcriptions checked for error?					
4. All client/project specific requirements met?					
5. Date/Time of analysis verified as correct?					

General

Comments:_____

Analyst & Date: _____ Second-Level Review & Date: _____

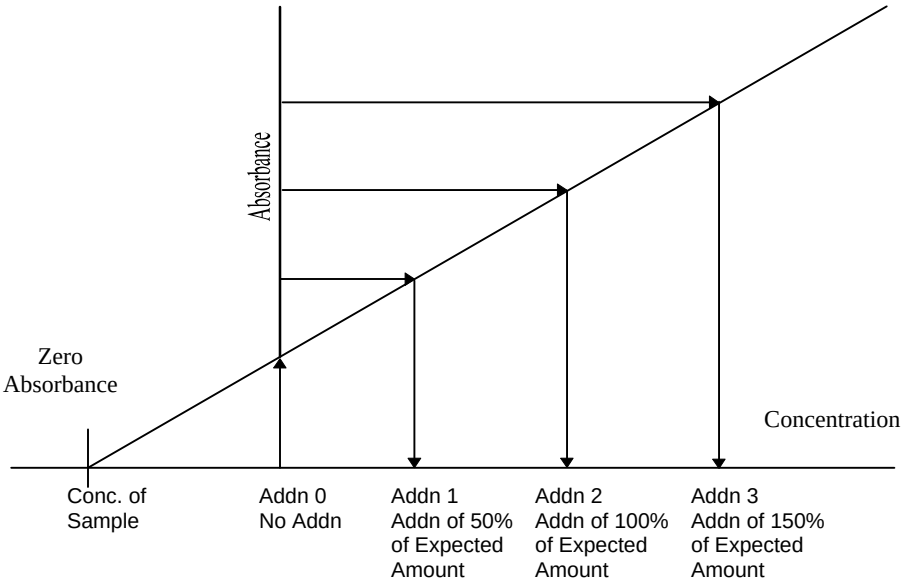
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D. PARTS MAINTENANCE GUIDE

Maintenance Schedule

The software offers a simple to use online Scheduled Maintenance page. To view the page go to Instrument:Scheduled Maintenance (F1 Menu, I, S). A page displaying all items necessary to keep the instrument well maintained is shown (see figure 6.1A).

```
RunProt:
RunFold:          Seq: 0    Batch:
                  Prnt: R/T Off
                  Rev: 3.390  15:40:47 14 Jan 1996 Xmit: Off  Gas:        LPM
 None                                                User:           A/S: On
INSTRUMENT:  Scheduled Maintenance
                                      Uses left     Last service    Next service
 replace: Pump tubing                    200        14-Jan-96       24-Jan-96
          Waste drain tubing            2500        14-Jan-96       29-Dec-96
          Liquid/gas separator          5000        14-Jan-96       14-Mar-96
          pump head                    10000          N/A             N/A
          Hg lamp                        N/A        14-Jan-96       12-Jun-96
          Reductant bottle               400        14-Jan-96       12-Jul-96
          process tubing                5000          N/A             N/A
 Clean optical cell                      300          N/A             N/A
 clean External optics                   N/A        14-Jan-96       12-Jul-96


* - needs maintenance

For help on <hotkey> press Shift <hotkey>
```

Figure 6.1a. Scheduled maintenance screen

Each scheduled maintenance item has a usage counter, timed usage, or both (N/A indicates that the usage counter or the timed usage is not applicable for that item). If either condition expires for a given item a maintenance message will alert the user at the top of the status box.

Maintenance Procedures

An asterisk(*) will appear next to the item requiring maintenance on the Scheduled Maintenance screen. To clear the message hit <Tab> or replace, clean, or replenish the item using the hot key for the item on the Scheduled Maintenance page. To perform the maintenance on a given item simply type the hot key (e.g. Type <P> for Pump tubing) and follow the directions. Once the directions are followed to completion, the usage counter and timed usage gets updated.

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 20% nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Hydra AA)

Daily	As Needed	Annually
Clean lens windows with methanol.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture reading.	Check pump tubing/drain tubing.	Check liquid/gas separator.
Check argon flow/pressure.	Clean optical cell	
Check tubing and replace, if needed.	Lubricate pump	
Check drain.		
Replace drying tube.		

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Acid Volatile Sulfides (AVS) and Simultaneously Extracted Metals (SEM) in Sediment

Approvals (Signature/Date):

Mike Wesoloski	11/18/2011 Date	Steve Jackson	10/5/2011 Date
Technical Specialist		Health & Safety Manager / Coordinator	
Nasreen DeRubeis	10/28/2011 Date	Deborah Lowe	11/2/2011 Date
Quality Assurance Manager		Laboratory Director	

1. SCOPE AND APPLICATION

1.1. This method describes the procedure for the determination of acid volatile sulfides (AVS) and for metals that are solubilized during the acidification step (Simultaneously Extracted Metals, SEM). The conditions used have been reported to measure amorphous or moderately crystalline monosulfides. As a precipitant of toxic heavy metals, sulfide is important in controlling the bioavailability of metals in anoxic sediments. If the molar ratio of toxic metals measured by SEM to AVS exceeds one, the metals are potentially bioavailable. Because the relative amounts of AVS and SEM are important in the prediction of potential metal bioavailability, it is important to use the SEM procedure for sample preparation for metal analysis. This uses the same conditions for release of both sulfide and metal from the sediment and thus provides the most predictive means of assessing the amount of metal associated with the sulfide.

1.2. Method 9034 is used to quantify the concentration of sulfide and Method 6010B is used to quantify the concentration of the routine SEM metals (arsenic, cadmium, chromium, copper, lead, nickel, silver and zinc). If mercury is requested as a SEM, Method 7470A is used for quantification. Reporting limits are listed in Attachment 1.

2. SUMMARY OF METHOD

2.1. The AVS in the sample is first converted to hydrogen sulfide (H2S) by acidification with hydrochloric acid at room temperature. The H2S is then purged from the sample and trapped. The amount of sulfide that is trapped is then determined titrimetrically following Method 9034. The SEM are metals liberated from the sediment during the acidification. These are determined following Method 6010B after filtration of the sample (plus 7470A if mercury is required).

3. DEFINITIONS

3.1. Acid Volatile Sulfides (AVS): Amorphous, moderately crystalline monosulfides, and other sulfides that form hydrogen sulfide under the conditions of this test.

3.2. Simultaneously Extracted Metals (SEM): Metals which form less soluble sulfides than do iron or manganese, and which are at least partially soluble under the conditions of this test. The routine SEMs are cadmium, copper, lead, nickel, and zinc. Mercury may also be determined on a project specific basis.

3.3. ICV: Initial Calibration Verification: An undistilled standard prepared by adding 1 mL of a 1000 ppm (or standardized concentration) sodium sulfide standard (different source than the standard used for the LCS and MS/MSD) to 50 mL of reagent water (20 ppm concentration).

3.4. ICB: Initial Calibration Blank: undistilled blank consisting of 50 mL of reagent water.

3.5. PBW: Prep Blank Water or Method Blank.

3.6. CCV: Continuing Calibration Verification: preparation is the same as the ICV.

3.7. CCB: Continued Calibration Blank: preparation is the same as the ICB.

3.8. LCS: Laboratory Control Sample.

4. INTERFERENCES

4.1. Oxygen in the reagents and apparatus is the primary interference reported. Samples must be taken with minimum aeration to avoid volatilization of sulfide or reaction with oxygen, which oxidizes sulfide to sulfur compounds that are not detected. Use deoxygenated, deionized water and reagents.

4.2. Reduced sulfur compounds, such as sulfite and hydrosulfite, may decompose in acid and form sulfur dioxide. This gas may carry over to the zinc acetate solutions and subsequently react with iodine during the titration, thus causing a positive bias to the results.

4.3. The iodometric method suffers interference from reducing substances that react with iodine, including thiosulfate, sulfite, and various organic compounds.

4.4. The pH of the sample after the addition of the acid and during the purge process must be below 3.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1. Specific Safety Concerns or Requirements

5.1.1. Hydrogen sulfide (H_2S) gas is generated by the addition of sulfuric acid. Inhalation of H_2S gas can cause headache, dizziness, nausea and unconsciousness and potentially death.

5.2. Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Iodine	Poison Corrosive Oxidizer	0.1 ppm-Ceiling	Vapors severely irritate and can burn the mucous membranes and respiratory tract. Liquid contact may cause blistering burns, irritation, and pain. Vapors may be severely irritating to the skin. Vapors are severely irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Dichromate	Oxidizer Corrosive Carcinogen	0.1 Mg/M3 TWA as CrO3	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. May cause ulceration and perforation of the nasal septum. Symptoms of redness, pain, and severe burn can occur. Dusts and strong solutions may cause severe irritation. Contact can cause blurred vision, redness, pain and severe tissue burns. May cause corneal injury or blindness.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium Sulfide	Corrosive	10 ppm-TWA 15 ppm-STEL	Will form Hydrogen Sulfide (HS) gas if combined with strong acids. Inhalation of HS gas may be fatal. Symptoms include painful conjunctivitis, headache, nausea, dizziness, coughing and, in extreme cases, pulmonary edema and possible death. Irritant. Contact with skin can produce serious caustic burns with painful inflammation and possible destruction of tissue. Inflammation, tearing and pain may be expected. Severe contact can cause destruction of tissue.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Procedures shall be carried out in a manner that protects the health and safety of all TestAmerica associates.

5.4. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.6. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.7. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor or a TestAmerica Emergency Coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Instrumentation

6.1.1. Not Applicable.

6.2. Supplies

6.2.1. Boiling tube.

6.2.2. Inlet adapter.

6.2.3. Dropping funnel.

6.2.4. Gas inlet.

6.2.5. Impinged bubbler.

6.2.6. Fritted bubbler.

6.2.7. Bubbler vessels.

6.2.8. WestClips®

6.2.9. Gas line “T” connector.

6.2.10. Class A Volumetric flasks, pipettes, and burettes.

6.2.11. High purity nitrogen gas.

6.2.12. Regulator.

6.2.13. 100 mL and 300 mL graduated disposable flasks.

6.2.14. 100 mL disposable beaker

6.2.15. Hot plate stirrer.

6.2.16. 50mL burette.

6.2.17. Parafilm

6.2.18. Filtering apparatus and 0.45 μm filter membrane.

7. REAGENTS AND STANDARDS

7.1. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2. Reagent water (Super Q/DI Water). All references to water in this method refer to reagent water.

7.3. Zinc acetate for the scrubber. Zinc acetate solution (approximately 0.5M). Dissolve about 110g zinc acetate dihydrate in 200mL of reagent water. Add 1mL hydrochloric acid (concentrated), to prevent precipitation of zinc hydroxide. Dilute to 1L.

7.4. Acid to acidify the sample. 6 M Hydrochloric acid, 1:1 HCl:reagent water. Purge with nitrogen for at least 30 minutes prior to use.

7.5. UHP/zero grade nitrogen gas. Gas chromatographic grade with two-stage regulator.

7.6. Starch indicator. 0.5%. Purchased.

7.7. 0.0250N $Na_2S_2O_3$. Purchased.

7.8. 0.025N Iodine. Purchased.

7.9. 1000ppm Sodium sulfide prepared by adding approximately 3.75g $Na_2S \bullet 9H_20$ to 500mL reagent water. May be commercially available.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Samples must be cooled to 4°C and stored headspace free. Typically a separate 4 oz jar is filled specifically for this test.

8.2. The acidification of the sample (H_2S generation) and sulfide determination must be performed within 14 days from the date of collection. The routine SEMs are stable up to six months after sample collection (28 days for mercury, if required).

8.3. If after distillation, the AVS distillate can not be immediately titrated it may be stored at $\leq$ 6°C for up to 24 hours before final titration provided the 7 day holding time is not exceeded.

9. QUALITY CONTROL

9.1. Sample QC

9.1.1. A Laboratory Control Sample (LCS) must be analyzed with each batch of 20 or fewer samples. A separate sulfide (AVS) LCS and metals (SEM) LCS is performed.

9.1.1.1. The LCS and ICV are the same standard. Therefore the ICV/LCS acceptance criteria are 85 to 115 percent. If the LCS is not used as the ICV, then the LCS must meet a 75 to 125 percent recovery criterion.

9.1.2. A matrix spike and a matrix spike duplicate (MS/MSD) must be analyzed with each batch of 20 or fewer samples. A separate sulfide (AVS) MS/MSD and metals (SEM) MS/MSD is performed.

9.1.2.1. The percent recovery for matrix spike and matrix spike duplicate should be $\pm$ 25 percent. If this criterion is not met, evaluate method process. If no errors are found, document in a Non-Conformance Memo (NCM).

9.1.2.2. The relative percent difference (RPD) between the MS and MSD must be within ± 20 percent. If this criterion is not met, then repeat the analysis once. The results with the better RPD will be reported. If the results for the reanalysis are the same as the original analysis, then report the original analysis.

9.1.3. A method blank must be analyzed with each batch of 20 samples or fewer processed at the same time. The prep blank (or method blank) can be used as the ICB if it meets the ICB acceptance criteria. The processing of a method blank will assure non-contamination of the reagents. The ICB result must be less than the Reporting Limit. The method blank result must be less than two times the Reporting Limit, otherwise all samples must be reprepared and reanalyzed. If this is not possible due to limited sample quantity (or there is no sample left) the corresponding samples will be flagged and the PM will be notified. If repreparation and reanalysis happen to be outside holding time, then approval from the client must be obtained before any reanalysis is performed.

9.2. Instrument QC

9.2.1. A sulfide run will consist of the following sequence: ICV, ICB, and up to 10 samples followed by a CCV and a CCB. See the appropriate metals SOP for the SEM analyses.

9.2.2. This can be followed by up to 10 more samples, followed by a CCV and CCB.

9.2.3. Repeat 9.2.1 and 9.2.2 sequence for additional samples.

9.2.4. The following QC requirements must be met for the sulfide (AVS) analyses:

9.2.4.1. The ICV must be within ± 15 percent. If this criterion is not met, then recalibrate and reanalyze the samples. The LCS can be used as an ICV if it meets the ICV acceptance criteria of 85 to 115 percent. If the LCS is not used as the ICV, then the LCS must meet a 75 to 125 percent recovery criterion.

9.2.4.2. The CCV must be within ± 15 percent. If this criterion is not met, then reanalyze the samples with a valid CCV. If the analysis sequence shows ICV, ICB, and 10 samples followed by CCV, CCB, and this CCV fails, then all those 10 samples must be reanalyzed. If with the above sequence 10 additional samples are analyzed following a CCV and a CCB and this second CCV fails, then all the samples up to the last acceptable CCV must be reanalyzed. The CCB criteria are the same as ICB.

9.3. All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by or under supervision of experienced analysts.

9.4. All sample preparation and analysis information will be documented on laboratory bench sheets, computer printouts, standard logbooks, etc. All the documents associated with an analysis will be forwarded for reporting and for inclusion in the project files.

10. PROCEDURE

10.1. Sample Preparation

10.1.1. Place the boiling tube containing approximately 10 grams of sample (record to the nearest 0.1 grams) and 50 mL of reagent water in the heater block (used as a holder only) and assemble the acid soluble sulfide distillation apparatus as shown in Figure 1. The sample can be weighed on a 2” x 2” piece of Parafilm and placed into the boiling tube.

10.1.2. Spike the sulfide (AVS) LCS, MS, and MSD with 1 mL of the 1000 ppm sodium sulfide solution (7.11) which is equivalent to 100 mg/Kg in a 10 gram sample. Spike the metals (SEM) LCS, MS, and MSD with 2.5 mLs of the metals ICP MS solution. If mercury is required, a mercury spike will need to be added to the LCS, MS, and MSD.

10.1.3. Place 2.0mL of 0.5M zinc acetate solution and 20.0mL of deionized water in each of two bubbler vessels. Place an impinged bubbler in the first (front) and second (back) vessel, and seal them with size 24/40 WestClips®. The sealed vessels and impingers function as the gas scrubbers. Connect the first scrubber to the inlet adapter and place the second bubbler vessel in the bubbler vessel rack. Connect the two impingers in series using Tygon® tubing.

10.1.4. Close stopcock of dropping funnel. Place 20 mL of the nitrogen purged 6 M hydrochloric acid in the dropping funnel.

10.1.5. Connect a high-purity (GC grade) nitrogen gas source to the main inlet of the gas manifold of the aluminum heater block as specified in the Heater Block Operation Manual. Use a two-stage gas tank regulator and set the pressure into the gas manifold to 20psi.

10.1.6. Connect a black gas line from each gas manifold valve to a "T" connector and a tygon gas line from the "T" to each of the two gas inlets of the apparatus. One at the top of the dropping funnel and one at the inlet adapter as shown in Figure 1.

10.1.7. Purge assembled apparatus with high-purity nitrogen for 10 minutes to remove atmospheric oxygen from the apparatus and contained solutions. During purge, adjust nitrogen flow such that 2-3 bubbles per second exit the base of the inlet adapter.

10.1.8. Open stopcock of dropping funnel and allow all of the 6M hydrochloric acid to drip into the boiling tube. Once dropping funnel is empty, close the stopcock to ensure sample is not lost into the funnel.

10.1.9. Purge the sample for 1 hour at room temperature. After the 1 hour purging period, remove the bubbler vessels. Turn off the nitrogen flow. Carefully combine the gas scrubber solutions in a 100 mL graduated disposable flask. Do not shake or mix solutions to avoid loss of sulfide. Bring up to 50 mL with reagent water. Determine the concentration of acid volatile sulfide in the zinc acetate gas scrubber solutions by using the Titrimetric-iodine method (9034)—proceed to Section 10.3.

10.1.10. After the generation of sulfide has been completed, the sediment suspension remaining in the boiling tube is filtered through a 0.45 μm membrane filter. The pH of the solution is determined using narrow range pH strips to verify that the pH is less than 3. If the pH is not less than 3, the group supervisor and QA Manager should be consulted. Document all actions in a Nonconformance Memo (NCM). The solution is brought up to a final volume of 250 mL in a 300 mL graduated disposable flask. This solution is analyzed directly by ICP for the routine SEMs (see SOP PT-MT-001). If mercury is required, an aliquot of this solution is prepared following Method 7470A and analyzed by CVAA (see SOP PT-MT-005).

10.2. Calibration

NOTE: All periodic standardizations of titrants can be found in the Wet Chemistry standardization logbook. Daily standardizations are found on the bench worksheet.

10.2.1. Stock sulfide standard is titrated daily before each distillation of sample sets. The stock standard must be reprepared every week.

10.2.2. Sodium thiosulfate (0.0250N) standardization—performed daily.

10.2.2.1. Use 0.0250 N Biiodate titrant: dissolve 0.8124g potassium biiodate (dried 2 hours) in Super-Q water and dilute to 1 L.

10.2.2.2. Place 2g KI in 250mL beaker and add 100mL Super-Q water and stir. Add 10mL 1:4 H_2SO_4 and 10mL biiodate.

10.2.2.3. Place in the dark for 5 minutes. Dilute to 150mL and add starch indicator (Section 7.8)

10.2.2.4. Titrate with $Na_2S_2O_3$ (7.9) to clear endpoint. Repeat procedure two additional times. Determine the normality of the $Na_2S_2O_3$ as follows:

$$N\ Na_2S_2O_3 = \frac{10\ mL\ biiodate \times 0.025\ N\ biiodate}{mL\ Na_2S_2O_3\ titrant}$$

10.2.3. Iodine standardization: performed daily

10.2.3.1. Place 20mL .0250N iodine in Erlenmeyer flask. Add 2mL 6 N HCl.

10.2.3.2. Titrate with $Na_2\ S_2O_3$ (7.9) to a pale yellow color.

10.2.3.3. Add starch indicator (7.8) and titrate with $Na_2S_2O_3$ (7.9) to clear endpoint. Determine the normality of the iodine (I) as follows:

$$N\ I = \frac{N Na_2S_2O_3 \times mL\ Na_2S_2O_3\ titrant}{mL\ I\ solution}$$

10.3. Sample Analysis

10.3.1. Pipette a known amount of standardized 0.025N iodine solution the 100mL disposable sample beaker, adding an amount in excess of that needed to oxidize the sulfide.

10.3.2. Add 2mL of 6N HCl to the iodine.

10.3.3. If at any point the amber/orange color of the iodine disappears or fades to yellow, more 0.025N iodine must be added. This additional amount must be added to the amount from Section 10.3.1 for calculations. Record the total volume of standardized 0.025N iodine solution used.

10.3.4. Add enough starch indicator (approximately 1 mL) for the solution to turn a dark blue color.

10.3.5. Titrate the solution in the flask with standard 0.025N sodium thiosulfate solution until the dark blue color disappears. Record the volume of titrant used.

10.3.6. For metals, the solution is analyzed directly by ICP for the routine SEMs (see SOP PT-MT-001). If mercury is required, an aliquot of this solution is prepared following Method 7470A and analyzed by CVAA (see SOP PT-MT-005).

11. CALCULATIONS / DATA REDUCTION

11.1. One mL of 0.0250 N standard iodine solution reacts with 0.4mg sulfide present in titration vessel.

11.2. $$\text{AVS mg/Kg-dry} = \frac{[(A \times B) - (C \times D)] \times 16000}{E \times F}$$

A = mL of iodine solution
B = N of iodine solution
C = mL of $Na_2S_2O_3$ solution
D = N of $Na_2S_2O_3$ solution
E = weight of sample (grams or mls)
F = Percent solids as decimal fraction (i.e., 50% solid is 0.50)

11.3. To convert the AVS concentration from mg/Kg-dry to μmoles/gram-dry, divide by 32.066 (molecular weight of sulfur).

11.4. Enter the completed data work sheet into computer program, sulfide analysis worksheet, for final results.

11.5. For each SEM, first determine concentration in mg/Kg-dry as follows:

$$\text{SEM mg/Kg-dry} = \frac{A \times B}{C \times D}$$

A = conc. of metal in solution as determined by 6010B or 7470A (mg/L)
B = final volume of solution in liters—typically 0.25 liters.
C = weight of sample in Kg.
D = Percent solids as decimal fraction (i.e., 50% solid is 0.50)

11.6. To convert the concentration of each SEM from mg/Kg-dry to μmoles/gram-dry, divide by the molecular weight of that metal (cadmium = 112.411; copper = 63.546; lead = 207.2; mercury = 200.59; nickel = 58.69; and zinc = 65.39).

11.7. Calculate the Total SEM molar concentration of the sample by summing each of the individual SEM concentrations in units of μmoles/gram-dry. If any one of the SEMs is not detected (ND), it is considered a zero (0) in the summation.

11.8. Calculate the molar ratio of SEM over AVS as follows:

SEM/AVS = A/B

A = Total SEM molar concentration (μmoles/gram-dry).
B = AVS molar concentration (μmoles/gram-dry).

Note: If AVS is not detected (ND), the molar ratio cannot be determined.

11.9. Matrix Spike percent recovery:

$$Theoretical\ Spike\ Conc. = \frac{\begin{pmatrix} Spike \\ Conc. \end{pmatrix} \times \begin{pmatrix} Vol.\ of \\ Spike\ Added \end{pmatrix}}{Final\ Vol.\ Spiked}$$

$$\%\ \text{Recovery} = \frac{\begin{pmatrix} Final \\ Spike + Sample \end{pmatrix} - Sample\ \text{Result}\left(\dfrac{\begin{pmatrix} Vol.\ Sample \\ Spiked \end{pmatrix}}{Final\ Vol.}\right)}{Theoretical\ Spike\ Conc.} \times 100$$

12. METHOD PERFORMANCE

12.1. Method Detection Limit Study (MDL)

12.1.1. Method Detection Limit (MDL) for Titrimetric Procedures - The detection limit for titrimetric procedures can be defined by the smallest amount of reagent that can be added during a titration to cause a chemical change. This is typically determined by the smallest size of the drop that can be produced on a particular burette or other titrating device. Drop size can be estimated by averaging the size of several (5 to 10 is a good number) repeated drops. The detection limit can then be calculated based on the titrant concentration, the sample size, and the minimum drop size.

12.1.2. Method Detection Limit (MDL) for Metals - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. Either an annual MDL study or quarterly MDL Verification can be done. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest that have been carried through the entire analytical procedure. MDLs must be determined in accordance with 40 CFR Part 136 Appendix B requirements as detailed in SOP: PT-QA-007. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the TestAmerica reporting limit.

12.2. Demonstration of Capabilities

12.2.1. Prior to analysis of any samples using this SOP, the following requirements must be met: Initial Demonstration Study: This requires the analysis of four QC check samples. The QC check sample is a well-characterized, laboratory-generated sample used to monitor method performance, which should contain the analyte(s) of interest. The results of the initial demonstration study must be acceptable before analysis of samples under this SOP may begin. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP. Acceptance criteria for the LCS are given in Section 9.1.1.1.

12.3. Training Qualifications

12.3.1. The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. The group/team leader must document the training and PE performance and submit the results to the QA Manager for inclusion in associate training files.

13. POLLUTION CONTROL

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental

Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

13.2. This method does not contain any specific modifications that serve to minimize or prevent pollution.

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1. Acidic waste generated by sample titration. This waste is collected in a waste container identified as "Acid Waste", Waste #33. This waste is neutralized to a final pH between 6 and 9 and discharged down into a lab sink.

14.1.2. Unused sample distillate. This waste is collected in a waste container identified as "Acid Waste", Waste #33. This waste is neutralized to a final pH between 6 and 9 and discharged down into a lab sink.

14.2. Waste generated in the procedure will be segregated, and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Coordinator should be contracted if additional information is required.

15. REFERENCES

15.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed.; U.S. EPA. Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1997; SW-846.

15.2. Allen, H.E. and F. Gongmin et al. 1991. Determination of Acid Volatile Sulfide and Simultaneously Extractable Metals in Sediment, April 1991 (Draft Analytical Method for the Determination of Acid Volatile Sulfide in Sediment, U.S. EPA Office of Water and Office of Science and Technology, Health and Ecological Criteria Division, Washington, D.C., August 1991.

15.3. SOP PT-MT-001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analyses, SW-846 Method 6010B, 6010C and EPA Method 200.7, current revision.

15.4. SOP PT-MT-005, Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW-846 7470A and MCAWW 245.1, current revision.

15.5. SOP PT-WC-010, Total Sulfide as Acid Soluble Sulfide, Method 9030B/9034, SM 20th Ed. 4500S-2F and EPA Method 376.1, current revision.

15.6. SOP PT-QA-007, Detection Limits, current revision.

15.7. SOP PT-QA-003, Glassware Clean-up for Organic/Inorganic Procedures, current version.

15.8. SOP PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability, current version.

15.9. SOP PT-QA-008, Thermometer Calibration and Temperature Monitoring, current version.

15.10. SOP PT-QA-011, Data Recording Requirements, current version.

15.11. SOP PT-QA-012, Selection and Calibration of Balances and Weights, current version.

15.12. SOP PT-QA-016, Nonconformance & Corrective Action System, current version.

15.13. SOP PT-QA-021, Quality Assurance Program, current version.

15.14. SOP PT-QA-022, Equipment Maintenance, current version.

15.15. SOP PT-QA-027, Sample Receiving and Chain of Custody, current version.

15.16. PT-LQAM, current version.

16. METHOD MODIFICATIONS

16.1. Not applicable.

17. ATTACHMENTS

17.1. Figure 1 – Acid Volatile Sulfide generation apparatus.

17.2. Attachment 1 – SEM and AVS Reporting Limits. MDLs listed in the two attachments for metals and sulfide are subject to change.

18. REVISION HISTORY

18.1. Revision 1, 5/16/08.

18.1.1. Renamed SOP as PT-WC-008.

18.1.2. Changed laboratory name to TestAmerica.

18.1.3. Updated SOP format to match corporate SOP format.

18.1.4. Corrected some typographical errors and several Section references that were incorrect.

18.1.5. Revised section 9.1.1.1: The LCS and ICV are the same standard. Therefore the ICV/LCS acceptance criteria are 85 to 115 percent. If the LCS is not used as the ICV, then the LCS must meet a 75 to 125 percent recovery criterion.

18.1.6. Added to Section 12.1.1: Method Detection Limit (MDL) for Titrimetric Procedures - The detection limit for titrimetric procedures can be defined by the smallest amount of reagent that can be added during a titration to cause a chemical change. This is typically determined by the smallest size of the drop that can be produced on a particular burette or other titrating device. Drop size can be estimated by averaging the size of several (5 to 10 is a good number) repeated drops. The detection limit can then be calculated based on the titrant concentration, the sample size, and the minimum drop size.

18.1.7. Modified Section 12.1.2 to add either annual MDL Study or quarterly MDL Verification can be done for metals..

18.1.8. All revisions are highlighted throughout the SOP.

18.2. Revision 2

18.2.1. Updated SOP reference numbers throughout the SOP.

18.2.2. Added TestAmerica Pittsburgh's SOP References in section 15.

18.3. Revision 3

18.3.1. Section 1.2, added As, Cr and Ag for ICP. Added: Reporting limits are in Attachment 1.

18.3.2. Formaldehyde is not used in executing this SOP, thus references to formaldehyde in sections 4.2, the Table under 5.2, 7.3 and 10.1.3.

18.3.3. Section 8.3 was added to clarify that a distillate will be refrigerated no more than 24 hours before final titration provide the 7 day holding time is still met.

18.3.4. In section 10.1.1, corrected the volume of reagent water added to the heater block from 100 ml to 50 ml.

18.3.5. Added section 10.3.5: For metals, the solution is analyzed directly by ICP for the routine SEMs (see SOP PT-MT-001). If mercury is required, an aliquot of this solution is prepared following Method 7470A and analyzed by CVAA (see SOP PT-MT-005).

18.3.6. In section 11.2, correct variable E to read weight of sample (grams or mLs).

18.3.7. In Section 15 References/Cross-References, references were added to all pertinent QA SOP's and the PT-LQAM.

18.4. Revision 4

18.4.1. Removed reference to the use of H_2SO_4 in the Table under section 5.2 and in section 7.5 since it is not used in this SOP.

18.4.2. In section 7.9, added "approximately" before 3.75 g.

18.4.3. In section 10.3.3 added amber/orange color.

18.4.4. Added section 10.3.4 to clarify that starch indicator is added to the sample to turn it dark blue before it is titrated with sodium thiosulfate in section 10.3.5.

18.4.5. In section 10.3.1 added the word sample between disposable and beaker.

18.4.6. Removed sentence one from 10.3.3 and removed "in transferring the zinc acetate solution" from sentence two in section 10.3.3.

Attachment 1 – Reporting Limits

TAL Reference Data Summary

Structured Analysis Code: A-**-OS-8G-03
Target Analyte List: All Analytes

Matrix: SOLID
Extraction: None specified.
Method: Simultaneously Extractable Metals in Sediment
QC Program: MARINE\SEDIMENT
Location: TestAmerica Pittsburgh

Analyte List		Detection Limits					Check List 3008							Spike List 3009						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
140	Arsenic	0.003337	umoles/gn	0.00038	umoles/gn	20061013	C	Y	0.6673	umoles/g	80	120	20	C	Y	0.667	umoles/g	75	125	20
411	Cadmium	0.001112	umoles/gn	0.00003	umoles/gn	20061013	C	Y	0.0111	umoles/g	80	120	20	C	Y	0.0111	umoles/g	75	125	20
2952	Chromium	0.002404	umoles/gn	0.00021	umoles/gn	20061013	C	Y	0.0961	umoles/g	80	120	20	C	Y	0.0961	umoles/g	75	125	20
643	Copper	0.009835	umoles/gn	0.00088	umoles/gn	20061013	C	Y	0.0983	umoles/g	80	120	20	C	Y	0.0983	umoles/g	75	125	20
1605	Lead	0.0007239	umoles/gn	0.00023	umoles/gn	20061013	C	Y	0.0603	umoles/g	80	120	20	C	Y	0.0603	umoles/g	75	125	20
1701	Mercury	0.0000623	umoles/gn	0.00000	umoles/gn	20061013	C	Y	0.0001	umoles/g	80	120	20	C	Y	0.0001	umoles/g	60	120	20
1956	Nickel	0.01704	umoles/gn	0.00049	umoles/gn	20061013	C	Y	0.2129	umoles/g	80	120	20	C	Y	0.2129	umoles/g	75	125	20
2285	Silver	0.001159	umoles/gn	0.00013	umoles/gn	20061013	C	Y	0.0115	umoles/g	80	120	20	C	Y	0.0115	umoles/g	75	125	20
2649	Zinc	0.03823	umoles/gn	0.00282	umoles/gn	20061013	C	Y	0.1911	umoles/g	80	120	20	C	Y	0.1911	umoles/g	75	125	20

Attachment 1 – Cont.

TAL Reference Data Summary

Structured Analysis Code: A-**-P7-8G-03
Target Analyte List: All Analytes

Matrix: SOLID
Extraction: None specified.
Method: Acid Volatile Sulfide in Sediment (AVS)
QC Program: MARINE\SEDIMENT
Location: TestAmerica Pittsburgh

Analyte List			Detection Limits				Check List 3000							Spike List 3001						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
3735	Acid Volatile Sulfide	0.499	umoles/gn	0.155	umoles/gn	20050101	C	Y			85	115	20	C	Y			75	125	25

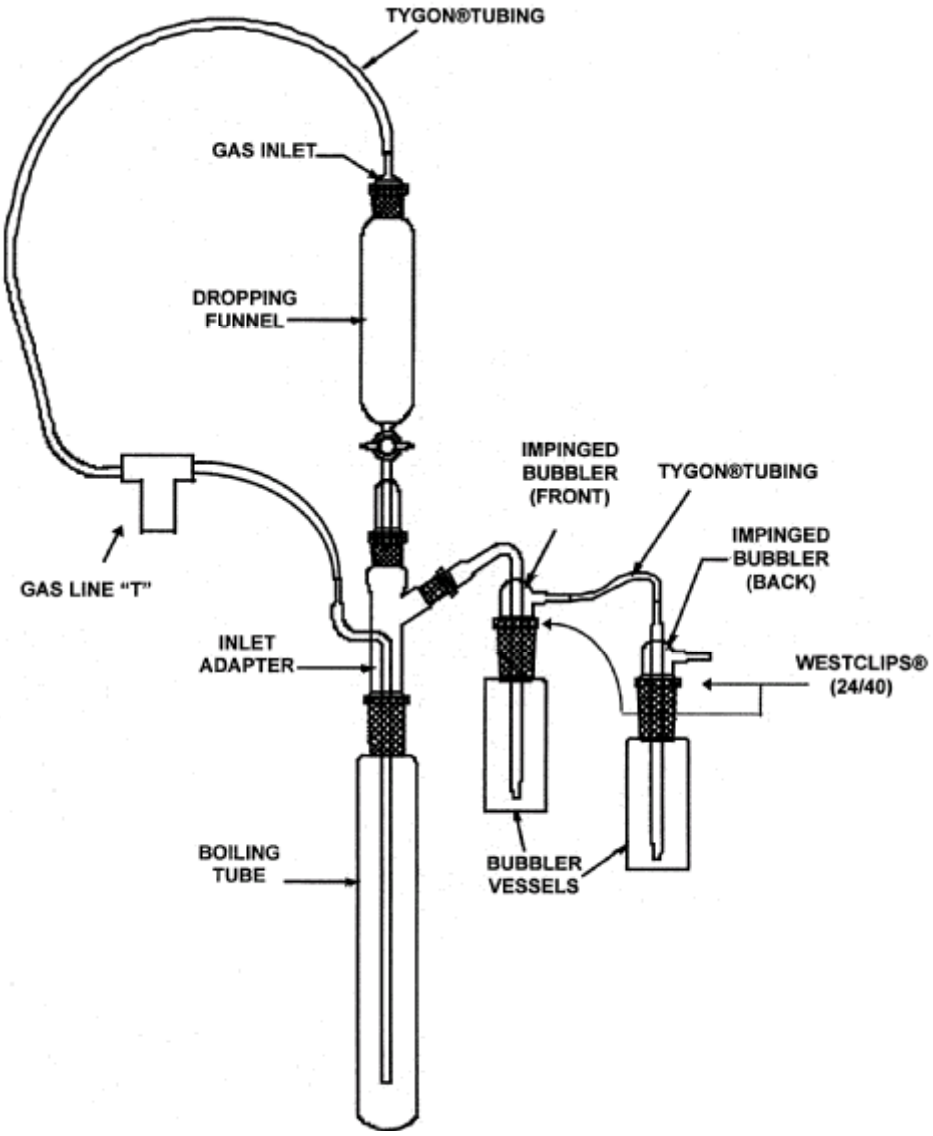


Figure 1 – Acid Volatile Sulfide generation apparatus.

EPA 8015B

DIESEL RANGE ORGANICS

1 SCOPE AND APPLICATION

1.1 This method is designed to measure the concentration of diesel range organics (DRO) in water and soil samples. This method should not be used to report hydrocarbon results in States where an alternative method has been mandated without approval from the regulatory authority.

Compound	CAS Number
DRO	Not Applicable

1.2 Instrumentation: HP 5890 Gas Chromatograph (GC) equipped with a flame ionization detector (FID) and a LEAP Technologies CTC A200S autosampler and Agilent Chemstation data acquisition software.

1.3 The method is primarily designed to measure mid-range petroleum products such as fuel oil. DRO corresponds to a hydrocarbon range of C_{10} - C_{28} and a boiling point range between approximately 170°C and 430°C. Hydrocarbons greater than C_{28} present in products such as motor oils or lubricating oils are also detectable under the conditions of this method. If, based on a review of the chromatogram, the presence of these heavier hydrocarbon products is noted, an additional analysis under different conditions may be necessary. An alternate analytical procedure is provided for heavier hydrocarbons.

1.4 Second column confirmation is not required for this method. If based on review of the chromatogram, it appears that it is likely that a major contribution to the DRO result is not a typical hydrocarbon pattern, a case narrative note should be made.

1.5 The estimated method detection limit (MDL) for DRO in sand and water is listed in Table 1. The detection limits given may vary based on sample size or sample matrix and/or regulatory requirements. The low standard, equal to 40 mg/kg for soil and 100 µg /L for water, is used as the reporting limit unless another reporting convention is required based on project or regulatory requirements.

1.6 Typical Demonstration of Capability (DOC) studies for sand and water are listed in Table 2.

1.7 This method is restricted to use by, or under the supervision of, analysts experienced in the use of a gas chromatograph and skilled in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2 SUMMARY OF METHOD

2.1 This method provides gas chromatographic conditions for the detection of semi-volatile petroleum fractions such as diesel, #2 fuel oil, or kerosene. Samples are extracted and injected into a capillary column gas chromatograph with FID. An alternate analytical approach is provided for heavier hydrocarbons such as motor oil or hydraulic oil.

2.2 Soil samples are dried with sodium sulfate and extracted with hexane. Water samples are extracted with hexane, solvent evaporated, and made to volume with hexane.

2.3 The extract is transferred to injection vials and analyzed by GC-FID.

3 DEFINITIONS AND ACRONYMS

3.1 There are many terms and acronyms used throughout this document. Check the definitions and acronyms sections of the Quality Manual for complete explanations.

4 INTERFERENCES

4.1 All materials including solvents, reagents, glassware and other sample processing materials must be demonstrated to be free from interferences under conditions of the analysis by analyzing method blanks. All glassware used to extract and analyze samples will be single use and disposable, which should eliminate typical glassware contamination problems associated with DRO analysis. However, even single use glassware may have potential interferences from the manufacturing and distribution process.

4.2 Because the FID is a “universal” detector there is a potential for many interferences, such as naturally occurring organics, fats, or phthalates. In most cases, prior site data will indicate that a potential problem may exist. Experienced analysts will aid the project in identifying interferences from true petroleum hydrocarbon results.

5 SAFETY

5.1 Employees must abide by the policies and procedures in the ECCS Chemical Hygiene Plan (CHP), and this document. Refer to the CHP for more detailed safety information or for information not listed in this document.

5.2 Eye protection that protects against splash and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled during this procedure. Lab coats are recommended.

5.3 Employees must handle glassware and equipment carefully in order to prevent injury and accidents. Any damaged or broken glassware is to be discarded or moved to the glass repair box.

5.4 ECCS maintains a Material Safety Data Sheet (MSDS) for every chemical used in the

laboratory. The MSDS file is kept in the main laboratory.

6 APPARATUS AND MATERIALS

6.1 Gas Chromatograph (GC)

6.1.1 Gas Chromatograph: HP5890
Autosampler: LEAP Technologies A200S
Detector: Flame Ionization
Injector: Split/splitless Injector
Data system: Agilent Chemstation Data Acquisition Software

6.1.2 Columns

6.1.2.1 Column 1: MXT-1, 30 m x 0.53 mm ID, 0.25 µm film thickness or equivalent

NOTE: This column is the preferred column for normal DRO analyses.

6.1.2.2 Column 2: MXT-1HT Sim Dist, 5 m x 0.53 mm ID, 0.1 µm film thickness or equivalent

NOTE: This column is the preferred column for heavier hydrocarbons such as motor oil or hydraulic fluids.

6.1.3 Injection hardware: Restek standard 4mm gooseneck liner and stainless steel cross seal.

6.2 Balances:

6.2.1 Top loader balance capable of weighting to 0.01 g

6.2.2 Analytical balance capable of weighting to 0.0001 g

6.3 Vials:

6.3.1 2 mL amber gas chromatograph injection vials with Teflon lined crimp seals

6.4 Bottles: 1000 ml amber glass bottles with Teflon lined screw caps

6.5 Volumetric flasks, various sizes

6.6 Pipettes, various sizes

6.7 Syringes: Gas-tight, various sizes

6.8 Disposable glass transfer pipettes and 2 mL rubber bulbs

6.9 Compressed Gas

6.9.1 Helium, Grade 5

6.9.2 Hydrogen, Grade 5

6.9.3 Air, standard

6.10 Refrigerator capable of maintaining 4 °C

6.11 Freezer capable of maintaining temperatures below -15 °C

7 REAGENTS

7.1 Solvents

7.1.1 Hexane

7.2 Solid Reagents – Not Applicable to this method

7.3 Acids and Bases

7.3.1 12 N Hydrochloric acid (HCl)

7.3.2 1:1 HCl

7.3.2.1 Add approximately 40 mL of de-ionized water to a 100 mL volumetric flask. Add 50 mL of 12 N HCl with a 50 mL pipette. Fill to the mark with de-ionized water, cap and mix. Fill to the mark again, mix, and transfer to a 100-mL bottle with LIMS label.

7.4 Stock Standards

7.4.1 Primary DRO stock standard (10 components) is purchased from Absolute Standards at certified solutions of 10,000 µg/mL for each of the 10 components (Part No. 91034).

7.4.2 Alternative stock standards such as fuel oil, motor oil, etc. can be utilized to accommodate specific project objectives.

7.5 Intermediate Standards – 5000 µg/mL total concentration

7.5.1 The intermediate DRO standard, each component at 500 µg/mL is prepared in a 50 mL volumetric flask by combining 5 mL of surrogate stock solution (7.7.2) with 2.5 mL of stock DRO solution (7.4.1) and bringing to the mark with hexane. The solution is documented in LIMS and transferred to LIMS labeled 40 mL VOA vials for refrigerated storage.

NOTE: The stock ampule(s) should be sonicated prior to use to insure the standard components are in solution.

7.5.2 If alternative standards are prepared for mixtures of hydrocarbons such as fuel oil or motor oil, the recommended concentration of intermediate standards is 2x or 10,000 µg/mL.

7.6 Calibration Standards

7.6.1 Calibration standards for DRO are prepared at seven concentrations 20, 50, 100, 200, 500, 1000, and 5000 µg/mL by serial dilution and use of the intermediate standard. See Table 6 for dilution scheme. The solutions are documented in LIMS and transferred to LIMS labeled 40 mL VOA vials for refrigerated storage.

7.7 Surrogate Spike

7.7.1 Surrogate stocks

7.7.1.1 Purchase neat n-nonane from Chem Service, Part No. F-1099

7.7.1.2 Purchase neat n-triacontane from Chem Service, Part No. O-2268.

7.7.2 Surrogate Spike Mix

7.7.2.1 Prepare the surrogate spike mix at 5,000 µg/mL by weighing 0.125 g of neat n-nonane and 0.125 g of n-triacontane into a 25 mL volumetric flask. Bring to the mark with hexane. The solution is documented in LIMS and transferred to LIMS labeled 40 mL VOA vials for refrigerated storage.

7.7.3 Concentrations and spiking volumes may be changed based on project specific goals and different final volumes. These changes must be documented.

7.8 Laboratory Control Sample (LCS) Spike

7.8.1 The LCS spike mix is the stock standard (7.4.1) at 10,000 µg/mL for each of the 10 components. For a final extract volume of 10 mL, spike with 50 µl for a nominal 100% DRO recovery of 500 µg/mL (each component 50 µg/mL).

7.9 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Spike

7.9.1 The MS/MSD spike mix is the stock standard (7.4.1) at 10,000 µg/mL for each of the 10 components. For a final extract volume of 10 mL, spike with 50 µl for a nominal 100% DRO recovery of 500 µg/mL (each component 50 µg/mL).

7.10 Second Source Calibration Standards

7.10.1 Second source DRO stock standards are purchased from Restek at certified solutions of 2,000 µg/mL for each of the 10 components (Part No. 31064).

7.10.2 Second source calibration check standard.

7.10.2.1 Prepare a second source calibration standard at 500 µg/mL total DRO. Using a gas tight syringe, aliquot 625 µL of second source stock (2,000 µg/mL) into a 25 mL volumetric flask. Dilute to volume with hexane. The solution is documented in LIMS and transferred to LIMS labeled 40 mL VOA vials for refrigerated storage.

7.11 Internal Standard – Not applicable to this method

8 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Water samples should be collected in 1 L amber glass bottles with Teflon lined caps containing 5 mL of 1:1 hydrochloric acid for preservation. Water samples must be extracted within 7 days of collection.

8.2 Soil samples should be collected in 4 ounce or larger amber glass jars with Teflon lined caps. Soil samples must be extracted within 14 days of collection.

8.3 All samples should be stored on ice or refrigerated at 4 °C immediately after collection. In the laboratory, store samples at 4 °C.

8.4 Extracts are stored in the freezer and must be analyzed within 40 days of extraction.

9 PROCEDURE

9.1 Water samples should be extracted in accordance with PRE-001, Separatory Funnel Extraction.

9.2 Soil samples should be extracted in accordance with PRE-003, Micro-scale Soil Extraction.

9.3 Water samples should be concentrated in accordance with PRE-001, Separatory Funnel Extraction. Soil sample extracts prepared in accordance with PRE-003, Micro-scale Soil Extraction, do not require concentration.

9.4 Clean-up and/or derivatization procedures do not apply to this method.

9.5 Instrument Conditions

9.5.1 MXT-1 Column (or equivalent)

Temperature Program	
Initial Temp:	55 °C
Initial Hold:	3 min
Initial Rate:	22 °C/min
Final Temp (1):	360 °C
Hold Time (1):	5 min
Injector Temp:	350 °C

Detector Temp:	380 °C
Carrier Gas:	Helium
Head Pressure:	~7 PSI
Make up Gas:	Helium
Flow Rate:	~30 mL/min
Oven Max	380° C
Splitless Valve	Splitless box not checked
On time	0.2 min
Off time	Initial value is off

9.5.2 MXT-1HT Sim Dist Column

Temperature Program	
Initial Temp:	60 °C
Initial Hold:	1 min
Initial Rate:	15 °C/min
Final Temp (1):	390 °C
Hold Time (1):	2.0 min
Injector Temp:	400 °C
Detector Temp:	400 °C
Carrier Gas:	Helium
Head Pressure:	~7 PSI
Make up Gas:	Helium
Flow Rate:	~30 mL/min
Oven Max	450° C
Splitless Valve	Splitless box not checked
On time	0.3 min
Off time	24.5 min

9.6 Preventive Maintenance

9.6.1 Routine maintenance consists of clipping the column, replacing the liner and seal, cleaning the hat, and installing a new septum.

9.6.2 Change the septum as needed based on age or number of injections that have been made on the GC. When operating continuously, change the septum daily.

9.6.3 Carryover on the GC is usually caused by a worn out injection syringe. When replacing the syringe, if a burr exists, use fine sandpaper to remove. Rinse the inside and outside of the syringe with hexane to remove any grit left in the syringe tip.

9.7 Calibration

9.7.1 For standard DRO analysis, prepare an initial calibration (ICAL) consisting of all six calibration standards; 20, 50,100, 200, 500, 1000, and 5000 µg/mL. Quantitation of DRO is performed by the external standard technique.

NOTE: For heavier hydrocarbons prepare a 5+ point calibration curve of the standard that best suits the data quality objective.

9.7.2 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph. The concentration of DRO in the sample is determined from a summation of the total response within the range of 0.1 minutes before the onset of elution of n-decane to 0.1 minutes after the end of the elution of n-octacosane using the initial calibration curve.

9.7.2.1 Integration should be baseline to baseline defined as a flat baseline parallel to the x-axis of the chromatogram that includes all responses within the retention time window. The optimal baseline placement would be a horizontal line drawn through the lowest point in the chromatogram. The lowest point is generally the baseline immediately after injection, but before the solvent elutes. A baseline hold integration event at approximately 0.7 minutes is generally used for a consistent and accurate baseline.

9.7.3 Regression

9.7.3.1 Plot the area summation against the concentration of the calibration standard using linear regression with a weighting factor of 1/concentration. The coefficient of determination (r^2) must be ≥0.990, which corresponds to a correlation coefficient of (r) of ≥0.995.

$$Y = AX^B \quad \text{or} \quad \ln Y = B \ln X + \ln A$$

Where: Y = area summation
X = Concentration in µg/mL
A = Constant
B = Exponent

9.7.4 Continuing calibration verification (CCV) The working calibration curve is verified on each working day by the injection of a 500 µg/mL CCV. If the response for any CCV varies from theory by more than ± 20%, a new calibration curve must be injected, and/or data is qualified.

$$Percent\ Difference = \frac{R2 - R1}{R1} \times 100$$

Where: R1 = Theoretical concentration.
R2 = Concentration from CCV.

9.8 Retention Time Windows

9.8.1 Retention times for the area summation and surrogates are obtained from the ICAL and used throughout the analytical run.

9.8.2 The surrogates are set as reference peaks. Retention windows for the surrogates are usually set as 0.06 minutes.

9.9 Sample Analysis

9.9.1 Set up the GC system using the conditions described in Section 9.5.1 or 9.5.2.

9.9.2 Samples are analyzed in a group referred to as an analysis sequence which is generated in LIMS to match the Chemstation data system sequence.

9.9.2.1 The initial calibration sequence will consist of a solvent blank followed by the ICAL standards, an initial calibration check standard (ICV), and the second source standard verification (SCV). Sample and quality control extracts are the added to the sequence interspersed with CCV standard every 10 injection and at the end of the run.

9.9.2.2 If a previous ICAL will be used, a new sequence is created in LIMS referencing that ICAL. The new sequence will consist of a solvent blank, an ICV, and a low level standard equal to or below the required reporting limit. Sample and quality control extracts are the added to the sequence interspersed with CCV standard every 10 injection and at the end of the run.

9.9.2.3 NOTE: The low level standard is analyzed to assure the previous ICAL is valid at the reporting limit.

9.9.3 Transfer an aliquot of each sample to 2 mL injection vials. Inject the samples and collect and process the data using the ChemStation data system.

9.9.4 Injection – Inject approximately 2 µL of each extract.

9.9.5 If any of the sample responses exceeds the theoretical value of the highest ICAL standard, dilute the extract and re-inject. Dilute the sample so expected concentration is in the upper half of the standard curve range.

9.9.6 Data Package Assembly and Review

9.9.6.1 The data package is to be assembled and reviewed in accordance with GEN-016, Data Review Procedures.

9.10 Calculations

9.10.1 The concentration of DRO in the sample extract is determined from the calibration curve in µg/ml through reverse extrapolation from the area summation

response in the sample using power regression. The concentration in µg/L or µg/kg is then calculated as follows:

9.10.1.1 Water Samples (µg/L)

$$Concentration\ (\mu g/L) = \frac{A_x \times D \times V_e}{V_s}$$

Where: A_x = Concentration of compound in the extract in µg/mL
D = Dilution factor, if applicable
V_e = Volume of extract in mL
V_s = Volume of sample extracted in Liters

9.10.1.2 Soil Samples (µg/kg)

$$Concentration\ (\mu g/g) = \frac{A_x \times D \times V_e}{W_s}$$

Where: A_x = Concentration of compound in the extract in µg/mL
D = Dilution factor, if applicable
V_e = Volume of extract in mL
W_s = Volume of sample extracted in kilograms

10 QUALITY CONTROL

10.1 Refer to Method 8000 for general quality control procedures for chromatography methods.

10.2 An analytical batch consists of 20 or fewer samples. Batch quality control samples should be analyzed with each set with the following frequency:

Blanks - One per 20 or fewer samples, minimum one per day
LCSs - One per 20 or fewer samples, minimum one per day
MS/MSDs - One MS/MSD per 20 or fewer samples, minimum one set per day

Note: If an MS/MSD cannot be prepared because of limited sample volume, a second LCS must be prepared.

10.3 Method blanks consist of an aliquot of laboratory reagent water or silica sand that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedure. If target analytes or interferences are present at concentrations that impact the analytical results for samples, the samples (including quality control samples) should be re-extracted or appropriately qualified in accordance with GEN-015, Qualification of Data.

10.4 LCSs consist of an aliquot of laboratory reagent water or silica sand spiked with the target analytes, prepared and processed simultaneously with and under the same conditions as samples through all steps of the analytical procedure. LCS control limits for precision and accuracy are established on at least a yearly basis through the use of at least 20 data points. Interim control limits are 70-130%. If the recovery of any of the target analytes is outside control limits, the samples (including quality control samples) should be re-extracted or appropriately qualified in accordance with GEN-015, Qualification of Data.

10.5 MS/MSD samples consist of duplicate aliquots of sample spiked with the target analytes, prepared and processed simultaneously with and under the same conditions as samples through all steps of the analytical procedure. MS/MSD control limits for precision and accuracy are established on at least a yearly basis through the use of at least 20 data points. MS/MSD control limits are advisory. Interim control limits are 60-140%. If the recovery or RPD of any of the target analytes is outside control limits, data should be appropriately qualified in accordance with GEN-015, Qualification of Data.

10.6 Initial calibration (ICAL) is performed using the internal/external standard technique by injecting a minimum of 5 of the available calibration standards. The lowest calibration point must be at or below the reporting limit. An acceptable calibration curve has a coefficient of determination (r^2) of 0.990 or greater.

10.7 The working calibration curve must be verified on each working day by the injection of one or more CCV standards. If the response for any analyte varies from the theoretical concentration by more than 20%, a new calibration curve must be prepared or data appropriately qualified in accordance with GEN-015, Qualification of Data.

10.8 Surrogates are added to every sample and QC sample. Surrogate control limits are generated on at least a yearly basis. Interim control limits are 60-140%. If a surrogate recovery is outside of control limits, the sample should be re-extracted and re-analyzed, if possible. If not, the data should be appropriately qualified in accordance with GEN-015, Qualification of Data.

10.9 A second source calibration verification standard must be analyzed with every initial calibration. The accepted limits are 70-130% for all analytes. If an SCV fails, immediate corrective action is required before proceeding with sample analysis. Affected data should be qualified according to GEN-015, Qualification of Data.

11 METHOD PERFORMANCE

11.1 Estimated MDLs for eight replicates of silica sand and water are listed in Table 1.

11.2 Performance data for four replicates of silica sand and water spiked at an LCS concentration are listed in Table 2.

12 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

12.1 Contingencies for out-of-control data should be evaluated on a case-by-case basis. A Corrective Action Form (CAF) must be completed for those times that acceptable QC results cannot be achieved. The CAF must be completed by the analyst and filed with the Quality Manager. Analytical results shall be qualified as necessary.

13 WASTE MANAGEMENT / POLLUTION PREVENTION

13.1 All waste will be disposed of in accordance with federal, state, and local regulations. This method has been prepared to minimize the waste produced and the potential for pollution of the environment. All ECCS employees shall follow this method and the guidance provided in the ECCS Health and Safety manual.

14 REFERENCES

14.1 Method 8015B, "Nonhalogenated Organics Using GC/FID," SW 846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, December 1996

14.2 "Modified DRO, Method for Determining Diesel Range Organics," Wisconsin DNR, September 1995.

TABLE 1

DRO MDLS
DB-1 COLUMN

WATER

Compound	Spike Conc. (µg/L)	Average (µg/L)	Average Rec (%)	Standard Deviation	RSD (%)	MDL (µg/L)
DRO	Not available when SOP was prepared.					

NOTES: [1] 10 component standard mix used as spike

SOIL

Compound	Spike Conc. (mg/kg)	Average (mg/kg)	Average Rec (%)	Standard Deviation	RSD (%)	MDL (mg/kg)
DRO	Not available when SOP was prepared.					

NOTES: [1] 10 component standard mix used as spike

TABLE 2

DEMONSTRATION OF CAPABILITY

WATER

Compound	Spike Conc. (µg/L)	Average (µg/L)	Average Rec (%)	Standard Deviation	RSD (%)	MDL (µg/L)
DRO [1]	Not available when SOP was prepared.					

NOTES: [1] 10 component standard mix used as spike

SOIL

Compound	Spike Conc. (mg/kg)	Average (mg/kg)	Average Rec (%)	Standard Deviation	RSD (%)	MDL (mg/kg)
DRO [1]	Not available when SOP was prepared.					

NOTES: [1] 10 component standard mix used as spike

TABLE 3

RETENTION TIMES

Compound	**MXT-1**
n-Nonane (Surr)	2.73
n-Decane	4.28
n-Octacosane	14.7
n-Triacontane (Surr)	15.19

TABLE 4

STOCK STANDARD SOLUTION CONCENTRATION

Compound	**Concentration (µg/mL)**
DRO[1]	100,000

NOTES: [1] 10 component standard mix (7.4.1)

TABLE 5

INTERMDEDIATE STANDARD CONCENTRATIONS

Compound	**Concentration (µg/mL)**
DRO[1]	5000

NOTES: [1] 10 component standard mix (7.5.1)

TABLE 6

INITIAL CALIBRATION CURVE PREPARATION

Concentration (µg/mL)

	L-1	**L-2**	**L-3**	**L-4**	**L-5**	**L-6**	**L-7**
DRO	20	50	100	200	500	1000	5000
Stock ID	L-4	L-5	Inter[1]	Inter[1]	Inter[1]	Inter[1]	See 6.5.1
Aliquot (mL)	5	5	1	2	5	10	N/A
Final Volume[2] (mL)	50	50	50	50	50	50	N/A

NOTES: [1] Intermediate 10 component stock standard (7.5.1)

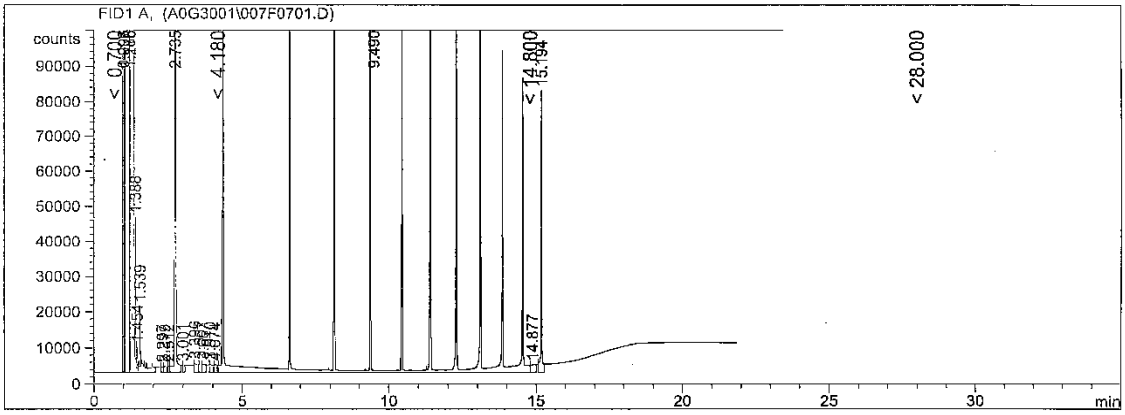
N/A – not applicable

FIGURE 1

EXAMPLE L-5 STANDARD CHROMATOGRAM – MXT-1 COLUMN

```
Data File C:\CHEM32\3\DATA\A0G3001\007F0701.D
Sample Name: A0G3001-CAL5
    ==========================================================================
    Acq. Operator    : cps                                Seq. Line :   7
    Acq. Instrument  : 3336A54843                          Location : Vial 7
    Injection Date   : 7/30/2010 6:14:33 PM                     Inj :   1
                                                          Inj Volume : Manually
    Acq. Method      : C:\CHEM32\3\DATA\073010\072910 2010-07-30 15-17-48\DRO1.M
    Last changed     : 7/30/2010 11:02:19 AM by CJM
    Analysis Method  : C:\CHEM32\3\METHODS\DROQ.M
    Last changed     : 8/3/2010 2:01:40 PM by cps
                       (modified after loading)
    Method Info      : DRO C9-C30, Nonane, Triacontane Surrogate

    ==========================================================================
```




```
    ==========================================================================
                          External Standard Report
    ==========================================================================

    Sorted By             :      Retention Time
    Calib. Data Modified  :      8/3/2010 2:03:34 PM
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A,

    RetTime Sig Type     Area      Amt/Area    Amount   Grp   Name
     [min]              counts*s                [ug/mL]
    -------|--|------|----------|----------|----------|--|---------------
      2.735  1 BB     2.78208e5  1.81707e-4   50.55246    Nonane
      9.490  1 BBA+   2.64366e6  1.82950e-4  483.65800    DRO
     15.194  1 BB     1.62175e5  3.09106e-4   50.12932    Triacontane

    Totals :                                  584.33978

    ==========================================================================
                             *** End of Report ***

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```

The signatures below indicate the following individuals have reviewed this document in its entirety and authorize its use to supersede prior revisions as of the effective date of this SOP.

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Chris Sauer, GC/MS Team Leader — Date: 02/18/11

Michael Linskens, Quality Manager — Date: 02/18/11

Approved By:

Nick Nigro, President — Date: 02/18/11

Title: Determination of Diesel Range Organics (DRO) and Petroleum Range Organics (PRO) [8015B, 8015C, 8015D, FL PRO, TN DRO, and Others]

Approvals (Signature/Date):

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Steve Wilhite Date	Stephanie Wilson Date
Technical Manager/Semivolatiles	Health & Safety Manager / Coordinator
Mandi Edwards 7/12/10	Susan Rembert 7/12/10
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Facility Distribution No. PS-GCS-010 **Distributed To: CONTROLLED SOPS**

Only Electronic Copies of this SOP are Controlled

1.0 Scope and Application

To provide the procedures necessary for the determination of Diesel Range Organics (DRO) and Petroleum Range Organics (PRO).

1.1 Analytes, Matrix(s), and Reporting Limits

This SOP applies to the analysis of a variety of matrices analyzed within the GC/Organic department. This method is designed to measure the concentration of diesel range organics in water and soil.

The method reporting limits for soils and waters are 2.5 mg/kg and 100 µg/L, respectively. Method detection limits (MDLs) for this method can be found in the laboratory Quality Assurance Manual (QAM).

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in the Quality Assurance Manual.

2.0 Summary of the Method

2.1 When no state requirements exist, this corresponds to an alkane range of C_{10}-C_{28} and a boiling point range between approximately 170°C and 480°C. This method provides an extraction procedure and the chromatographic conditions for the detection of fuel hydrocarbons in the carbon range of C_{10}-C_{28} or state-specified carbon range. A weighed amount of the solid matrix is extracted using methylene chloride as the extraction solvent. A measured volume of aqueous matrix is extracted with methylene chloride. Quantitative analysis is done using direct injection of 1.0 µl of sample extract into a gas chromatograph (GC). A temperature program is used in the GC to separate the organic compounds. Detection is achieved by a flame ionization detector (FID). Quantitation is performed by comparing the total chromatographic area between n-C_{10} and n-C_{28} (or state-specified carbon range), including resolved and unresolved components, to the response of a multi-component calibration standard. Otherwise, the following carbon ranges apply:

Table 1

State	Petroleum Range Organics	Diesel Range Organics
Alabama		Any recognized 8015 method
Arkansas		Any recognized 8015 method
Colorado		Any recognized 8015 method
Florida	C_8-C_{40} (FL PRO)	C_{10}-C_{28}
Illinois		C_{10}-C_{28}
Indiana		Any recognized 8015 method
Iowa		IDNR OA-2 (entire response integrated)
Louisiana		C_{10}-C_{28}
Kansas		Any recognized 8015 method
Massachusetts		MADEP EPH (see SOP PS-GCS-011)
Mississippi		C_{10}-C_{25}
New Jersey		C_{10}-C_{28}
North Carolina		Modified MADEP EPH (see SOP PS-GCS-011)
North Dakota		Any recognized 8015 method

State	Petroleum Range Organics	Diesel Range Organics
Ohio		compare to free product standard
Oklahoma		OK DRO (C_{10}-C_{28})
Oregon		C_{10}-C_{28}
Pennsylvania		C_{10}-C_{28}
Rhode Island		C_{10}-C_{28}
Tennessee		C_{12}-C_{40}
Texas	C_6-C_{10}, >C_{10}-C_{28}	C_{10}-C_{28}
Virginia		WI DNR modified DRO (C_{10}-C_{28})
West Virginia		C_{10}-C_{28}

2.2 The method is designed to measure mid-range petroleum products such as diesel or fuel oil. Components greater than C_{28} present in products such as motor oils or lubricating oils are detectable under the conditions of the method. If, based on a review of the chromatogram, the presence of these product types is suspected, additional efforts may be performed including, but not limited to, analysis of additional reference materials. These additional efforts are not contained in this SOP.

3.0 Definitions

3.1 Diesel Range Organics (DRO)**:** All chromatographic peaks eluting between decane (n-C_{10}) and octacosane (n-C_{28}). Quantitation is based on direct comparison of the area within this range to the total area of the 10-components in the Total Petroleum Hydrocarbon standard.

3.2 Petroleum Range Organics (PRO): All chromatographic peaks eluting between octane (n-C_8) and Tetracontane (n-C_{40}). Quantitation is based on direct comparison of the area within this range to the total area of the 17-components in the Total Petroleum Hydrocarbon standard.

3.3 Additional definitions and acronyms may be found in the QAM.

4.0 Interferences

Other organic compounds; including chlorinated hydrocarbons, phenols, and phthalate esters are measurable. As defined in the method, the DRO results include these compounds.

The flame ionization detector (FID) is a non-selective detector. There is a potential for many non-target compounds present in samples to interfere with this analysis.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document.

5.1 Specific Safety Concerns Or Requirements

The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in both the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Diesel Fuel	Flammable	N/A	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

Equipment maintenance is described in the manufacturer's manuals. All maintenance is documented per SOP PS-LAB-004 (Logbook Format, Review and Control).

Refer to the instrument operating manual for maintenance requirements and suggestions.

Refer to the QAM for the maintenance schedule.

6.1 Instrumentation

- Gas chromatograph HP 5890 flame ionization detector (FID).
- Computer with Enviroquant Software
- Gas chromatographic column and operating conditions for the instrument are:

  - Flash column RTX-5 capillary column or RTX-1 capillary column, 5 meters, 0.25 mm id, 0.25 µm film thickness.
  - Detector: flame ionization detector
  - Injection method: Splitless mode
  - Program temperature:
    Initial temperature = 45°C, hold = 20 seconds;
    Rate = 315°C/75 seconds, hold 270 seconds;
    Total run time 4.5 minutes.
  - Gas flows:

Hydrogen	= 30 ml/minute
Air	= 300 ml/minute
Slit (He)	= 100 ml/minute
Septum Sweep	= 5 ml/minute

  - Column pressure = 12 psi

6.2 Supplies

- 2000 ml separatory funnels
- Zymark Turbo Vap
- 1 ml Endpoint Tubes for use with Turbo Vap
- Spatula
- 4 and 8 ml glass vials
- Water bath
- Sonic disrupter
- 250 ml beakers
- Gas-tight syringes
- Autosampler vials – 1.8 ml
- Drying oven
- Mettler balance (top loader) - Calibration of balances is performed per SOP PS-QAD-016 (Calibration of Laboratory Balances and Laboratory Weights).

7.0 Reagents and Standards

All standards and surrogate solutions are prepared in methylene chloride and/or carbon disulfide. Standards are prepared, labeled, and stored in accordance with the guidelines in EPA SW846 Method 8000. NIST standards are used whenever available.

7.1 Methylene chloride - Pesticide quality

7.2 Carbon disulfide – low benzene

CAUTION

Carbon disulfide is extremely flammable. Vapor may cause a flash fire. Harmful if swallowed, inhaled, or absorbed through the skin. Causes eyes, skin, and respiratory tract irritation.

7.3 Sodium sulfate (Na_2SO_4) - granular, kiln dried

7.4 Reagent water: reagent water is defined as water free of analyte(s) of interest [i.e., analyte(s) of interest not observed at MDL] when employed in this procedure.

7.5 Silica Gel, 28 to 200 mesh, reagent grade 12 or equivalent (deactivated with 1 to 2% water).

7.6 Total petroleum hydrocarbon standard - A seventeen (C_8-C_{40}) component blend of typical petroleum components (Attachment 1) containing the even numbered carbons. This standard serves as a quantitation standard and a retention time window defining mix for diesel and petroleum range organics. Additional components that may be added include C_6, C_9, and C_{19}. If these are added it will alter the total amounts in each standard.

7.7 Fuel (Diesel) Standard - Diesel purchased from a local service station or obtained from the sample site or from a commercial standards vendor. Prepare the Fuel standard by weighing out 2500 mg of diesel into a 250 ml volumetric flask and dilute to volume with methylene chloride. This yields a 10000 μg/ml stock calibration standard.

7.8 Custom Florida TRPH standard

7.9 Surrogate standards - The surrogate standards ortho ter phenyl (OTP) and nonatriacontane (C_{39}) are purchased as neat compounds. Stock (intermediate) standards are made by diluting 1000 mg of OTP into 100 ml methylene chloride and 150 mg of C_{39} into 100 ml of carbon disulfide The resulting concentrations are 10000 μg/ml OTP and 1500 μg/ml C_{39}. A working standard is prepared by diluting both 6.25 ml of the stock OTP standard and 16.67 ml of the stock C_{39} standard into 250 ml of methylene chloride with 10-15% carbon disulfide to help keep the C_{39} in solution. This will produce a working standard with a 250 μg/ml concentration of OTP and 100 μg/ml concentration of C_{39}. If the surrogate is also to be used for North Carolina and Massachusetts EPH analyses, 1-Chlorooctadecane (COD) should be prepared and added the same way as the OTP.

7.10 The required working (calibration) standards and surrogate standards are prepared in the following proportions:

Optional C_6 (10000 μg/ml)	Optional C_9 (10000 μg/ml)	Optional C_{19} (10000 μg/ml)	TPH Standard (5000 μg/ml)	OTP Stock (10000 μg/ml)	COD Stock (10000 μg/ml)	C_{39} Stock (1500 μg/ml)	Final Conc.	Final Volume
1 ml	1 ml	1 ml	2 ml	1 ml	1 ml	6.67 ml	400 μg/ml	25 ml
0.5 ml	0.5 ml	0.5 ml	1 ml	0.5 ml	0.5 ml	3.33 ml	200 μg/ml	25 ml
1 ml	1 ml	1 ml	2 ml	1ml	1ml	6.67 ml	100 μg/ml	100 ml
0.125 ml	0.125 ml	0.125 ml	0.25 ml	0.125 ml	0.125 ml	0.83 ml	50 μg/ml	25 ml
0.05 ml	0.05 ml	0.05 ml	0.1 ml	0.05 ml	0.05 ml	0.333 ml	20 μg/ml	25 ml
0.0125 ml	0.0125 ml	0.0125 ml	0.025 ml	0.125 ml	0.125 ml	0.083 ml	5 μg/ml	25 ml

8.0 Sample Collection, Preservation, Shipment, and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Waters	Glass	1000 mLs	Cool 4 ± 2°C	7/40 Days	40 CFR Part 136.3
Soils	Glass	30 grams	Cool 4 ± 2°C	14/40 Days	N/A

[1] To Extraction/To Analysis.

Holding Times, Preservation and Container Requirements:
State DRO, PRO, - Aqueous

STATE	METHOD	CONTAINER	PRESERVATION Temp	PRESERVATION Chemical	HOLDING TIME
Florida	FL PRO	1 liter glass, Teflon cap	4°C	HCl or H_2SO_4 to pH < 2	Extraction 7 days Analysis 40 days
Iowa	Method for Determination of DRO	One liter glass, Teflon caps	4°C	None	Extraction 7 days Analysis 40 days
Kansas	Extractable Petroleum Products	1 liter glass, Teflon lid	4°C	None	Extraction 7 days Analysis 40 days
Kentucky	Methods for sample collection, sample preservation, chain of custody (COC), sampling equipment, decontamination procedures, sample containers, sample sizes, and maximum sample holding times shall be conducted according to 40 CFR 260.11, specifically, US EPA SW-846.				
Maine	Modified DRO	1 liter amber bottles, Teflon cap	4 ± 2°C	1:1 HCl or $NaHSO_4$ to pH < 2	7 days
Mississippi	Method for Determination of Diesel Hydrocarbons	1 liter glass, Teflon lid	4°C	None	Extraction 7 days Analysis 40 days
Montana	Method for Determination of DRO	1 liter glass containers	4°C	Acidified to pH 2	Extraction 7 days Analysis 40 days
New York	Petroleum Fingerprint Identification	1 liter glass mason jar, Teflon cap	4°C	None	Transport to lab within 24 hours
Oklahoma	DRO	1 liter amber, Teflon cap	4°C	5ml of 50% HCl	Extraction 7 days Analysis 40 days
Tennessee	Method of Determination of EPH by GC/FID	1 liter glass	4°C	Acid	Extract 7 days Analysis 40 days
Virginia	Refer to Wisconsin Methods				
Wisconsin	Modified DRO[1]	One liter amber glass, Teflon cap	4°C	5 ml 50% HCl at time of collection	Extraction 7 days Analysis 47 days

Key to Table
1. Acid can be added to bottle prior to adding sample. Samples from carbonate aquifers should be preserved with sodium azide or extracted unpreserved within 48 hours. These samples must be flagged on the COC

9.0 Quality Control

Please refer to the QAM for quality parameters not addressed in this SOP.

Refer to SOP PS-QAD-017 (Non-conforming Events) for corrective action procedures.

Quality Controls	Frequency	Control Limit	Corrective Action[5]
Method Blank (MB)	1 in 20 or fewer samples	< Rpt. Limit	MB > ½ the RL. Request re-extracts.
Laboratory Control Sample (LCS)/(LCSD)[1]	1 in 20 or fewer samples	Statistical Limits [4]	LCS is outside limits, request re-extract.
Matrix Spike (MS)[2]	1 in 20 or fewer samples	Statistical Limits [4]	
MS Duplicate (MSD)[2]	1 in 20 or fewer samples	Statistical Limits [4]	MS/MSD if the samples confirm flag the data and report. If they do not "match" re-extract.
Surrogates	every sample[3]	Statistical Limits [4]	Outside control limits high – 1) no hits = flag and report. Hits, request re-extracts. Low – request re-extract unless matrix interference is evident.

[1] LCS Duplicate (LCD) is required when MS/MSD is not available to determine precision.
[2] The sample selection for MS/MSD are randomly selected, unless specifically requested by a client.
[3] Analytical and QC samples (MB, LCS, MS/MSD)
[4] Statistical control limits are updated annually and are updated into LIMS.
[5] For a complete description of Corrective Actions refer to PS-QAD-017 (Non-conforming Events).

10.0 Procedures

10.1 Sample Preparation

- Aqueous matrices are extracted and concentrated using SOP PS-EXT-001 (Continuous Liquid-Liquid Extraction) or SOP PS-EXT-002 (Separatory Funnel Liquid-Liquid Extraction); however, the final concentrate volume is adjusted to 5 ml (2 ml final volume for FLPRO only, 1 ml final volume for OA-2 and Wisconsin).
- Solid matrices are extracted and concentrated using SOP PS-EXT-005 (Preparation of Soil/Sediment by Pulsed Sonication for the Analysis of Semivolatile Organic Compounds), but final concentrate volume is adjusted to 5 ml (2 ml final volume for FLPRO only, 1 ml final volume for OA-2 and Wisconsin).
- Silica Gel Cleanup (Mandatory for FLPRO analysis) - Add 0.3 g of loose silica gel to the extract and shake the mixture for five (5) minutes. Transfer cleaned extract to a labeled vial with a sealed Teflon-lined septum vial for analysis.

NOTE
When using loose silica gel, filter the extract through a plug of precleaned silanized glass wool in a disposable glass pipette or allow to settle and decant extract into appropriate vial.

10.2 Calibration (if state method does not specify) - External Standard Method

A calibration curve should be run initially or when a new column is put in place, major maintenance takes place, or if the CCV will not pass criteria. The initial calibration correlation coefficient must be **≥ 0.995** or meet relative standard deviation **(%RSD)** criteria (see 10.2.3) for 8015B in order to proceed with analysis.

10.2.1 Calibrate the GC with an initial six-point calibration using the TPH standards listed in section 7.10. See Attachment 3 for calibration point concentrations.

For 8015B, the initial calibration is generated using the diesel standard discussed in section 7.7. For all other DRO methods including FLPRO, the initial calibration curve is generated using the TPH standard.

10.2.3 Tabulate the concentration injected against the area response of the 10 components (C_{10}-C_{28}) for DRO and the 17 components (C_8-C_{40}) for FLPRO. If C_6, C_9 and/or C_{19} were added to the standards, the number of expected components will increase to include these. The ratio of the concentration injected to the area response, defined as the calibration factor (CF), can be calculated for the standard at each concentration. If the percent relative standard deviation (%RSD) is less the 25% over the working range, linearity through the origin can be assumed, and the average continuing calibration factor can be used in place of a calibration curve.

$$CF = \frac{\text{concentration of standard (mg/L)}}{\text{total area of TPH components}}$$

NOTE
For Iowa, 8015B %RSD must be less than 20%.

10.2.4 The working calibration factor or calibration curve must be verified on each working day by the injection of a continuing calibration verification standard - CCV (100 µg/ml mid-point). The CCV is run every 10 samples and followed by an instrument blank. If the response for this standard varies from the predicted response by more than ± 25% (or other as noted below), the CCV analysis must be repeated. Second exceedence requires initial calibration and/or corrective action.

$$\text{Percent difference (\%D)} = \frac{R_1 - R_2}{R_{avg}} \times 100$$

where:

R_1 = Average CF from the calibration curve
R_2 = Calibration Factor from CCV
$R_{avg} = (R_1 + R_2)/2$

NOTE
For El Paso work, 85%-115% will be used for continuing calibration checks for all GC methods.
For Iowa, the %D must not vary by more than ± 20%.

10.3 Sample Analysis

10.3.1 Retention Time Windows

Retention time (RT) windows are established for all compounds of interest. Retention time windows are calculated according to the procedure in SW846 method 8000B, section 7.6. The retention times of all analytes in all verification standards must fall within the absolute RT windows. If an analyte falls outside the RT window in a calibration verification standard, new absolute RT windows must be calculated, unless instrument maintenance corrects the problem.

- The TPH alkane standard is injected after the calibration curve and as frequently as needed throughout the run for retention time verification (RTV) of individual hydrocarbon ranges.

- Samples, blanks and QC samples are analyzed by GC/FID. Suggested injection volumes are 1.0 µl using the conditions established in section 7.9.

- If initial calibration has been performed, verify the calibration by analysis of a mid-point CC.

- The mid-point standard must also be analyzed every 10 injections and at the end of each sequence.

- A methylene chloride blank must be run in every sequence to determine the area generated on normal baseline bleed under the conditions prevailing in the 24 hour period. Methylene chloride blanks should also be run as needed after samples suspected of being highly concentrated to prevent carryover.

- If the product concentration exceeds the linear range of the method in the final extract, the extract must be diluted and reanalyzed.

11.0 Calculations and Data Reduction

The concentration of hydrocarbons in an extracted sample is calculated by using a total area sum between C_{10} and C_{28}. The area of the surrogate OTP is subtracted from the total sample when applicable.

11.1 Soil Samples

$$\text{Concentration (mg/kg)} = \frac{(CF)(V)(T)(d)}{(D)\ (\text{amount of soil extracted})}$$

11.2 Water Samples

$$\text{Concentration (mg/L)} = \frac{(CF)(T)(d)}{(C)}$$

Where: C = concentration factor, i.e., the volume of sample divided by the volume of the extract (ml).
CF = Calibration Factor
D = dry weight of soil sample (in kilograms)
d = dilution factor, if samples extract was diluted
T = total response area of sample

V = volume of sample extract (in liters)

11.3 Results are reported as ND (no detection) if the sample results are below the reporting limits described in section 1.1.

11.4 Linear regression: If this method is used, employ software to calculate sample results using the linear regression equations.

11.5 Enviroquant automatically calculates surrogate recovery.

$$\text{OTP \% Recovery} = \frac{\text{Amount of OTP in Sample}}{\text{250 (surr. Spiked into sample)}} \times 100$$

$$C_{39}\text{ \% Recovery} = \frac{\text{Amount of } C_{39} \text{ in Sample}}{\text{100 (surr. Spiked into sample)}} \times 100$$

11.6 QC calculations are discussed in the laboratory QAM.

11.7 Acceptance criteria is available in the laboratory LIMS and in the Quality Assurance Manual.

11.8 Calculations for calibration curves may be found in Corporate SOP CA-Q-S-005, Calibration Curves.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure of the QAM. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capabilities

Refer to the QA Manual for general procedures and specific concentrations that must be used. Also, reference SOP PS-QAD-021 (Demonstrations of Capability).

12.3 Training Requirements

The QA Manual or the Training SOP PS-LAB-014 (Training Program and Documentation) should be referenced for training requirements.

13.0 Data Reporting

- Iowa requires product type identification of common petroleum products.

14.0 Pollution Control

It is the laboratory's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to laboratory SOP PS-LAB-015 (Waste Handling and Disposal Practices).

The following waste streams are produced when this method is carried out.

- Solvent waste generated in the department is placed in a 4 liter satellite waste container labeled Organic Waste and stored in a secondary waste container. The containers are dumped in the Hazardous waste room in the Organic Solvent Waste Drum and recorded in the hazardous waste book.
- The samples vials are disposed of in the sample vial drum located in the hazardous waste room and the recorded in the hazardous waste book.
-

16.0 References / Cross-References

16.1 Florida DEP Method for Determination of Petroleum Range Organics (Method # FL-PRO).

16.2 The Mississippi Method for the Determination of Diesel Hydrocarbons.

16.3 Tennessee Department of Health and Environment's Analysis of Gasoline and Other Petroleum Products for Total Petroleum Hydrocarbons Using Gas Chromatography.

16.4 Virginia DEQ Petroleum Program Manual.

16.5 Modified DRO, Method for Determining Diesel Range Organics, Wisconsin DNR, September 1995.

16.6 Iowa DNR, OA-2, Method for Extractable Petroleum Products and Related Low Volatility Organic Compounds, Revision 7/27/93)

16.7 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996, Final Update IV, 2008. (8015B, 8015C, 8015D)

16.8 Standard Methods for the Examination of Water and Wastewater, 18th/19th /20th edition /Online; Eaton, A.D. Clesceri, L.S. Greenberg, A.E. Eds; American Water Works

Association, Water Pollution Control Federation, American Public Health Association: Washington, D.C.

16.9 Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, and Appendix A-C; 40 CFR Part 136, USEPA Office of Water. Revised as of July 1, 1995, Appendix A to Part 136 - Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (EPA 600 Series)

16.10 Laboratory Quality Assurance Manual, PS-QAM-001.

16.11 Laboratory SOP, PS-LAB-004 Logbook Format, Review and Control.

16.12 Laboratory SOP, PS-QAD-017 Non-conforming Events.

16.13 Laboratory SOP, PS-QAD-016 Calibration of Laboratory Balances and Laboratory Weights.

16.14 Laboratory SOP, PS-LAB-015 Waste Handling and Disposal Practices

16.15 Corporate SOP, CA-Q-S-001 Solvent and Acid Testing and Approval.

16.16 Corporate SOP, CA-Q-S-005 Calibration Curves.

16.17 Corporate SOP, CW-E-M-001 Corporate Environmental Health and Safety Manual.

17.0 Method Modifications

N/A

18.0 Attachments

Attachment 1: TPH Standard
Attachment 2: Acceptance criteria for QC Samples
Attachment 3: Total Amount of TPH in Standards
Attachment 4: El Paso Technical Requirements

19.0 Revision History

- Revision 0, dated 01/21/2008.
  - Add El Paso Technical Requirements

- Revision 1, dated 01/16/2009.
  - Updated State carbon ranges in Table 1
  - Revised layout to be consistent with TA Template Method SOP R1
  - Corrected typographical errors
  - Corrected internal and external references
  - Removed obsolete state references and requirements
  - Added caution note for Carbon disulfide

- Revision 2, dated 07/16/2010.
  - Added Holding Times, Preservation and Container Requirements: State DRO, PRO, - Aqueous to Section 8.

- Updated Reference Section 16

Attachment 1

TPH Standard

Component	Mid-point Concentration (mg/L)	Component	Mid-point Concentration (mg/L)
Octane	100	Hexacosane	100
Decane	100	Octacosane	100
Dodecane	100	Triacontane	100
Tetradecane	100	Dotriacontane	100
Hexadecane	100	Tetratriacontane	100
Octadecane	100	Hexatriacontane	100
Eicosane	100	Octatriacontane	100
Decosane	100	Tetracontane	100
Tetracosane	100		

Attachment 2

Acceptance criteria for QC Samples

01/27/00	FLPRO		8015/DRO-TNEPH		TX 1005	
	WATER	SOIL	WATER	SOIL	WATER	SOIL
RL (ppb)	100	2500	100	2500	5000	50000
SPK TV (ppb)	3400	113333	10,000	333,333		
LCS CLs (%)	41-133	50-124	55-142	56-152	70-130	70-130
MS/D CLs (%)	41-101	11-154	21-144	36-156	70-130	70-130
MS/D RPD CLs (%)	20	50	33	40	30	30
OTP CLs (%)	49-143	50-121	65-144	68-141	50-150	50-150
C39 CLs (%)	20-176	37-138				

01/27/00	NC/MA TPH (C19-C36)		NC/MA TPH (C9-C18)		NC/MA PAH (C11-C22)	
	WATER	SOIL	WATER	SOIL	WATER	SOIL
RL (ppb)	50	1,600	50	1,600	50	1,600
SPK TV (ppb)	100	3,333	150	5,000	250	8,333
LCS CLs (%)	40-140	40-140	40-140	40-140	40-140	40-140
LCS CLs (ppb)	40-140	1,333-4,667	60-210	2,000-7,000	60-210	2,000-7000
MS/D CLs (%)	40-140	40-140	40-140	40-140	40-140	40-140
MS/D CLs (ppb)	40-140	1,333-4,667	60-210	2,000-7,000	60-210	2,000-7000
MS/D RPD CLs (%)	50	50	50	50	50	50
MS/D RPD CLs (ppb)	50	1,667	75	2,500	75	2,500
OTP TV (ug/ml)					125	125
OTP CLs (%)					40-140	40-140
OTP CLs (ug/ml)					50-175	50-175
COD TV (ug/ml)	125	125	125	125		
COD CLs (%)	40-140	40-140	40-140	40-140		
COD CLs (ug/ml)	50-175	50-175	50-175	50-175		
FBP TV (ug/ml)					100	100
FBP CLs (%)					40-140	40-140
FBP CLs (ug/ml)					40-140	40-140
2BN TV (ug/ml)					100	100
2BN CLS (%)					40-140	40-140
2BN CLS (ug/ml)					40-140	40-140

Attachment 3

Total Amount of TPH in Standards

#Peaks	calibration point concentrations (ppm/peak)					
1	5	20	50	100	200	400
2	10	40	100	200	400	800
3	15	60	150	300	600	1200
4	20	80	200	400	800	1600
5	25	100	250	500	1000	2000
6	30	120	300	600	1200	2400
7	35	140	350	700	1400	2800
8	40	160	400	800	1600	3200
9	45	180	450	900	1800	3600
10	50	200	500	1000	2000	4000
11	55	220	550	1100	2200	4400
12	60	240	600	1200	2400	4800
13	65	260	650	1300	2600	5200
14	70	280	700	1400	2800	5600
15	75	300	750	1500	3000	6000
16	80	320	800	1600	3200	6400
17	85	340	850	1700	3400	6800
18	90	360	900	1800	3600	7200
19	95	380	950	1900	3800	7600
20	100	400	1000	2000	4000	8000

Attachment 4

El Paso GC Semivolatile TPH Tech Requirements

General

Dual column/detector confirmation not required for VOA or GRO
Ret Time Window reset only once per 24hr.

QC Requirements

LCS

All targets must pass LCS (If LCSD, all targets must pass both LCS and LCSD) Contact PM if no extra volume for re-analysis

- Ok to report if LCS high and sample ND
- Re-analyze LCS only once; if fail again re-prep/analyze samples if in hold
- Re-analyze for all low LCS

Surrogate

Re-analyze for any Surr failure

- Unless MS/MSD out on Elpaso sample, or
- Surr high and sample ND, or
- Obvious, documentable matrix interference….
- If re-analysis ok and in hold, report re-analysis only
- If re-analysis also fails or is run out of hold; report both runs

Blanks

Blank Criteria →

- no hit above RL; Surr pass
- hit ok if ND in sample or if sample hit > 10x blank hit
- can re-analyze blank once; if still hit re-prep/analyze samples (with same hit) if in hold
- If samples out of hold or if re-prep/analysis still has blank hit, report original analysis and notify PM

Instrument Blanks OK, but cannot use only before CCV.

Matrix Spikes

MS/MSD failure ok if LCS good; NCM probable matrix interference
Spike Elpaso if >10 samples in Batch

Calibration

IC RSD ≤ 20% for avg RF
Linear R ≥ 0.99; Quadratic R^2 ≥ 0.99; force thru 0; cannot use 0 as point
Cannot use Grand Mean
CCV/ICV ≤ 15%D
CCV every 10 samples

- Reanalyze samples bracketed by failing CCV

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Isotope Dilution Analysis of Selected Semivolatile Organic Compounds and Alkylated PAHs by Gas Chromatography/Mass Spectrometry - Selected Ion Monitoring (GC/MS-SIM)

(SUPERSEDES: KNOX-ID-0016, Rev. 7)

Prepared By: _____

Reviewed By: _____
Technical Specialist

Approved By: _____ 08/19/10
Quality Assurance Manager

Approved By: _____ 8-17-10
Environmental, Health and Safety Coordinator

Approved By: _____ 8-19-10
Laboratory Director

1. Scope and Application

1.1. This procedure is used for the determination of selected semivolatile organic compounds and alkylated polynuclear aromatic hydrocarbons (PAHs) in water, soil, sediment, sludge, tissue, emissions from stationary sources and other sample matrices.

1.2. The individual compounds and homologue groups listed in Table 1 may be determined by this procedure.

1.3. The standard reporting limits for this method are approximately 10 ng/L for aqueous samples, 1 ng/g for soil/sediment/tissue samples, and 10 ng/g for air (XAD & filter) samples. Some analytes have higher reporting limits (refer to Table 1). Reporting limits will be proportionately higher for samples and extracts that require dilution.

1.4. This procedure is written for use by analysts who are experienced with residue analysis and skilled in GC/MS SIM.

1.5. Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PAHs and other target compounds. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2. Summary of Method

2.1. This procedure uses capillary column gas chromatography/mass spectrometry (GC/MS) techniques. The mass spectrometer is operated in the selected ion monitoring (SIM) mode.

2.2. Samples are spiked with a solution of known amounts of the isotopically labeled internal standards listed in Table 4. The samples are then extracted using matrix specific extraction and cleanup techniques. The final extract is prepared by adding a known amount of the labeled recovery standard and concentrating to the final volume.

2.3. An aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a mass spectrometer.

2.4. The identification of the target compounds is based on their retention time relative to the labeled internal standards as established during routine calibration and the simultaneous detection of a quantitation and confirmation ion.

2.5. Quantitation of the target compounds is based on their relative response to the internal standards. A multipoint calibration is performed to establish mean response factors for the target analytes. Alkylated homologues are quantitated on the basis of response factors of the parent PAH. The instrument performance is routinely checked by the analysis of continuing calibration standards. Method performance is demonstrated by the analysis of method blanks and laboratory control samples (LCS), as well as an initial demonstration of capability.

3. Definitions

3.1. Alternate Surrogate Standard - A labeled compound which is used in 2 cases: (1) It is added to source air impinger contents prior to extraction to estimate the extraction efficiency for PAHs and other target compounds in the impinger sample. It is only used when the impinger extract is to be combined with the XAD sample extract prior to analysis. (2) It is added to the second liter of aqueous sample when the extracts from two separatory funnel extractions are to be combined for analysis.

3.2. Continuing Windowing Standard (Win) – A dilute mixture of coal tar and crude oils, selected for light, medium and heavy molecular weight distributions. This standard is used to verify and update the retention times of the characteristic peaks of PAH homologue groups (e.g., C2 Alkylnaphthalenes and C3 Alkylnaphthalenes). The solution is analyzed at the beginning of each shift during which homologue data is to be acquired.

3.3. Data Acquisition Parameters – Parameters affecting the scanning operation and conversion of the analytical signal to digitized data files. These include the configuration of the ADC circuitry, the ion dwell time, the MID cycle time, and acquisition modes set up for the method. Examples of acquisition modes for the MS include SIM mode, and Low Mass Resolution mode.

3.4. Labeled Internal Standards - Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the sample before extraction and are used to calculate the concentration of the target analytes.

3.5. Recovery Standard - Labeled compounds which are added to every sample, blank, and quality control spike sample extract prior to analysis. They are used to measure the recovery of the internal standards and the alternate surrogate standard.

3.6. Sampling Surrogate Standard - A labeled compound added in a known amount to the XAD-2 resin of the sampling train, and allowed to equilibrate with the matrix before sampling is performed. The sampling surrogate standard has to be a component that can be completely resolved, is not present in the sample, and does not have any interference effects. Its measured concentration in the extract is an indication of how effectively the sampling train retains the target compounds collected on the XAD-2 resin. The recovery of the sampling surrogate standards in the field blanks can be used to determine whether there are any matrix effects caused by time or conditions under which the sample is transported and stored prior to analysis.

3.7. Additional definitions can be found in the TestAmerica Knoxville QAM glossary.

4. Interferences

4.1. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of analysis by performing laboratory method

blanks. Analysts should avoid using PVC gloves, powdered gloves, or gloves with measurable levels of phthalates.

4.2. The use of high purity reagents and solvents helps minimize interference problems.

4.3. Transformation of PAHs and the formation of artifacts can occur in the sampling train. PAH degradation and transformation on sampling train filters have been demonstrated. Certain reactive PAHs such as benzo(a)pyrene, benz(a)anthracene, and fluoranthene when trapped on filters can readily react in corrosive matrices. These PAHs are transformed by reaction with low levels of nitric acid and higher levels of nitrogen oxides, ozone, and sulfur oxides.

4.4. Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.5. Non-target interferences may cause peaks on selected ion current profiles (SICPs) intended for PAHs and their alkylated homologues. Pattern recognition must be employed for identifying interfering peaks that should not be considered for the homologue or target PAH under consideration. Analysts should be intimately familiar with both parent and alkyl PAH analyses in complex environmental samples. This procedure is particularly important for newer operators. See Figure 3 for chromatograms for identifying alkyl PAHs.

4.6. Atmospheric contamination can cause significant background peaks, especially for lower molecular weight parent and alkyl PAHs. The source of contamination can be significant in areas containing atmospheric PAHs (e.g., from diesel exhaust). Quality control requirements for the blank and appropriately qualifying the data are discussed in section 9.3.

5. Safety

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. Safety Concerns or Requirements.

5.2.1. The preparation of all standards and reagents, and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.2.2. The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or pass through an appropriate filter.

5.2.3. Training: Workers must complete the new employee Corporate Safety Manual safety orientation prior to working in the laboratory.

5.2.4. Personal Hygiene: Thoroughly washing of hands and forearms is recommended after each manipulation and before breaks.

5.2.5. Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

5.2.6. Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE:** This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	**Hazards**	**Exposure Limit[1]**	**Signs and symptoms of exposure**
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable, Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause light-headedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Isooctane	Flammable, Toxic, Irritant	None Established	Inhalation of vapors may cause respiratory tract irritation. Overexposure may cause drowsiness and dizziness. Toxic if absorbed through skin. May cause skin irritation. May cause eye irritation. May be harmful if swallowed.
Methylene Chloride	Carcinogen, Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3.1. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include the following PAHs: benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

5.4. Exposure to chemicals will be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. All work must be stopped in the event of a known or potential compromise to the health or safety laboratory personnel. The situation must be reported immediately to a laboratory supervisor.

5.6. The autosampler, gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.7. The mass spectrometer is under high vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.8. There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off or disconnect it from its source of power.

6. Equipment and Supplies

6.1. Gas Chromatograph/Mass Spectrometer (GC/MS) System – Analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, autosampler, analytical columns, and gases. The GC capillary column is directly coupled to the MS source.

6.2. GC column - 30m x 0.25mm ID x 25µm film thickness. RTX-5MS with Integra-guard fused silica capillary column, or equivalent.

6.3. Mass Spectrometer - Electron impact ionization with the filament eVs optimized for best instrument sensitivity, stability and signal to noise ratio, shall be capable of repetitively selectively monitoring 20 exact masses minimum during a period of approximately 1 second.

6.4. Data System - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. Target™ software is used and can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). This software allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended

6.5. Carrier gas - Ultra high purity helium.

6.6. Volumetric flask (class A) of appropriate sizes with ground-glass stoppers.

6.7. Balance capable of weighing 0.0001g.

6.8. Syringe: various sizes, Hamilton Laboratory grade syringes or equivalent.

6.9. Glass bottles with PTFE-lined screw caps or crimp tops.

7. Reagents and Standards

7.1. Acetone, pesticide quality, or equivalent.

7.2. Methylene chloride, pesticide quality, or equivalent.

7.3. Hexane, pesticide quality, or equivalent.

7.4. Isooctane, pesticide quality, or equivalent.

7.5. Perfluorotributylamine (FC-43) is used in neat form to tune and calibrate the mass spectrometer. Scientific Instruments Services Catalog No. FC-43-100, or equivalent.

7.6. Standards and Calibration Solutions: Obtained as individual solutions and prepared solutions from Cambridge Isotope Laboratories (CIL), Cerilliant, Accustandard, Supelco or equivalent. Refer to Table 4 for details.

7.6.1. Refer to SOP KNOX-QA-0001, "Standard/Reagent Labeling and Documentation", current revision, for guidance on standard documentation and labeling.

7.6.2. Initial Calibration Standards: CS1-CS7. See Table 3 for a complete list of compounds and their concentrations. Solutions are prepared with hexane as the solvent.

7.6.3. Initial Calibration Verification Standard (ICV): A second source calibration standard different from that used to prepare the initial calibration. A 0.5 µg/mL solution is prepared and combined with internal standard stock solutions in order to prepare a second source standard (the same concentration as a CS4 standard; see Table 3).

7.6.4. Continuing Windowing Standard:

7.6.4.1. The Crude Oil Intermediate solution is prepared by weighing 2.5 g of stock crude oil into 100 mL of hexane (final conc. = 25,000 µg/mL).

7.6.4.2. The Coal Tar Intermediate solution (stock solution = 20% coal tar in 83% alcohol/5%Polysorbate-80) is prepared by taking a known amount of solution and concentrating on a water bath/nitrogen stream to remove as much alcohol as possible, then bringing back to volume with isooctane. A 2 % solution (20,000 µg/mL) is then prepared by diluting a portion with isooctane.

7.6.4.3. 10 mL of each of these are put through a silica gel clean-up and brought back to volume with hexane.

7.6.4.4. The Alkyl Window Spiking solution is prepared by combining 100 µL of the 25,000 µg/mL crude oil stock and 100 µL of the 20,000 µg/mL coal tar stock into 1 mL of hexane. The final

concentration of the crude oil and the coal tar is 2,500 µg/mL and 2,000 µg/mL, respectively.

7.6.5. LCS Spiking Solutions: See Table 4 for a complete list of compounds and their concentrations. Solutions are prepared with acetone as the solvent.

7.6.6. Internal Standard Spiking Solutions: See Table 4 for a complete list of compounds and their concentrations. Solutions are prepared with acetone as the solvent.

7.6.7. Recovery Standard Spiking Solution: See Table 4 for a complete list of compounds and their concentrations. Solution is prepared with hexane as the solvent.

7.6.8. Alternate Surrogate Standard Spiking Solution: See Table 4 for a complete list of compounds and their concentrations. Solution is prepared with acetone as the solvent.

7.6.9. Sampling Surrogate Standard Spiking Solution: See Table 4 for a complete list of compounds and their concentrations. Solution is prepared with hexane as the solvent.

7.6.10. Stability of Solutions: Sealed standard solutions used for quantitative purposes expire 3 years from the date received or on the manufacturer's expiration date, unless otherwise specified by program requirements. Lab prepared stock solutions expire 2 years after preparation; lab prepared spiking solutions expire 1 year after preparation. No daughter solution expiration date can exceed the parent expiration date. Standards are stored at 6^{o}C or less, or per manufacturer's recommendation.

7.6.11. Since the alkyl window standard is used for qualitative purposes only, the coal tar and crude oil stock materials and intermediate solutions have no expiration date. The alkyl window spiking solution expires 1 year after preparation. If degradation of any alkyl window pattern is observed, a new spiking solution is to be prepared. If degradation is still observed, a new intermediate solution is to be prepared.

8. Sample Collection, Preservation and Storage

8.1. Sampling is not performed for this method by TestAmerica Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, "Sample Receipt and Log In", current revision.

8.2. All extracts must be analyzed within 40 days from the start of extraction.

8.3. Store extracts in the dark at 4±2°C.

8.4. Sample holding times:

8.4.1. Solid samples have a 14 day holding time from collection to extraction. Water samples have a 7 day holding time from extraction to extraction.

Tissue samples have a 1 year holding time from collection to extraction. Air samples collected using method CARB 429 have a 21 day holding time from collection to extraction, whereas, air samples collected using SW-846 method 0010 have a 14 day holding time from collection to extraction.

9. Quality Control

9.1. Initial Demonstration of Capability and Method Detection Limit Studies: For the standard analyte list (Table 1), the initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin. Refer to Table 7 for the initial demonstration of capability acceptance criteria.

9.2. Internal standards are spiked into all samples, blanks, and LCS (LCSD and MS/MSD, if requested) to assess method performance on the sample matrix.

9.2.1. See Table 7 for the acceptance criteria for the recoveries of the internal standards and spiked compounds in field samples, method blanks, and other QC samples.

9.2.2. The isotope dilution technique assumes that results are independent of internal standard recovery (i.e., the target analyte is expected to behave similarly to the internal standard, thus the quantitation of the target analyte should not be impacted by the recovery of the internal standard).

9.2.3. If the recovery of any internal standard is not within the specified limits, one or more of the following steps may be useful in diagnosing the problem and determining the impact to the data:

9.2.3.1. Determine if the outlying recoveries are associated with a pattern, such as 1) an association of the outliers with a specific recovery standard or 2) a trend of low bias early in the chromatogram.

9.2.3.2. Verify that the selection and integration of the recovery standard and the internal standard is appropriate.

9.2.3.3. Verify that the calculations are correct.

9.2.3.4. Inspect the extract volume for discrepancies. Inspect the extraction notes for problems encountered during extraction.

9.2.3.5. Verify that the instrument sensitivity and retention time has not been compromised. Inspect the area counts of the recovery standards for diagnosis. An acceptable bracketing analysis may be used to determine that the instrument was in control and only that specific analysis is suspect.

9.2.3.6. If matrix interference is suspected, a dilution to reduce the matrix effect may be warranted.

9.2.3.7. High internal standard recovery may indicate matrix interferences on the internal standard or a suppression of the recovery standard.

9.2.3.8. Low internal standard recovery may also indicate matrix interferences on the internal standard, or a high recovery of the recovery standard. If a low internal standard recovery is determined to be due to a loss of instrument sensitivity, the impact on the ability to support the reporting limit should be considered.

9.2.3.9. If the poor internal standard recovery is judged to be a result of sample matrix interferences, a reduced portion of the sample may be re-extracted or additional cleanups may be employed.

9.2.4. If it has been determined that the data has been impacted due to the recovery of the internal standard being outside limits, reanalysis at a dilution or a re-extraction of the sample should be performed

9.2.5. If it has been determined that the data has not been impacted, generate a nonconformance memo and discuss the situation in the case narrative. This should be done in consultation with the client.

9.3. Method Blank: A method blank must be extracted with each extraction batch of 20 or fewer samples. The method blank (or an instrument blank) must be analyzed before the samples and must not contain any of the compounds of interest at a concentration above the reporting limit or 10 percent of the analyte concentration in the field samples.

9.3.1. Samples associated with a contaminated method blank must be re-extracted and reanalyzed with an acceptable method blank. The project manager may consult the client to determine project needs. If the client prefers that the original data be reported, the associated data may be reported in lieu of reanalysis. A nonconformance memo and narrative addressing the analytical issues must be generated.

9.3.2. If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.4. A laboratory control sample (LCS) is extracted and analyzed along with each extraction batch of 20 or fewer samples. LCS spike components, and control limits are listed in Table 7.

9.4.1. If any LCS compounds of interest are calculated outside the control limits, the associated samples must be re-extracted and reanalyzed with a compliant LCS. (Refer to QA-003 for additional guidance.) The project manager may consult the client to determine project needs. If the client prefers that the original data be reported, the associated data may be reported in lieu of reanalysis. A nonconformance memo and narrative

addressing the analytical issues must be generated.

9.5. Client-specified matrix spike / matrix spike duplicate samples may be analyzed to provide additional precision and accuracy data.

9.6. Nonconformance and Corrective Action: Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the QA Manager.

9.7. Quality Assurance Summaries: Certain clients or regulatory programs may require specific project or program QC that may supersede these method requirements. Quality Assurance Summaries are developed to address these requirements.

10. Calibration and Standardization

10.1. Refer to CA-Q-S-002, current revision, Acceptable Manual Integration Practices and the TestAmerica Knoxville attachment for information on manual integration practices and documentation requirements.

10.2. Setup the autosampler, GC/MS, and establish the instrument operating conditions. Example GC/MS instrument conditions are shown in Figure 1.

10.3. Tune the mass spectrometer as needed using perfluorotributylamine (PFTBA) and the instrument data system autotune program. Select the DFTPP tune optimization profile for the autotune program.

10.4. Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by the results of continuing calibration procedures described below. The other type, continuing calibration, consists of analyzing the calibration solution (CS4). No samples are to be analyzed until acceptable initial and continuing calibrations are demonstrated and documented.

10.5. Setup the MS to acquire data in MID mode. Setup MID descriptors using the masses listed in Table 6.

10.5.1. Prior to analyzing initial calibration standards for the first time and afterwards as needed, analyze the Continuing Alkyl Window standard and CS4 standard in full scan mode to determine the elution retention time window of the target alkyl PAH groups and target parent analytes.

10.5.2. Use the retention times from the full scan analyses to set the MID switchpoints so that the target analytes and alkyl PAH retention time windows fall within their respective MID groups.

10.6. Initial Calibration

10.6.1. Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 3.

10.6.2. The 12-hour time period begins at the moment of injection of the first

calibration analysis that is used to demonstrate the linearity. The time period ends when 12 hours has elapsed according to the system clock. Analysis may proceed until 12 hours from the injection of the calibration have passed.

10.6.3. Analyze 1µL of each of the seven calibration standards and calculate the relative response factor (RRF) of each analyte vs. the appropriate internal standard and each internal standard vs. the appropriate recovery standard listed in Table 5 using the following equation:

$$RRF = \frac{As \times Cis}{Ais \times Cs}$$

Where:

As = area of the quantitation ion of the compound of interest.
Ais = area of the quantitation ion of the appropriate reference standard.
Cis = concentration of the appropriate reference standard.
Cs = concentration of the compound of interest.

NOTE: Alkylated PAH homologues are assigned the RRF calculated for the parent PAH. See table 8 for parent response factor assignment for the alkylated homologues.

10.6.4. Calculate the mean relative response factor and the standard deviation of the relative response factors for each calibration standard solution using the following equations:

$$\overline{RRF} = \frac{1}{n}\sum_{i=1}^{n}(RRF)_i$$

Where:

RRF_i = RRF calculated for calibration solution "i" using the equation in section 10.6.3.
n = The number of calibration points in the curve.

$$\%RSD = \frac{SD}{\overline{RRF}} \times 100$$

Where:

$\overline{RRF}$ = Mean relative response factor calculated above.
SD = the sample standard deviation of the relative response factors used to calculate the mean RRF.

$$SD = \sqrt{\sum_{i=1}^{N}\frac{\left(RFi - \overline{RF}\right)^2}{N-1}}$$

Where:

RFi = RF for each of the calibration levels.

N = Number of RF values.

10.6.5. Criteria for Acceptable Calibration - The percent relative standard deviation (%RSD) for the mean relative response factors for both the target analytes and the internal standards must not exceed 30 percent.

10.6.5.1. If acceptable initial calibration is not achieved, identify the root cause, perform corrective action, and repeat the initial calibration. If the root cause can be traced to an abnormal disruption of an individual acquisition (e.g., low injection volume or the instrument inadvertently loses communication during elution), repeat the individual analysis and recalculate the percent relative standard deviation. (See the current revision of P-T-001, "Selection of Calibration Points".) If the calibration is acceptable, document the problem and proceed; otherwise repeat the initial calibration.

10.6.6. Initial Calibration Verification Standard (2nd source standard)

Prepare the ICV as described in section 7.6.3. The ICV must contain all the target analytes analyzed in the initial calibration.

Analyze 1µL of the ICV standard under the same conditions as the initial calibration. Calculate the concentration of the ICV using the average RRFs from the initial calibration. Calculate the percent recovery (%R) between the expected and the calculated ICV concentration. The %R must not exceed ± 30% (see Table 7).

10.7. Continuing Calibration

10.7.1. Continuing calibration is performed at the beginning of a 12-hour period. The 12-hour time period begins at the moment of injection of the continuing calibration standard (CCAL). The time period ends when 12 hours has elapsed according to the system clock. Analyses may proceed until 12 hours from the injection of the CCAL have passed. A sample injected less than 12 hours after the CCAL is acceptable.

10.7.2. Analyze 1µL of the CS4 continuing calibration standard (see Table 3). Use the same data acquisition parameters as those used during the initial calibration. Check for GC resolution and peak shape.

10.7.3. If total homologues are to be acquired during the analytical shift, analyze 1µL of the Continuing Alkyl Windowing Standard Solution (section 7.6.4). Use the same data acquisition parameters as those used during the continuing calibration.

Examine and identify the presence of first and last peaks for the isomers of any total homologues to be quantified during the shift. Representative selected ion chromatograms for alkyl PAH windows are shown in Figure 3.

10.7.4. Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met at the beginning of each 12 hour period during which samples are analyzed. If continuing calibration criteria are not met, identify the root cause, perform corrective action and repeat the continuing calibration. If the second consecutive continuing calibration does not meet acceptance criteria, additional corrective action must be performed. Acceptable performance must be demonstrated after two consecutive failing continuing calibrations by the analysis of two consecutive acceptable continuing calibrations or by analysis of a new initial calibration.

10.7.4.1. The measured RRFs of all target analytes and internal standards must be within 30 percent difference or drift of the mean values established during the initial calibration. If this criterion is not satisfied, a new initial calibration curve must be established before sample extracts can be analyzed.

$$\%\text{Drift} = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100$$

Where:

C_{actual} = Known concentration in standard
C_{found} = Measured concentration

$$\%\text{Difference} = \frac{\overline{RF} - RF}{\overline{RF}} \times 100$$

Where:

$\overline{RF}$ = Average analyte response factor from initial calibration
RF = Measured analyte response factor from calibration verification

10.7.4.2. The recovery standard response must be within 50-200% of the response in the corresponding CS4 calibration level of the initial calibration.

11. Procedure

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure, except those specified by project specific instructions, shall be completely documented using a nonconformance memo and approved by a Technical Specialist, Project Manager, and QA Manager. If contractually required, the client shall be notified.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. GC/MS Analysis

11.3.1. Calibrate the instrument as described in Section 10.

11.3.2. Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 1 µL into the GC/MS and acquire data until benzo(ghi)perylene has eluted from the column.

11.3.3. Record analysis information in the instrument logbook. The following information is required:

- Date of analysis
- Time of analysis
- Instrument data system filename
- Analyst
- Lab sample identification
- Bench dilution factor

Additional information may be recorded in the logbook if necessary.

11.3.4. Generate ion chromatograms for the masses listed in Table 6 that encompass the expected retention windows of the target analytes. Integrate the selected ion current profiles of the quantitation ions shown in the table. Representative selected ion chromatograms for alkyl PAH windows are shown in Figure 3.

11.3.5. Dilutions: If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12. Data Analysis and Calculations

12.1. Qualitative identification criteria for individual analytes: For a gas chromatographic peak to be identified as a target analyte, it must meet all of the following criteria:

12.1.1. The quantitation ion must be present.

12.1.2. The internal standard quantitation ions must be present.

12.1.3. The relative intensities of confirmation ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%). The absence of confirmation ions should be considered carefully when making decisions regarding qualitative identification. Confirmation ions may have lower response than

quantitation ions and may not always be present at lower concentrations. Their absence in this case may not be cause for determining that the analyte is not present. The absence of confirmation ions at higher levels where they should have been detectable may be cause for determination that an analyte is not present.

12.1.4. The sample component retention time must compare to within ± 0.2 min. of the retention time of the internal standard component. For reference, the standard must be run within the same 12 hour period as the sample.

12.1.5. If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

12.2. Qualitative identification criteria for total homologue groups (e.g., total C2 or C3 alkylnaphthalenes) - For gas chromatographic peaks to be identified as a member of the homologue, it must meet all of the following criteria:

12.2.1. The retention time (RT) of the analyte must be no more than 5 seconds before and no more than 5 seconds after the expected RT of the first and last isomer in the homologue, based on the continuing windowing solution analysis.

12.2.2. Manual integration of the alkyl PAH homologues (e.g., total C2 or C3 alkylnaphthalenes) by an experienced analyst is required. Proper identification of the alkyl clusters is critical, as is the proper identification and elimination of non-target compounds that occur at the same nominal mass. Retention time window criterion alone is insufficient for correctly identifying alkyl PAH clusters and non-target compounds. Pattern recognition must be used to avoid including non-target species that may occur at the same mass and within the retention time window as the target alkyl PAHs. All alkyl clusters should be integrated baseline to baseline to sum the total area of the cluster (adjusting the baseline for detector drift), but not valley to valley. Manual control and adjustment of the integration parameters is required for proper integration.

12.3. Quantitation for Target Analytes.

12.3.1. Calculate the internal standard recoveries (Ris) relative to the recovery standard according to the following equation:

$$\text{Ris} = \frac{\text{Ais} \times \text{Qrs} \times \text{S}}{\text{Ars} \times \text{RRFis} \times \text{Qis}} \times 100\%$$

Where:

Ais	=	area of the quantitation ion of the appropriate internal standard
Ars	=	area of the quantitation ion of the recovery standard
Qrs	=	ng of recovery standard added to the extract
Qis	=	ng of internal standard added to the sample

RRFis = mean relative response factor of internal standard obtained during initial calibration
S = Prep split factor, i.e., the inverse of the proportion of extract used after the addition of internal standards and before the addition of recovery standard.

Example:
Ais = 104067
Ars = 63273
Qrs = 10,000 ng/mL x 0.025 mL = 250 ng
Qis = 250 ng/mL x 3 mL = 750 ng/mL
RRFis = 2.12963
S = 3 (i.e., 1/3 of extract was taken through cleanup after the addition of internal standards)

$$\text{Ris} = \frac{104067 \times 250\,\text{ng} \times 3}{63273 \times 2.12963 \times 750\,\text{ng/mL}} \times 100\% = 77.2\%$$

12.3.2. See Table 7 for the acceptance criteria for recoveries of the internal standards and spiked compounds in field samples, method blanks, and other QC samples. See section 9.2 for guidance for corrective action when internal standards are outside control limits.

12.3.3. Calculate the concentration of individual target analytes according to the following equation:

$$\text{Concentration} = \frac{\text{As} \times \text{Qis}}{\text{Ais} \times \text{RRF} \times \text{W} \times \%\text{S}}$$

Where:
As = area of the quantitation ion of the compound of interest. In the case of total homologues, As = the sum of areas of all peaks which meet the qualitative criteria listed in Section 12.2.
Ais = area of the quantitation ion of the appropriate internal standard
Qis = ng of internal standard added to the sample
RRF = mean relative response factor of compound obtained during initial calibration
W = amount of sample extracted (grams or mL)
%S = % solids decimal fraction (i.e., % solids/100)

Example:
As = 2082058
Ais = 104067
Qis = 250 ng/mL x 3 mL = 750 ng
RRF = 0.92745
W = 30 g
%S = 0.750

$$\text{Concentration} = \frac{2082058 \times 750\text{ng}}{104067 \times 0.92745 \times 30\text{g} \times 0.750} = 719\ \text{ng/g}$$

NOTE: Alkylated PAH homologues are assigned the RRF calculated for the parent PAH. See table 8 for parent response factor assignment for the alkylated homologues.

12.3.4. If the concentration in the final extract of any target analyte exceeds the upper method calibration level, a dilution of the extract or a re-extraction of a smaller portion of the sample must be performed. Dilutions of up to 50x may be performed on the extract. Since the internal standards are diluted in the extracts, the internal standards that are used for calculation should be inspected to ensure that they are not diluted below a 10 to 1 signal to noise ratio. If the compounds which exceed the calibration range cannot be brought within the calibration range by a 50x dilution, extraction of a smaller aliquot of sample may be performed or the sample may be analyzed by a more appropriate analytical technique such as full scan GC/MS. Consultation with the client should occur before any re-extraction is performed.

12.3.5. The isotope dilution technique accounts for the dilution factor in the extract. If a sample extract is diluted, the internal standard and recovery standard are also diluted, so a dilution factor is not used in the equation. However, the analyst must apply the dilution factor in QuantIMS to adjust the RL and MDL appropriately.

12.4. Flag all compound results in the sample which were detected in the method blank with a “B” qualifier.

12.5. Flag all compound results in the sample which are below the reporting limit and above the MDL with a “J” qualifier. See Table 1.

12.6. Flag all compound results in the sample which are above the upper calibration limit with an “E” qualifier.

12.7. Total alkyl homologue concentrations are considered estimated and are qualified with the EST flag. The qualitative criteria for these homologues are not as rigorous as they are for individual targets (i.e., the retention times of all the compounds are not known). The compounds are identified as eluting within a retention time window established by examining a variety of coal tar and crude oil standards.

12.8. Data Review

12.8.1. The analyst who performs the initial data calculations must initial and date the QuantIMS data review form.

12.8.2. Refer to Figure 2 for an example data review checklist used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data. The analyst who performs the initial data calculations must

initial and date the data review checklist.

12.8.3. All qualitative peak identifications must be verified by a second analyst. If discrepancies are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.8.4. All hand calculations and data entries into calculation programs, databases, or spreadsheets must be checked by a second analyst at a frequency of 100 percent. If discrepancies are found, the data must be returned to the analyst who performed the initial calculation for resolution.

12.8.5. The analyst that performed the second level review must fill out, initial and date the data review checklist.

13. Method Performance

13.1. Method Detection Limit (MDL): An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples (this does not apply to alkyl homologues). Method detection limits are determined and verified as specified in the current revision of SOP CA-Q-S-006 (and attachment) based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit.

13.2. Initial Demonstration of Capability: Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in TestAmerica Knoxville SOP KNOX-QA-0009. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample is listed in Table 7.

13.2.2. Calculate the average recovery and relative standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in Table 7. Historical matrix specific laboratory control sample acceptance criteria may also be used for evaluation of method demonstrations.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. Pollution Prevention

14.1. All attempts will be made to minimize the use of solvents and standard materials.

15. Waste Management

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. The following waste streams are produced when this procedure is carried out.

- Solvent waste shall be placed in the flammable waste stream, contained in a steel satellite accumulation container type or flammable solvent container.
- Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials shall be placed in the incinerable laboratory waste stream, contained in a steel or poly satellite accumulation container type.

16. References

16.1. TestAmerica Knoxville Quality Assurance Manual (QAM), current revision.

16.2. Method 429 - Determination of Polycyclic Aromatic Hydrocarbon (PAH) emissions from Stationary Sources, California Environmental Protection Agency Air Resources Board, Adopted: September 12, 1989, Amended: July 28, 1997.

16.3. NOAA Technical Memorandum NOS ORCA 130, National Status and Trends Program for Marine Environmental Quality, Sampling and Analytical Methods of the National Status and Trends Program Mussel Watch Project: 1993-1996 Update, March 1998.

17. Miscellaneous

17.1. Deviations from reference methods: Not applicable. This TestAmerica Knoxville laboratory SOP was developed using information from various sources, including the reference methods listed in section 16. This stand alone procedure is not intended to be compliant with all requirements of the reference methods.

17.2. The NOAA Technical Memorandum NOS ORCA 130 document is used to reference the alkyl groups only and not used for calibration, etc.

17.3. List of appendices, tables and figures referenced in the body of the SOP.

17.3.1. Table 1 – Target Analytes and Reporting Limits

17.3.2. Table 1A – Additional Analytes and Reporting Limits

17.3.3. Table 2 – Matrix, Sample Size, IS Spiking Level, and Final Volume

17.3.4. Table 3 – Concentration of Target Analytes in Calibration Solutions

17.3.5. Table 4 – Concentration of Stock Standards and Spiking Solutions

17.3.6. Table 5 – Quantitation References

17.3.7. Table 6 – Selected Ion Monitored and SIM Groups

17.3.8. Table 7 – Acceptance Criteria for Performance Tests and QC Samples

17.3.9. Table 8 – Response Factor Assignment for the Alkylated Homologues

17.3.10. Figure 1 – Recommended GC and GC/MS Conditions

17.3.11. Figure 2 – Example Data Review Checklist

17.3.12. Figure 3 – C1-C4 Alkyl Homologue Peak Patterns

Table 1 - Standard Target Analytes and Reporting Limits

Analyte	CAS No.	Aqueous (ng/L)	Solid/Sediment and Tissue (ng/g)	Air (Filter) (ng/sample)	Air (XAD) (ng/sample)	Air (Combined) (ng/sample)
Naphthalene	91-20-3	50	20	50	400	400
2-Methylnaphthalene	91-57-6	20	10	20	50	50
1-Methylnaphthalene	90-12-0	10	5	20	50	50
Acenaphthylene	208-96-8	10	1	20	20	20
Acenaphthene	83-32-9	10	1	20	20	20
Fluorene	86-73-7	10	1	10	10	10
Phenanthrene	85-01-8	20	1	20	30	30
Anthracene	120-12-7	10	1	10	10	10
Fluoranthene	206-44-0	10	1	10	10	10
Pyrene	129-00-0	10	1	60	20	60
Benz(a)anthracene	56-55-3	10	1	10	10	10
Chrysene	218-01-9	10	1	10	10	10
Benzo(b)fluoranthene	205-99-2	10	1	10	100	100
Benzo(k)fluoranthene	207-08-9	10	1	10	100	100
Benzo(e)pyrene	192-97-2	10	1	10	10	10
Benzo(a)pyrene	50-32-8	10	1	10	10	10
Perylene	198-55-0	10	1	10	10	10
Indeno(1,2,3-c,d)-pyrene	193-39-5	10	1	10	10	10
Dibenz(ah)anthracene	53-70-3	10	1	10	10	10
Benzo(ghi)perylene	191-24-2	10	1	10	10	10
C2 Naphthalenes	NA	10	2	NA	NA	NA
C3 Naphthalenes	NA	10	2	NA	NA	NA
C4 Naphthalenes	NA	10	1	NA	NA	NA
C1 Fluorenes	NA	10	1	NA	NA	NA
C2 Fluorenes	NA	10	1	NA	NA	NA
C3 Fluorenes	NA	10	1	NA	NA	NA
C1 Phenanthrenes & Anthracenes	NA	10	1	NA	NA	NA
C2 Phenanthrenes & Anthracenes	NA	10	1	NA	NA	NA
C3 Phenanthrenes & Anthracenes	NA	10	1	NA	NA	NA
C4 Phenanthrenes & Anthracenes	NA	10	1	NA	NA	NA
C1 Fluoranthenes & Pyrenes	NA	10	1	NA	NA	NA
C1 Benz(a)anthracenes & Chrysenes	NA	10	1	NA	NA	NA
C2 Benz(a)anthracenes & Chrysenes	NA	10	1	NA	NA	NA
C3 Benz(a)anthracenes & Chrysenes	NA	10	1	NA	NA	NA
C4 Benz(a)anthracenes & Chrysenes	NA	10	1	NA	NA	NA

Table 1A - Additional Analytes and Reporting Limits

Analyte	CAS No.	Aqueous (ng/L)	Solid/Sediment and Tissue (ng/g)	Air (Filter) (ng/sample)	Air (XAD) (ng/sample)	Air (Combined (ng/sample)
Biphenyl	92-52-4	10	1	20	50	50
1-Methylphenanthrene	832-69-9	10	1	10	10	10
2,6-Dimethylnaphthalene	581-42-0	10	2	20	30	30
2,3,5-Trimethylnaphthalene	2245-38-7	10	2	10	10	10
Dibenzothiophene	132-65-0	10	1	10	10	10
C1 Dibenzothiophenes	NA	10	1	NA	NA	NA
C2 Dibenzothiophenes	NA	10	1	NA	NA	NA
C3 Dibenzothiophenes	NA	10	1	NA	NA	NA
C4 Dibenzothiophenes	NA	10	1	NA	NA	NA

Table 2 - Matrix, Sample Size, IS Spiking Level and Final Volume

	Water	**Soil/ Sediment**	**Tissue**	**Wipe**	**Air**	**Waste**
Weight/volume/ sample amount	1 L	10 g	10 g	Entire Sample	Entire Sample	1 g
IS Spiking Levels	250 ppt	25 ppb	25 ppb	250 ng	250 ng	250 ng
Final Extract Vol. (mL)	0.5	0.5	0.5	0.5	0.5	0.5

Table 3 - Concentration of Target Analytes in Calibration Solutions

Analyte	CS1 (µg/mL)	CS2 (µg/mL)	CS3 (µg/mL)	CS4 (µg/mL)	CS5 (µg/mL)	CS6 (µg/mL)	CS7 (µg/mL)
Naphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Biphenyl	0.02	0.10	0.25	0.50	1.0	2.5	5.0
2-Methylnaphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
1-Methylnaphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Acenaphthylene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Acenaphthene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Fluorene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Phenanthrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
1-Methylphenanthrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
2,3,5-Trimethylnaphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Anthracene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
2,6-Dimethylnaphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Fluoranthene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Pyrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benz(a)anthracene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Chrysene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(b)fluoranthene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(k)fluoranthene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(e)pyrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(a)pyrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Perylene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Indeno(1,2,3-cd)pyrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Dibenz(ah)anthracene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(ghi)perylene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Dibenzothiophene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Sampling Surrogates							
d_{10}-Fluorene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
d_{14}-p-Terphenyl	0.02	0.10	0.25	0.50	1.0	2.5	5.0
^{13}C-Fluorene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Internal Standards							
d_{10}-Anthracene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_4-1,4-Dichlorobenzne	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_8 Naphthalene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-2-Methylnaphthalene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-1-Methylnaphthalene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_8-Acenaphthylene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-Phenanthrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-2,6-Dimethylnaphthalene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-Fluoranthene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benz(a)anthracene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Chrysene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(b)fluoranthene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(k)fluoranthene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(a)pyrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Perylene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Indeno(1,2,3-cd)pyrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{14}-Dibenz(ah)anthracene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(ghi)perylene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_8-Dibenzothiophene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Recovery Standards							
d_{10}-Acenaphthene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-Pyrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(e)Pyrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Alternate Surrogate							
$^{13}C_6$-Anthracene	0.50	0.50	0.50	0.50	0.50	0.50	0.50

Table 4 - Concentration of Stock Standards and Spiking Solutions

Compound	Recommended Sources*	Catalog Number	Vendor Conc (µg/mL)	Stock Solution (µg/mL)	Spiking Solution (µg/mL)
Native Analytes					
Naphthalene	Supelco	21084612	100	50	0.25
Biphenyl	Supelco	21084612	100	50	0.25
2-Methyl naphthalene	Supelco	21084612	100	50	0.25
1-Methyl naphthalene	Supelco	21084612	100	50	0.25
Acenaphthylene	Supelco	21084612	100	50	0.25
Acenaphthene	Supelco	21084612	100	50	0.25
Fluorene	Supelco	21084612	100	50	0.25
Phenanthrene	Supelco	21084612	100	50	0.25
1-Methylphenanthrene	Supelco	21084612	100	50	0.25
2,3,5-Trimethylnaphthalene	Supelco	21084612	100	50	0.25
Anthracene	Supelco	21084612	100	50	0.25
2,6-Dimethylnaphthalene	Supelco	21084612	100	50	0.25
Fluoranthene	Supelco	21084612	100	50	0.25
Pyrene	Supelco	21084612	100	50	0.25
Benz(a)anthracene	Supelco	21084612	100	50	0.25
Chrysene	Supelco	21084612	100	50	0.25
Benzo(b)fluoranthene	Supelco	21084612	100	50	0.25
Benzo(k)fluoranthene	Supelco	21084612	100	50	0.25
Benzo(e)pyrene	Supelco	21084612	100	50	0.25
Benzo(a)pyrene	Supelco	21084612	100	50	0.25
Perylene	Supelco	21084612	100	50	0.25
Indeno(1,2,3-cd)pyrene	Supelco	21084612	100	50	0.25
Dibenz(a,h)anthracene	Supelco	21084612	100	50	0.25
Benzo(ghi)perylene	Supelco	21084612	100	50	0.25
Dibenzothiophene	Supelco	21084612	100	50	0.25
Internal Standards					
d_8-Naphthalene	Accustandard	S-18004	200	10	0.25
d_{10}-2-Methyl naphthalene	Accustandard	S-18004	200	10	0.25
d_{10}-1-Methyl naphthalene	Accustandard	S-18004	200	10	0.25
d_8-Acenaphthylene	Accustandard	S-18004	200	10	0.25
d_{10}-Phenanthrene	Accustandard	S-18004	200	10	0.25
d_{12}- 2,6-Dimethylnaphthalene	Accustandard	S-18004	200	10	0.25
d_{10}-Fluoranthene	Accustandard	S-18004	200	10	0.25
d_{12}-Benz(a)anthracene	Accustandard	S-18004	200	10	0.25
d_{12}-Chrysene	Accustandard	S-18004	200	10	0.25
d_{12}-Benzo(b)fluoranthene	Accustandard	S-18004	200	10	0.25
d_{12}-Benzo(k)fluoranthene	Accustandard	S-18004	200	10	0.25
d_{12}-Benzo(a)pyrene	Accustandard	S-18004	200	10	0.25
d_{12}-Perylene	Accustandard	S-18004	200	10	0.25
d_{12}-Indeno(1,2,3-cd)pyrene	Accustandard	S-18004	200	10	0.25
d_{14}-Dibenz(a,h)anthracene	Accustandard	S-18004	200	10	0.25
d_{12}-Benzo(ghi)perylene	Accustandard	S-18004	200	10	0.25
d_8-Dibenzothiophene	Accustandard	S-18004	200	10	0.25
d_{10}-Anthracene	Accustandard	S-18004	200	10	0.25
Recovery Standards					
d_{10}-Acenaphthene	CIL	DLM-108-S	200	NA	10
d_{10}-Pyrene	CIL	DLM-155-S	200	NA	10
d_{12}-Benzo(e)pyrene	CIL	DLM-257-S	200	NA	10
Alternate Surrogate					
$^{13}C_6$-Anthracene	Cerilliant	CLM-1333-1.2	100	10	0.25
Sampling Surrogates					
$^{13}C_6$-Fluorene	Cerilliant	CLM-3596-1.2	100	20	5.0
d_{10}-Fluorene	CIL	DLM-1123-S	200	20	5.0
d_{14}-p-Terphenyl	CIL	DLM-382-S	200	20	5.0

* Other sources of standards may be used.

Table 5 – Quantitation References

Analyte	Analyte Type	Quantitation Standard (QS)	QS Type
Naphthalene	Native Analyte	d_8-Naphthalene	IS
Biphenyl	Native Analyte	d_{10}-2-Methylnaphthalene	IS
2-Methylnaphthalene	Native Analyte	d_{10}-2-Methylnaphthalene	IS
1-Methylnaphthalene	Native Analyte	d_{10}-1-Methylnaphthalene	IS
Acenaphthylene	Native Analyte	d_8-Acenaphthylene	IS
Acenaphthene	Native Analyte	d_8-Acenaphthylene	IS
Fluorene	Native Analyte	d_{10}-Phenanthrene	IS
Dibenzothiophene	Native Analyte	d_8-Dibenzothiophene	IS
Phenanthrene	Native Analyte	d_{10}-Phenanthrene	IS
1-Methylphenanthrene	Native Analyte	d_{10}-Phenanthrene	IS
2,3,5-Trimethylnaphthalene	Native Analyte	d_{12}-2,6-Dimethylnaphthalene	IS
Anthracene	Native Analyte	d_{10}-Anthracene	IS
2,6-Dimethylnaphthalene	Native Analyte	d_{12}-2,6-Dimethylnaphthalene	IS
Fluoranthene	Native Analyte	d_{10}-Fluoranthene	IS
Pyrene	Native Analyte	d_{10}-Fluoranthene	IS
Benz(a)anthracene	Native Analyte	d_{12}-Benz(a)anthracene	IS
Chrysene	Native Analyte	d_{12}-Chrysene	IS
Benzo(b)fluoranthene	Native Analyte	d_{12}-Benzo(b)fluoranthene	IS
Benzo(k)fluoranthene	Native Analyte	d_{12}-Benzo(k)fluoranthene	IS
Benzo(e)pyrene	Native Analyte	d_{12}-Benzo(a)pyrene	IS
Benzo(a)pyrene	Native Analyte	d_{12}-Benzo(a)pyrene	IS
Perylene	Native Analyte	d_{12}-Perylene	IS
Indeno(1,2,3-cd)pyrene	Native Analyte	d_{12}-Indeno(1,2,3-cd)pyrene	IS
Dibenz(ah)anthracene	Native Analyte	d_{14}-Dibenz(ah)anthracene	IS
Benzo(ghi)perylene	Native Analyte	d_{12}-Benzo(ghi)perylene	IS
C2 Naphthalenes	Alkyl Group	d_8-Naphthalene*	IS
C3 Naphthalenes	Alkyl Group	d_8-Naphthalene*	IS
C4 Naphthalenes	Alkyl Group	d_8-Naphthalene*	IS
C1 Fluorenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C2 Fluorenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C3 Fluorenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C1 Dibenzothiophene	Alkyl Group	d_8-Dibenzothiophene*	IS
C2 Dibenzothiophene	Alkyl Group	d_8-Dibenzothiophene*	IS
C3 Dibenzothiophene	Alkyl Group	d_8-Dibenzothiophene*	IS
C4 Dibenzothiophene	Alkyl Group	d_8-Dibenzothiophene*	IS
C1 Phenanthrenes & Anthracenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C2 Phenanthrenes & Anthracenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C3 Phenanthrenes & Anthracenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C4 Phenanthrenes & Anthracenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C1Fluoranthenes & Pyrenes	Alkyl Group	d_{10}-Fluoranthene*	IS
C1 Benz(a)anthracenes & Chrysenes	Alkyl Group	d_{12}-Chrysene *	IS
C2 Benz(a)anthracenes & Chrysenes	Alkyl Group	d_{12}-Chrysene *	IS
C3 Benz(a)anthracenes & Chrysenes	Alkyl Group	d_{12}-Chrysene *	IS
C4 Benz(a)anthracenes & Chrysenes	Alkyl Group	d_{12}-Chrysene *	IS
d_{10}-Fluorene	Sampling Surrogate	d_{10}-Phenanthrene	IS
d_{14}-p-Terphenyl	Sampling Surrogate	d_{10}-Fluoranthene	IS
$^{13}C_6$-Fluorene	Sampling Surrogate	d_{10}-Phenanthrene	IS

* Response factor for alkyls taken from parent PAH. See Table 8.

Table 5 – Quantitation References (continued)

Analyte	Analyte Type	Quantitation Standard (QS)	QS Type
d_{-8}-Naphthalene	IS	d_{10}-Acenaphthene	RS
d_{10}-2-Methylnaphthalene	IS	d_{10}-Acenaphthene	RS
d_{10}-1-Methylnaphthalene	IS	d_{10}-Acenaphthene	RS
d_{12}-2,6-Dimethylnaphthalene	IS	d_{10}-Acenaphthene	RS
d_8-Acenaphthylene	IS	d_{10}-Acenaphthene	RS
d-8 dibenzothiophene	IS	d_{10}-Pyrene	RS
d_{10}-Phenanthrene	IS	d_{10}-Pyrene	RS
d_{10}-Anthracene	IS	d_{10}-Pyrene	RS
d_{10}-Fluoranthene	IS	d_{10}-Pyrene	RS
d_{12}-Benz(a)anthracene	IS	d_{10}-Pyrene	RS
d_{12}-Chrysene	IS	d_{10}-Pyrene	RS
d_{12}-Benzo(b)fluoranthene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Benzo(k)fluoranthene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Benzo(a)pyrene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Perylene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Indeno(1,2,3-cd)pyrene	IS	d_{12}-Benzo(e)pyrene	RS
d_{14}-Dibenz(ah)anthracene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Benzo(ghi)perylene	IS	d_{12}-Benzo(e)pyrene	RS
$^{13}C_6$-Anthracene	Alternate Surrogate	d_{10}-Pyrene	RS

IS = Labeled Internal Standard
RS = Recovery Standard

Table 6 - Selected Ions Monitored and SIM Groups

Analyte	Classification	Quantitation	Confirmation	SIM Group
d_8-Naphthalene	Internal Standard	136	134	2
Naphthalene	Native Analyte	128	102	2
d_{10}-2-Methylnaphthalene	Internal Standard	152	151	3
2-Methylnaphthalene	Native Analyte	142	141	3
d_{10}-1-Methylnaphthalene	Internal Standard	152	151	3
1-Methylnaphthalene	Native Analyte	142	141	3
Biphenyl	Native Analyte	154	152	4
C2-naphthalenes	Alkyl Group	156	141	4,5
d_{12}-2,6-Dimethylnaphthalene	Internal Standard	168	167	4
2,6-Dimethylnaphthalene	Native Analyte	156	155	4
C3-naphthalenes	Alkyl Group	170	155	5,6
d_8-Acenaphthylene	Internal Standard	160	158	5
Acenaphthylene	Native Analyte	152	151	5
d_{10}-Acenaphthene	Recovery Standard	164	163	5
Acenaphthene	Native Analyte	154	153	5
C4-Naphthalenes	Alkyl Group	184	169	5,6,7
2,3,5-Trimethylnaphthalene	Native Analyte	170	169	6
d_{10}-Fluorene	Sampling Surrogate	176	174	6
$^{13}C_6$-Fluorene	Sampling Surrogate	171	172	6
Fluorene	Native Analyte	166	165	6
C1-Fluorenes	Alkyl Group	180	165	6,7
Dibenzothiophene	Native Analyte	184	139	7
d_8-Dibenzothiophene	Internal Standard	192	191	7
d_{10}-Phenanthrene	Internal Standard	188	184	7
Phenanthrene	Native Analyte	178	176	7
C2-Fluorenes	Alkyl Group	194	179	7
d_{10}-Anthracene	Internal Standard	188	184	7
Anthracene	Native Analyte	178	176	7
$^{13}C_6$-Anthracene	Alternate Surrogate	184	182	7
C1-Dibenzothiophenes	Alkyl Group	198	197	7,8
C3-Fluorenes	Alkyl Group	208	193	7,8,9
C1-Phenanthrenes_Anthracenes	Alkyl Group	192	191	7,8
1-Methylphenanthrene	Native Analyte	192	191	8
C2-Dibenzothiophenes	Alkyl Group	212	211	8,9
C2-Phenanthrenes_Anthracenes	Alkyl Group	206	191	8,9
C3-Dibenzothiophenes	Alkyl Group	226	211	8,9
d_{10}-Fluoranthene	Internal Standard	212	208	9
Fluoranthene	Native Analyte	202	200	9
C3-Phenanthrenes_Anthracenes	Alkyl Group	220	205	9
C4-Dibenzothiophenes	Alkyl Group	240	225	8,9
d_{10}-Pyrene	Recovery Standard	212	208	9
Pyrene	Native Analyte	202	200	9
C4-Phenanthrenes_Anthracenes	Alkyl Group	234	219	9

Table 6 - Selected Ions Monitored and SIM Groups (continued)

Analyte	Classification	Quantitation	Confirmation	SIM Group
d_{14}-Terphenyl	Sampling Surrogate	244	242	9
C1-Fluoranthenes_Pyrenes	Alkyl Group	216	215	9
d_{12}-Benz(a)anthracene	Internal Standard	240	236	10
Benz(a)anthracene	Native Analyte	228	226	10
d_{12}-Chrysene	Internal Standard	240	236	10
Chrysene	Native Analyte	228	226	10
C1-Benz(a)anthracenes_Chrysenes	Alkyl Group	242	241	10,11
C2-Benz(a)anthracenes_Chrysenes	Alkyl Group	256	241	10,11
C3-Benz(a)anthracenes_Chrysenes	Alkyl Group	270	255	10,11
d_{12}-Benzo(b)fluoranthene	Internal Standard	264	260	11
Benzo(b)fluoranthene	Native Analyte	252	253	11
d_{12}-Benzo(k)fluoranthene	Internal Standard	264	260	11
Benzo(k)fluoranthene	Native Analyte	252	253	11
C4-Benz(a)anthracenes_Chrysenes	Alkyl Group	284	269	11
d_{12}-Benzo(e)pyrene	Recovery Standard	264	260	11
Benzo(e)pyrene	Native Analyte	252	253	11
d_{12}-Benzo(a)pyrene	Internal Standard	264	260	11
Benzo(a)pyrene	Native Analyte	252	253	11
d_{12}-Perylene	Internal Standard	264	260	11
Perylene	Native Analyte	252	253	11
d_{14}-Dibenz(ah)anthracene	Internal Standard	292	288	12
Dibenz(ah)anthracene	Native Analyte	278	139	12
d_{12}-Indeno(1,2,3-cd)pyrene	Internal Standard	288	284	12
Indeno(1,2,3-cd)pyrene	Native Analyte	276	138	12
d_{12}-Benzo(ghi)perylene	Internal Standard	288	284	12
Benzo(ghi)perylene	Native Analyte	276	138	12

Table 7 - Acceptance Criteria for Performance Tests and QC Samples

Analyte	IDOC Test Conc[1] (ng/µL)	IDOC %RSD	IDOC %R	ICV %R	LCS %R	Method Blank %R	Sample %R
Naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
2-Methyl naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
1-Methyl naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
Biphenyl	0.5	30	60-140	70-130	60-140	NA	NA
2,6-Dimethyl naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
Acenaphthylene	0.5	30	60-140	70-130	60-140	NA	NA
Acenaphthene	0.5	30	60-140	70-130	60-140	NA	NA
2,3,5-Trimethyl naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
Fluorene	0.5	30	60-140	70-130	60-140	NA	NA
Phenanthrene	0.5	30	60-140	70-130	60-140	NA	NA
Anthracene	0.5	30	60-140	70-130	60-140	NA	NA
1-Methyl phenanthrene	0.5	30	60-140	70-130	60-140	NA	NA
Fluoranthene	0.5	30	60-140	70-130	60-140	NA	NA
Pyrene	0.5	30	60-140	70-130	60-140	NA	NA
Benz(a)anthracene	0.5	30	60-140	70-130	60-140	NA	NA
Chrysene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(b)fluoranthene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(k)fluoranthene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(e)pyrene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(a)pyrene	0.5	30	60-140	70-130	60-140	NA	NA
Perylene	0.5	30	60-140	70-130	60-140	NA	NA
Indeno(1,2,3-cd)pyrene	0.5	30	60-140	70-130	60-140	NA	NA
Dibenz(ah)anthracene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(ghi)perylene	0.5	30	60-140	70-130	60-140	NA	NA
Dibenzothiophene	0.5	30	60-140	70-130	60-140	NA	NA
Internal Standards							
d_8-Naphthalene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-2-Methyl naphthalene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-1-Methyl naphthalene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-2,6-Dimethyl naphthalene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_8-Acenaphthylene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-Phenanthrene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-Fluoranthene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benz(a)anthracene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Chrysene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benzo(b)fluoranthene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benzo(k)fluoranthene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benzo(a)pyrene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Perylene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Indeno(1,2,3-cd)pyrene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{14}-Dibenz(a,h)anthracene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benzo(ghi)perylene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-Anthracene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_8-Dibenzothiophene	0.5	30	60-140	70-130	60-140	60-140	30-120
Alternate Surrogate							
$^{13}C_6$-Anthracene	0.5	30	60-140	70-130	60-140	60-140	30-120
Sampling Surrogate							
d_{10}-Fluorene	NA	NA	NA	NA	NA	NA	50-150
d_{14}-p-Terphenyl	NA	NA	NA	NA	NA	NA	50-150
$^{13}C_6$-Fluorene	NA	NA	NA	NA	NA	NA	50-150

[1]Test concentration in the final extract, assuming a 0.5 mL volume.

Table 8 – Response Factor Assignment for the Alkylated Homologues

Alkyl Group	Parent to reference for RF
C2 Naphthalenes	Naphthalene
C3 Naphthalenes	Naphthalene
C4 Naphthalenes	Naphthalene
C1 Fluorenes	Fluorene
C2 Fluorenes	Fluorene
C3 Fluorenes	Fluorene
C1 Dibenzothiophene	Dibenzothiophene
C2 Dibenzothiophene	Dibenzothiophene
C3 Dibenzothiophene	Dibenzothiophene
C4 Dibenzothiophene	Dibenzothiophene
C1 Phenanthrenes & Anthracenes	Phenanthrene
C2 Phenanthrenes & Anthracenes	Phenanthrene
C3 Phenanthrenes & Anthracenes	Phenanthrene
C4 Phenanthrenes & Anthracenes	Phenanthrene
C1Fluoranthenes & Pyrenes	Pyrene
C1 Benz(a)anthracenes & Chrysenes	Chrysene
C2 Benz(a)anthracenes & Chrysenes	Chrysene
C3 Benz(a)anthracenes & Chrysenes	Chrysene
C4 Benz(a)anthracenes & Chrysenes	Chrysene

Figure 1 Recommended GC & GC/MS Conditions

```
                              INSTRUMENT CONTROL PARAMETERS:    MP
                              ----------------------------------

   C:\MSDCHEM\1\METHODS\KNX_00161.M
      Tue Sep 15 10:30:44 2009

Control Information
------- -----------

Sample Inlet      :  GC
Injection Source  :  GC ALS
Mass Spectrometer :  Enabled

================================================================================
                                  6890 GC METHOD
================================================================================


OVEN
   Initial temp:  45 'C (On)                  Maximum temp:  375 'C
   Initial time:  0.50 min                    Equilibration time:  0.50 min
   Ramps:
      #  Rate  Final temp  Final time
      1 30.00       240        0.00
      2 21.00       310        0.00
      3  4.00       320        0.10
      4 35.00       335        2.64
      5   0.0(Off)
   Post temp:  0 'C
   Post time:  0.00 min
   Run time:  16.00 min


FRONT INLET (SPLIT/SPLITLESS)              BACK INLET (UNKNOWN)
   Mode:  Pulsed Splitless
   Initial temp:  250 'C (On)
   Pressure:  15.73 psi (On)
   Pulse pressure:  25.0 psi
   Pulse time:  0.50 min
   Purge flow:  10.0 mL/min
   Purge time:  1.25 min
   Total flow:  14.2 mL/min
   Gas saver:  Off
   Gas type:  Helium


COLUMN 1                                   COLUMN 2
   Capillary Column                           (not installed)
   Model Number:  Restek 12623-124
   Rtx-5MS w/Integra-Guard
   Max temperature:  360 'C
   Nominal length:  30.0 m
   Nominal diameter:  250.00 um
   Nominal film thickness:  0.25 um
   Mode:  constant flow
   Initial flow:  1.2 mL/min
   Nominal init pressure:  15.73 psi
   Average velocity:  26 cm/sec
   Inlet:  Front Inlet
   Outlet:  MSD
   Outlet pressure:  3.80 psi


FRONT DETECTOR (NO DET)                    BACK DETECTOR (NO DET)


SIGNAL 1                                   SIGNAL 2

KNX_00161.M Tue Sep 15 10:30:43 2009 Test America Knoxville                Page: 2
```

Figure 1 Recommended GC & GC/MS Conditions (continued)

```
   Data rate:  20 Hz                    Data rate:  20 Hz
   Type:  test plot                     Type:  test plot
   Save Data:  Off                      Save Data:  Off
   Zero:  0.0 (Off)                     Zero:  0.0 (Off)
   Range:  0                            Range:  0
   Fast Peaks:  Off                     Fast Peaks:  Off
   Attenuation:  0                      Attenuation:  0

COLUMN COMP 1                        COLUMN COMP 2
   (No Detectors Installed)             (No Detectors Installed)

THERMAL AUX 2                        AUX PRESSURE 3
   Use:  MSD Transfer Line Heater       Description:  Quick Swap
   Description:                         Gas Type:  Helium
   Initial temp:  300 'C (On)           Initial pressure:  0.00 psi (Off)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)

AUX PRESSURE 4                       AUX PRESSURE 5
   Description:                         Description:
   Gas Type:  Helium                    Gas Type:  Helium
   Initial pressure:  0.00 psi (Off)    Initial pressure:  0.00 psi (Off)

                                     POST RUN
                                        Post Time: 0.00 min

TIME TABLE
   Time       Specifier                  Parameter & Setpoint


                              GC Injector


     Front Injector:
        Sample Washes                 0
        Sample Pumps                  6
        Injection Volume           1.00 microliters
        Syringe Size              10.0 microliters
        PreInj Solvent A Washes       0
        PreInj Solvent B Washes       0
        PostInj Solvent A Washes      3
        PostInj Solvent B Washes      3
        Viscosity Delay               1 seconds
        Plunger Speed              Fast
        PreInjection Dwell         0.00 minutes
        PostInjection Dwell        0.00 minutes


     Back Injector:
No parameters specified

 Column 1 Inventory Number : 915849
 Column 2 Inventory Number :

                              MS ACQUISITION PARAMETERS


General Information
------- -----------

Tune File               : dftpp.u

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```

Figure 1 Recommended GC & GC/MS Conditions (continued)

```
Acquistion Mode          : Scan/SIM


MS Information
-- -----------

Solvent Delay            : 4.40 min

EMV Mode                 : Relative
Relative Voltage         : 141
Resulting EM Voltage     : 1647

[Scan Parameters]

Low Mass                 : 35.0
High Mass                : 550.0
Threshold                : 500
Sample #                 : 1       A/D Samples    2
[Sim Parameters]

GROUP 1
Group ID                 : 1
Resolution               : Low
Plot 1 Ion               : 146.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (146.00,     40) (148.00,     40) (150.00,     40)
                         (152.00,     40)

GROUP 2
Group ID                 : 2
Resolution               : Low
Group Start Time         : 5.52
Plot 1 Ion               : 102.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (102.00,     40) (128.00,     40) (134.00,     40)
                         (136.00,     40)

GROUP 3
Group ID                 : 3
Resolution               : Low
Group Start Time         : 6.12
Plot 1 Ion               : 141.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (141.00,     35) (142.00,     35) (151.00,     35)
                         (152.00,     35) (156.00,     35)

GROUP 4
Group ID                 : 4
Resolution               : Low
Group Start Time         : 6.50
Plot 1 Ion               : 152.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (141.00,     15) (152.00,     15) (154.00,     15)
                         (155.00,     15) (156.00,     15) (167.00,     15)
                         (168.00,     15)

GROUP 5
Group ID                 : 5
Resolution               : Low
Group Start Time         : 6.81
Plot 1 Ion               : 151.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (141.00,     10) (151.00,     10) (152.00,     10)
                         (153.00,     10) (154.00,     10) (155.00,     10)
                         (156.00,     10) (158.00,     10) (160.00,     10)
                         (163.00,     10) (164.00,     10) (169.00,     10)
                         (170.00,     10) (184.00,     10)

GROUP 6

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```

Figure 1 Recommended GC & GC/MS Conditions (continued)

```
Group ID                : 6
Resolution              : Low
Group Start Time        : 7.30
Plot 1 Ion              : 165.00
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (139.00,     10) (155.00,     10) (165.00,     10)
                        (166.00,     10) (169.00,     10) (170.00,     10)
                        (171.00,     10) (172.00,     10) (174.00,     10)
                        (176.00,     10) (180.00,     10) (184.00,     10)

GROUP 7
Group ID                : 7
Resolution              : Low
Group Start Time        : 8.00
Plot 1 Ion              : 139.00
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (139.00,      5) (165.00,      5) (169.00,      5)
                        (176.00,      5) (178.00,      5) (179.00,      5)
                        (180.00,      5) (182.00,      5) (184.00,      5)
                        (186.00,      5) (188.00,      5) (191.00,      5)
                        (192.00,      5) (193.00,      5) (194.00,      5)
                        (197.00,      5) (198.00,      5) (208.00,      5)

GROUP 8
Group ID                : 8
Resolution              : Low
Group Start Time        : 8.80
Plot 1 Ion              : 191.00
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (191.00,     10) (192.00,     10) (193.00,     10)
                        (197.00,     10) (198.00,     10) (206.00,     10)
                        (208.00,     10) (211.00,     10) (212.00,     10)
                        (225.00,     10) (226.00,     10) (240.00,     10)

GROUP 9
Group ID                : 9
Resolution              : Low
Group Start Time        : 9.20
Plot 1 Ion              : 200.00
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (191.00,      5) (193.00,      5) (200.00,      5)
                        (202.00,      5) (205.00,      5) (206.00,      5)
                        (208.00,      5) (211.00,      5) (212.00,      5)
                        (215.00,      5) (216.00,      5) (219.00,      5)
                        (220.00,      5) (225.00,      5) (226.00,      5)
                        (234.00,      5) (240.00,      5) (242.00,      5)
                        (244.00,      5)

GROUP 10
Group ID                : 10
Resolution              : Low
Group Start Time        : 10.70
Plot 1 Ion              : 226.00
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (226.00,     25) (228.00,     25) (236.00,     25)
                        (240.00,     25) (241.00,     25) (242.00,     25)

GROUP 11
Group ID                : 11
Resolution              : Low
Group Start Time        : 11.20
Plot 1 Ion              : 252.00
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (241.00,     30) (242.00,     30) (252.00,     30)
                        (253.00,     30) (255.00,     30) (256.00,     30)
                        (260.00,     30) (264.00,     30) (269.00,     30)
                        (270.00,     30) (284.00,     30)

GROUP 12

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```

Figure 1 Recommended GC & GC/MS Conditions (continued)

```
Group ID                : 12
Resolution              : Low
Group Start Time        : 14.00
Plot 1 Ion              : 292.00
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (138.00,     25) (139.00,     25) (276.00,     25)
                        (278.00,     25) (284.00,     25) (288.00,     25)
                        (292.00,     25)

[MSZones]

MS Source               : 230 C   maximum 250 C
MS Quad                 : 150 C   maximum 200 C

                            END OF MS ACQUISITION PARAMETERS

                             TUNE PARAMETERS for SN: US81839504
                          ------------------------------

 Trace Ion Detection is OFF.

 EMISSION     :      34.610
 ENERGY       :      69.922
 REPELLER     :      29.620
 IONFOCUS     :      87.310
 ENTRANCE_LE  :       0.000
 EMVOLTS      :    1505.882
                               Actual EMV  :    1647.06
                               GAIN FACTOR :       2.04
 AMUGAIN      :    1914.000
 AMUOFFSET    :     125.688
 FILAMENT     :       1.000
 DCPOLARITY   :       0.000
 ENTLENSOFFS  :     19.325@  3    19.325@ 50    15.561@ 69    16.816@131    16.565@219    17.06
7@414    16.816@502    16.816@1049
 MASSGAIN     :    -652.000
 MASSOFFSET   :     -44.000

                           END OF TUNE PARAMETERS
                       -----------------------------------

PostRun InstCntl macro(s) exist: msacq2.mac

                            END OF INSTRUMENT CONTROL PARAMETERS
                            -----------------------------------
```

Figure 2 Example Data Review Checklist

TestAmerica Knoxville GC/MS-SIM Initial Calibration Data Review / Narrative Checklist
Method: PAHs and Selected SVOCs - KNOX-ID-0016, Revision 8

Analysis Date:		Instrument::		ICAL Batch/Scan Name:		Scanned ☐

A. Review Items	N/A	Yes	No	Why is data reportable?	2nd √
1. Were all standards injected within 12 hr of first calibration standard?					
2. Was date/time of analysis verified between header and logbook?					
3. Are peak integrations appropriate?					
4. Were ≥ 5 levels of each analyte/IS analyzed?					
5. Was the high point standard checked for saturation?					
6. Was low level standard at or below RL?					
7. Are all %RSD ≤30% ?					
8. Are the MID descriptors properly set?					
9. Are correct RFs listed in ICAL summary?					
10. Was ICAL summary form processed using the correct method?					
11. Are the ICAL start and end dates/times correct on ICAL summary?					
12. Elution order checked on isomeric pairs?					
• 2-methylnaphthalene before 1-methylnaphthalene (& d10 isomers)					
• acenaphthylene before acenaphthene (& d10 isomers)					
• dibenzothiophene before anthracene					
• phenanthrene before anthracene (& d10 isomers)					
• fluoranthene before pyrene (& d10 isomers)					
• benzo(a)anthracene before chrysene (& d12 isomers)					
• benzo(b)fluoranthene before benzo(k)fluoranthene (& d12 isomers)					
• benzo(e)pyrene before benzo(a)pyrene benzo(a)pyrene before perylene (& d12 isomers)					
• Indeno(1,2,3-cd)pyrene before benzo(g,h,I)perylene (& d12 isomers)					
13. Is the 2nd source ICV with +/- 30% of the expected value?					
14. Are the Alkyl RFs correct (i.e., same as the parent RF)?					
15. If criteria were not met, was a NCM generated and approved by supervisor?					
16. Does the ICAL folder contain **complete** data in the following order? ICAL data review checklist, runlog, Target Initial Calibration Report, followed by the quan report and chromatograms for all calibration and 2nd source standards.					

1st Level Reviewer:	Date:
Comments:	
2nd Level Reviewer:	Date:
Comments:	

ID028R20.doc, 081810

Figure 2 Example Data Review Checklist (continued)

TestAmerica Knoxville GC/MS-SIM Continuing Calibration Review / Narrative Checklist
Method: LRPAH PAHs and Selected SVOCs - KNOX-ID-0016, Revision 8

Analysis Date:		CCAL Batch/ Scan Name:		Instrument:		ICAL Batch/ Scan Name:		Scanned ☐

A. Review Items	N/A	Yes	No	Why is data reportable?	2nd √
1. Were all injections in sequence within 12 hr of CCAL?					
2. Was date/time of analysis verified between header and logbook?					
3. Are peak integrations appropriate?					
4. Is the %D or drift <30% for all analytes					
5. Are the recovery standards within 50-200% of the ICAL CS4 level?					
6. Are the MID descriptors properly set?					
7. Are correct RFs listed in CCAL summary?					
8. Was the correct ICAL used for quantitation? (Verify 1 RF.)					
9. Elution order checked on isomeric pairs/coeluters?					
• 2-methylnaphthalene before 1-methylnaphthalene (& d10 isomers)					
• acenaphthylene before acenaphthene (& d10 isomers)					
• dibenzothiophene before anthracene					
• phenanthrene before anthracene (& d10 isomers)					
• fluoranthene before pyrene (& d10 isomers)					
• benzo(a)anthracene before chrysene (& d12 isomers)					
• benzo(b)fluoranthene before benzo(k)fluoranthene (& d12 isomers)					
• benzo(e)pyrene before benzo(a)pyrene benzo(a)pyrene before perylene (& d12 isomers)					
• Indeno(1,2,3-cd)pyrene before benzo(g,h,I)perylene (& d12 isomers)					
10. Were the first/last RTs for each alkyl PAH homologue group properly identified and indicated on the chromatogram?					
11. If criteria were not met, was a NCM generated and approved by supervisor?					
12. Does the CCAL folder contain **complete** data in the following order? CCAL data review checklist, runlog, Target Continuing Calibration Report, followed by the quan report and chromatograms for the CCAL and window standard.					

1st Level Reviewer:	Date:
Comments:	
2nd Level Reviewer:	Date:
Comments:	

Figure 2 Example Data Review Checklist (continued)

TestAmerica Knoxville GC/MS-SIM Data Review / Narrative Checklist
Method: PAHs and Selected SVOCs - KNOX-ID-0016, Revision 8
Page 1 of 3

Lot Number:			Instrument:		
Scanned Filenames:					

A. Tune / Calibration	N/A	Yes	No	Why is data reportable?	2nd √
1. Were all samples injected within 12 hr of CCAL?					
2. Was the correct ICAL used for quantitation? (Check 1 RF per sample/QC sample.)					
B. Sample Results	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd √**
1. Were all special project requirements met?					
2. Were sample preparation and analytical HTs met? If no, list NCM#_____				☐ [ht1] HT expired upon receipt. ☐ [ht2] Client requested analysis after HT expired.* ☐ **Re-extraction done after HT expired.**	
3. Was prep info (sample amount, final vol, split factors, units, prep dates/times) verified?					
4. For sediment samples, were the RLs and MDLs adjusted for % moisture using QuantIMS DF?					
5. Was date/time of analysis verified between header and logbook?					
6. Was header information (WO#, data file, initial wt/vol, extract vol, DF) verified?					
7. Were peaks properly identified?					
8. Are peak integrations appropriate?					
9. Were alkyl group start/end times and patterns verified?					
10. Are internal standards (30-120% R), alternate standards and sampling surrogates (30-140% R) within QC limits for samples and matrix spikes? Sample Reason Sample Reason _____				☐ **[is1] IS above QC limits.** ☐ **[is2] IS below QC limts.** ☐ **[sur1] Surrogates outside QC limits.**	
11. If amount extracted was <80% of nominal amount, were the RLs/MDLs adjusted? List samples:_____				☐ [elev6] Elevated RLs for all analytes due to insufficient sample amount received.	
12. For initial analysis that's a dilution, was the largest analyte >20% of calibration range? List dilutated samples and reason (e.g elev1) Sample Reason Sample Reason _____				☐ [elev1] Elevated RL for (ANALYTE) due to sample matrix interferences. ☐ [elev2] Elevated RL for (ANALYTE) due to interfering analyte. ☐ [elev3] Elevated RLs for all analytes due to difficult sample matrix. ☐ [elev4] Diluted based on screening results. ☐ [elev5] Elevated RLs for all analytes due to presence of non-target compounds.	

NOTE: Nonconformance memos are required for **bold** autotext statements.

Figure 2 Example Data Review Checklist (continued)

TestAmerica Knoxville GC/MS-SIM Data Review / Narrative Checklist
Method: LRPAH PAHs and Selected SVOCs - KNOX-ID-0016, Revision 8
Page 2 of 3

Lot Number:					
13. If bench dilutions were required, were results within calibration range? Sample Reason Sample Reason _____				☐ [E1] 1 g reprep performed. ☐ [E2] 1 g multi-spike reprep performed. ☐ [E3] Post-extraction spike performed. ☐ [E4] E values reported per client.	
14. For secondary diluted analyses to bring compounds in calibration range, was the largest analyte targeted to be above 50% of calibration range? List diluted samples and reason (e.g., dil1): Sample Reason Sample Reason _____				☐ [dil1] Conc. of (ANALYTE) > calibration range. RLs adjusted accordingly. ☐ [dil2] Conc. of several compounds > calibration range. RLs adjusted accordingly. ☐ [dil3] Conc. of (ANALYTE) > calibration range. Both analyses reported to provide lowest RLs. ☐ [dil4] Conc. of several compounds > calibration range. Both analyses reported to provide lowest RLs.	
15. Was the upper calibration range (UCL) calculated correctly and were hits >UCL flagged with "E"?					
16. If manual integrations were performed, are they clearly identified, initialed, dated and reason given?				Reasons: 1) Corrected split peak; 2) Unresolved peak; 3) Tailing; 4) RT shift; 5) Wrong peak selected; 6) Other	
17. Have alternate hits and manual integrations been verified as correct?					
C. Preparation/Matrix QC Results	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd √**
1. LCS native analyte %R within QC limits (60-140%)? If no, list NCM#:: _____				☐ **[lcs1] Insufficient sample for reanalysis.** ☐ **[lcs2] Samples consumed during prep.** ☐ **[lcs3] LCS %R high but analyte <RL in associated samples.**	
2. LCS IS %R within QC limits (60-140%)?				☐ **[is3] IS above QC limits.** ☐ **[is4] IS below QC limts.**	
3. Method blank done per prep batch and method blank or instrument blank analyzed with each sequence?					
4. Method blank IS %R within QC limits (60-140%)?.				☐ **[is5] IS above QC limits.** ☐ **[is6] IS below QC limts.**	
5. Are all analytes present in the method blank ≤ RL?				☐ **[mb1] Reported blank after client consultation.** ☐ **[mb3] Analyte < RL in associated samples.** ☐ **[mb4] Sample results >10x blank.** ☐ **[mb5] Insufficient sample for reanalysis.** ☐ **[mb7] Samples consumed during prep.**	
6. Were MS run #'s assigned correctly?					
7. Are MS/MSD recoveries and RPDs within QC limits?				☐ [ms1] LCS acceptable. High native analyte concentration relative to spike level and/or lack of sample homogeneity.	
D. Final Report	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd √**
1. Final report acceptable? (Results correct, RLs calculated correctly, units correct, IS %R correct, appropriate flags used, dilution factor correct, and extraction/ analysis dates correct.)					

Figure 2 Example Data Review Checklist (continued)

TestAmerica Knoxville GC/MS-SIM Data Review / Narrative Checklist
Method: LRPAH PAHs and Selected SVOCs - KNOX-ID-0016, Revision 8
Page 3 of 3

Lot Number:					
2. If samples were split, are the dilution factors & prep factors applied properly & MDL/RLs adjusted				☐ [elev7] Elevated RLs for all analytes due to split; list samples: _____ _____	
3. For alkyl PAHs, are hits fagged with EST?					
4. Were all non-associated internal standards turned to 'NA'?					
5. Was a narrative prepared and all deviations noted?					
6. Are all non-conformances documented appropriately and copy included with deliverable?					
7. Are the correct scanned file names listed?					
8. Were all CCALs and window standards scanned?					
1st Level Reviewer:		**Date:**			
Comments:					
2nd Level Reviewer:		**Date:**			
Comments:					

Figure 3: C1-C4 Alkyl Homologue Peak Patterns

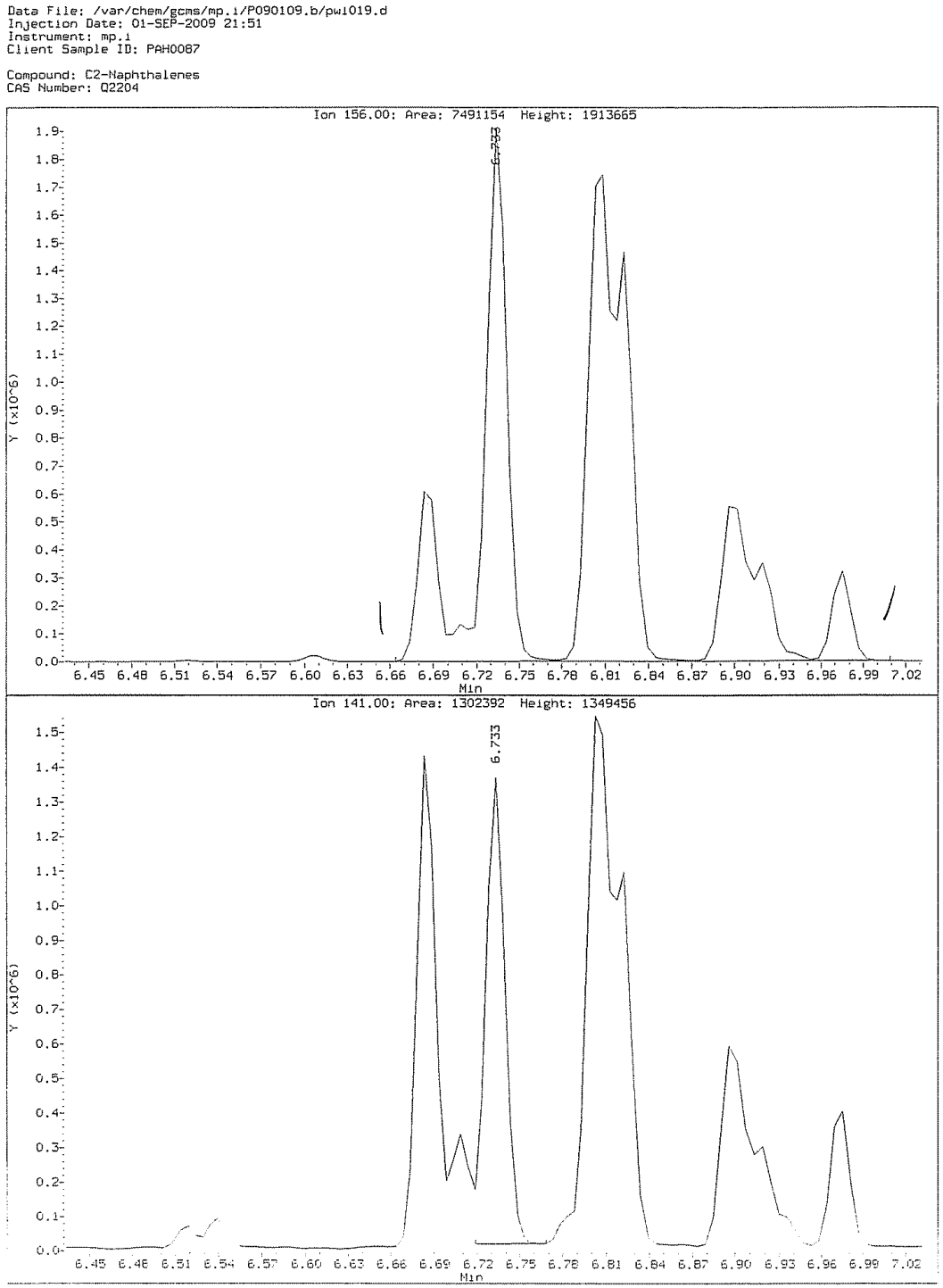


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

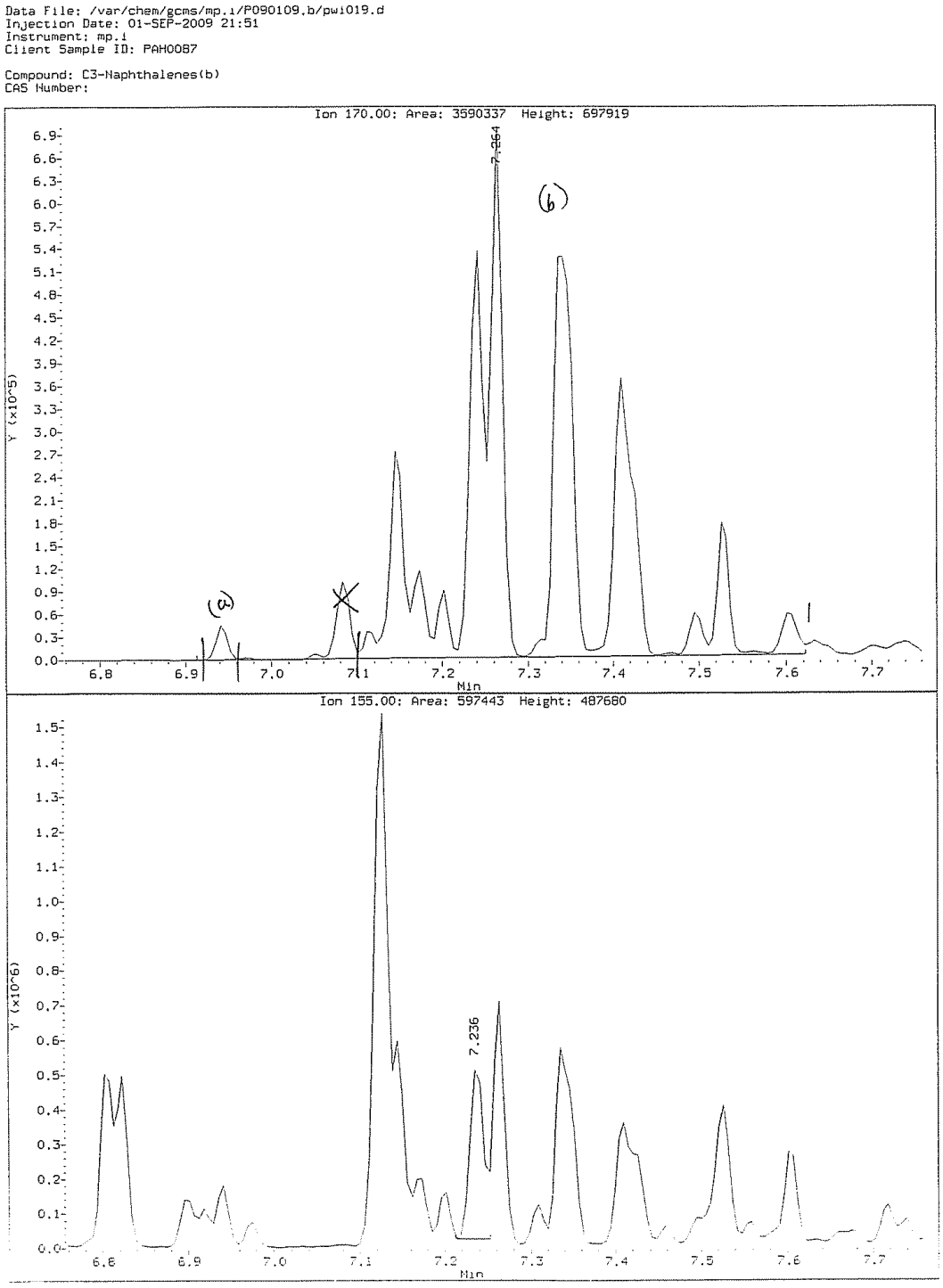


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

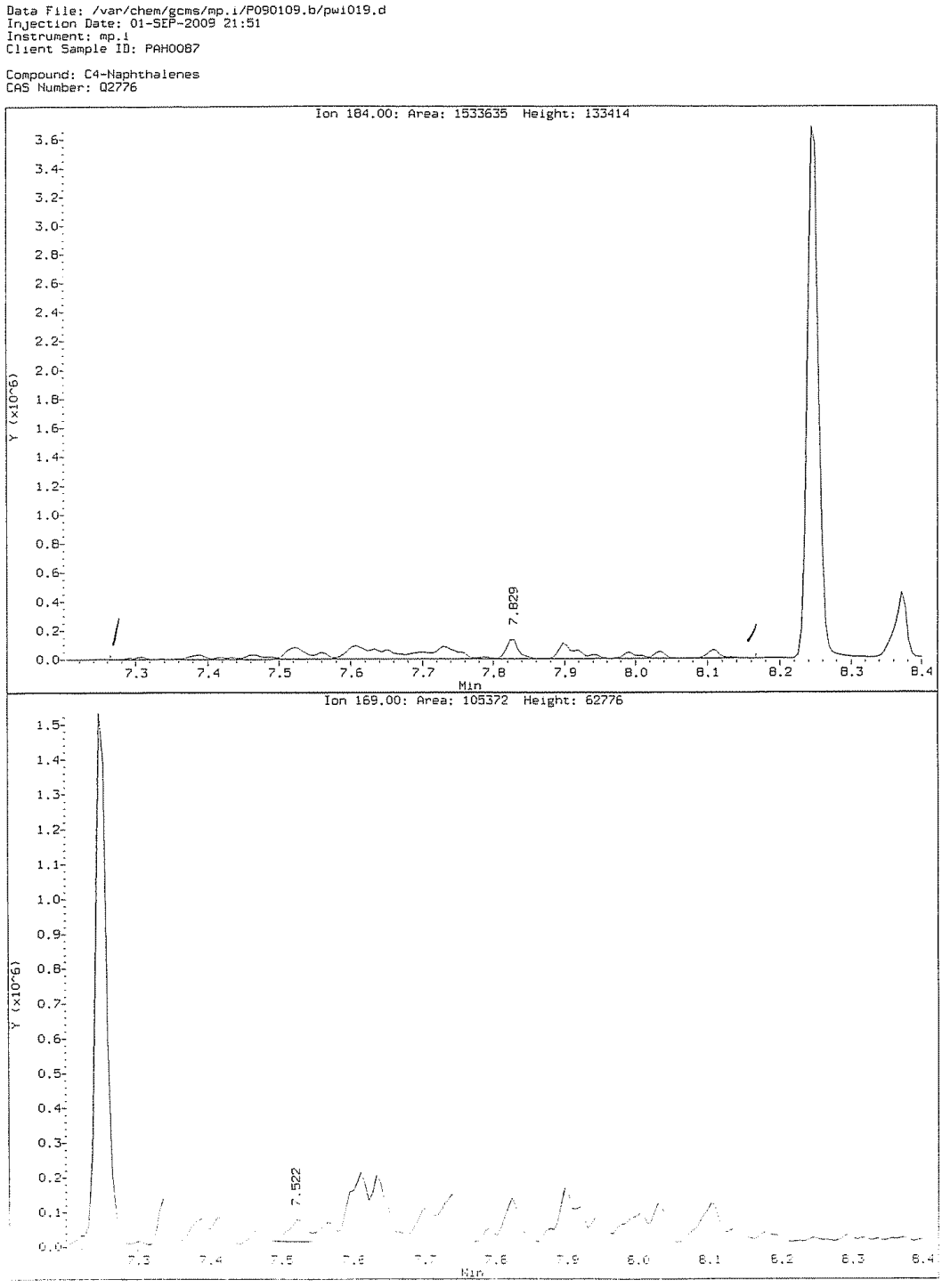
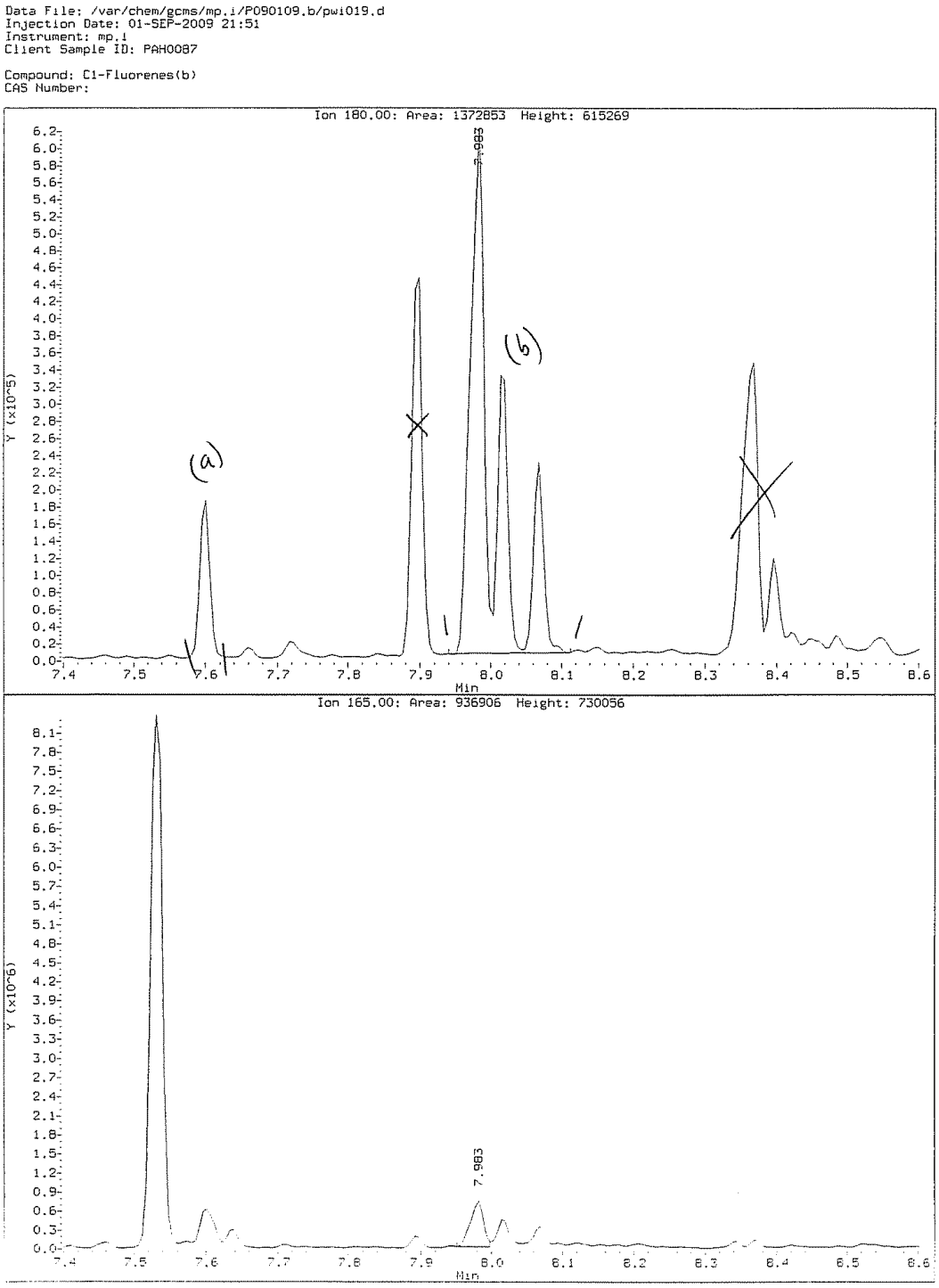


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)



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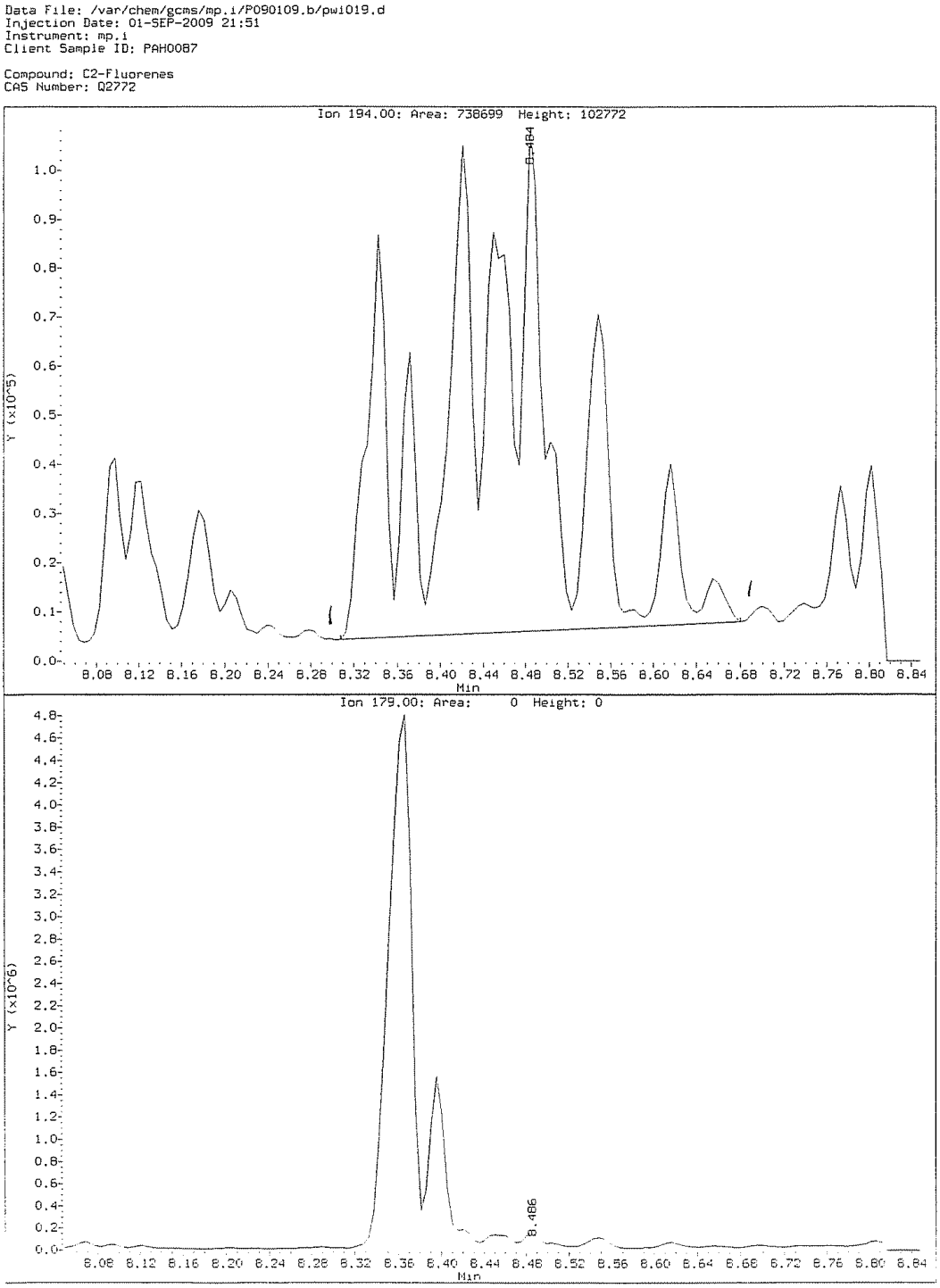

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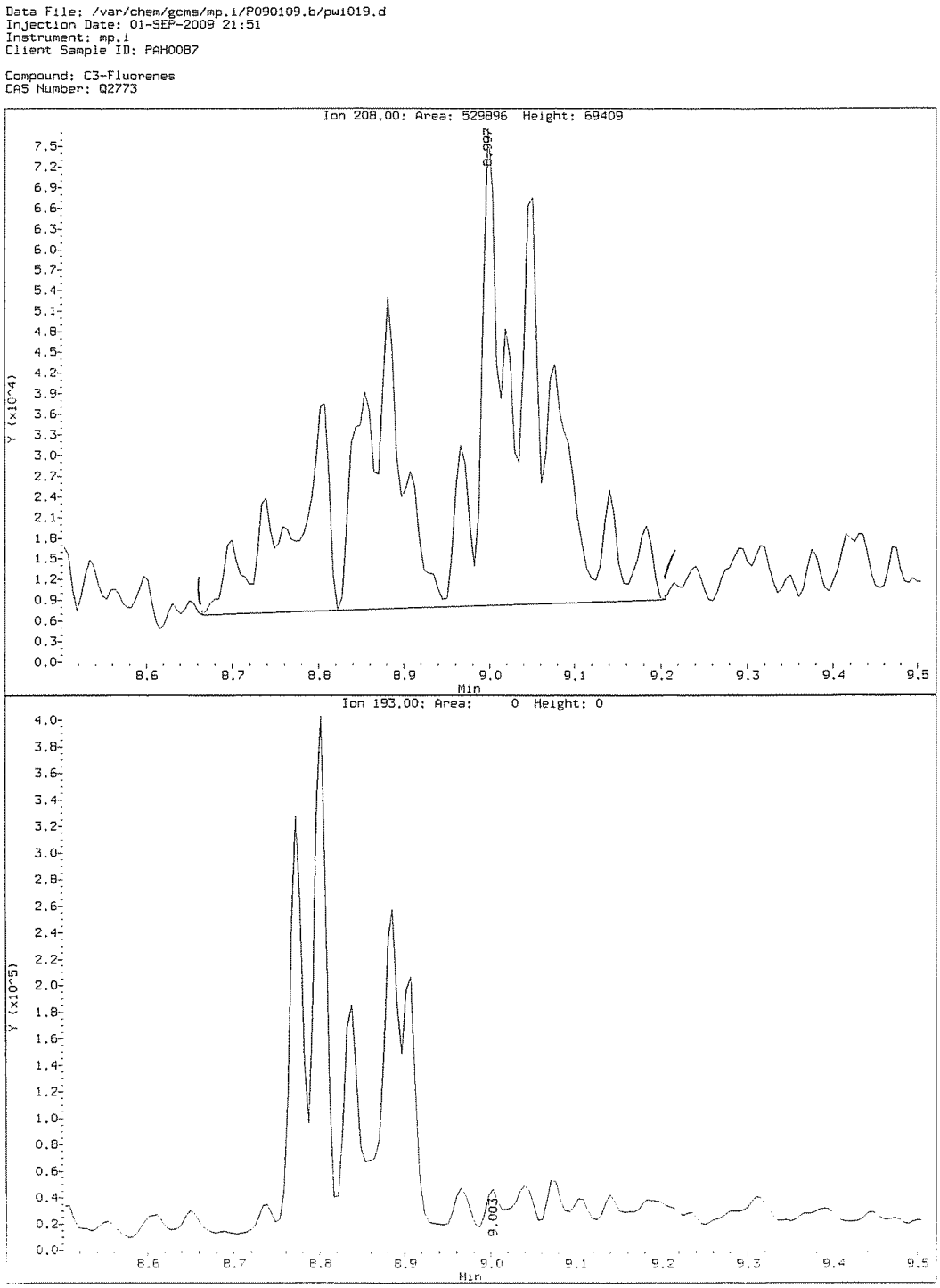

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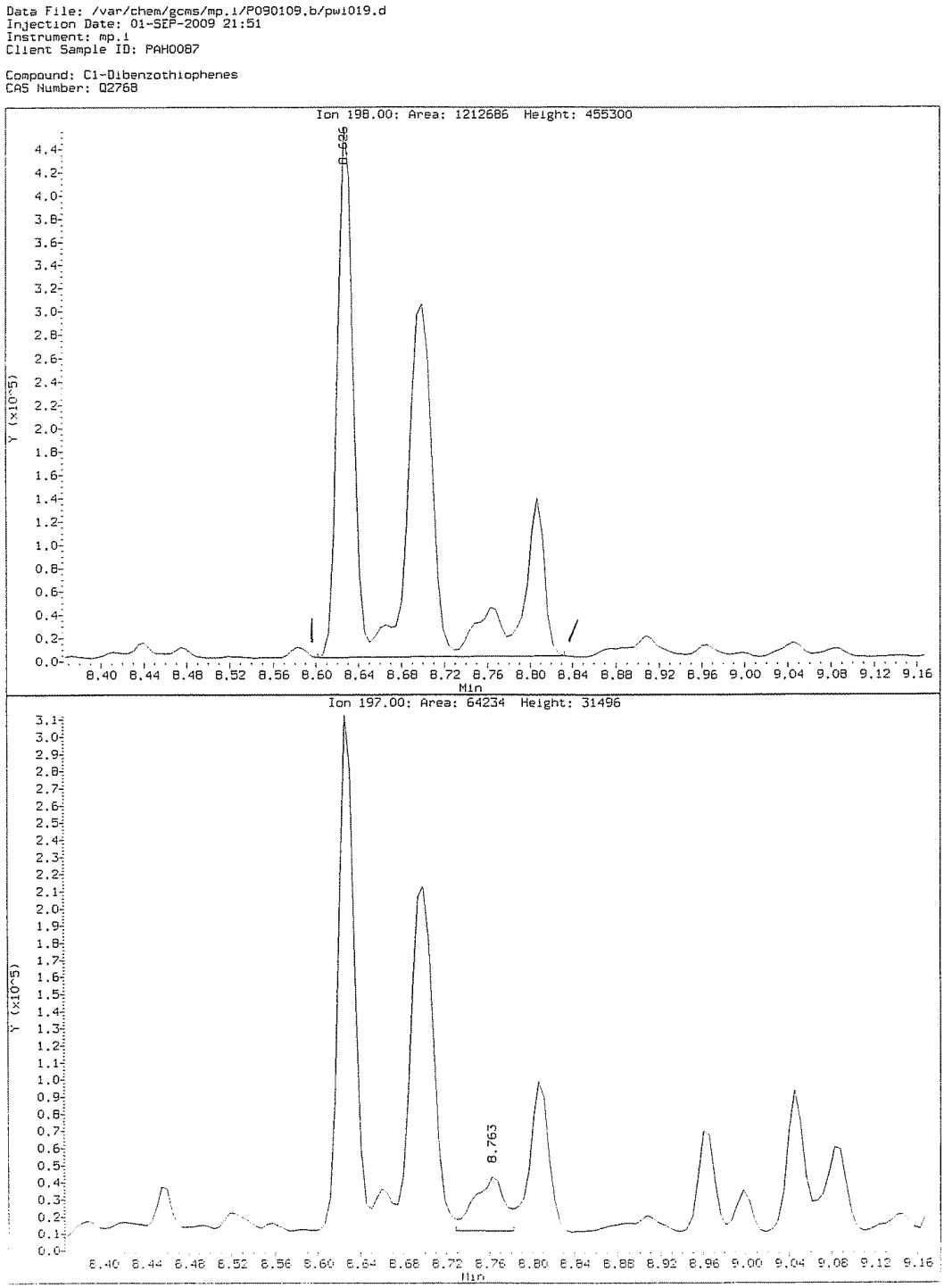

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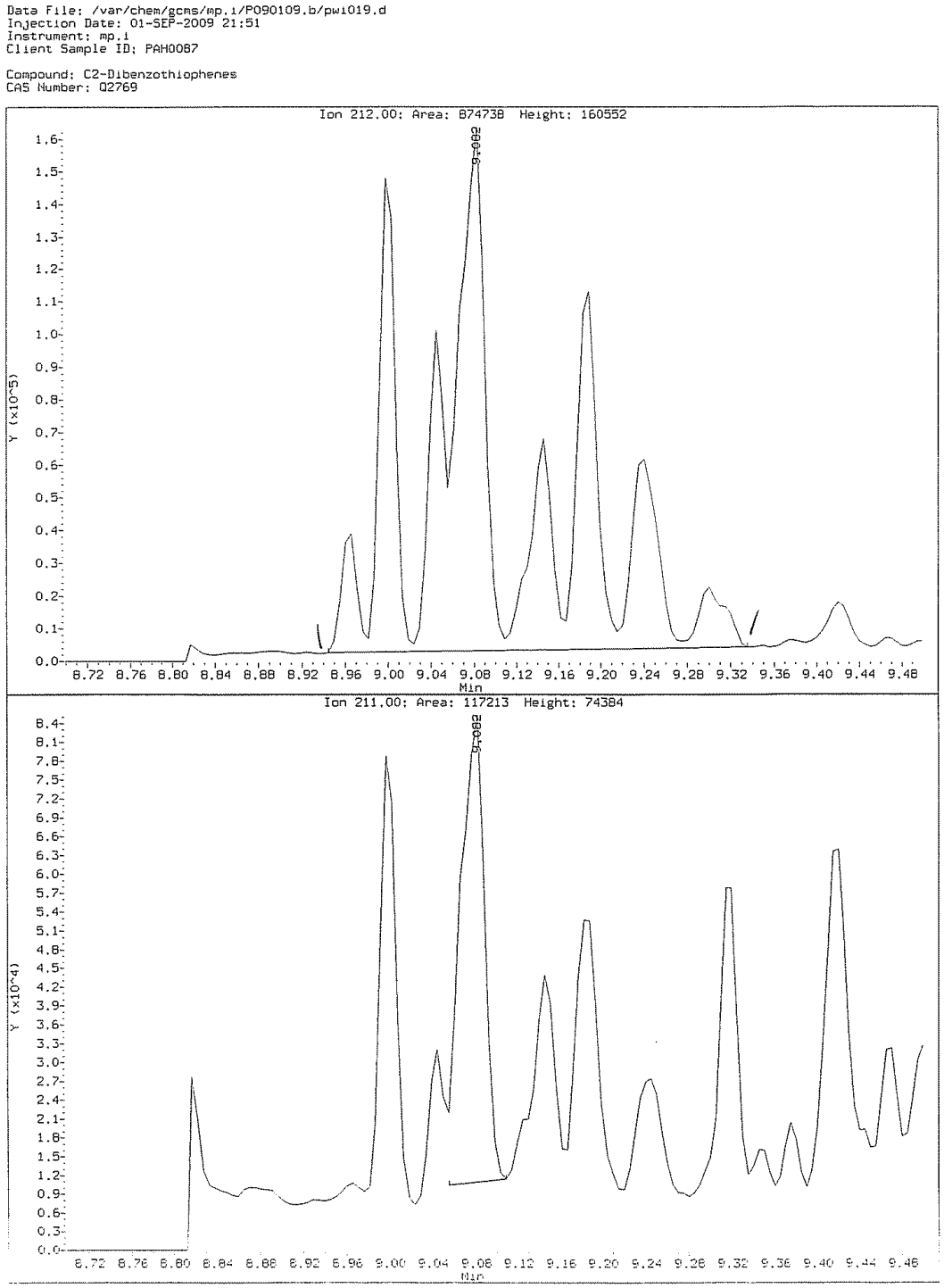

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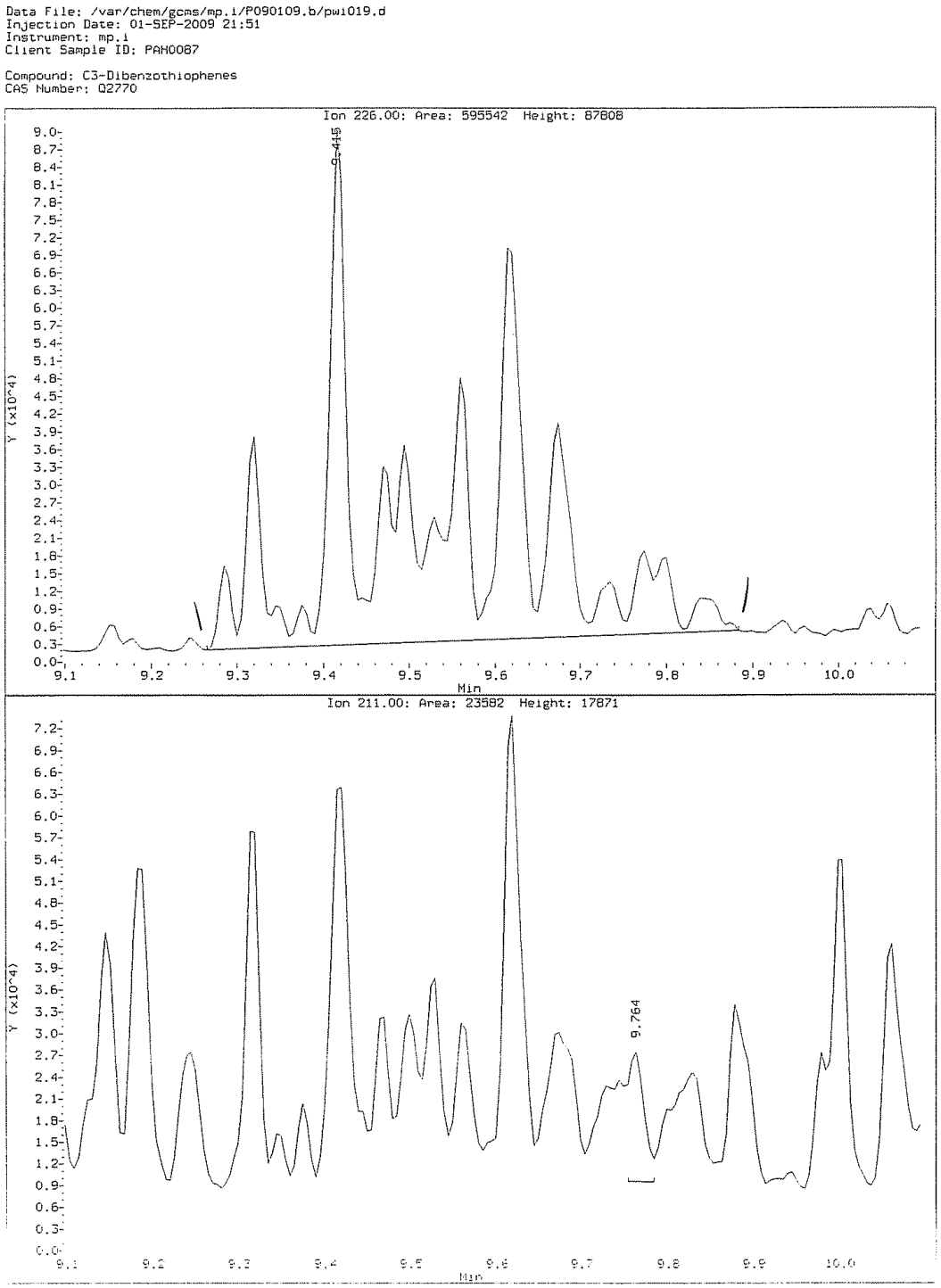

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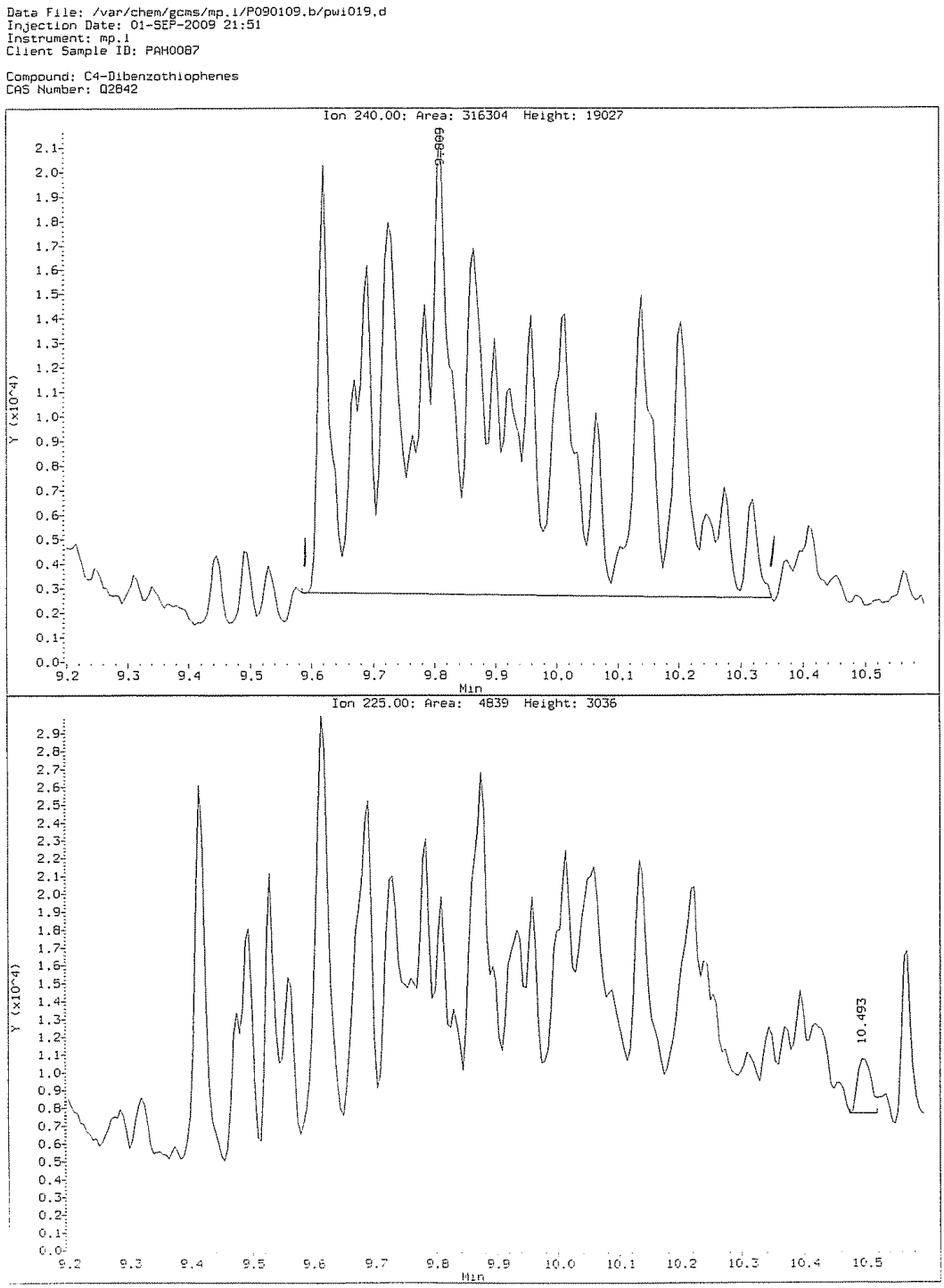


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

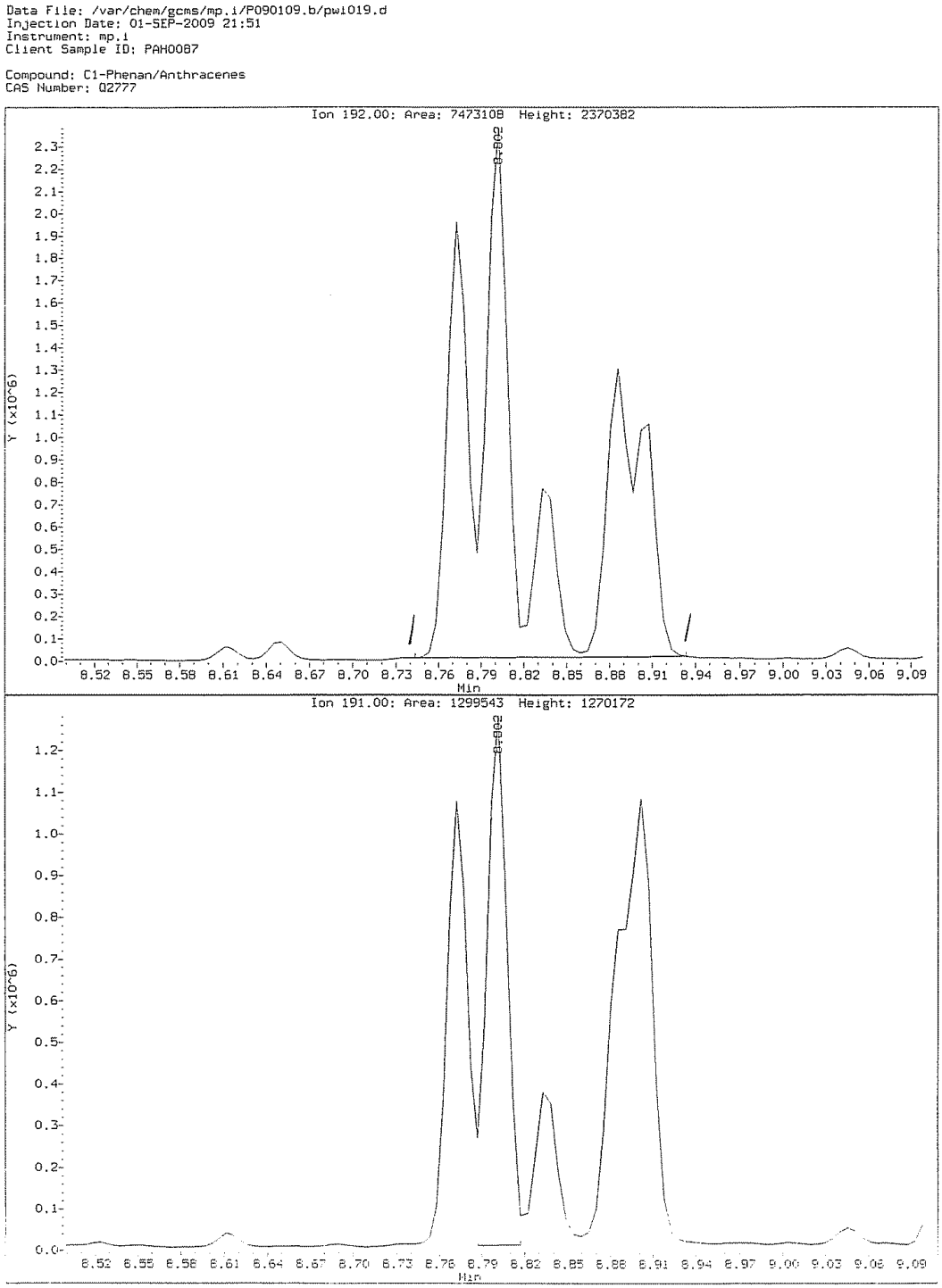
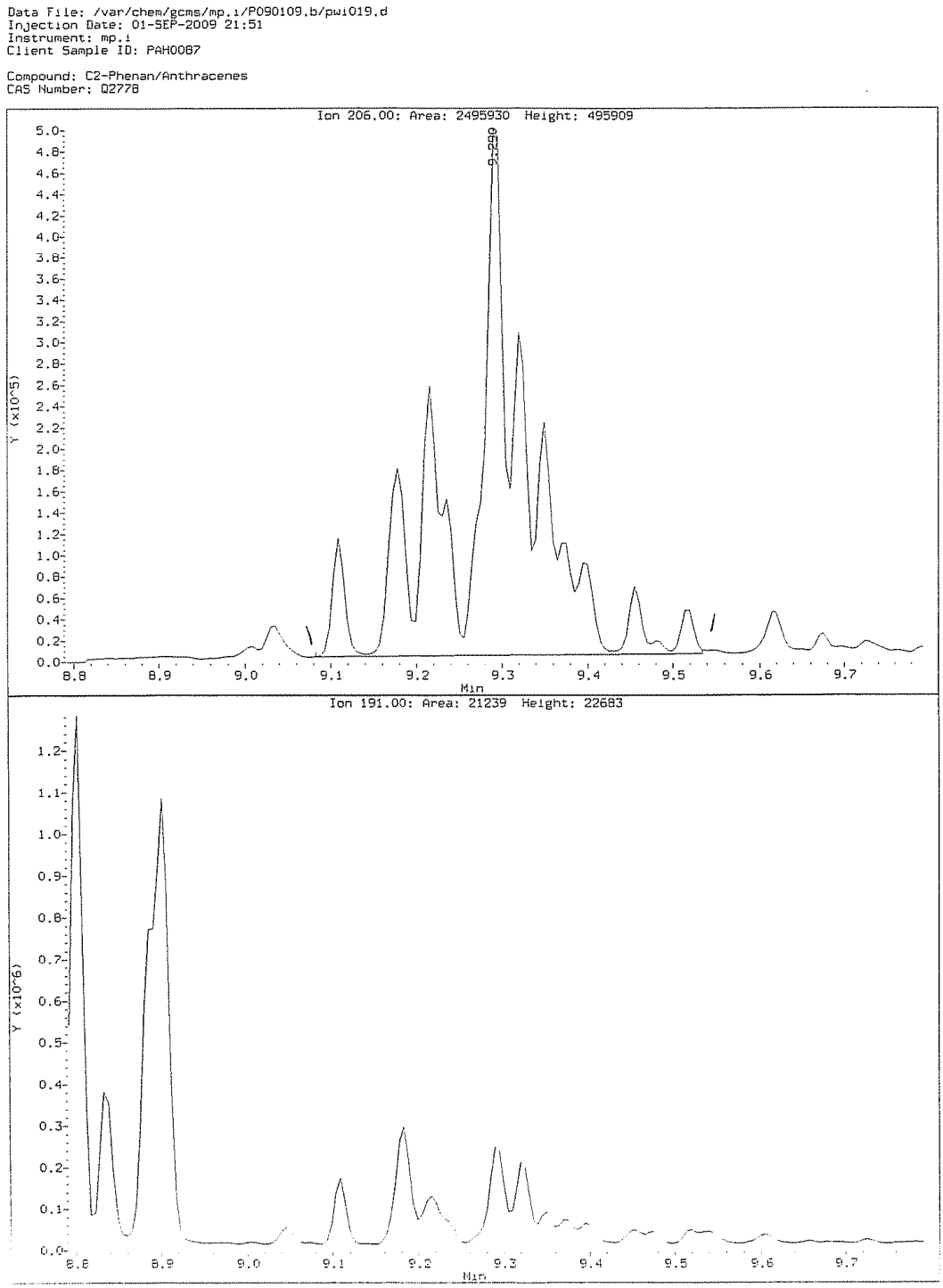


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)



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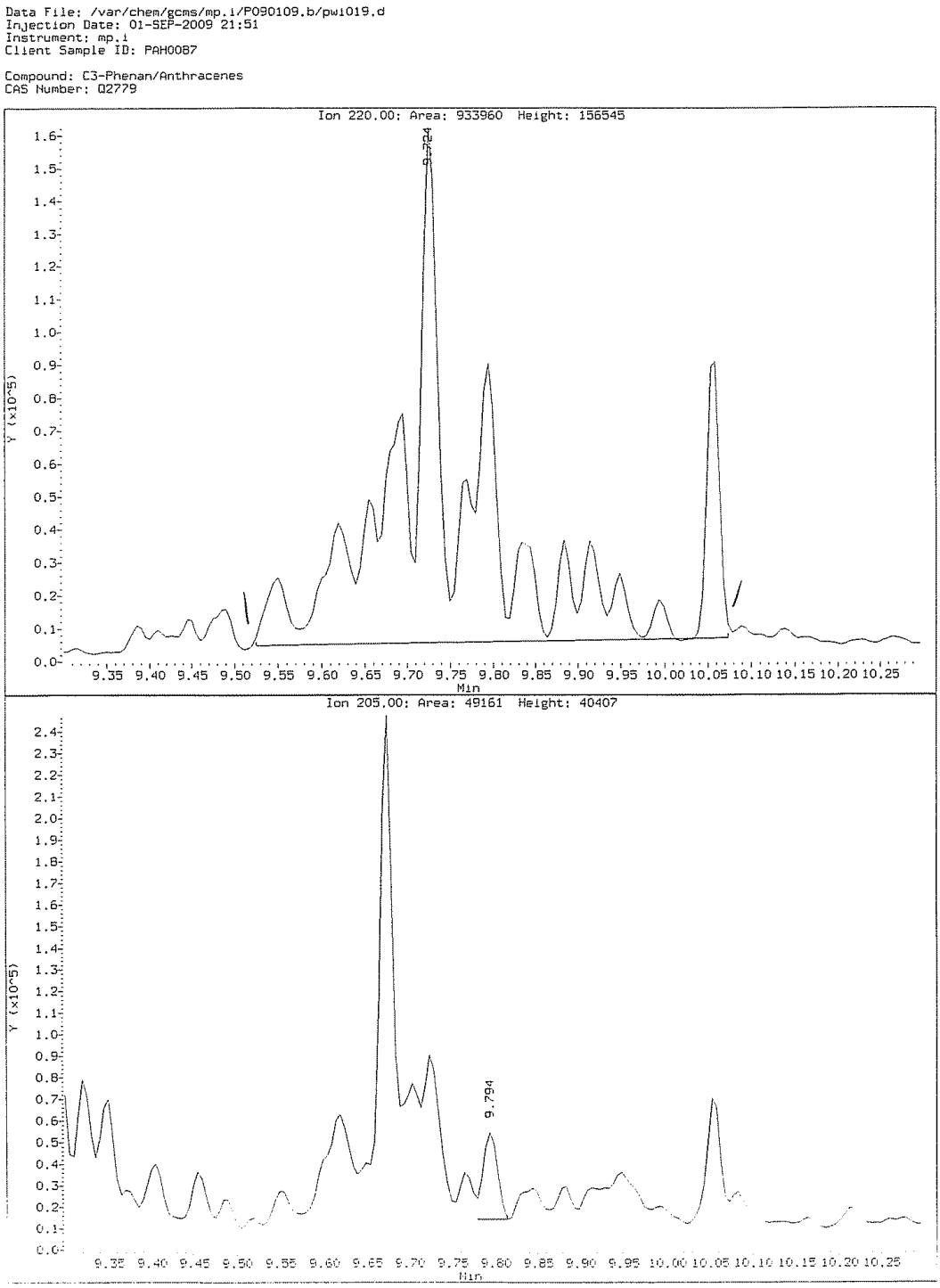

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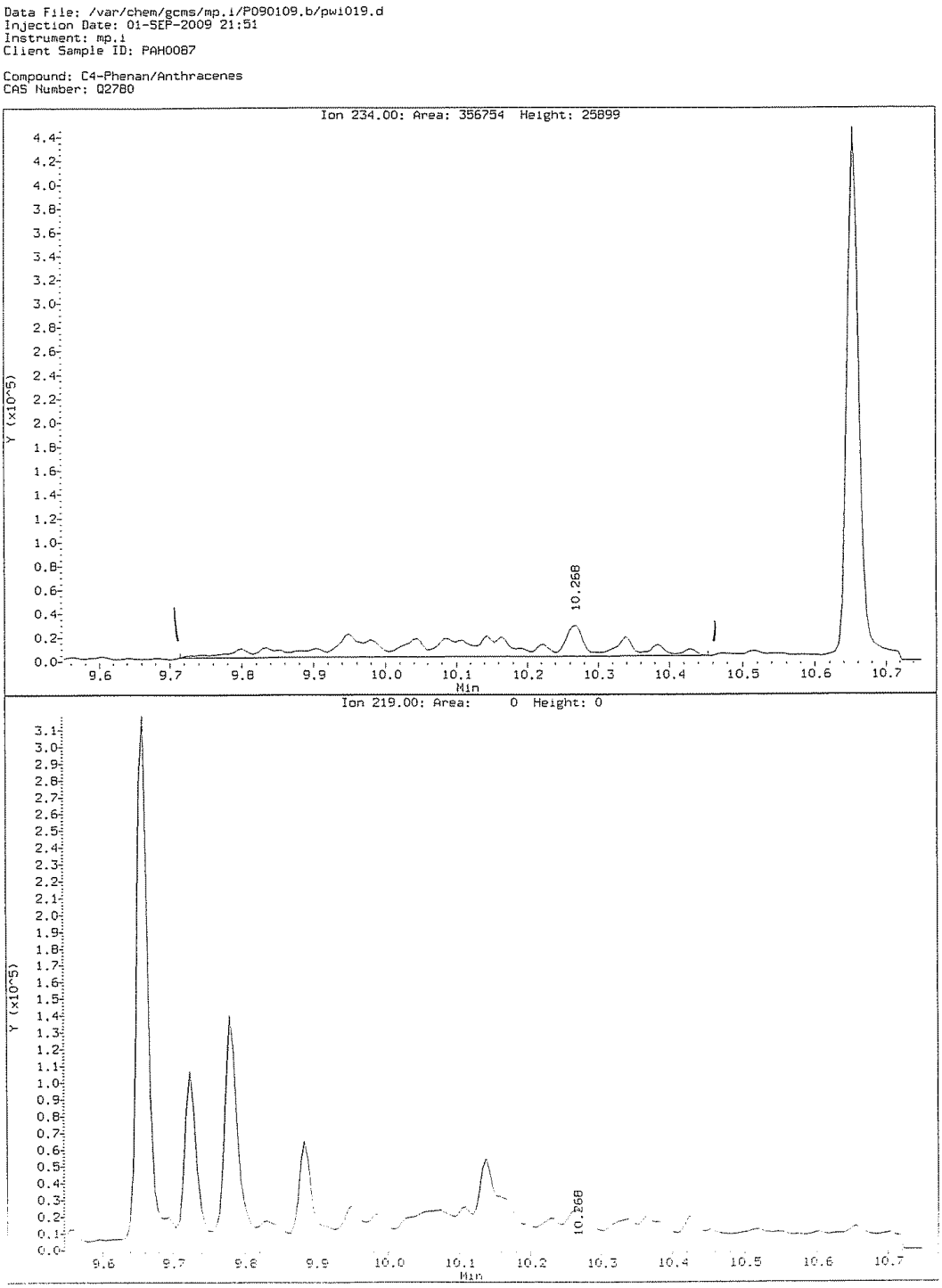

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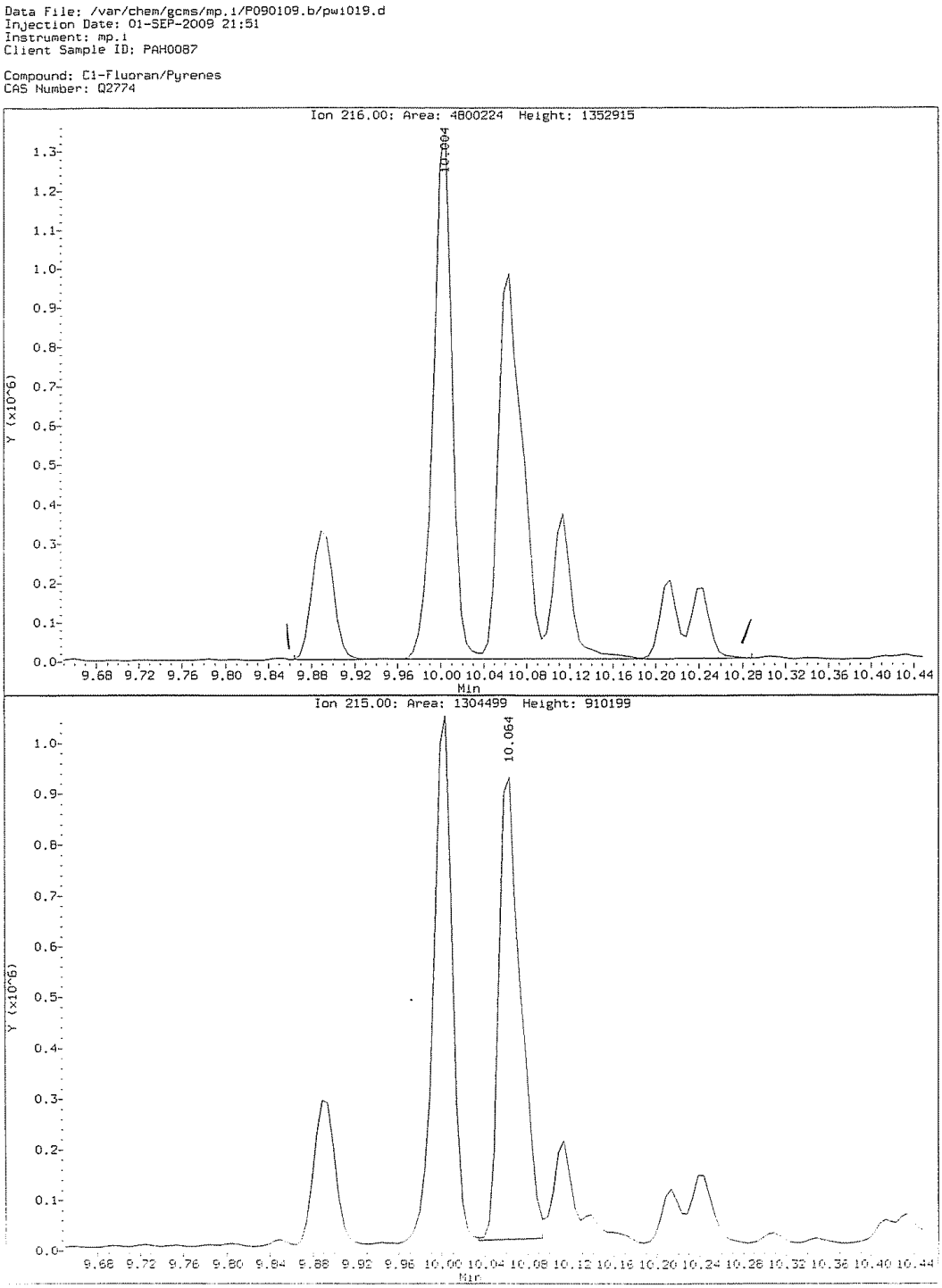

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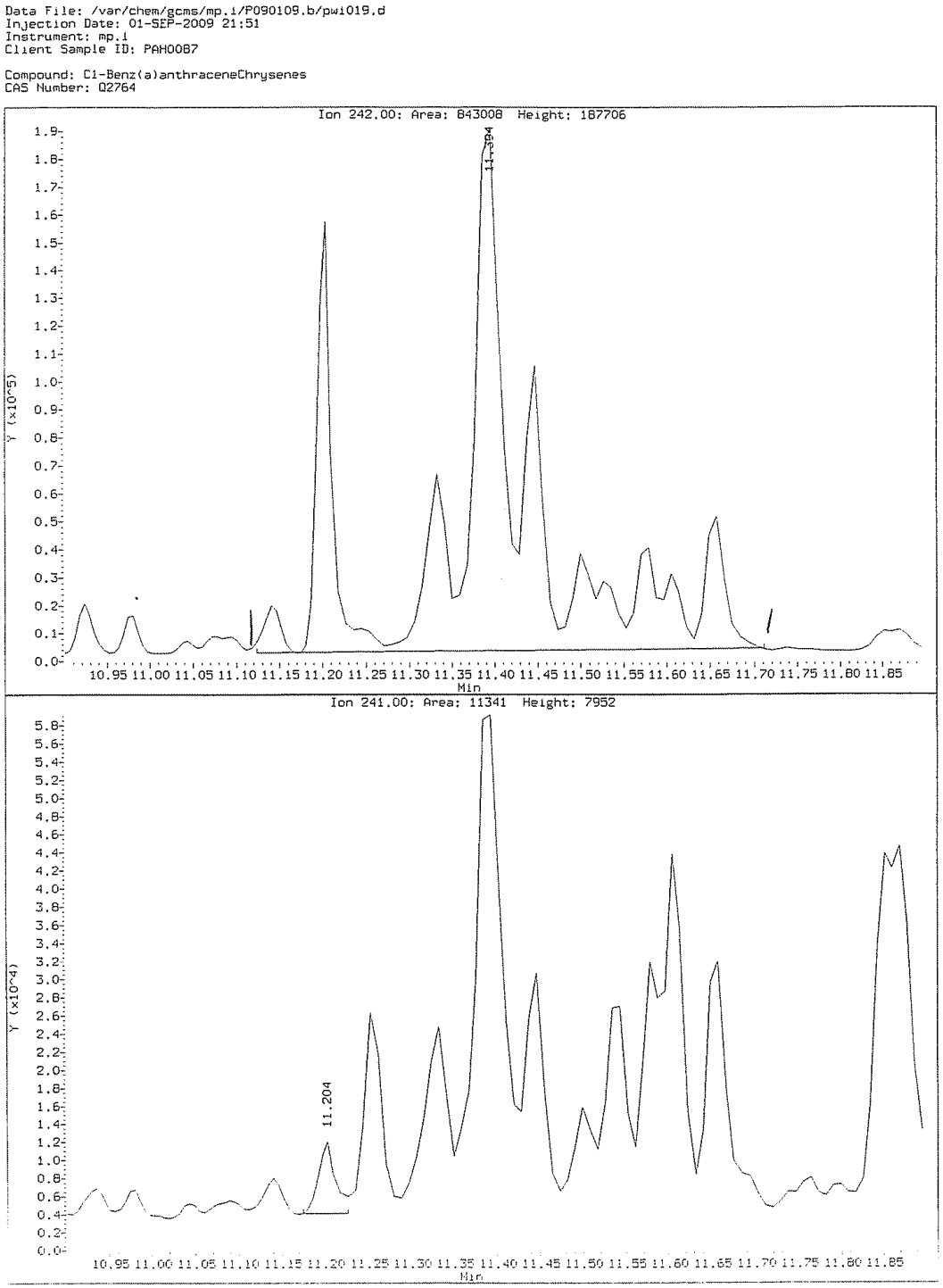

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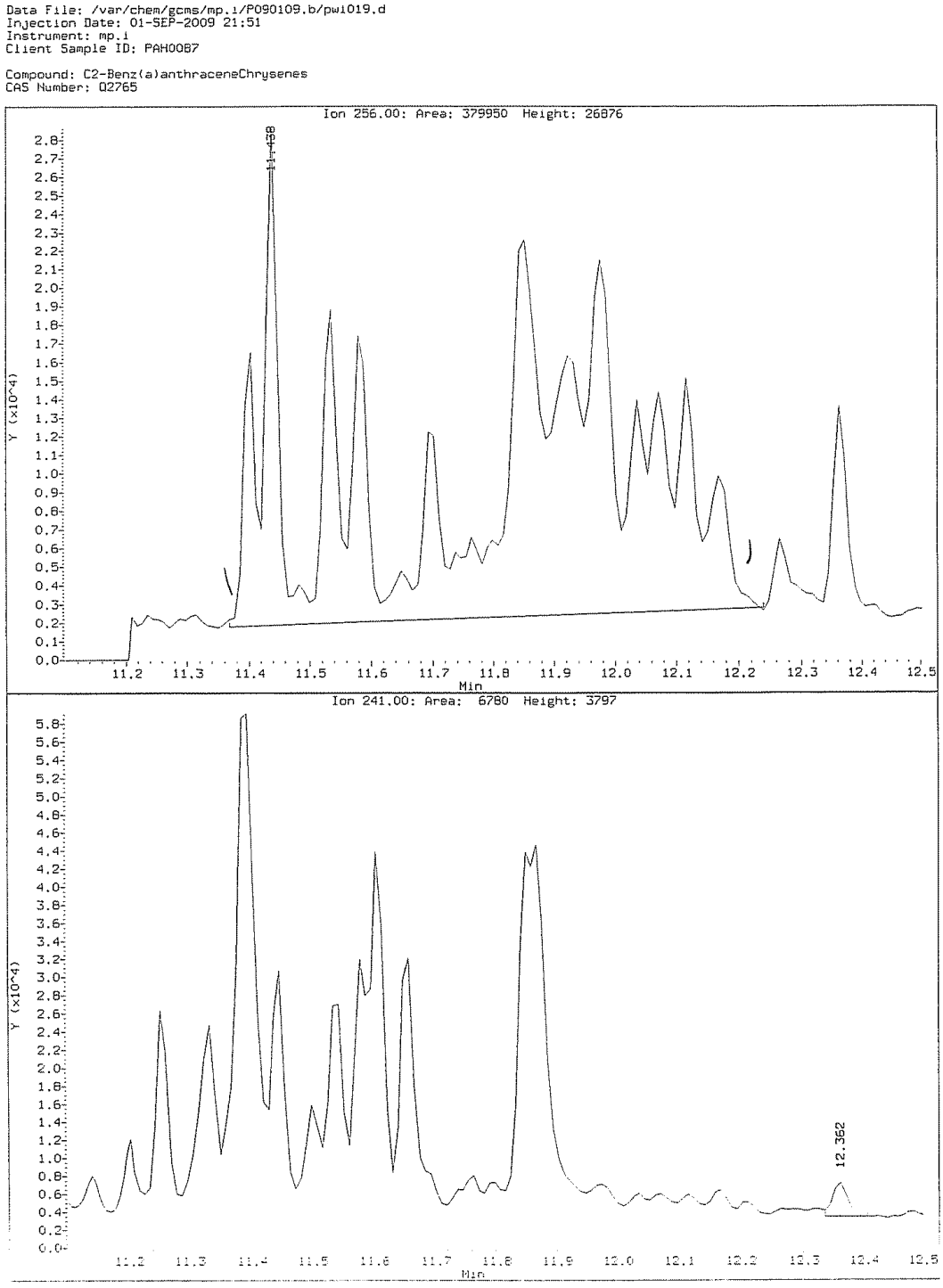


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

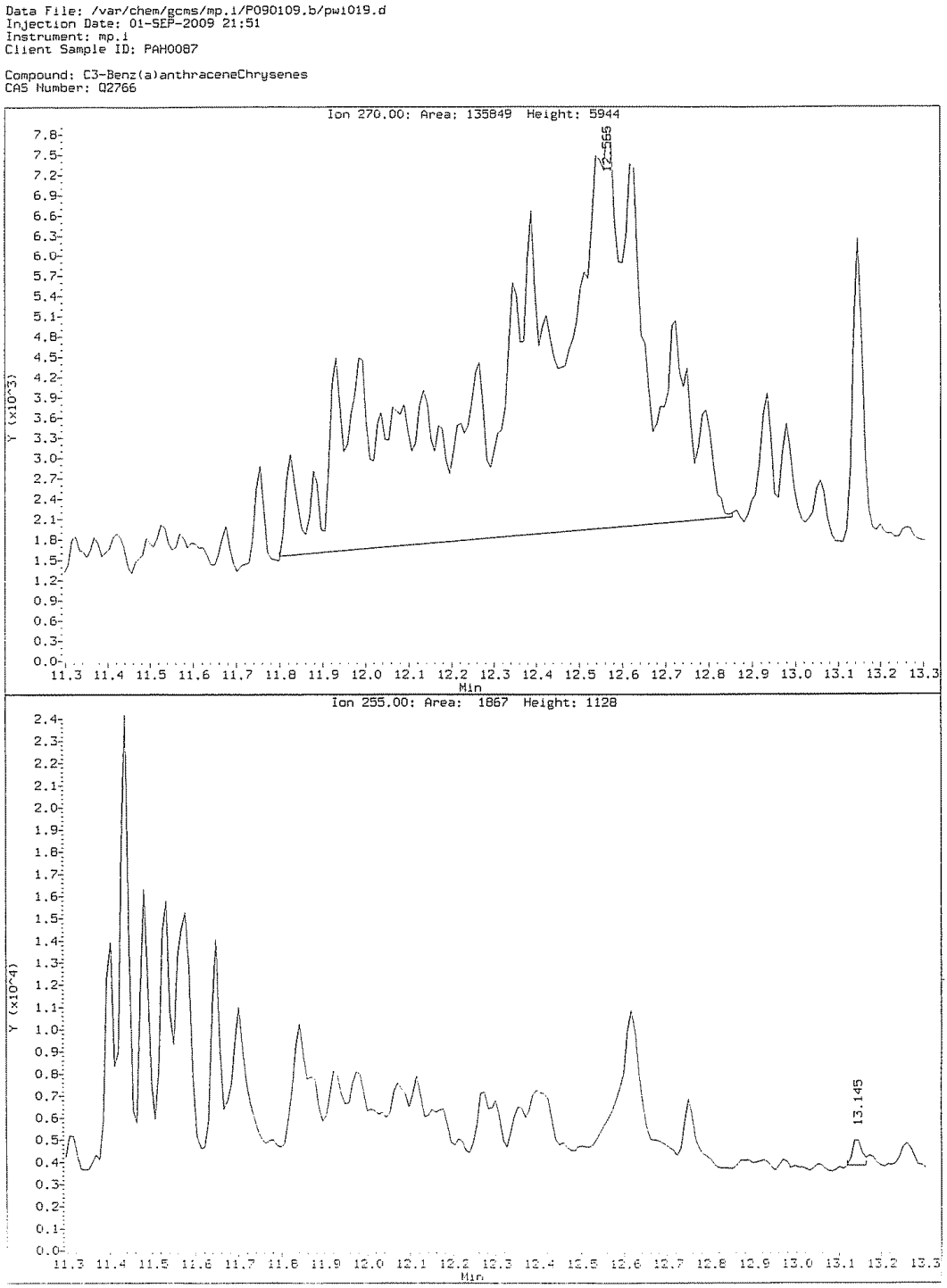
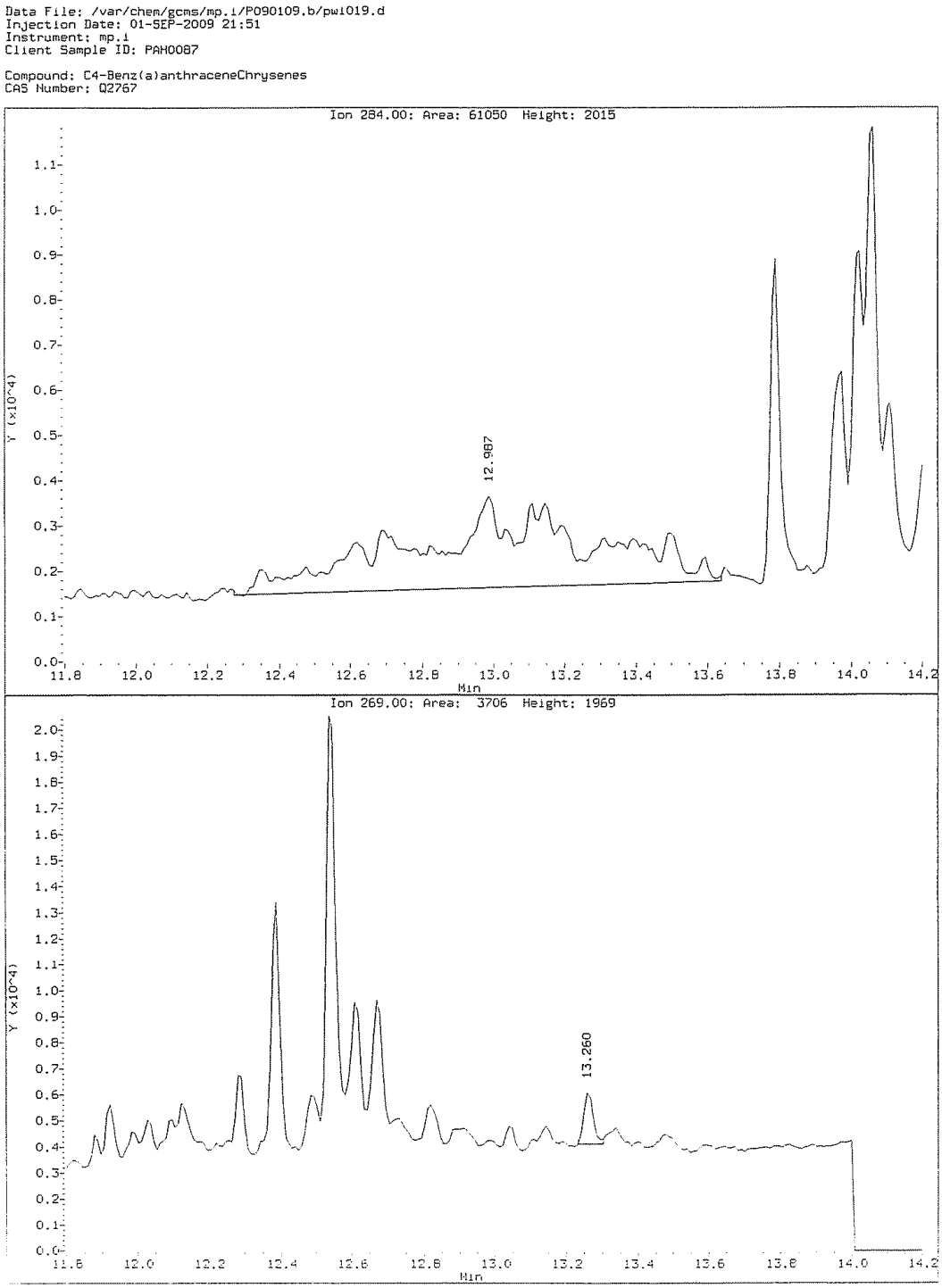


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)



TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Analysis of Polychlorinated Dioxins/Furans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Based on Methods 8290, 8290A, 1613B, 23, 0023A, and TO-9A

(SUPERSEDES: KNOX-ID-0004, Rev. 10)

Prepared By: _____ 3/23/12

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Laboratory Director

1. Scope and Application

1.1 This procedure is used for the determination of tetra- through octa- chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in water, soils, solids, sediments, wipes, biological samples, fly ash, XAD resin, filters, still bottoms, waste oils, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). This procedure is designed to meet analytical program requirements where US EPA Method 8290, 8290A, 1613B, 23, 0023A, or TO-9A is specified.

1.2 The seventeen 2,3,7,8-substituted and total Tetra-Hepta PCDDs/PCDFs listed in Table 1 can be determined by this procedure. Specifications are also provided for separate determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF). In addition, total homologs (i.e., Total TCDD, Total TCDF, etc.) can be identified by this method.

1.3 The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The minimum levels (MLs) in Table 2 are the levels at which the PCDDs/PCDFs can be quantitated with no interferences present.

1.4 This procedure is designed for use by analysts who are experienced with residue analysis and skilled in HRGC/HRMS. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.5 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2. Summary of Method

2.1 This procedure uses high resolution capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS) techniques. Refer to SOPs KNOX-OP-0001, current revision and KNOX-ID-0012, current revision for the procedures used for sample extraction and cleanup.

2.2 Samples are spiked with a solution of known amounts of the isotopically labeled internal standards listed in Table 13 and Table 15. The samples are then extracted using matrix specific extraction procedures.

2.2.1 Water samples are extracted using separatory funnel techniques with methylene chloride as the extraction solvent.

2.2.2 Solid samples are extracted by Soxhlet extraction with the appropriate solvent.

2.2.3 Organic liquid waste samples are diluted in solvent.

2.3 After extraction, the sample is concentrated and solvent exchanged to hexane. The extract is then subjected to one or more optional cleanup steps to remove the sample of interferences. The final extract is prepared by adding a known amount of the labeled recovery standards ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD) and concentrating to the final volume.

2.4 The acid-base cleanup of the sample is used before column chromatography for samples that contain large amounts of basic and acidic coextractable compounds. If such interferences are not removed before column chromatography, they can cause a shift in the predicted elution pattern. Conditions which can indicate the need for this procedure are as follows: Samples which are highly colored, samples which contain lipids or other oxidizable compounds or samples which contain known large amounts of polar organics.

2.5 Dual Column Cleanup: Silica gel is effective in removing chlorophenoxy herbicide residues, while alumina partitions PCBs, 2,4,5-trichlorophenol and hexachlorophene.

2.6 When the above cleanup techniques do not completely remove interferences, an activated carbon cleanup is used to remove interferences.

2.7 An aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high resolution ($\geq$10,000 resolution) mass spectrometer (HRMS). Two exact m/z's are monitored for each analyte.

2.8 The identification of the target 2,3,7,8 substituted isomers is based on their retention time relative to the labeled internal standards as established during routine calibration and the simultaneous detection of the two most abundant ions in the molecular ion region. All other PCDD/PCDF congeners are identified by their retention times falling within retention time windows as established during routine calibration, and the simultaneous detection of the two most abundant ions in the molecular ion region. Confirmation of identification is based on comparing the calculated ion ratios with the theoretical ion abundances. The identification of 2,3,7,8-TCDF is confirmed on an isomer specific (DB-225) GC column.

2.9 Quantitation of the 2,3,7,8-substituted PCDD/PCDF isomers, total PCDDs, and total PCDFs is based on their relative response to the internal standards. A multipoint calibration is performed to establish mean response factors for the target analytes. The instrument performance is routinely checked by the analysis of continuing calibration standards. Method performance is demonstrated by the analysis of method blanks, initial precision and recovery samples, and ongoing precision and recovery samples.

3. Definitions

3.1 Analyte: A PCDD or PCDF tested for by this method. The analytes are listed in Table 1.

3.2 Calibration Standard: A solution prepared from a secondary standard and/or stock solution and used to calibrate the response of the instrument with respect to analyte concentration.

3.3 Calibration Verification Standard (VER): The mid-point calibration standard (CS3) that is used to verify calibration. See Table 5 and Table 6.

3.4 Cleanup Standard: Solution containing $^{37}Cl_4$-2,3,7,8-TCDD that is added to the calibration solutions and to every 1613B sample, blank, and quality control spike sample. It is added after extraction but prior to extract cleanup, and the analysis results are used to judge the efficiency of the cleanup procedures.

3.5 Column Performance Solution Mixture (CPSM): A mixture of TCDD or TCDF isomers (including the 2,3,7,8-TCDD or 2,3,7,8-TCDF isomer) known to elute close to the retention time of 2,3,7,8-TCDD or 2,3,7,8-TCDF on the analytical column being used. It is used to demonstrate acceptable resolution between the 2,3,7,8-TCDD or 2,3,7,8-TCDF isomer and all other TCDD or TCDF isomers on analytical column (percent valley ≤ 25).

3.6 Congener: Any member of a particular homologous series, for example, 1,2,3,7,8-pentachlorodibenzofuran.

3.7 CS1, CS2, CS3, CS4, CS5: See Calibration Standard and Table 5 and Table 6.

3.8 Estimated Detection Limit (EDL): The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level.

3.9 Estimated Maximum Possible Concentration (EMPC): The calculated concentration of a signal in the same retention time region as a target analyte but which does not meet the other qualitative identification criteria defined in the procedure.

3.10 GC: Gas chromatograph or gas chromatography

3.11 Homologous Series: A series of compounds in which each member differs from the next member by a constant amount. The members of the series are called homologs.

3.12 HRGC: High resolution GC

3.13 HRMS: High resolution MS

3.14 ICV: Initial Calibration Verification Standard. A calibration standard from a second source, traceable to a national standard if possible. The ICV is analyzed after the initial calibration to verify the concentration of the Initial Calibration Standards.

3.15 Internal Standards: Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the sample before extraction and are used to calculate the concentration of the target analytes or detection limits.

3.16 Initial Precision and Recovery (IPR): See Initial Demonstration of Capability in Sections 9.1 and 13.2.

3.17 Isomer: Chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example, 1,2,3,4-TCDD and 2,3,7,8-TCDD are structural isomers.

3.18 Laboratory Blank: See Method Blank.

3.19 Laboratory Control Sample (LCS): A laboratory blank spiked with known quantities of analytes. The LCS is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery..

3.20 Maximum Level (MaxL): The concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. Also referred to as the upper method calibration limit (UMCL). It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.21 Method Blank: An aliquot of reagent water, sand, sodium sulfate, or other representative matrix, free of the targets of interest and interferences, that is extracted and analyzed along with the samples to monitor for laboratory contamination.

3.22 Minimum Level (MinL): The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. Also referred to as the lower method calibration limit (LMCL). It is equivalent to the concentration of the lowest calibration standard assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.23 MS: Mass spectrometer or mass spectrometry.

3.24 Multiple Ion Detection (MID): A MS operational mode in which only selected ions are monitored rather than scanning the instrument to obtain a complete mass spectrum.

3.25 Ongoing precision and recovery standard (OPR): See Laboratory Control Sample.

3.26 PCDD: Polychlorinated dibenzo-p-dioxins.

3.27 PCDF: Polychlorinated dibenzofurans.

3.28 PFK: Perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

3.29 FC-43 (PFTBA): Perfluorotributylamine

3.30 Recovery Standard: Solution containing $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD that is added to every sample, blank, and quality control spike sample extract prior to analysis. The results are used to measure the recovery of the internal standards and the cleanup standard.

3.31 Percent Difference (%D): A measure of the difference between two values normalized to one of the values. It is used to determine the accuracy of the concentration measurements of second source verification standards.

3.32 Relative Response Factor (RRF): The ratio of the response of the mass spectrometer to a known amount of a compound relative to that of a known amount of a reference standard as measured in the initial and continuing calibrations. It is used to determine instrument performance and it is used to calculate the concentration of target analytes, internal standard recoveries, or detection limits in samples, blanks, and quality control samples.

3.33 Signal to Noise Ratio: The ratio of the mass spectrometer response of a GC peak to the background noise signal.

3.34 Split Ratio (S): The decimal expression of the proportion of extract used from splits taken after the addition of internal standards and before the addition of recovery standards.

3.35 Window Defining Mix: A solution which contains the first and last eluting isomers of each homologue group and is used to verify that the switching times between the MID descriptors have been appropriately set.

3.36 Additional definitions can be found in the Test America Knoxville QAM.

4. Interferences

4.1 Solvents, reagents, glassware and other sample processing hardware can yield discrete artifacts or elevated baselines that can cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of analysis by performing laboratory method blanks. Analysts must not use PVC gloves, powdered gloves, or gloves with levels of phthalates which cause interference.

4.2 The use of high purity reagents and solvents (pesticide grade) helps minimize interference problems. Where necessary, reagents are cleaned by extraction or solvent rinse.

4.3 Interferences coextracted from the samples can vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated alkyldibenzofurans that can be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. While certain cleanup techniques are provided as part of this method, unique samples can require additional cleanup steps to achieve lower detection limits.

5. Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated must be removed and discarded, other gloves must be cleaned immediately.

5.2.1 Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. For the operations described herein, Nitrile gloves are to be worn. For operations using solvents that may splash, SilverShield® gloves are recommended. SilverShield® gloves protect against breakthrough for most of the solvents used in this procedure.

5.3 The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.4 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them or use thermal protection when working on them while they are above room temperature.

5.5 The mass spectrometer is under high vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source. Alternatively, the source can be removed from the vacuum manifold through a vacuum interlock.

5.6 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power. If the work involved requires measurement of voltage supplies, the instrument can be left on.

5.7 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene chloride	Carcinogen, Irritant	25 ppm-TWA, 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. Can be absorbed through skin.
Hexane	Flammable, Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure can cause lightheadedness, nausea, headache, and blurred vision. Vapors can cause irritation to the skin and eyes.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable, Poison, Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure can include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and can cause skin to become dry and cracked. Skin absorption can occur; symptoms can parallel inhalation exposure. Irritant to the eyes.
Toluene	Flammable, Poison, Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation can cause irritation of the upper respiratory tract. Symptoms of overexposure can include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness can be produced. Causes severe eye and skin irritation with redness and pain. Can be absorbed through the skin.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Can cause coughing, dizziness, dullness, and headache.
Cyclohexane	Flammable, Irritant	300 ppm TWA	Inhalation of vapors causes irritation to the respiratory tract. Symptoms can include coughing, shortness of breath. High concentrations have a narcotic effect.
Tetradecane	Irritant	None established	Inhalation of vapors can cause difficulty breathing, headache, intoxication and central nervous system damage.
Benzene	Flammable, Toxic, Carcinogen	PEL: 1 ppm TWA ; 5 ppm, 15 min. STEL	Causes skin irritation. Toxic if absorbed through skin. Causes severe eye irritation. Toxic if inhaled. Vapor or mist causes irritation to mucous membranes and upper respiratory tract. Exposure can cause narcotic effect. Inhalation at high concentrations can have an initial stimulatory effect on the central nervous system characterized by exhilaration, nervous excitation and/or giddiness, depression, drowsiness or fatigue. Victim can experience tightness in the chest, breathlessness, and loss of consciousness.
Nonane	Flammable	None established	Harmful if inhaled/swallowed. Vapor/mist is irritating to eyes, mucous membranes and upper respiratory tract. Causes skin irritation.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.7.1 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA regulations include benzene and methylene chloride, 2,3,7,8-TCDD and all other 2,3,7,8- substituted PCDD or PCDF isomers.

NOTE: The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound must be treated as a potential health

hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

5.8 Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers must be kept closed unless transfers are being made.

5.9 All procedures that involve solvents such as acetone, toluene, methylene chloride, and hexane (e.g., glassware cleaning and the preparation of standards and reagents) must be conducted in a fume hood with the sash closed as far as the operations permit.

5.10 Personal Hygiene: Thorough washing of hands and forearms is recommended after each manipulation and before breaks (coffee, lunch, and shifts).

5.11 All work must be stopped in the event of a known or potential compromise to the health or safety of an associate. The situation must be reported immediately to a laboratory supervisor.

6. Equipment and Supplies

6.1 Sample Analysis Equipment.

6.1.1 Gas Chromatograph – Must have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and must meet all of the performance specification in Section 10.

6.1.1.1 GC column for PCDDs/PCDFs and for isomer specificity for 2,3,7,8-TCDD – 60m x 0.32mm ID x 0.25µm film thickness DB-5 or RTX-5 fused silica capillary column (J&W No. 123-5062, Restek No.10227 or 10227-125 IntegraGuard) or equivalent is required.

6.1.1.2 GC column for isomer specificity for 2,3,7,8-TCDF – 30m x 0.32mm ID x 0.25µm film thickness DB-225 or RTX-225 fused silica capillary column (J&W No. 123-2232 or Restek No.14024) or equivalent is required.

6.1.2 Mass Spectrometer – Electron impact ionization with the filament electron volts (eV) optimized for best instrument sensitivity, stability and signal to noise ratio. Must be capable of repetitively selectively monitoring 12 exact m/z's minimum at high resolution (≥10,000) during a period of approximately 1 second and must meet all of the performance specifications in Section 10.

6.1.3 GC/MS Interface – The mass spectrometer (MS) must be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beam.

6.1.4 Data System – Capable of collecting, recording, and storing MS data.

7. Reagents and Standards

7.1 Standards and Calibration Solutions: Certified Reference Standards purchased from Cambridge Isotope Laboratories (CIL, Andover Massachusetts), and Wellington Laboratories (Guelph, Ontario, Canada). If the chemical purity is 98% or greater, the weight can be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at room temperature in screw-capped vials with PTFE-lined caps. Standards are used as received after being sonicated and transferred to 2.0 mL amber glass vials with PTFE lined caps.

7.1.1 Stability of Solutions: Standards have an expiration of ten (10) years from date of receipt unless otherwise specified by the manufacturer. Standard solutions used for quantitative purposes must be analyzed periodically, and must be assayed against reference standards before use.

7.2 Initial Calibration Standards:

7.2.1 1613B/8290/8290A: CS1-CS5. CIL Catalog No. EDF-9999. (See Table 5).

7.2.2 23/0023A/TO-9A: CS1-CS5. Wellington Catalog No. EPA-23 CS1-5. (See Table 6).

7.3 Initial Calibration Verification Standards:

7.3.1 1613B/8290/8290A: Wellington Catalog No. EPA-1613-CS3.

7.3.2 23/0023A/TO-9A: CS3. CIL Catalog No. EDF-4052-3.

7.4 Daily Calibration Verification Standards

7.4.1 1613B/8290/8290A: CS3. CIL Catalog No. EDF-9999-3. (See Table 7).

7.4.2 1613B/8290/8290A: CS3. CIL Catalog No. EDF-4141. (See Table 7).

NOTE: This standard can be used as both the Continuing Calibration Standard and the DB/Rtx-5 GC Window Defining Mix/Column Performance Check Solution.

7.4.3 23/0023A/TO-9A: CS3. Wellington Catalog No. EPA-23-CS3. (See Table 8).

7.5 Native Standards

7.5.1 Native Standard Stock Solution: CIL Catalog No. EDF-7999-10x, 400-4000 ng/mL in nonane, 1.2 mL.

7.5.2 Native Standard Working Stock Solution: Dilute 0.300 mL of the native standard stock solution to 3.0 mL in a volumetric flask with nonane for a final concentration of 40-400 ng/mL.

7.5.3 Native LCS Spiking Solution: Dilute 500 µL of the native standard working stock solution to 100 mL in a 125 mL amber bottle with a PTFE lined cap

with iso-octane to a final concentration of 0.2-2.0 ng/mL. 1.0 mL of this solution is added to each LCS, LCSD or MS/MSD sample. See Table 11 for a complete list of compounds and their concentrations.

7.6 1613B/8290/8290A Internal Standards

7.6.1 1613B/8290/8290A Internal Standard Stock Solution: CIL Catalog No. EDF-8999, 100 ng/mL ($^{13}C_{12}$-OCDD 200 ng/mL) in nonane, 500 µL.

7.6.2 1613B/8290/8290A Internal Standard Spiking Solution: Dilute 2000 µL of the internal standard stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with iso-octane to a final concentration of 1.0 ng/mL ($^{13}C_{12}$-OCDD 2.0 ng/mL). 1.0 mL of this solution is added to each sample, method blank and QC sample. See Table 12 for a complete list of compounds and their concentrations.

7.7 2,3,7,8-TCDD/2,3,7,8-TCDF Internal Standards

7.7.1 $^{13}C_{12}$-2,3,7,8-TCDD Internal Standard Stock Solution: CIL Catalog No. ED-900, 50 µg/mL in nonane, 1.2 mL

7.7.2 $^{13}C_{12}$-2,3,7,8-TCDF Internal Standard Stock Solution: CIL Catalog No. EF-904, 50 µg/mL in nonane, 1.2 mL

7.7.3 $^{13}C_{12}$-TCDD/$^{13}C_{12}$-TCDF Internal Standard Secondary Stock Solution: Dilute 0.100 mL of the stock solutions above to 5 mL in a volumetric flask with nonane to a final concentration of 1000 ng/mL.

7.7.4 $^{13}C_{12}$-TCDD/$^{13}C_{12}$-TCDF Internal Standard Spiking Solution: Dilute 200 µL of the internal standard secondary stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with iso-octane to a final concentration of 1.0 ng/mL. 1.0 mL of this solution is added to each sample, method blank and QC sample extract that is extracted for TCDD and/or TCDF analysis only. See Table 2 for a complete list of compounds and their concentrations.

7.8 23/0023A/TO-9A Internal Standards

7.8.1 23/0023A/TO-9A Internal Standard Stock Solution: Wellington Catalog No. EPA-23ISS, 1000 ng/mL ($^{13}C_{12}$-OCDD 2000 ng/mL) in nonane/toluene (80:20 v:v), 1.2 mL.

7.8.2 23/0023A/TO-9A Internal Standard Spiking Solution: Dilute 200 µL of the internal standard stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with iso-octane to a final concentration of 1.0 ng/mL ($^{13}C_{12}$-OCDD 2.0 ng/mL). 1.0 mL of this solution is added to each sample, method blank, and QC sample. See Table 15 for a complete list of compounds and their concentrations.

7.9 Recovery Standards

7.9.1 $^{13}C_{12}$-1,2,3,4-TCDD Recovery Standard Stock Solution: CIL Catalog No. ED-911, 50 µg/mL in nonane, 1.2 mL

7.9.2 $^{13}C_{12}$-1,2,3,7,8,9-HxCDD Recovery Standard Stock Solution: CIL Catalog No. ED-996, 50 µg/mL in nonane, 1.2 mL

7.9.3 Recovery Standard Secondary Stock Solution: Dilute 1.0 mL of the stock solutions above to 10 mL in a volumetric flask with nonane to a final concentration of 5.0 µg/mL.

7.9.4 Recovery Standard Spiking Solution: Add 10 mL of nonane to a 12 mL amber vial with a Class A glass pipette. With a syringe, remove 200 µL of nonane from the vial and add 200 µL of the recovery standard secondary stock solution to a final concentration of 0.1 µg/mL. 20 µL of this solution is added to each sample, method blank and QC sample extract. See Table 2 for a complete list of compounds and their concentrations.

7.10 1613B Cleanup Standards

7.10.1 Cleanup Standard Stock Solution: CIL Catalog No. ED-907, 50 µg/mL in nonane, 1.2 mL

7.10.2 Cleanup Standard Secondary Stock Solution: Dilute 0.100 mL of the 50 µg/mL cleanup standard stock solution to 1.0 mL in a volumetric flask with nonane to a final concentration of 5.0 µg/mL.

7.10.3 Cleanup Standard Working Stock Solution: Dilute 0.120 mL of the 5.0 µg/mL cleanup standard secondary stock solution to 3.0 mL in a volumetric flask with nonane to a final concentration of 200 ng/mL.

7.10.4 Cleanup Standard Spiking Solution: Dilute 200 µL of the 200 ng/mL working stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with hexane to a final concentration of 0.20 ng/mL. 1.0 mL of this solution is added to each 1613B sample, method blank and QC sample extract prior to cleanup. See Table 17 for a complete list of compounds and their concentrations.

7.11 23/0023A/TO-9A Surrogate Standards

7.11.1 23/0023A/TO-9A Surrogate Standard Stock Solution: Wellington Catalog No. EPA-23SSS, 1000 ng/mL in nonane/toluene (95:5 v:v), 1.2 mL.

7.11.2 23/0023A/TO-9A Surrogate Standard Spiking Solution: Dilute 500 µL of the surrogate standard stock solution to 25 mL in a graduated cylinder with nonane to a final concentration of 20 ng/mL. 100 µL of this solution is added

to each sample train components before sampling. See Table 16 for a complete list of compounds and their concentrations.

7.12 PCDD/PCDF Window Defining and Isomer Specificity Standard

7.12.1 PCDD/PCDF Window Defining and Isomer Specificity Mixture: CIL Catalog No. EDF-4141. This standard contains the daily standard, window defining mix and the isomer specificity mix.

7.13 Perfluorokerosene (PFK) is used in neat form to tune and calibrate the mass spectrometer. Fluka (Catalog No. - 77275) has been found to be superior to other sources of PFK.

7.14 FC-43 (PFTBA) is used in neat form to tune and calibrate the mass spectrometer. (Scientific Instrument Services Catalog No. FC-43-35).

8. Sample Collection, Preservation and Storage

8.1 Sampling is not performed for this method by TestAmerica Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, "Sample Receipt and Log In", current revision. Sample container and preservation recommendations are listed in the table below.

Method:	**1613B**	**8290/8290A[1]**	**23**	**0023A[1]**	**TO-9A**
Holding Times	Samples – 1 year from collection to extraction Extracts – 1 year from extraction to analysis	Samples – 30 days from collection to extraction Extracts – 45 days from extraction to analysis Tissue Extracts –45 days from collection to analysis	Samples – 30 days from collection to extraction Extracts – 45 days from extraction to analysis	Samples – 30 days from collection to extraction Extracts – 45 days from extraction to analysis	Samples – 7 days from collection to extraction Extracts – 40 days from extraction to analysis
Containers	Amber Glass	Amber Glass	See KNOX-ID-0012	See KNOX-ID-0012	See KNOX-ID-0012
Preservation:					
Aqueous Samples	≤6 °C in the dark If residual chlorine is present, add 80 mg/L sodium thiosulfate. If pH > 9, adjust to pH 7-9 with sulfuric acid	≤6 °C in the dark If residual chlorine is present, add 80 mg/L sodium thiosulfate.	N/A	N/A	N/A
Solid Samples	<-10 °C in the dark	≤6 °C in the dark	N/A	N/A	N/A
Tissue Samples	<-10 °C in the dark	<-20 °C in the dark[2]	N/A	N/A	N/A
Air Samples	N/A	≤6 °C in the dark	≤6 °C in the dark	≤6 °C in the dark	≤6 °C in the dark

1 If the freezer used to store samples is not capable of reaching a temperature of <-20 °C when the temperature control is set to its maximum limit, a storage higher temperature is acceptable as long as it is <-10 °C.

9. Quality Control

9.1 The Initial Demonstration of Capability (IDOC) studies described in Section 13 must be completed with acceptable results before analysis of samples can begin.

9.2 The Method Detection Limit (MDL) study described in Section 13 must be completed with acceptable results before analysis of samples can begin.

9.3 A laboratory method blank must be run along with each analytical batch of 20 (10, including field blank if provided, for TO-9A) or fewer samples. The method blank is normally analyzed immediately after the calibration standards. The method blank must meet the following acceptance criteria:

9.3.1 The concentration of target analytes in the method blank must be less than the minimum level (ML) and "B" qualifiers are added to all associated samples with analytes detected in the method blank above the estimated detection limit (EDL).

9.3.2 If the concentration of target analytes in the method blank is greater than minimum level (ML) but less than 10% of the concentration in the associated samples, corrective action is required but the associated data can be reported. At a minimum, corrective action must include the addition of "B" qualifiers to all associated samples with analytes detected in the method blank above the ML and documentation in the case narrative.

9.3.3 If the method blank sample fails to meet the acceptance criteria, the Project Manager is notified and the entire sample batch is re-extracted. If there is insufficient sample volume remaining for re-extraction, the client is contacted for information about the availability of additional sample volume. If there is no additional sample available, the original sample data is flagged and reported. A nonconformance memo is initiated describing the problem and corrective action. The problem and corrective action is documented in the project narrative.

9.3.4 If there is no target analyte greater than the minimum levels (ML) in the samples associated with an unacceptable method blank, the data can be reported with qualifiers. Such action must be done in consultation with the client.

9.3.5 The method blank internal standard recoveries must be within established control limits. In the situation where method blank internal standard recoveries are below acceptance limits, method blank results can be used if the following criteria are met:

- All internal standards peaks must exhibit a 10:1 signal to noise ratio or greater
- The estimated detection limit (EDL) is at or above the minimum level (ML)

9.3.5.1 The application of the above criteria must be noted in the case narrative.

9.3.6 Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.4 Instrument Blank

9.4.1 Instruments must be evaluated for contamination during each 12 hour analytical sequence. This is accomplished by analysis of a method blank if available. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of solvent with the internal standards and recovery standards added. It is evaluated in the same way as the method blank.

9.5 Laboratory Control Sample

An LCS is analyzed along with each analytical batch of 20 (10, including field blank if provided, for TO-9A) or fewer samples. The LCS consists of reagent water for aqueous samples, and a clean solid matrix (sodium sulfate) for solid samples. The LCS extract must be subject to the same clean up procedures as the associated sample extracts. LCS spike components, concentrations, and control limits are given in Table 11.

9.5.1 If any analyte in the LCS is outside the control limits, corrective action must occur. Corrective action includes:

9.5.1.1 If the LCS fails to meet the acceptance criteria, the Project Manager is notified and the entire sample batch is re-extracted. If there is insufficient sample volume remaining for re-extraction, the client is contacted for information about the availability of additional sample volume. If there is no additional sample available, the original sample data is flagged and reported. A nonconformance memo is initiated describing the problem and corrective action. The problem and corrective action is documented in the project narrative.

9.5.1.2 If the batch is not re-extracted and reanalyzed, an NCM must be initiated and the reasons for accepting the batch must be clearly presented in the project records and the report. (An example of an acceptable reason for not reanalyzing might be that the matrix spike and matrix spike duplicate recoveries are within control limits, the method blank and sample internal standard recoveries are within limits, and the data clearly demonstrates that the problem was confined to the LCS).

9.5.1.3 For method TO-9A calculate the precision (%D) from the LCS/LCSD. The precision must be within ± 30%.

9.5.2 Ongoing monitoring of the LCS provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.6 Internal Standards

Internal standards are spiked into all samples, blanks, and laboratory control samples to assess method performance on the sample matrix. The recovery of each labeled internal standard must be within the limits in Table 13 for methods 1613B, 8290 and 8290A or in Table 15 for methods 23, 0023A, and TO-9A.

9.6.1 If the recovery is outside these limits the following corrective action must be taken:

9.6.1.1 Check all calculations for error.

9.6.1.2 Ensure that instrument performance is acceptable.

9.6.1.3 Recalculate the data and/or reanalyze if either of the above checks reveal a problem.

9.6.1.4 If the recovery of any internal standard is less than the lower control limit, calculate the S/N ratio of the internal standard. If the S/N is > 10 and the estimated detection limits (EDLs) are less than the minimum levels (MLs), report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the estimated detection limits (EDLs) are greater than the minimum levels (MLs), re-extract and re-analyze the sample. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample can be re-extracted or additional clean-ups can be employed. The decision to reanalyze or flag the data is made in consultation with the client.

9.7 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – Method 8290 only.

When method 8290 is performed a matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every 20 samples of a given matrix. **Note that a MS/MSD is not required for Method 8290A**. The MS/MSD is spiked with the same subset of analytes as the LCS (See Table 12). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

9.7.1 If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action is to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis can proceed. The reasons for accepting the batch must be documented in the report narrative.

9.7.2 If the recovery for any component is outside QC limits for both the MS/MSD and the LCS, the analysis is out of control and corrective action must be taken. Corrective action normally includes repreparation and reanalysis of the batch.

9.7.3 If a MS/MSD is not possible due to limited sample, then a LCSD must be analyzed. The LCSD is evaluated using the same acceptance criteria as the LCS. The RPD of the LCS and LCSD are compared to the acceptance limits in Table 12.

9.7.4 The MS/MSD must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds are diluted out.

9.8 Surrogate Standards – Methods 23, 0023A, TO-9A

Field surrogate standards are added to the collection media prior to sample collection when performing methods 23, 0023A, or TO-9A. The surrogate recoveries are calculated relative to the internal standards and are a measure of sampling efficiency. The recovery of the surrogate standards must be within the limits specified in Table 16. Poor recoveries of the surrogate standards can indicate breakthrough in the sampling train.

9.8.1 If the recovery is outside these limits the following corrective action must be taken:

9.8.1.1 Check all calculations for error.

9.8.1.2 Ensure that instrument performance is acceptable.

9.8.1.3 Recalculate the data and/or reanalyze if either of the above checks reveal a problem.

9.8.1.4 Flag the results that are outside control limits and notify the Project Manager. The client must be notified and consulted for additional corrective action.

10. Calibration and Standardization

10.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by the results of continuing calibration procedures described below. The other type, continuing calibration, consists of analyzing the column performance check solution and a calibration solution (CS3). No samples are to be analyzed until acceptable calibration as described in sections 10.2 and 10.2.9.1 is demonstrated and documented. A 2uL injection volume is specified for all extracts, blanks, calibration solutions and performance check samples. A 1uL injection volume can be used; however, the laboratory must keep the injection volume the same throughout calibration and analysis.

10.2 Initial Calibration

10.2.1 Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 5 for methods 1613B and 8290/8290A or in Table 6 for methods 23, 0023A, or TO-9A. Store calibration standards at room temperature in the dark. Calibration standard solutions have an expiration date of ten (10) years from date of receipt unless otherwise specified by the manufacturer/supplier.

10.2.2 Establish operating parameters for the GC/MS system (suggested operating conditions are displayed in Figure 1 and Figure 2). For method 1613B adjust the GC conditions to meet the relative retention times for the PCDDs/PCDFs listed in Table 3. The cycle time for MID descriptors must be ≤ 1 sec.

10.2.3 By using a PFK or FC-43 molecular leak, tune the instrument to meet the minimum resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or 313.9838 (FC-43) or any other reference signal close to the m/z 303.9016 (from TCDF).

10.2.4 By using peak matching conditions and the aforementioned either PFK or FC-43 reference peak, verify that the exact mass of m/z 380.9760 (PFK) or m/z 363.9807 (FC-43) is within 5 ppm of the required value. Document that the resolving power at reduced accelerating voltage of m/z 380.9760 (PFK) or m/z 363.9807 (FC-43) is greater than 10,000 (10 percent valley).

10.2.5 Analyze 2µL of the Window Defining Mixture and set the switchpoints for the MID descriptors. The switchpoints must be set to encompass the retention time window of each congener group.

10.2.6 If the initial calibration is being performed on the DB-5 or RTX-5 column, analyze 2µL of the Column Performance solution. The chromatographic peak separation between 2,3,7,8-TCDD and the closest eluting non-2,3,7,8-TCDD isomer must be resolved with a % Valley of $\underline{<}$ 25, where

$$\%\ \text{Valley} = \frac{\text{baseline to valley height of closest eluting isomer}}{\text{peak height of 2,3,7,8-TCDD}} \times 100$$

If the initial calibration is being performed on the DB-225 or RTX-225 column, analyze 2µL of the TCDF Column Performance solution. The chromatographic peak separation between 2,3,7,8-TCDF and the closest eluting non-2,3,7,8-TCDF isomer must be resolved with a % Valley of ≤ 25, where

$$\%\ \text{Valley} = \frac{\text{baseline to valley height of closest eluting isomer}}{\text{peak height of 2,3,7,8-TCDF}} \times 100$$

10.2.7 Analyze 2µL of each of the five calibration standards and calculate the RRF of each analyte vs. the appropriate internal standard listed in Table 3 for

methods 1613B, 8290/8290A or in Table 4 for methods 23, 0023A, and TO-9A using the following equation;

$$RRF = \frac{As \times Cis}{Ais \times Cs}$$

where:

As =]sum of the areas of the quantitation ions of the compound of interest
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Cis = concentration of the appropriate internal standard
Cs = concentration of the compound of interest

10.2.7.1 Calculate the mean relative response factor (mean RRF) and the percent relative standard deviation (RSD) of the relative response factors for each compound of interest in the five calibration standard solutions using the following equations;

$$\overline{RRF}_{n=5} = \frac{1}{n} \times \sum_{i=1}^{n} RF_i$$

$$RSD_{n=5} = \sqrt{\frac{\sum_{i=1}^{n} \left(RF_i - \overline{RF}\right)^2}{n-1}} \times \frac{100}{\overline{RRF}}$$

10.2.8 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met for each initial calibration standard before sample analyses are performed. If acceptable initial calibration is not achieved, identify the root cause, perform corrective action, and repeat the initial calibration. If the root cause can be traced to problems with an individual analysis within the calibration series, follow the procedure in Test America Policy CA-T-P-002 Selection of Calibration Points, current revision (see reference section 16.10).

10.2.8.1 The percent relative standard deviation (RSD) for the mean relative response factors must be within the acceptance criteria listed in Table 5 for methods 1613B, 8290/8290A or in Table 6 for methods 23, 0023A, and TO-9A.

10.2.8.2 The peaks representing the PCDDs/PCDFs and labeled compounds in the calibration standards must have signal-to-noise ratios (S/N) ≥ 10.

10.2.8.3 The ion abundance ratios must be within the specified control limits in Table 22.

10.2.8.4 For method 1613B the absolute retention time of $^{13}C_{12}$-1234-TCDD must exceed 25.0 minutes on the DB/Rtx-5 column and 15.0 minutes on the DB/Rtx-225 column.

10.2.8.5 Corrective action can include replacing the injector port liner, replacing the injector port septum, removal of a small portion of the front of the analytical column, replacing the autosampler syringes and rinse solvent, adjusting the instrument tuning, cleaning the ion volume or ion source, installing a new analytical column and replacing the calibration standard solutions.

10.2.9 Analyze 2µL of the Initial Calibration Verification (ICV) Standard in section 7.3 after the completion of the initial calibration prior to sample analysis. Calculate the concentration of the ICV using the RRFs from the CS3 standard analyzed in section 10.2.7 and the formula in section 12.3.4. Calculate the percent difference (%D) between the expected and the calculated ICV concentration using the following formula.

$$\%D = \frac{(C_{Exp} - C_{Calc})}{C_{Exp}} \times 100$$

Where:
C_{Exp} = The expected concentration of the Standard.
C_{Calc} = The calculated concentration of the Standard.

10.2.9.1 The general criteria for percent difference acceptance limits is ±25% for all native compounds. The warning limits for percent difference is ±25% to ±35%.

10.2.9.2 All data associated with compounds with percent differences in the warning limits must be reviewed before acceptance.

10.2.9.3 All data associated with compounds with percent differences outside the warning limits must be documented as an NCM. Corrective action must be taken and can include the following:

- Reanalyze the ICV Standard
- Replace and reanalyze the ICV Standard
- Evaluate the instrument performance
- Evaluate the Initial Calibration Standards

10.3 Continuing Calibration

10.3.1 Continuing calibration is performed at the beginning of a 12 hour period after successful mass resolution and GC resolution performance checks. A calibration check is also required at the end of a 12 hour period when performing method 8290/8290A or 0023A.

10.3.2 Document the mass resolution performance as specified in sections 10.2.3 and 10.2.4. The mass resolution checks must be performed at the beginning and at the end of each 12-hour shift.

10.3.3 Analyze 2µL of the Window Defining Mixture and/or Column Performance Solution Mixture under the same instrument conditions used to perform the initial calibration. Determine and document acceptable column performance as described in section 10.2.5 and 10.2.6.

10.3.4 Analyze 2µL of the Daily Calibration Standard Solution (CS3). Calculate the concentrations and percent difference of the standard using the formulas in sections 12.3.4 and 10.2.9.

NOTE: The combined Continuing Calibration Standard/Window Defining Mix/Column Performance Solution specified in section 7.4.2 can be used in section 10.3.2, 10.3.4, and 10.3.6.

10.3.5 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met at the beginning of each 12 hour period that samples are analyzed. If acceptable beginning continuing calibration criteria is not met, identify the root cause, perform corrective action and repeat the continuing calibration. If the second consecutive beginning continuing calibration does not meet acceptance criteria, additional corrective action must be performed. Acceptable performance must be demonstrated after two consecutive failing beginning continuing calibrations by the analysis of two consecutive acceptable beginning continuing calibrations or by analysis of a new initial calibration.

10.3.5.1 The measured concentration or percent difference for each compound must be within the acceptance criteria limits in Table 7 for method 1613B, 8290/8290A or in Table 8 for methods 23, 00231A and TO-9A.

10.3.5.2 For method 1613B the relative retention times of PCDDs/PCDFs and labeled compounds in the standard must be within the limits in Table 3.

10.3.5.3 The peaks representing the PCDDs/PCDFs and labeled compounds in the calibration standard must have signal-to-noise ratios (S/N) $\geq$ 10.

10.3.5.4 The ion abundance ratios must be within the specified control limits in Table 22.

10.3.5.5 Corrective action can include all of the items specified in section 10.2.8.5.

10.3.5.6 When performing method 8290/8290A or 0023A, if the continuing calibration fails at the beginning of a 12-hour shift, the instructions in section 10.3.5 must be followed. If the continuing calibration check performed at the end of a 12 hour period fails by no more than ±25 %D for unlabeled native analytes and ±35 %D for labeled standards, the closing standard must not be used as a beginning calibration standard for the next 12-hour shift and the requirements in section 10.3.5 must be met before analysis can continue. Use the mean RRF from the two daily continuing calibration runs to compute the analyte concentrations instead of the RRFs obtained from the initial calibration. If the continuing calibration check performed at the end of a 12 hour period fails by more than ±25 %D for unlabeled native analytes and ±35 %RPD for labeled standards initiate corrective action and reanalyze all sample extracts analyzed during the 12 hour period encompassing the failed end of shift calibration check.

It is realized that it might not always be possible to achieve all RF criteria. For example, the RF criteria for $^{13}C_{12}$-HpCDD and $^{13}C_{12}$-OCDD were not met, however the RF values for the corresponding unlabeled compounds were within the criteria established in this procedure. The data quality for the unlabeled HpCDD and OCDD values were not compromised as a result of the calibration event. In these situations, the analyst must consult with the group manager and the project manager to assess the impact on the data quality objectives on the affected samples. Corrective action must be taken and any decision to report sample data in this situation must be made in conjunction with the client. An NCM must be initiated if the data is to be reported.

10.3.6 Daily calibration must be performed every 12 hours of instrument operation. The 12 hour shift begins with the documentation of the mass resolution followed by the injection of the Window Defining Mixture or Column Performance Solution Mixture and the Daily Calibration Standard.

10.3.6.1 For methods 1613B, 23, TO-9A- The mass resolution documentation must also be performed at the end of the 12 hour shift. If the lab is operating consecutive 12 hour shifts, the mass resolution check from the end of the previous period can be used for the beginning of the next period.

10.3.6.2 For method 8290/8290A or 0023A - The Continuing Calibration Standard check and mass resolution documentation must also be

performed at the end of the 12 hour shift. If the lab is operating consecutive 12-hour shifts, the Window Defining Mixture and/or Column Performance Solution Mixture must be analyzed at the beginning of each 12-hour period. The mass resolution and continuing calibration checks from the previous period can be used for the beginning of the next period.

11. Procedure

11.1 One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variations in the procedure, except those specified by project specific instructions, must be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager and QA Manager. If contractually required the client must be notified.

11.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3 Sample Extract Analysis

11.3.1 Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 2 µL into the GC/MS and acquire data until OCDF has eluted from the column.

11.3.2 Record analysis information in the instrument logbook. The following information is required:

Date of analysis
Time of analysis
Instrument data system filename
Analyst
Lab sample identification

Additional information can be recorded in the logbook if necessary.

11.3.3 Generate ion chromatograms for the masses listed in Table 21 that encompass the expected retention windows of the PCDD and PCDF homologous series.

11.4 Refer to the TestAmerica Knoxville Quality Assurance Manual, current revision for the GC/MS instrument equipment maintenance table.

11.5 Refer to TestAmerica Knoxville SOP KNOX-IT-0001, current revision for requirements for computer hardware and software.

12. Data Analysis and Calculations

12.1 Refer to Figure 3 for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data.

12.2 Qualitative identification criteria for PCDDs and PCDFs. For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

12.2.1 The ion current response for both ions used for quantitative purposes must reach maximum simultaneously (± 2 seconds).

12.2.2 The signal-to-noise ratio (S/N) for each GC peak at each exact m/z must be ≥ 2.5 for positive identification of a PCDD/PCDF compound.

12.2.3 The ratio of the integrated areas of the two exact m/z's specified in Table 21 must be within the limits specified in Table 22, or alternatively when performing method 1613B, within ±10 percent of the ratio in the midpoint (CS3) calibration or the calibration verification (VER), whichever is most recent.

12.2.4 Method 1613B only - The relative retention time of the peak for a 2,3,7,8-substituted PCDD or PCDF must be within the limits in Table 3.

12.2.5 Method 8290, 8290A and 0023A only - For 2,3,7,8-substituted isomers, which have an isotopically labeled internal standard or recovery standard present in the sample extract, the retention time of the two ions used for quantitation purposes must be within -1 to +3 seconds of the isotopically labeled standard.

12.2.6 Method 23 and TO-9A only - For 2,3,7,8-substituted isomers, which have an isotopically labeled internal standard or recovery standard present in the sample extract, the retention time of the two ions used for quantitation purposes must be within ±3 seconds of the isotopically labeled standard.

12.2.7 Method 8290, 8290A, 23, 0023A, and TO-9A only - For 2,3,7,8-substituted isomers, which do not have an isotopically labeled internal standard present in the sample extract, the retention time must fall within 0.005 retention time units of the relative retention times measured in the routine calibration.

12.2.8 The retention time of peaks representing non-2,3,7,8-substituted PCDDs/PCDFs must be within the retention time windows established in section 10.2.5.

12.2.9 No peaks detected in the polychlorinated diphenyl-ether (PCDPE) mass channel in the same retention time region (± 2 sec for method 8290, 8290A & 0023A) as a PCDF peak.

12.3 Quantitation for PCDDs and PCDFs.

12.3.1 Calculate the Internal Standard and Cleanup Standard Recoveries (Ris) relative to the Recovery Standard according to the following equation:

$$\text{Ris} = \frac{\text{Ais} \times \text{Qrs}}{\text{Ars} \times \text{RRFis} \times \text{Qis}} \times 100\%$$

Where:

Ais= sum of the areas of the quantitation ions of the appropriate internal standard (cleanup standard is single ion)
Ars= sum of the areas of the quantitation ions of the recovery standard
Qrs= ng of recovery standard added to extract
Qis= ng of internal standard or cleanup standard added to sample
RRFis = mean relative response factor of internal standard obtained during initial calibration

NOTE: In some situations, such as high-volume water sampling or air train samples, the extract is split for multiple analyses. In this case, Qrs must be correctly calculated to account for the splitting of extracts before the recovery standard was added.

$$Qrs = \frac{Crs \times Vrs}{S}$$

Where:
Qrs= ng of recovery standard added to extract
Crs= concentration of recovery standard added to the split portion of the extract
Vrs= volume of recovery standard added to the split portion of the extract
S = split ratio of the extract (decimal fraction of the extract used)

12.3.2 The split ratio represents the proportion of extract used from splits taken after the addition of internal standards and before the addition of recovery standards. The split ratio is calculated as the product of all split ratios generated between these steps:

$$S = Spis \times Spcs \times Spfc$$

Where:

Spis = the decimal fraction of extract used from split taken once the internal standard has been added and the extraction is performed.

Spcs = the decimal fraction of extract used from split taken once the cleanup standard (if used) has been added.

Spfc = the decimal fraction of extract used from split taken once the cleanup fractionation column has been run.

12.3.3 When properly applied, isotope dilution techniques produce results that are independent of recovery. The recovery of each internal standard must be within the limits specified in Table 13 for method 1613B, 8290 or 8290A or in Table 15 for method 23, 0023A, or TO-9A. If the recovery of any internal standard is not within the specified limits, calculate the S/N ratio of the

internal standard. If the S/N is ≥ 10 and the method minimum levels are met, report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the minimum levels are not achieved, re-extract and re-analyze the sample. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample can be re-extracted or additional clean-ups can be employed.

12.3.4 Calculate the concentration of the 2,3,7,8 isomers according to the following equation:

$$C_{2,3,7,8\,\text{isomers}} = \frac{\text{Ata} \times \text{Qis}}{\text{Ais} \times \text{RRF} \times \text{Ws}}$$

Where:
C = Concentration of 2,3,7,8 isomers
Ata = sum of the areas of the quantitation ions of the target analyte
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor from initial calibration.
Ws = amount of sample spiked and extracted (grams or liters)

12.3.5 The concentrations of non-2,3,7,8-isomers are calculated using the RRF for the corresponding 2,3,7,8-isomer. If more than one 2,3,7,8-isomer exist for a particular level of chlorination, the average of the individual 2,3,7,8-isomer RRFs is used in the calculation.

$$C_{\text{non 2,3,7,8 isomer}} = \frac{\text{Ata} \times \text{Qis}}{\text{Ais} \times \text{RRF} \times \text{Ws}}$$

Where:
Ata = sum of the areas of the quantitation ions of the non-2,3,7,8 isomer
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor from initial calibration for the corresponding 2,3,7,8 isomer.
Ws = amount of sample spiked and extracted (grams or liters)

12.3.6 Calculate the total concentration of all isomers within each homologous series of PCDDs and PCDFs by summing the concentrations of the individual PCDD or PCDF 2,3,7,8 and non-2,3,7,8 isomers.

$$C_{\text{Total}} = \sum C_{2,3,7,8\,\text{isomers}} + \sum C_{\text{non 2,3,7,8 isomers}}$$

12.3.7 If solid samples are to be reported on a dry weight basis, the laboratory LIMS system performs the following calculation:

$$\text{Concentration (Dry Weight)} = \frac{C}{\%\text{Solids} \div 100}$$

Where:
C= Concentration of the target analyte
%Solids = the sample percent solids determined by moisture analysis

12.3.8 If no peaks are present in the region of the ion chromatogram where the compounds of interest are expected to elute, calculate the estimated detection limit (EDL) for that compound according to the following equation:

$$\text{EDL} = \frac{N \times 2.5 \times Qis}{His \times RRFs \times Ws \times Ssl}$$

Where:
N = average peak to peak noise of quantitation ion signals in the region of the ion chromatogram where the compound of interest is expected to elute
His = peak height of quantitation ions for appropriate internal standard
Qis = ng of internal standard added to sample
RRFs = mean relative response factor of compound from initial calibration
W = amount of sample spiked and extracted (grams or liters)
Ssl = decimal expression of percent solids (optional, if results are requested to be reported on dry weight basis)

NOTE: The percent solids calculation is performed by the laboratory LIMS system prior to final reporting.

12.3.9 If peaks are present in the region of the ion chromatogram which do not meet the qualitative criteria listed in section 12.2, calculate an Estimated Maximum Possible Concentration (EMPC). Two different calculation formulas can be used depending upon specific client requirements.

12.3.9.1 When performing methods 8290, 8290A for EPA regulated analyses where the currently promulgated method is required by law (e.g. Trial Burns) and for all other analyses unless the client has specified otherwise, use the equation in section 12.3.4, except that Ata represents the sum of the area under the one peak and of the other peak area calculated using the theoretical chlorine isotope ratio. The peak selected to calculate the theoretical area is the one which gives the lower of the two possible results (i.e. the EMPC is lower than the result calculated from the uncorrected areas).

12.3.9.2 When the client has specifically requested, use the equation in section 12.3.4 without correcting the areas. This method gives an

EMPC which is always higher than the method above and would be considered the worst case.

12.3.10 If peaks are present in the diphenyl ether mass channel at the same retention time as a PCDF peak, the peak cannot be identified as a PCDF. Calculate the concentration of the peak using the equation in section 12.3.4 but report the concentration as an Estimated Maximum Possible Concentration.

12.3.11 If the concentration in the final extract of any 2,3,7,8-substituted PCDD/PCDF isomer (except OCDD or OCDF) exceeds the upper method calibration limits, a dilution of the extract or a re-extraction of a smaller portion of the sample must be performed. For OCDD and OCDF, report the measured concentration and indicate that the value exceeds the calibration limit by flagging the results with "E". Dilutions of up to 1/10 can be performed on the extract. If the compounds that exceed the calibration range cannot be brought within the calibration range by a 1/10 dilution, extraction of a smaller aliquot of sample can be performed or the sample can be analyzed by a more appropriate analytical technique such as HRGC/LRMS. Consultation with the client must occur before any re-extraction is performed.

12.3.12 Evaluate the ion chromatograms of the PFK or FC-43 lock mass and calibration mass for each MID group. The PFK or FC-43 mass intensity must be consistent throughout the retention time of the target compounds. Negative excursions or variations in the PFK or FC-43 mass intensity indicate the elution of interferences from the GC column that are causing suppression in the ion source of the mass spectrometer. This ion suppression can reduce the instrument sensitivity and quantitative result of any peaks that elute at the same retention time. Either additional extract cleanup or dilutions can reduce ion suppression. The quantitative results must be carefully evaluated when there is evidence of ion suppression present in the PFK or FC-43 mass traces.

12.4 The DB-5 (RTX-5) column does not provide for isomer specificity of 2,3,7,8-TCDF using the operating condition required for this method. If a peak is determined to be present at the expected retention time of 2,3,7,8-TCDF and its calculated concentration is above the MinL, the sample extract must be analyzed on the DB-225 (RTX-225) column.

12.5 The Minimum Level (MinL) is defined as the level at which the instrument gives acceptable calibration assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures. Deviation from the extraction amounts or final volumes listed Table 2 changes the MinL. The MinL is calculated as shown in the following equation:

$$\text{MinL} = \frac{C\,\text{min} \times Vfe}{W\text{s}}$$

Where:

Cmin = the concentration the analyte in the lowest calibration standard
Ws = amount of sample spiked and extracted (grams or liters)
Vfe = the final volume of the extract, corrected for all splits and dilutions

$$\mathrm{V}fe = \frac{Vdel \times DFpr}{Spr \times S}$$

Where:

Vdel = the volume of extract delivered to the analysis
DFpr = the dilution factor for dilutions performed to the final extract
Spr = the split ratio for any post-recovery standard splits
S = the split ratio for any post-internal standard and post-cleanup standard splits

12.6 The Maximum Level (MaxL) is defined as the concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The MaxL is calculated as shown in the following equation:

$$\mathrm{M}axL = \frac{C\,\mathrm{max} \times Vfe}{W\mathrm{s}}$$

Where:

Cmax = the concentration the analyte in the highest calibration standard Vfe and Ws are defined in Section 12.5.

12.7 Flag all compound results in the sample that were detected in the method blank with a “B” qualifier.

12.8 Flag all compound results in the sample that are below the minimum level with a “J” qualifier.

12.9 Flag all compound results in the sample that are above the upper calibration limit with an “E” qualifier.

12.10 Flag all compound results in the sample that are “Estimated Maximum Possible Concentrations” with a “Q” qualifier.

12.11 Flag compound results in the sample that exhibit chromatographic evidence of co-eluting compounds with a “C” qualifier.

12.12 Flag compound results in the sample that are affected by ion suppression with a “S” qualifier.

12.13 Data Review

12.13.1 The analyst who performs the initial data calculations must initial and date the front chromatogram of the raw data package to document that they have performed the qualitative and quantitative analysis on the sample data.

12.13.2 A second analyst must verify all qualitative peak identifications. If discrepancies are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.13.3 A second analyst must check all hand calculation and data entry into calculation programs, databases, or spreadsheets at a frequency of 100 percent. If discrepancies are found, the data must be returned to the analyst who performed the initial calculation for resolution.

12.13.4 The reviewing analyst must initial and date the front chromatogram of the raw data package to document that they have performed the second level review on the sample data.

12.13.5 All items listed on the data review check list must be checked by both the analyst who performed the initial qualitative and quantitative analysis and the analyst who performed the second level review. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data. An example data review check list is shown in Figure 3.

13. Method Performance

13.1 Method Detection Limit (MDL): An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in the SOP CA-Q-S-006, current revision, based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit.

13.2 Initial Demonstration of Capability: Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in Test America Knoxville SOP KNOX-QA-0009, current revision. Demonstration for both aqueous and solid matrices is required.

13.2.1 For aqueous samples, extract, concentrate, and analyze four 1-L aliquots of reagent water spiked with labeled internal standards and native analytes according to the procedures in section 11. For non-aqueous samples, extract, concentrate, and analyze four aliquots of sodium sulfate spiked with labeled internal standards and native analytes according to the procedures in section 11. It is recommended that a method blank be prepared with the IDOC samples. Extracts must be stored in the dark at room temperature in amber or clear glass vials prior to analysis.

13.2.2 Using the results of the set of four analyses, compute the average concentration (X) of the extracts in ng/mL and the standard deviation (S) of the concentration in ng/mL for each compound.

13.2.3 For each compound, compare S and X with the corresponding limits for initial precision and recovery in Table 9 for method 1613B and Table 10 for methods 8290, 8290A 23, 0023A, and TO-9A. If S and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples can begin. If, however, any individual S exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test.

13.3 Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. Refer to SOP KNOX-QA-0009, current revision for further requirements for performing and documenting initial and on-going demonstrations of capability.

14. Pollution Prevention

14.1 All attempts will be made to minimize, as far as practical, the use of solvents and standard materials.

15. Waste Management

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 See the current revision of SOP KNOX-HS-0002 for specific waste handling guidelines.

15.3 The following waste streams are produced when this method is carried out.

15.3.1 Waste solvents must be placed in the flammable waste stream, contained in a steel satellite accumulation container or flammable solvent container.

15.3.2 Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials that may or may not be contaminated/hazardous must be placed in the incinerable laboratory waste stream, contained in a HDPE satellite accumulation container.

16. References

16.1 TestAmerica Knoxville Quality Assurance Manual (QAM), current revision.

16.2 EPA Method 1613: Tetra- Through Octa- Chlorinated Dioxins and Furans by Isotope Dilutions HRGC/HRMS, Revision B, October 1994.

16.3 SW-846 Method 8290, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), Revision 0, September 1994.

16.4 SW-846 Method 8290A, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), Revision 1, February 2007.

16.5 SW-846 Method 0023A, Sampling Method for Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofuran Emissions from Stationary Sources, Revision 1, December 1996.

16.6 USEPA Method 23 – Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors. 40 CFR Part 60 Appendix A.

16.7 Method TO-9A: Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition EPA/625/R-96/010b.

16.8 TestAmerica Knoxville SOP KNOX-ID-0012, "Method 0023A and Method 0010 Sampling Train Pre-Sampling Preparation and Sample Extraction Procedure (Includes TO-9A Sampling Components)", current revision.

16.9 TestAmerica Knoxville SOP KNOX-OP-0001, "Extraction of Polychlorinated Dioxins/Furans for Analysis by HRGC/HRMS Based on Methods 8290, 8290A and 1613B", current revision.

16.10 TestAmerica Policy, CA-T-P-002, Selection of Calibration Points, current revision.

17. Miscellaneous

17.1 Deviations from Reference Methods.

17.1.1 Spiking levels have been reduced to minimize the amount of dioxin contaminated waste generated by this procedure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.2 The absolute retention time requirements in Method 1613 section 15.4.1.1 is not required in this procedure. The routine maintenance required of GC columns when analyzing samples from hazardous waste sites makes this requirement virtually impossible to meet in a commercial laboratory environment. This requirement provides no additional quality assurance purpose beyond those already provided by the use of labeled internal standards and required relative retention time limits.

17.1.3 This procedure provides for additional calculation and reporting of sample specific detection limits and estimated maximum possible concentrations not required by Method 1613. These reporting conventions are similar to those required by EPA SW-846 Method 8290 and expected by data users familiar with EPA Office of Solid Waste program requirements.

17.1.4 Methods 8290/8290A do not require dilution and reanalysis of samples for which OCDD/OCDF and non-2378s exceed the calibration range. Although this allowance is not made by method 1613B, this procedure does not require dilution for OCDD/OCDF and non-2378s on samples analyzed by that method.

17.1.5 The calibration standards specified in method 23 are used for method 0023A and TO-9A.

17.1.6 Extracts are stored at room temperature rather than at <10 °C as specified in method 1613B. Methods 8290 and 8290A allow for the storage of extracts at room temperature in the dark. All of the reference methods require that standards be stored at room temperature. Recovery studies performed by Cambridge Isotopes Laboratories (CIL) indicate freezing or refrigeration of standards causes problems with precipitation and irreversible adsorption to the inside surface of the vial. CIL recommends the storage of standards and extracts at room temperature as long as they are protected from exposure to UV and evaporative losses.

17.1.7 This procedure allows for the use of perfluorotributylamine (FC43) for mass calibration and resolution instead of the method recommended reference compound, Perfluorokerosene (PFK). FC43 is used on the newest HRMS instrument in the laboratory based on the manufacturer's recommendation. The use of another mass reference substance is noted in both reference methods 1613B and 8290A. FC43 provides for less noise and less ion source contamination than the method recommended PFK.

17.1.8 The percent valley column resolution criteria is ≤ 25% for this SOP. Among the reference methods both ≤ 25% and < 25% are represented.

17.2 List of tables and figures referenced in the body of the SOP.

17.2.1 Table 1 – Polychlorinated Dibenzodioxins and Furans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography /High Resolution Mass Spectrometry (HRGC/HRMS)

17.2.2 Table 2 – Methods – All, Minimum Levels by Matrix

17.2.3 Table 3 – Methods – 1613B and 8290/8290A, Retention Time References, Quantitation References, and Relative Retention Times

17.2.4 Table 4 – Methods – 23, 0023A, and TO-9A, Retention Time References and Quantitation References

17.2.5 Table 5 – Methods – 1613B and 8290/8290A, Initial Calibration Standard Concentrations and Acceptance Criteria

17.2.6 Table 6 – Methods – 23, 0023A, and TO-9A, Initial Calibration Standard Concentrations and Acceptance Criteria

17.2.7 Table 7 – Methods – 1613B and 8290/8290A, Daily Verification Standard (VER) Concentrations and Acceptance Criteria

17.2.8 Table 8 – Methods – 23, 0023A, and TO-9A, Daily Verification Standard (VER) Concentrations and Acceptance Criteria

17.2.9 Table 9 – Method – 1613B, Initial Demonstration of Capability (IDOC) Acceptance Criteria

17.2.10 Table 10 – Methods – 8290/8290A, 23, 0023A, and TO-9A, Initial Demonstration of Capability (IDOC) Acceptance Criteria

17.2.11 Table 11 – Laboratory Control Sample (LCS) Spiking Solution Component Concentrations and Acceptance Limits

17.2.12 Table 12 – Method – 8290/8290A. Matrix Spike and Matrix Spike Duplicate Sample (MS/MSD) Spiking Solution Component Concentrations and Acceptance Limits

17.2.13 Table 13 - Methods – 1613B and 8290/8290A, Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

17.2.14 Table 14 – Method – 1613B, Cleanup Standard Spiking Solution Component Concentrations and Acceptance Limits

17.2.15 Table 15 – Methods – 23, 0023A, and TO-9A, Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

17.2.16 Table 16 – Methods – 23, 0023A, and TO-9A, Surrogate Standard Spiking Solution Component Concentrations and Acceptance Limits

17.2.17 Table 17 – Methods – All, Recovery Standard Spiking Solution Component Concentrations

17.2.18 Table 18 – Rtx-5/DB-5 Column Window Defining Standard Mixture Components. – Rtx-5 (DB-5) Column Performance Standard Mixture Components

17.2.19 Table 19 – Rtx-5/DB-5 Column Performance Standard Mixture Components

Table 1

Polychlorinated Dibenzo-p-dioxins/Dibenzofurans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)

PCDDs/PCDFs [1] Isomer/Congener	CAS Registry	Labeled Analog	CAS Registry
2,3,7,8-TCDD	1746-01-6	$^{13}C_{12}$-2,3,7,8-TCDD $^{37}Cl_4$-2,3,7,8-TCDD	76523-40-5 85508-50-5
Total TCDD	41903-57-5		
2,3,7,8-TCDF	51207-31-9	$^{13}C_{12}$-2,3,7,8-TCDF	89059-46-1
Total TCDF	55722-27-5		
1,2,3,7,8-PeCDD	40321-76-4	$^{13}C_{12}$-1,2,3,7,8-PeCDD	109719-79-1
Total PeCDD	36088-22-9		
1,2,3,7,8-PeCDF	57117-41-6	$^{13}C_{12}$-1,2,3,7,8-PeCDF	109719-77-9
2,3,4,7,8-PeCDF	57117-31-4	$^{13}C_{12}$-2,3,4,7,8-PeCDF	116843-02-8
Total PeCDF	30402-15-4		
1,2,3,4,7,8-HxCDD	39227-28-6	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	109719-80-4
1,2,3,6,7,8-HxCDD	57653-85-7	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	109719-81-5
1,2,3,7,8,9-HxCDD	19408-74-3	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	109719-82-6
Total HxCDD	34465-46-8		
1,2,3,4,7,8-HxCDF	70648-26-9	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	114423-98-2
1,2,3,6,7,8-HxCDF	57117-44-9	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	116843-03-9
2,3,4,6,7,8-HxCDF	60851-34-5	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	116843-05-1
1,2,3,7,8,9-HxCDF	72918-21-9	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	116843-04-0
Total HxCDF	55684-94-1		
1,2,3,4,6,7,8-HpCDD	35822-46-9	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	109719-83-7
Total HpCDD	37871-00-4		
1,2,3,4,6,7,8-HpCDF	67562-39-4	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	109719-84-8
1,2,3,4,7,8,9-HpCDF	55673-89-7	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	109719-94-0
Total HpCDF	38998-75-3		
OCDD	3268-87-9	$^{13}C_{12}$-OCDD	114423-97-1
OCDF	39001-02-0	none	

Notes:

1. Polychlorinated dioxins and furans

TCDD	= Tetrachlorodibenzo-p-dioxin	TCDF	= Tetrachlorodibenzofuran
PeCDD	= Pentachlorodibenzo-p-dioxin	PeCDF	= Pentachlorodibenzofuran
HxCDD	= Hexachlorodibenzo-p-dioxin	HxCDF	= Hexachlorodibenzofuran
HpCDD	= Heptachlorodibenzo-p-dioxin	HpCDF	= Heptachlorodibenzofuran
OCDD	= Octachlorodibenzo-p-dioxin	OCDF	= Octachlorodibenzofuran

Table 2

Methods – All
Minimum Levels by Matrix

Analyte	Extract (ng/mL) [1]	Water (pg/L) [2]	Solids (pg/g) [3]	Biological Tissue (pg/g) [3]	Waste (pg/g) [4]	Air/Wipe (pg) [5]
2,3,7,8-TCDD	0.5	10	1	1	10	10
2,3,7,8-TCDF	0.5	10	1	1	10	10
1,2,3,7,8-PeCDD	2.5	50	5	5	50	50
1,2,3,7,8-PeCDF	2.5	50	5	5	50	50
2,3,4,7,8-PeCDF	2.5	50	5	5	50	50
1,2,3,4,7,8-HxCDD	2.5	50	5	5	50	50
1,2,3,6,7,8-HxCDD	2.5	50	5	5	50	50
1,2,3,7,8,9-HxCDD	2.5	50	5	5	50	50
1,2,3,4,7,8-HxCDF	2.5	50	5	5	50	50
1,2,3,6,7,8-HxCDF	2.5	50	5	5	50	50
2,3,4,6,7,8-HxCDF	2.5	50	5	5	50	50
1,2,3,7,8,9-HxCDF	2.5	50	5	5	50	50
1,2,3,4,6,7,8-HpCDD	2.5	50	5	5	50	50
1,2,3,4,6,7,8-HpCDF	2.5	50	5	5	50	50
1,2,3,4,7,8,9-HpCDF	2.5	50	5	5	50	50
OCDD	5.0	100	10	10	100	100
OCDF	5.0	100	10	10	100	100

Notes:
1 Concentration in the extract assuming a 20 µL volume.
2 Based on a sample volume of 1.0 L.
3 Based on a sample weight of 10.0 g.
4 Based on a sample weight of 1.0 g.
5 Based on extraction of the entire sample.

Table 3

Methods – 1613B and 8290/8290A
Retention Time References, Quantitation References and Relative Retention Times

Analyte	Retention Time and Quantitation Reference	Relative Retention Time
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the recovery standard		
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0.999-1.002
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	0.999-1.003
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.999-1.002
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0.999-1.002
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0.999-1.002
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.976-1.043
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.989-1.052
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0.923-1.103
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.567
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.425
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.011-1.526
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the recovery standard		
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0.999-1.001
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.998-1.004
1,2,3,7,8,9-HxCDD	--[1]	1.000-1.019
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0.999-1.001
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	0.997-1.005
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	0.999-1.001
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0.999-1.001
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0.999-1.001
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0.999-1.001
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0.999-1.001
OCDD	$^{13}C_{12}$-OCDD	0.999-1.001
OCDF	$^{13}C_{12}$-OCDD	0.999-1.008
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.000
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.981-1.003
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.944-0.970
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.949-0.975
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.959-1.021
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.047
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.086-1.110
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.043-1.085
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.057-1.151
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.032-1.311

Notes:

1 The retention time reference for 1,2,3,7,8,9-HxCDD is $^{13}C_{12}$-1,2,3,6,7,8-HxCDD. 1,2,3,7,8,9-HxCDD is quantified using the averaged responses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD.

Table 4

Methods – 23, 0023A and TO-9A
Retention Time References and Quantitation References

Analyte	Retention Time and Quantitation Reference
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the recovery standard	
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the recovery standard	
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
OCDD	$^{13}C_{12}$-OCDD
OCDF	$^{13}C_{12}$-OCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD

Table 5

Methods – 1613B and 8290/8290A
Initial Calibration Standard Concentrations and Acceptance Criteria

	CS1	CS2	CS3	CS4	CS5	1613B	8290	8290A
Analyte	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**%RSD**	**%RSD**	**%RSD**
Native PCDD's and PCDF's								
2,3,7,8-TCDD	0.5	2.0	10	40	200	±20	±20	±20
2,3,7,8-TCDF	0.5	2.0	10	40	200	±20	±20	±20
1,2,3,7,8-PeCDD	2.5	10	50	200	1000	±20	±20	±20
1,2,3,7,8-PeCDF	2.5	10	50	200	1000	±20	±20	±20
2,3,4,7,8-PeCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000	±20	±20	±20
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000	±20	±20	±20
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000	±35	±20	±20
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000	±20	±20	±20
2,3,4,6,7,8-HxCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000	±20	±20	±20
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000	±20	±20	±20
OCDD	5.0	20	100	400	2000	±20	±20	±20
OCDF	5.0	20	100	400	2000	±35	±20	±20
Labeled Internal Standards								
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-OCDD	200	200	200	200	200	±35	±30	±20
Labeled Cleanup Standard								
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2.0	10	40	200	±35	-	-
Labeled Recovery Standard								
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	-	-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	-	-	-

Table 6

Methods – 23, 0023A and TO-9A
Initial Calibration Standard Concentrations and Acceptance Criteria

	CS1	CS2	CS3	CS4	CS5	23 / TO-9A	0023A
Analyte	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**%RSD**	**%RSD**
Native PCDDs and PCDFs							
2,3,7,8-TCDD	0.5	1.0	5	50	100	±25	±20
2,3,7,8-TCDF	0.5	1.0	5	50	100	±25	±20
1,2,3,7,8-PeCDD	2.5	5	25	250	500	±25	±20
1,2,3,7,8-PeCDF	2.5	5	25	250	500	±25	±20
2,3,4,7,8-PeCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,6,7,8-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,7,8,9-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,6,7,8-HxCDF	2.5	5	25	250	500	±25	±20
2,3,4,6,7,8-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,7,8,9-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,6,7,8-HpCDD	2.5	5	25	250	500	±25	±20
1,2,3,4,6,7,8-HpCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500	±25	±20
OCDD	5.0	10	50	500	1000	±25	±20
OCDF	5.0	10	50	500	1000	±30	±20
Labeled Internal Standards							
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	±25	±30
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	±25	±30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-OCDD	200	200	200	200	200	±30	±30
Surrogate Standards							
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	1.0	5	50	100	±25	±30
$^{13}C_{12}$-2,3,4,7,8-PeCDF	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500	±25	±30
Labeled Recovery Standard							
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	-	-

Table 7

Methods – 1613B and 8290/8290A
Daily Verification Standard (VER) Concentrations and Acceptance Criteria

		1613B			8290/8290A	
Analyte	**VER (ng/mL)**	**All Isomers (ng/mL)**	**Tetra only (ng/mL)**		**Shift Open %D**	**Shift Close[1] %D**
Native PCDDs and PCDFs						
2,3,7,8-TCDD	10	7.8-12.9	8.2-12.3		±20	±25
2,3,7,8-TCDF	10	8.4-12.0	8.6-11.6		±20	±25
1,2,3,7,8-PeCDD	50	39-65	-		±20	±25
1,2,3,7,8-PeCDF	50	41-60	-		±20	±25
2,3,4,7,8-PeCDF	50	41-61	-		±20	±25
1,2,3,4,7,8-HxCDD	50	39-64	-		±20	±25
1,2,3,6,7,8-HxCDD	50	39-64	-		±20	±25
1,2,3,7,8,9-HxCDD	50	41-61	-		±20	±25
1,2,3,4,7,8-HxCDF	50	45-56	-		±20	±25
1,2,3,6,7,8-HxCDF	50	44-57	-		±20	±25
2,3,4,6,7,8-HxCDF	50	44-57	-		±20	±25
1,2,3,7,8,9-HxCDF	50	45-56	-		±20	±25
1,2,3,4,6,7,8-HpCDD	50	43-58	-		±20	±25
1,2,3,4,6,7,8-HpCDF	50	45-55	-		±20	±25
1,2,3,4,7,8,9-HpCDF	50	43-58	-		±20	±25
OCDD	100	79-126	-		±20	±25
OCDF	100	63-159	-		±20	±25
Labeled Internal Standards						
$^{13}C_{12}$-2,3,7,8-TCDD	100	82-121	85-117		±30	±35
$^{13}C_{12}$-2,3,7,8-TCDF	100	71-140	76-131		±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	62-160	-		±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	76-130	-		±30	±35
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	77-130	-		±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	85-117	-		±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	85-118	-		±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	76-131	-		±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	70-143	-		±30	±35
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	73-137	-		±30	±35
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	74-135	-		±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	72-138	-		±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	78-129	-		±30	±35
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	77-129	-		±30	±35
$^{13}C_{12}$-OCDD	200	96-415	-		±30	±35
Labeled Cleanup Standard						
$^{37}Cl_4$-2,3,7,8-TCDD	10	7.9-12.7	8.3-12.1		-	-
Labeled Recovery Standard						
$^{13}C_{12}$-1,2,3,4-TCDD	100	-	-		-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	-	-		-	-

Notes:

1 If the closing standard %D exceeds the opening %D criteria, the average of the Opening and Closing RF is used instead of the Initial Calibration RF to calculate sample concentrations.

Table 8

Methods – 23, 0023A and TO-9A
Daily Verification Standard (VER) Concentrations and Acceptance Criteria

			0023A	
	VER	23 and TO-9A	Shift Open	Shift Close[1]
Analyte	(ng/mL)	%D	%D	%D
Native PCDDs and PCDFs				
2,3,7,8-TCDD	5	±25	±20	±25
2,3,7,8-TCDF	5	±25	±20	±25
1,2,3,7,8-PeCDD	25	±25	±20	±25
1,2,3,7,8-PeCDF	25	±25	±20	±25
2,3,4,7,8-PeCDF	25	±25	±20	±25
1,2,3,4,7,8-HxCDD	25	±25	±20	±25
1,2,3,6,7,8-HxCDD	25	±25	±20	±25
1,2,3,7,8,9-HxCDD	25	±25	±20	±25
1,2,3,4,7,8-HxCDF	25	±25	±20	±25
1,2,3,6,7,8-HxCDF	25	±25	±20	±25
2,3,4,6,7,8-HxCDF	25	±25	±20	±25
1,2,3,7,8,9-HxCDF	25	±25	±20	±25
1,2,3,4,6,7,8-HpCDD	25	±25	±20	±25
1,2,3,4,6,7,8-HpCDF	25	±25	±20	±25
1,2,3,4,7,8,9-HpCDF	25	±25	±20	±25
OCDD	50	±25	±20	±25
OCDF	50	±30	±20	±25
Labeled Internal Standards				
$^{13}C_{12}$-2,3,7,8-TCDD	100	±25	±30	±35
$^{13}C_{12}$-2,3,7,8-TCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	±25	±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	±30	±30	±35
$^{13}C_{12}$-OCDD	200	±30	±30	±35
Surrogate Standards				
$^{37}Cl_4$-2,3,7,8-TCDD	5	±25	±30	±35
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	±25	±30	±35
Labeled Recovery Standard				
$^{13}C_{12}$-1,2,3,4-TCDD	100	-	-	
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	-	-	

Notes:

1 If the closing standard %D exceeds the opening %D criteria, the average of the Opening and Closing RF is used instead of the Initial Calibration RF to calculate sample concentrations.

Table 9

Method – 1613B
Initial Demonstration of Capability (IDOC) Acceptance Criteria

	Test	1613B			1613B Tetra Only	
Analyte	Conc. (ng/mL) [1]	s^2 (ng/mL) [1]	X^3 (ng/ml) [1]		s^2 (ng/mL) [1]	X^3 (ng/ml) [1]
Native PCDDs and PCDFs						
2,3,7,8-TCDD	10	2.8	8.3-12.9		2.7	8.7-12.4
2,3,7,8-TCDF	10	2.0	8.7-13.7		2.0	9.1-13.1
1,2,3,7,8-PeCDD	50	7.5	38-66		-	-
1,2,3,7,8-PeCDF	50	7.5	43-62		-	-
2,3,4,7,8-PeCDF	50	8.6	36-75		-	-
1,2,3,4,7,8-HxCDD	50	9.4	39-76		-	-
1,2,3,6,7,8-HxCDD	50	7.7	42-62		-	-
1,2,3,7,8,9-HxCDD	50	11.1	37-71		-	-
1,2,3,4,7,8-HxCDF	50	8.7	41-59		-	-
1,2,3,6,7,8-HxCDF	50	6.7	46-60		-	-
2,3,4,6,7,8-HxCDF	50	7.4	37-74		-	-
1,2,3,7,8,9-HxCDF	50	6.4	42-61		-	-
1,2,3,4,6,7,8-HpCDD	50	7.7	38-65		-	-
1,2,3,4,6,7,8-HpCDF	50	6.3	45-56		-	-
1,2,3,4,7,8,9-HpCDF	50	8.1	43-63		-	-
OCDD	100	19	89-127		-	-
OCDF	100	27	74-146		-	-
Labeled Internal Standards						
$^{13}C_{12}$-2,3,7,8-TCDD	50	18.5	14-67		17.5	16-57.5
$^{13}C_{12}$-2,3,7,8-TCDF	50	17.5	15.5-56.5		17	17.5-49.5
$^{13}C_{12}$-1,2,3,7,8-PeCDD	50	19.5	13.5-92		-	-
$^{13}C_{12}$-1,2,3,7,8-PeCDF	50	17.0	13.5-78		-	-
$^{13}C_{12}$-2,3,4,7,8-PeCDF	50	19.0	8-139.5		-	-
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	50	20.5	14.5-73.5		-	-
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	50	19.0	17-61		-	-
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	50	21.5	13.5-76		-	-
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	50	17.5	15-61		-	-
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	50	18.5	14.5-68		-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	50	20.0	12-78.5		-	-
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	50	17.5	17-64.5		-	-
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	50	20.5	16-55		-	-
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	50	20.0	14-70.5		-	-
$^{13}C_{12}$-OCDD	100	47.5	20.5-138		-	-
Labeled Cleanup Standard						
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9-15.4		3.4	4.5-13.4

Notes:

1 All specifications are given as concentration in the final extract, assuming a 20-µL volume.

2 s = standard deviation of the concentration

3 X = average concentration. The acceptance range for average recovery can be normalized (shifted to center on 100% recovery) to compensate for the bias in the collaborative study used to develop the acceptance criteria.

Table 10

Methods – 8290/8290A, 23, 0023A and TO-9A
Initial Demonstration of Capability (IDOC) Acceptance Criteria

Analyte	Test Conc (ng/mL) [1]	s[2] (%Rec)	X[3] (%Rec)
Native PCDDs and PCDFs			
2,3,7,8-TCDD	10	15[4]	70-130[4]
2,3,7,8-TCDF	10	15[4]	70-130[4]
1,2,3,7,8-PeCDD	50	15[4]	70-130[4]
1,2,3,7,8-PeCDF	50	15[4]	70-130[4]
2,3,4,7,8-PeCDF	50	15[4]	70-130[4]
1,2,3,4,7,8-HxCDD	50	15[4]	70-130[4]
1,2,3,6,7,8-HxCDD	50	15[4]	70-130[4]
1,2,3,7,8,9-HxCDD	50	15[4]	70-130[4]
1,2,3,4,7,8-HxCDF	50	15[4]	70-130[4]
1,2,3,6,7,8-HxCDF	50	15[4]	70-130[4]
2,3,4,6,7,8-HxCDF	50	15[4]	70-130[4]
1,2,3,7,8,9-HxCDF	50	15[4]	70-130[4]
1,2,3,4,6,7,8-HpCDD	50	15[4]	70-130[4]
1,2,3,4,6,7,8-HpCDF	50	15[4]	70-130[4]
1,2,3,4,7,8,9-HpCDF	50	15[4]	70-130[4]
OCDD	100	15[4]	70-130[4]
OCDF	100	15[4]	70-130[4]

Notes:
1 All specifications are given as concentration in the final extract, assuming a 20 µL volume.
2 s = standard deviation of the percent recovery
3 X = average percent recovery
4 Inhouse generated historical control limits can be used in place of the specified limit.

Table 11

Laboratory Control Sample (LCS) Spiking Solution Component Concentrations and Acceptance Limits

Analyte	LCS Solution Conc. (ng/mL)[1]	Final Extract Conc (ng/mL)[2]	1613B LCS Conc (ng/mL)[2]	8290/8290A, 23, 0023A, TO-9A Recovery (%Rec)
2,3,7,8-TCDD	0.2	10	6.7-15.8	70-130[4]
2,3,7,8-TCDF	0.2	10	7.5-15.8	70-130[4]
1,2,3,7,8-PeCDD	1.0	50	35-71	70-130[4]
1,2,3,7,8-PeCDF	1.0	50	40-67	70-130[4]
2,3,4,7,8-PeCDF	1.0	50	34-80	70-130[4]
1,2,3,4,7,8-HxCDD	1.0	50	35-82	70-130[4]
1,2,3,6,7,8-HxCDD	1.0	50	38-67	70-130[4]
1,2,3,7,8,9-HxCDD	1.0	50	32-81	70-130[4]
1,2,3,4,7,8-HxCDF	1.0	50	36-67	70-130[4]
1,2,3,6,7,8-HxCDF	1.0	50	42-65	70-130[4]
2,3,4,6,7,8-HxCDF	1.0	50	35-78	70-130[4]
1,2,3,7,8,9-HxCDF	1.0	50	39-65	70-130[4]
1,2,3,4,6,7,8-HpCDD	1.0	50	35-70	70-130[4]
1,2,3,4,6,7,8-HpCDF	1.0	50	41-61	70-130[4]
1,2,3,4,7,8,9-HpCDF	1.0	50	39-69	70-130[4]
OCDD	2.0	100	78-144	70-130[4]
OCDF	2.0	100	63-170	70-130[4]
Tetras Only				
2,3,7,8-TCDD	0.2	10	7.3-14.6	70-130[4]
2,3,7,8-TCDF	0.2	10	8.0-14.7	70-130[4]

Notes:

1 1.0 mL of this solution is added to the LCS before extraction (see section 7.11.2).

2 The final extract concentration is based on an extract volume of 20 µL.

3 Spike concentrations are based on a 1.0 L extraction for water, 10.0g extraction for solids, and entire sample extraction for air/wipe samples.

4 Inhouse generated historical control limits can be used in place of the specified limit.

Table 12

Method – 8290/8290A
Matrix Spike and Matrix Spike Duplicate Sample (MS/MSD) Spiking Solution Component Concentrations and Acceptance Limits[1]

Analyte	LCS Solution Conc. (ng/mL)[2]	Final Extract Conc (ng/mL)[3]	8290 Recovery (%Rec)	8290 Precision (RPD)
2,3,7,8-TCDD	0.2	10	70-130[4]	±15[4]
2,3,7,8-TCDF	0.2	10	70-130[4]	±15[4]
1,2,3,7,8-PeCDD	1.0	50	70-130[4]	±15[4]
1,2,3,7,8-PeCDF	1.0	50	70-130[4]	±15[4]
2,3,4,7,8-PeCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,6,7,8-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,7,8,9-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,6,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
2,3,4,6,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,7,8,9-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,6,7,8-HpCDD	1.0	50	70-130[4]	±15[4]
1,2,3,4,6,7,8-HpCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8,9-HpCDF	1.0	50	70-130[4]	±15[4]
OCDD	2.0	100	70-130[4]	±15[4]
OCDF	2.0	100	70-130[4]	±15[4]

Notes:
1 If insufficient sample exists for MS/MSD analysis, these limits apply to LCS/LCSD samples.
2 1.0 mL of this solution is added to the LCS before extraction (see section 1.1).
3 The final extract concentration is based on an extract volume of 20 µL.
4 Inhouse generated historical control limits can be used in place of the specified limit.

Table 13

Methods – 1613B and 8290/8290A
Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	1613B LCS Conc (ng/mL)[2]	1613B Sample Conc (ng/mL)[2]	8290 Recovery (%Rec)
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	10.0-87.5	12.5-82.0	40-135
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	11.0-76.0	12.0-84.5	40-135
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1.0	50	10.5-113.5	12.5-90.5	40-135
$^{13}C_{12}$-1,2,3,7,8-PeCDF	1.0	50	10.5-96.0	12.0-92.5	40-135
$^{13}C_{12}$-2,3,4,7,8-PeCDF	1.0	50	6.5-164.0	10.5-89.0	40-135
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	1.0	50	10.5-96.5	16.0-70.5	40-135
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1.0	50	12.5-81.5	14.0-65.0	40-135
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1.0	50	9.5-101.0	13.0-76.0	40-135
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1.0	50	10.5-79.5	13.0-61.5	40-135
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	1.0	50	11.0-88.0	14.0-68.0	40-135
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	1.0	50	8.5-102.5	14.5-73.5	40-135
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1.0	50	13.0-83.0	11.5-70.0	40-135
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1.0	50	10.5-79.0	14.0-71.5	40-135
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	1.0	50	10.0-93.0	13.0-69.0	40-135
$^{13}C_{12}$-OCDD	2.0	100	13.0-198.5	17.0-157	40-135
Tetras Only					
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	12.5-70.5	15.5-68.5	40-135
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	13.0-63.0	14.5-70.0	40-135

Notes:
1 1.0 mL of the Internal Standard Spiking Solution is added to each sample, method blank and LCS prior to extraction (see section 1.1).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

Table 14

Method – 1613B
Cleanup Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	1613B LCS Conc (ng/mL)[2]	1613B Sample Conc (ng/mL)[2]	1613B LCS Tetra Only Conc (ng/mL)[2]	1613B Sample Tetra Only Conc (ng/mL)[2]
$^{37}Cl_4$-2,3,7,8-TCDD	0.2	10	3.1-19.1	3.5-19.7	3.7-15.8	4.2-16.4

Notes:
1 1.0 mL of the Cleanup Standard Spiking Solution is added to each sample, method blank and LCS prior to cleanup (see section 7.11.6).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

Table 15

Methods – 23, 0023A and TO-9A
Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	23 Recovery (%Rec)	0023A Recovery (%Rec)	TO-9A Recovery (%Rec)
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,7,8-PeCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1.0	50	25-130	40-135	40-120
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1.0	50	25-130	40-135	40-120
$^{13}C_{12}$-OCDD	2.0	100	25-130	40-135	40-120

Notes:

1 1.0 mL of the Internal Standard Spiking Solution is added to each sample, method blank and LCS prior to extraction (see section 7.11.4).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

Table 16

Methods – 23, 0023A, and TO-9A
Surrogate Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	23 Recovery (%Rec)	0023A Recovery (%Rec)	TO-9A Recovery (%Rec)
$^{37}Cl_4$-2,3,7,8-TCDD	20	100	70-130	70-130	50-120
$^{13}C_{12}$-2,3,4,7,8-PeCDF	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	20	100	70-130	70-130	40-120

Notes:

1 100 µL of the Surrogate Standard Spiking Solution is added to each sample train prior to sampling (see section 1.1).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

Table 17

Methods – All
Recovery Standard Spiking Solution Component Concentrations

Labeled Analyte	Solution Conc (µg/mL)[1]	Test Conc. (ng/mL)[2]
$^{13}C_{12}$-1,2,3,4-TCDD	0.1	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.1	100

Notes:
1 20 µL of the Recovery Standard Spiking Solution is added to each sample, method blank and LCS prior to analysis (see section 1.1).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

Table 18

Rtx-5/DB-5 Column Window Defining Standard Mixture Components

Congener	First Eluted	Last Eluted
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,6,8-/1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-/1,2,4,6,8,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

Table 19

Rtx-5 (DB-5) Column Performance Standard Mixture Components

Isomer
1,2,3,7/1,2,3,8-TCDD
1,2,3,9-TCDD
2,3,7,8-TCDD

Table 20

DB-225 (Rtx-225) Column Performance Standard Mixture Components

Isomer
2,3,4,7-TCDF
2,3,7,8-TCDF
1,2,3,9-TCDF

Table 21

Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

Descriptor	Accurate Mass[1]	Ion ID	Elemental Composition	Analyte
1	292.9825 (313.9834)	LOCK	C_7F_{11} ($C_6NF_{12}^+$)	PFK (FC43)
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9338	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	342.9792 (363.9802)	QC	C_8F_{13} ($C_7NF_{14}^+$)	PFK (FC43)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
2	330.9792 (313.9834)	LOCK	C_7F_{13} ($C_6NF_{12}^+$)	PFK (FC43)
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	380.9760 (375.9802)	QC	C_8F_{15} ($C_8NF_{14}^+$)	PFK (FC43)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	380.9760 (375.9802)	LOCK	C_8F_{15} ($C_8NF_{14}^+$)	PFK (FC43)
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	404.9760 (413.9770)	QC	$C_{10}F_{15}$ ($C_8NF_{16}^+$)	PFK (FC43)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE

Table 21 (Continued)

Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

Descriptor	Accurate Mass[1]	Ion ID	Elemental Composition	Analyte
4	404.9760 (413.9770)	LOCK	$C_{10}F_{15}(C_8NF_{16}^+)$	PFK (FC43)
	407.7818	M+2	$C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0$	HpCDF
	409.7788	M+4	$C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0$	HpCDF
	417.8250	M	$^{13}C_{12}H\ ^{35}Cl_7\ 0$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0$	HpCDF (S)
	423.7767	M+2	$C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0_2$	HpCDD
	425.7737	M+4	$C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0_2$	HpCDD (S)
	442.9728 (463.9738)	QC	$C_{10}F_{17}(C_9NF_{18}^+)$	PFK (FC43)
	479.7165	M+4	$C_{12}H\ ^{35}Cl_7\ ^{37}Cl_2\ 0$	NCDPE
5	430.9728 (425.9770)	LOCK	$C_9F_{17}(C_9NF_{16}^+)$	PFK (FC43)
	441.7428	M+2	$C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0$	OCDF
	443.7399	M+4	$C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0$	OCDF
	457.7377	M+2	$C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0_2$	OCDD
	459.7348	M+4	$C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0_2$	OCDD
	469.7780	M+2	$^{13}C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0_2$	OCDD (S)
	480.9696 (501.9706)	QC	$C_{10}F_{19}(C_9NF_{20}^+)$	PFK (FC43)
	513.6775	M+4	$C_{12}\ ^{35}Cl_8\ ^{37}Cl_2\ 0$	DCDPE

Notes:

1 Nuclidic masses used:

H = 1.007825	C = 12.00000	^{13}C = 13.003355	F = 18.9984
O = 15.994915	^{35}Cl = 34.968853	^{37}Cl = 36.965903	

Table 22

Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

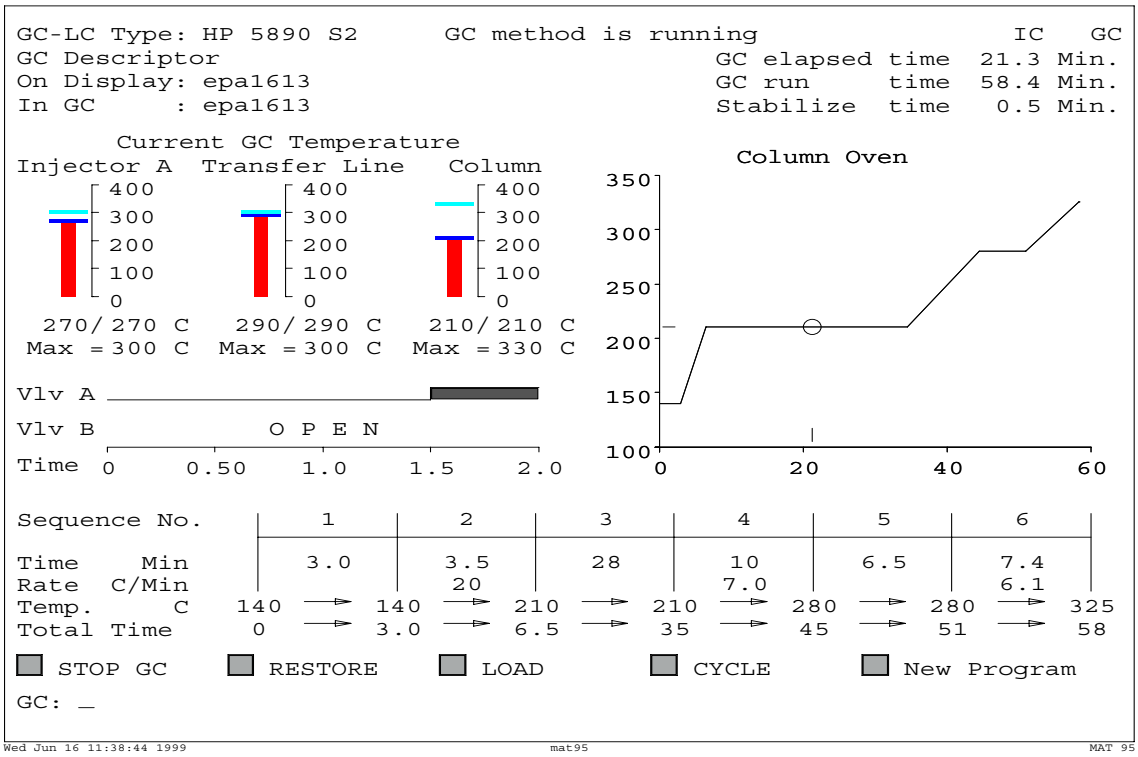
Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6 [1]	M/M+2	0.51	0.43	0.59
7	M+2/M+4	1.04/1.05[3]	0.88	1.20
7 [2]	M/M+2	0.44	0.37	0.51
8	M+2/M+4	0.89	0.76	1.02

Notes:

1 Used for ^{13}C-HxCDF (IS).
2 Used for ^{13}C-HpCDF (IS).
3 Method 1613B Theoretical Ratio

Figure 1

Rtx-5 Recommended GC Operating Conditions



DB-225 Recommended GC Operating Conditions

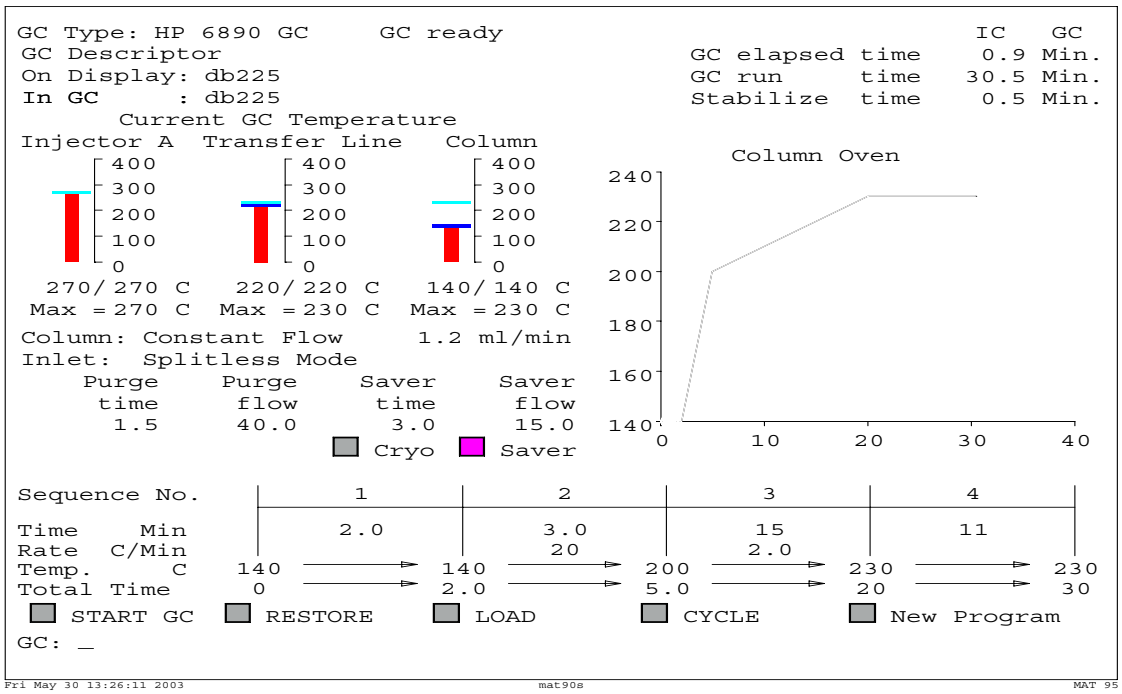
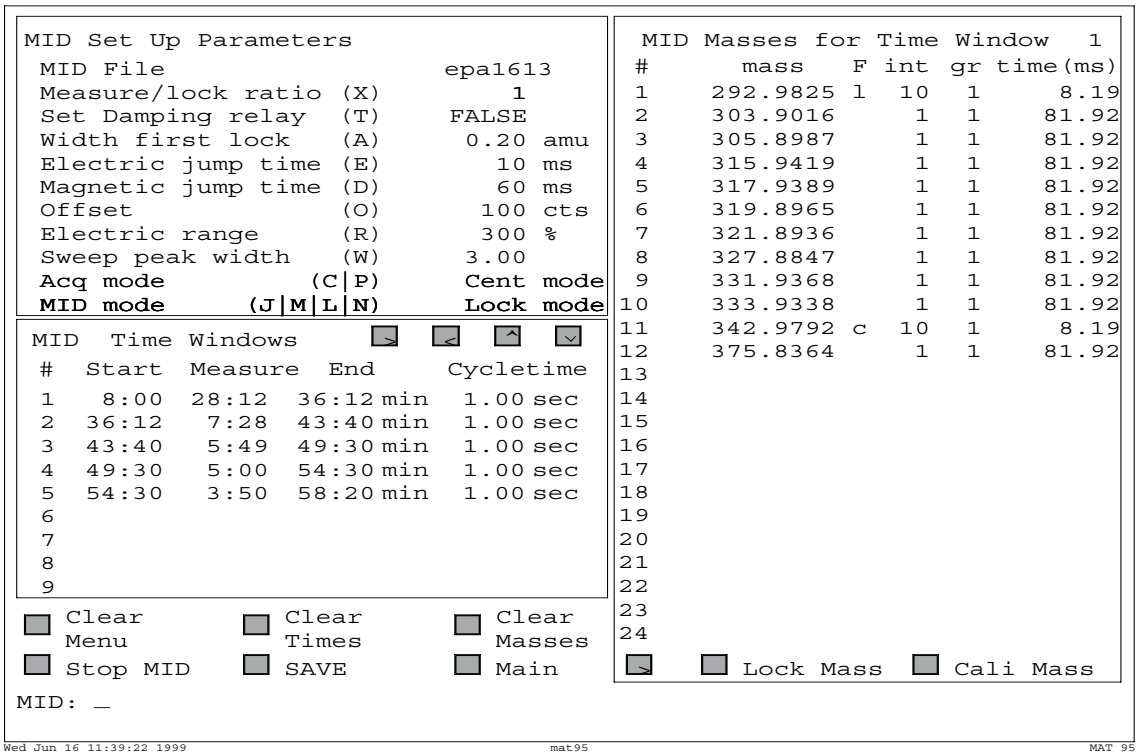


Figure 2

Rtx-5 Recommended MID Descriptors



```
MID Set Up Parameters
 MID File                    epa1613
 Measure/lock ratio (X)        1
 Set Damping relay  (T)      FALSE
 Width first lock   (A)       0.20 amu
 Electric jump time (E)         10 ms
 Magnetic jump time (D)         60 ms
 Offset             (O)        100 cts
 Electric range     (R)        300 %
 Sweep peak width   (W)        3.00
 Acq mode          (C|P)       Cent mode
 MID mode      (J|M|L|N)       Lock mode

MID  Time Windows
 #   Start  Measure  End      Cycletime
 1    8:00  28:12  36:12 min   1.00 sec
 2   36:12   7:28  43:40 min   1.00 sec
 3   43:40   5:49  49:30 min   1.00 sec
 4   49:30   5:00  54:30 min   1.00 sec
 5   54:30   3:50  58:20 min   1.00 sec
 6
 7
 8
 9

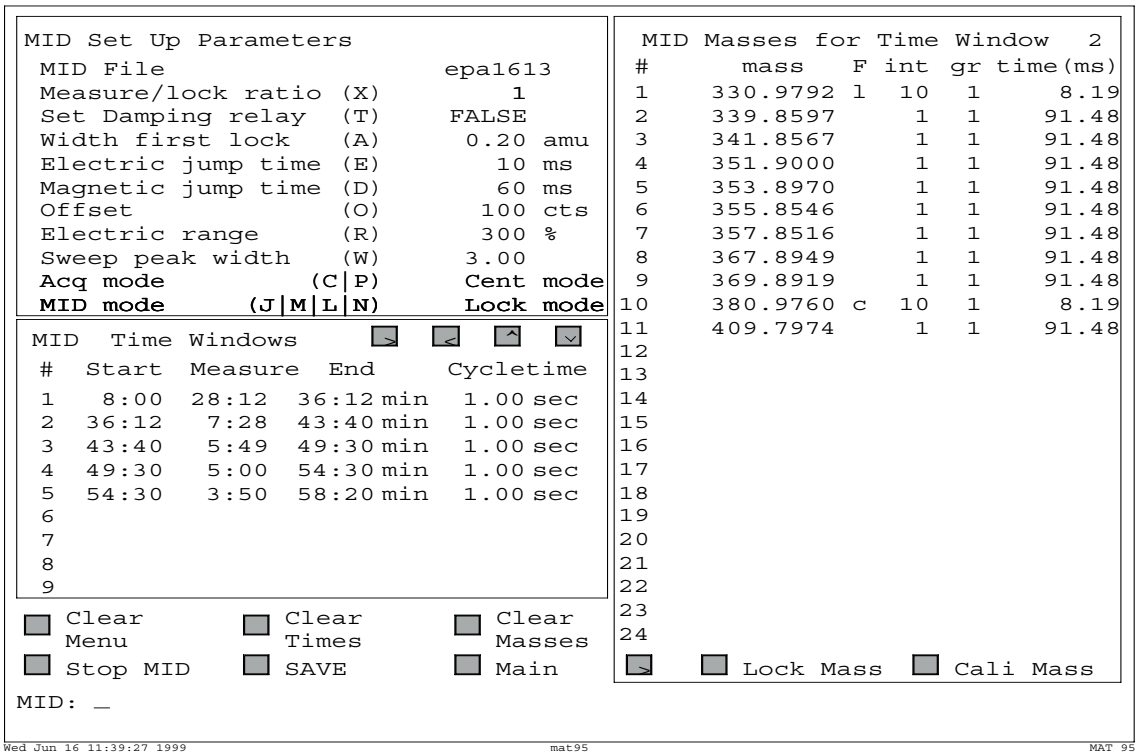
 Clear Menu    Clear Times    Clear Masses
 Stop MID      SAVE           Main

MID: _
```

```
 MID Masses for Time Window   1
 #       mass    F int  gr time(ms)
 1     292.9825 l  10   1      8.19
 2     303.9016      1   1     81.92
 3     305.8987      1   1     81.92
 4     315.9419      1   1     81.92
 5     317.9389      1   1     81.92
 6     319.8965      1   1     81.92
 7     321.8936      1   1     81.92
 8     327.8847      1   1     81.92
 9     331.9368      1   1     81.92
10     333.9338      1   1     81.92
11     342.9792 c  10   1      8.19
12     375.8364      1   1     81.92
13
14
15
16
17
18
19
20
21
22
23
24

 Lock Mass   Cali Mass
```

```
Wed Jun 16 11:39:22 1999        mat95        MAT 95
```



```
MID Set Up Parameters
 MID File                    epa1613
 Measure/lock ratio (X)        1
 Set Damping relay  (T)      FALSE
 Width first lock   (A)       0.20 amu
 Electric jump time (E)         10 ms
 Magnetic jump time (D)         60 ms
 Offset             (O)        100 cts
 Electric range     (R)        300 %
 Sweep peak width   (W)        3.00
 Acq mode          (C|P)       Cent mode
 MID mode      (J|M|L|N)       Lock mode

MID  Time Windows
 #   Start  Measure  End      Cycletime
 1    8:00  28:12  36:12 min   1.00 sec
 2   36:12   7:28  43:40 min   1.00 sec
 3   43:40   5:49  49:30 min   1.00 sec
 4   49:30   5:00  54:30 min   1.00 sec
 5   54:30   3:50  58:20 min   1.00 sec
 6
 7
 8
 9

 Clear Menu    Clear Times    Clear Masses
 Stop MID      SAVE           Main

MID: _
```

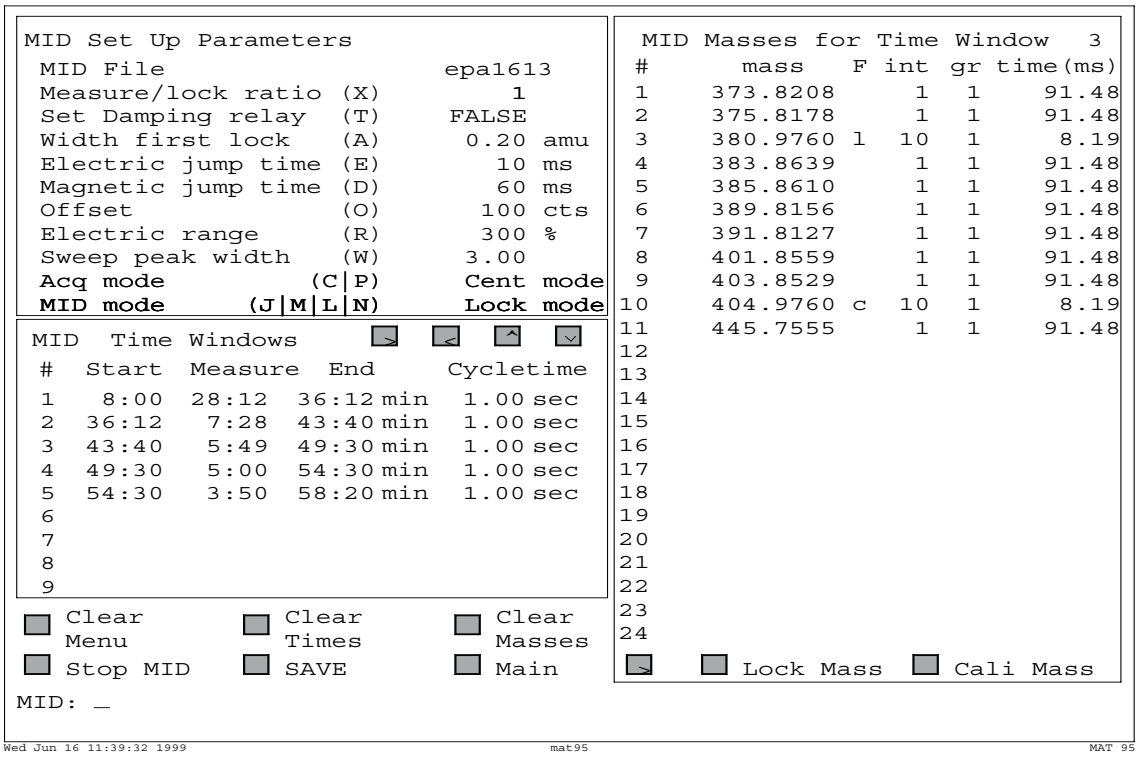
```
 MID Masses for Time Window   2
 #       mass    F int  gr time(ms)
 1     330.9792 l  10   1      8.19
 2     339.8597      1   1     91.48
 3     341.8567      1   1     91.48
 4     351.9000      1   1     91.48
 5     353.8970      1   1     91.48
 6     355.8546      1   1     91.48
 7     357.8516      1   1     91.48
 8     367.8949      1   1     91.48
 9     369.8919      1   1     91.48
10     380.9760 c  10   1      8.19
11     409.7974      1   1     91.48
12
13
14
15
16
17
18
19
20
21
22
23
24

 Lock Mass   Cali Mass
```

```
Wed Jun 16 11:39:27 1999        mat95        MAT 95
```

Figure 2 (Continued)

Rtx-5 Recommended MID Descriptors



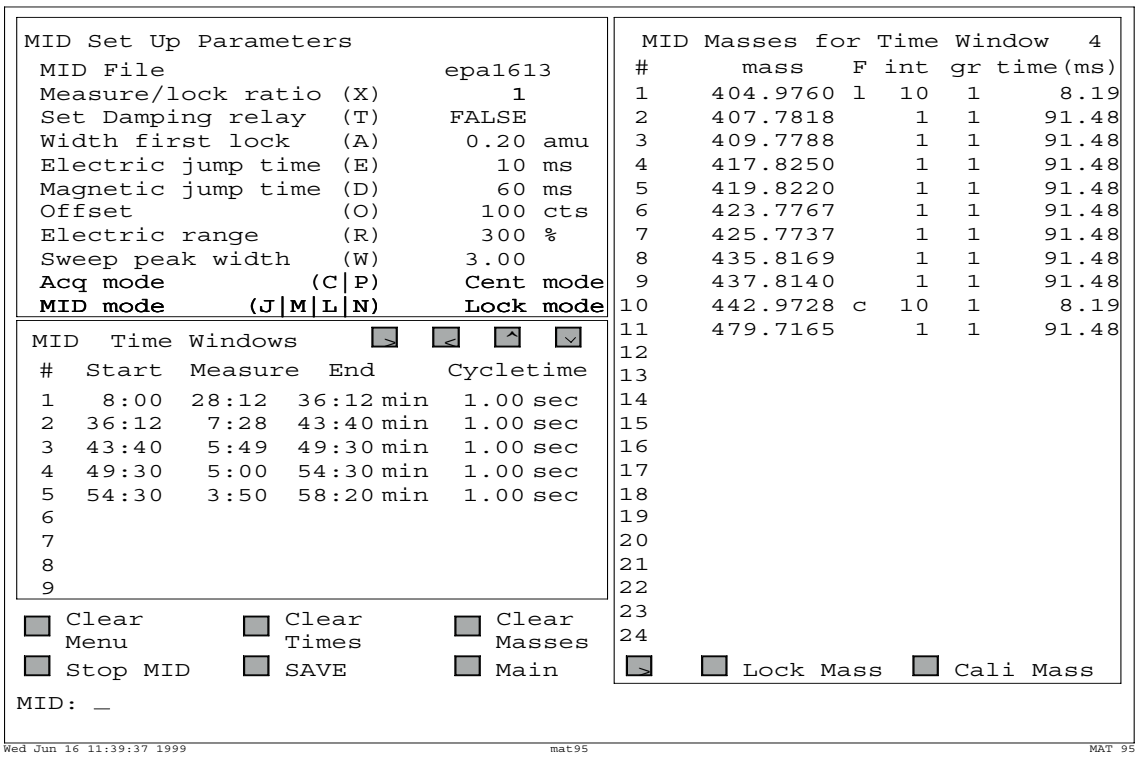
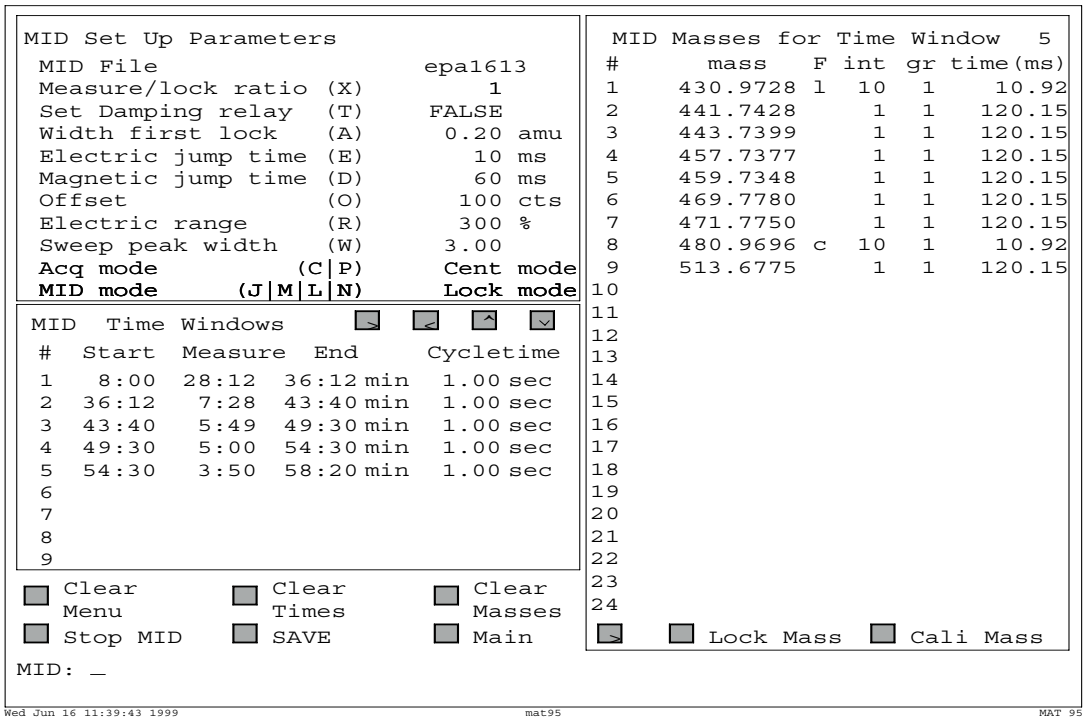


Figure 2 (Continued)

Rtx-5 Recommended MID Descriptors



DB-225 Recommended MID Descriptor

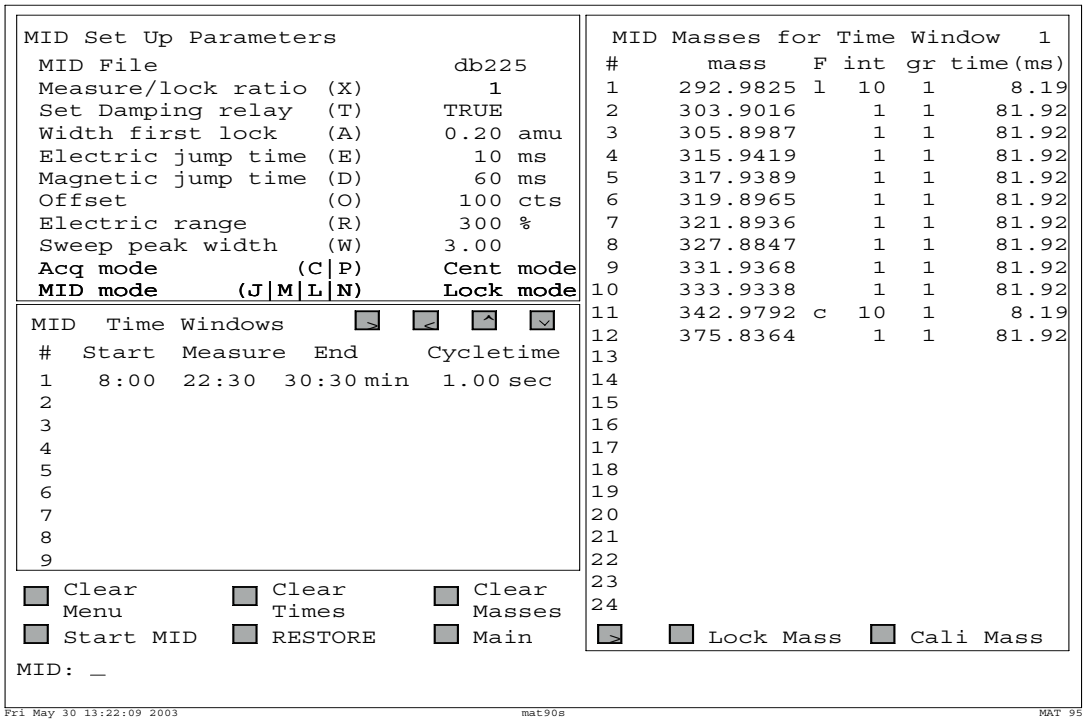


Figure 3

Example Sample Data Review Checklist

TestAmerica Knoxville Dioxin GC/MS Initial Calibration Data Review / Narrative Checklist
Method: 8290/8290A - KNOX-ID-0004-R11

Mass Res. ✓ Date/Time:		Inst:		Win Filename:		Col Perf Filename:	

CS1 Filename	CS2 Filename	CS3 Filename	CS4 Filename	CS5 Filename

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented before beginning the initial calibration?					
2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 or FC43 m/z 313.9838 and m/z 363.9807?					
3. Was the measured exact mass of m/z 380.9760 (PFK) or 363.9807 (FC43) within 5 ppm at reduced accelerating voltage?					
4. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group?					
5. Was the Column Performance solution analyzed and the %Valley ≤25 for separation between 2378-TCDD/F and the closest eluting non-2378 isomer?					
6. Were the five calibration standard solutions, at the concentrations specified in Table 5 of the SOP, analyzed?					
7. Was date/time of analysis verified between analysis header and logbook as correct?					
8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound (Table 5), quantitation ions (Table 22), and formula (Section 10.2.6)?					
9. Are the relative retention times of all PCDDs/PCDFs and all labeled compounds within the limits specified in Table 3?					
10. Are %RSD ≤20% for all unlabeled native analytes?					
11. **8290**, are %RSD ≤30% for all labeled internal standards?					
12. **8090A**, are %RSD ≤20% for all labeled internal standards?					
13. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
14. Are the ion abundance ratios for all labeled and unlabeled analytes within the control limits specified in Table 22 of the SOP?					
15. Was the second source (Wellington) ICV standard analyzed, and the %D calculated and within the acceptance criteria of < ±35%?					
16. If manual integrations were performed, are they clearly identified, initialed and dated?					
17. Were before/after chromatograms reviewed to determine whether the software and manual integrations were appropriate?.					
18. Were manual integrations performed properly?.					
19. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
20. Does the ICAL folder contain **complete** data in the following order? Data review checklist, a **complete** runlog, Avg. %RSD summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation; Total RIC, EICP's and manual integration - for window and all standards, in order from low to high standard, ICV Summary Table, Calculation Summary, and chromatograms?					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

ID022R16.doc, 031212

Figure 3 (Continued)

Example Data Review Checklist

TestAmerica Knoxville Dioxin GC/MS Continuing Calibration Review / Narrative Checklist
Method: 8290/8290A - KNOX-ID-0004-R11

Start Mass Res. ✓:		**Ver Filename:**		**Inst:**	
End Mass Res. ✓:		**Win Filename:**		**ICAL Date:**	
		Col Perf Filename:			
		End Ver Filename:			

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented at both the beginning and end of the 12 hour shift?					
2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 or FC43 m/z 313.9838 and m/z 363.9807?					
3. Was the measured exact mass of m/z 380.9760 (PFK) or 363.9807 (FC43) within 5 ppm at reduced accelerating voltage?					
4. Was date/time of analysis verified between analysis header and logbook as correct?					
5. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group?					
6. Was the Column Performance solution analyzed and the %Valley ≤25 for separation between 2378-TCDD/F and the closest eluting non-2378 isomer?					
7. Were continuing calibrations performed at the beginning and end of the 12-hour period, with successful mass resolution and GC resolution performance checks?					
8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound (Table 3), quantitation ions (Table 22), and formula (Section 10.2.6)?					
9. Are the measured RRFs for each compound within the specified control limits in Table 7 for all PCDDs/PCDFs?					
10. Are the relative retention times of all PCDDs/PCDFs and all labeled compounds within the limits specified in Table 3?					
11. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
12. Are the ion abundance ratios for all labeled and unlabeled analytes within the control limits specified in Table 22 of the SOP?					
13. If manual integrations were performed, are they clearly identified, initialed and dated?					
14. Were before/after chromatograms reviewed to determine whether the software and manual integrations were appropriate?.					
15. Were manual integrations performed properly?.					
16. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
17. Does the CCAL folder contain **complete** data in the following order: Data review checklist, a **complete** runlog, CCAL summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation; Total RIC, EICP's and manual integration - for window and all standards?					

Analyst:	**Date:**	**2nd Level Reviewer :**	**Date:**
Comments:		**Comments:**	

ID022R16.doc, 031212

Figure 3 (Continued)

Example Data Review Checklist

TestAmerica Knoxville Dioxin GC/MS Data Review / Narrative Checklist LOT #_____
Method: 8290/8290A- KNOX-ID-0004-R11 Page 1 of 1 Batch#_____

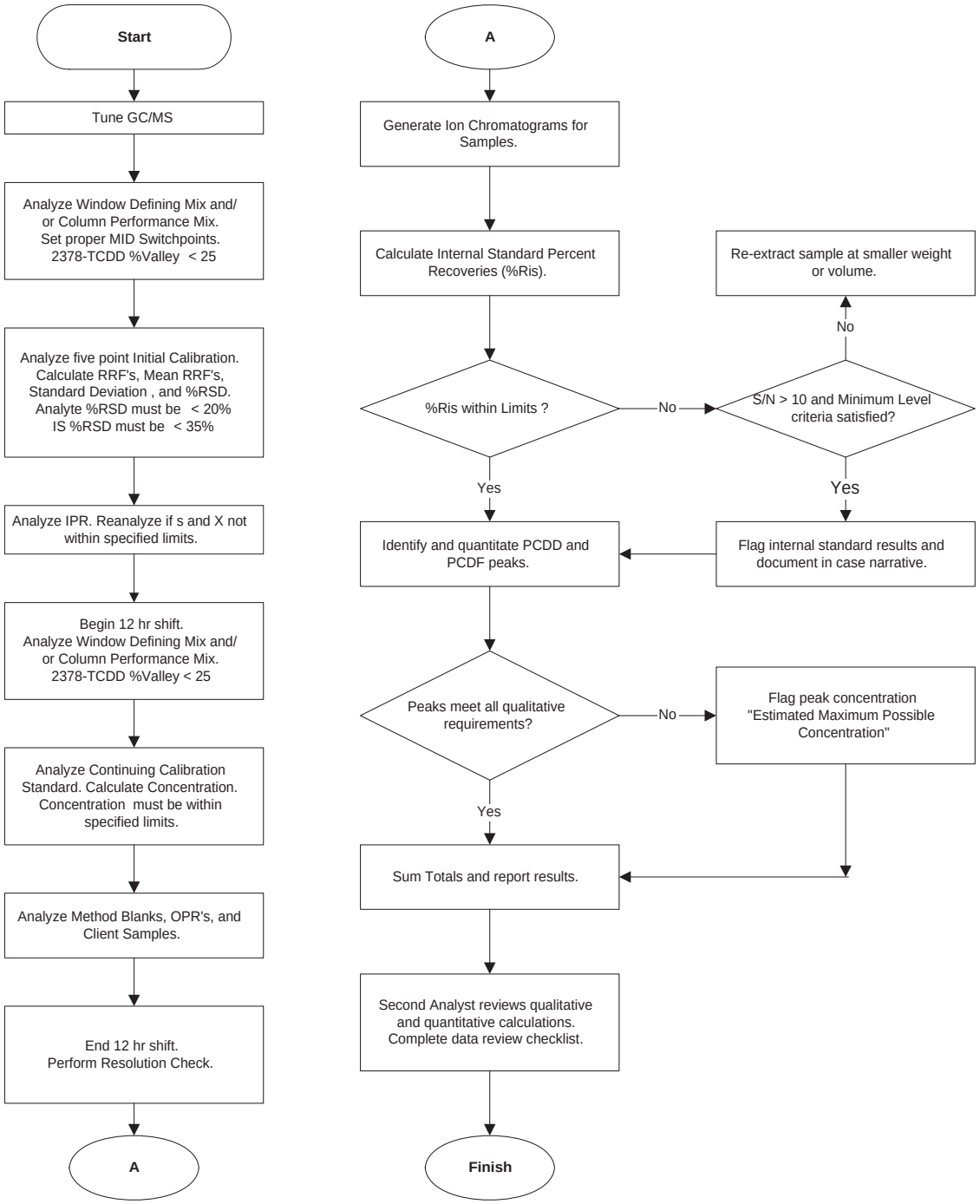
Review Items **A. Initial Calibration**	N/A	Yes	No	Why is data reportable?	2nd Level
1. Was the correct ICAL used for quantitation? (Check 1-2 compounds for batch by manually calculating concentration using the ICAL avg. RF.)					
B. Continuing Calibration	N/A	Yes	No		2nd
1. Has a Continuing Calibration Checklist been completed for each analytical batch?					
C. Client Sample AND QC Sample Results	N/A	Yes	No		2nd
1. Were all special project requirements met?					
2. Were the header information, prep factors, and dilution factors verified?					
3. Is logbook date/time of analysis correct?					
4. Sample analyses done within preparation and analytical holding time (HT)? *If no, list samples:*_____				☐ HT expired upon receipt. ☐* Client requested analysis after HT expired. ☐ Re-extraction done after HT expired.	
5. Are internal standards within QC limits specified in Table 13? *If no, list samples and reason (e.g.,* **sur1***):* Sample Reason Sample Reason _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____				☐* **[sup]** Ion suppression due to matrix. ☐* **[low]** Low recovery. S/N >10 and EDL<ML. ☐ **[sam]** Not enough sample to re-extract. ☐ **[dil]** Dilution showed acceptable %R. ☐ **[mtx]** Obvious matrix interference. Further cleanup not possible. ☐* **[unk]** At client's request, data was flagged as estimated and released without further investigation.	
6. Were reported PCDD/Fs which did not meet the criteria below, properly calculated and reported as EMPCs?: • RT of 2378 isomers within -1 to +3 seconds of associated labeled isomer. • RT of non-2378 isomers within established first/last windows. • Both native ions maximized within ±2 seconds. • Ion abundance ratios within the control limits specified in Table 22. • No corresponding peak at PCDPE mass.					
7. Were all 2378-TCDF hits ≥ ML confirmed by analysis on DB-225?					
8. Are positive results > ML within calibration range? *If no, list samples:*_____				☐ OCDD/F or non-2378 exceeded calibration range ☐ Sample extracted at lowest possible volume	
9. Are all manual integrations performed properly and clearly identified and approved?					
10. Were before/after chromatograms reviewed to determine whether the software and manual integrations were appropriate?.					
11. Final report acceptable? (Results correct, DLs calculated correctly, units correct, IS %R correct, appropriate flags used, dilution factor correct, and extraction/ analysis dates correct.)					
12. Was a narrative prepared and all deviations noted?					
D. Preparation/Matrix QC	N/A	Yes	No	Why is data reportable?	2nd
1. LCS/LCSD done per prep batch and all analytes within the limits specified in QuantIMS reference data?				☐* Reanalysis not possible-insufficient sample. ☐LCS/LCSD %R high and affected analyte(s) were <ML in associated samples. ☐ See comment/narrative	
2. Method blank done per prep batch, method/instrument blank analyzed with each sequence and analytes present in the method blank ≤ ML? *If no, list blank ID:* _____				☐ Sample results are > 10x higher than blank. ☐* There is no analyte > RL in the samples associated with method blank. ☐* Reanalysis not possible-insufficient sample	
3. MS/MSD recoveries and RPDs within laboratory generated QC limits? *If no, list MS/MSD* _____				☐ LCS acceptable, indicating sample matrix effects. ☐ LCS acceptable, high analyte concentration. ☐ LCS acceptable, lack of sample homogeneity.	
E. Other	N/A	Yes	No		2nd
1. Are all nonconformances documented appropriately and copy included with deliverable?					

Analyst:	**Date:**	**Analyst:**	**Date:**
Comments:		**Comments:**	

* Such action must be taken in consultation with client.

Figure 4

Analysis of PCDDs and PCDFs by HRGC/HRMS



Appendix B

Additional Information for Table 1

Analysis Group Description	Method Description	Method Code								
Soil Analysis	**Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography**	8082A								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	DCB Decachlorobiphenyl	2051-24-3							60	140
	PCB-1016	12674-11-2	70	130	20	60	140	20		
	PCB-1221	11104-28-2	70	130	20	60	140	20		
	PCB-1232	11141-16-5	70	130	20	60	140	20		
	PCB-1242	53469-21-9	70	130	20	60	140	20		
	PCB-1248	12672-29-6	70	130	20	60	140	20		
	PCB-1254	11097-69-1	70	130	20	60	140	20		
	PCB-1260	11096-82-5	70	130	20	60	140	20		
	Tetrachloro-m-xylene	877-09-8							60	140
	PCB-1262	37324-23-5	NA	NA	NA	NA	NA	NA		
	PCB-1268	11100-14-4	NA	NA	NA	NA	NA	NA		

Analysis Group Description	Method Description	Method Code								
Soil Analysis	Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography	8081A_8082A								
	Analyte Description	CAS Number	LCSREC Recovery Low %	LCSREC Recovery High %	LCSRPD Precision %	MSREC Recovery Low %	MSREC Recovery High %	MSRPD Precision %	SUREC Recovery Low %	SUREC Recovery High %
	Aldrin	309-00-2	50	150	20	50	150	20		
	alpha-BHC	319-84-6	50	150	20	50	150	20		
	beta-BHC	319-85-7	50	150	20	50	150	20		
	delta-BHC	319-86-8	20	124	20	20	124	20		
	gamma-BHC (Lindane)	58-89-9	50	150	20	50	150	20		
	alpha-Chlordane	5103-71-9	50	150	20	50	150	20		
	gamma-Chlordane	5103-74-2	50	150	24	50	150	24		
	4,4'-DDD	72-54-8	50	150	20	50	150	20		
	4,4'-DDE	72-55-9	50	150	20	50	150	20		
	4,4'-DDT	50-29-3	50	150	37	50	150	37		
Analyte Description	CAS Number	LCSREC Recovery Low %	LCSREC Recovery High %	LCSRPD Precision %	MSREC Recovery Low %	MSREC Recovery High %	MSRPD Precision %	SUREC Recovery Low %	SUREC Recovery High %	Analyte Description
	Dieldrin	60-57-1	50	150	20	50	150	20		
	Endosulfan I	959-98-8	50	150	23	50	150	23		
	Endosulfan II	33213-65-9	50	150	33	50	150	33		
	Endosulfan sulfate	1031-07-8	44	140	26	44	140	26		
	Endrin	72-20-8	50	150	20	50	150	20		
	Endrin aldehyde	7421-93-4	50	150	20	50	150	20		
	Endrin ketone	53494-70-5	50	150	20	50	150	20		
	Heptachlor	76-44-8	50	150	20	50	150	20		
	Heptachlor epoxide	1024-57-3	50	150	20	50	150	20		
	Methoxychlor	72-43-5	50	150	26	50	150	26		
	Toxaphene	8001-35-2								
	Tetrachloro-m-xylene	877-09-8							45	140
	DCB Decachlorobiphenyl (Surr)	2051-24-3							45	140

Analysis Group Description	Method Description	Method Code								
Soil Analysis	Closed System Purge and Trap (Low-Level)	5035A								
Soil Analysis	**Volatile Organic Compounds (GC/MS)**	8260B								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	1,1,1-Trichloroethane	71-55-6	67	126	31	67	126	31		
	1,1,2,2-Tetrachloroethane	79-34-5	60	139	24	60	139	24		
	1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	55	130	37	55	130	37		
	1,1,2-Trichloroethane	79-00-5	70	128	22	70	128	22		
	1,1-Dichloroethane	75-34-3	66	124	23	66	124	23		
	1,1-Dichloroethene	75-35-4	59	129	25	59	129	25		
	1,2,3-Trichlorobenzene	87-61-6	37	144	40	37	144	40		
	1,2,4-Trichlorobenzene	120-82-1	51	136	40	51	136	40		
	1,2-Dibromo-3-Chloropropane	96-12-8	35	136	40	35	136	40		
	1,2-Dibromoethane (EDB)	106-93-4	70	131	20	70	131	20		
	1,2-Dichlorobenzene	95-50-1	71	124	22	71	124	22		
	1,2-Dichloroethane	107-06-2	61	127	23	61	127	23		
	1,2-Dichloroethane-d4 (Surr)	17060-07-0							52	124
	1,2-Dichloropropane	78-87-5	72	122	20	72	122	20		
	1,3-Dichlorobenzene	541-73-1	75	118	20	75	118	20		
	1,4-Dichlorobenzene	106-46-7	77	116	20	77	116	20		
	1,4-Dioxane	123-91-1	10	160	40	10	160	40		
	2-Butanone (MEK)	78-93-3	35	149	36	35	149	36		
	2-Hexanone	591-78-6	32	150	32	32	150	32		
	4-Bromofluorobenzene (Surr)	460-00-4							63	120
	4-Methyl-2-pentanone (MIBK)	108-10-1	44	148	30	44	148	30		
	Acetone	67-64-1	20	150	40	20	150	40		
	Benzene	71-43-2	77	120	20	77	120	20		
	Bromochloromethane	74-97-5	67	126	29	67	126	29		
	Bromodichloromethane	75-27-4	70	125	21	70	125	21		

Analysis Group Description	Method Description	Method Code								
Soil Analysis	Closed System Purge and Trap (Low-Level)	5035A								
Soil Analysis	**Volatile Organic Compounds (GC/MS)**	8260B								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	Bromoform	75-25-2	53	140	23	53	140	23		
	Bromomethane	74-83-9	25	150	40	25	150	40		
	Carbon disulfide	75-15-0	50	127	23	50	127	23		
	Carbon tetrachloride	56-23-5	69	122	22	69	122	22		
	Chlorobenzene	108-90-7	79	120	20	79	120	20		
	Chloroethane	75-00-3	22	150	40	22	150	40		
	Chloroform	67-66-3	72	120	25	72	120	25		
	Chloromethane	74-87-3	44	131	27	44	131	27		
	cis-1,2-Dichloroethene	156-59-2	80	118	20	80	118	20		
	cis-1,3-Dichloropropene	10061-01-5	73	120	20	73	120	20		
	Cyclohexane	110-82-7	64	130	21	64	130	21		
	Dibromochloromethane	124-48-1	70	132	20	70	132	20		
	Dibromofluoromethane (Surr)	1868-53-7							68	121
	Dichlorodifluoromethane	75-71-8	25	150	34	25	150	34		
	Ethylbenzene	100-41-4	78	125	21	78	125	21		
	Isopropylbenzene	98-82-8	70	133	22	70	133	22		
	Methyl acetate	79-20-9	27	142	40	27	142	40		
	Methyl tert-butyl ether	1634-04-4	48	132	36	48	132	36		
	Methylcyclohexane	108-87-2	66	135	23	66	135	23		
	Methylene Chloride	75-09-2	58	127	28	58	127	28		
	m-Xylene & p-Xylene	179601-23-1	75	126	21	75	126	21		
	o-Xylene	95-47-6	83	127	20	83	127	20		
	Styrene	100-42-5	83	129	20	83	129	20		
	Tetrachloroethene	127-18-4	78	129	20	78	129	20		
	Toluene	108-88-3	78	124	21	78	124	21		

Analysis Group Description	Method Description	Method Code								
Soil Analysis	Closed System Purge and Trap (Low-Level)	5035A								
Soil Analysis	**Volatile Organic Compounds (GC/MS)**	8260B								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	Toluene-d8 (Surr)	2037-26-5							72	127
	trans-1,2-Dichloroethene	156-60-5	77	121	20	77	121	20		
	trans-1,3-Dichloropropene	10061-02-6	74	129	20	74	129	20		
	Trichloroethene	79-01-6	76	119	21	76	119	21		
	Trichlorofluoromethane	75-69-4	20	150	40	20	150	40		
	Vinyl chloride	75-01-4	63	124	27	63	124	27		
	Xylenes, Total	1330-20-7	83	126	20	83	126	20		

Analysis Group Description	Method Description	Method Code								
Water Analysis	Liquid-Liquid Extraction (Separatory Funnel)	3510C								
Aqueous Analysis	**Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography**	8081A_8082A								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	PCB-1016	12674-11-2	60	110	27	60	110	27		
	PCB-1221	11104-28-2								
	PCB-1232	11141-16-5								
	PCB-1242	53469-21-9								
	PCB-1248	12672-29-6								
	PCB-1254	11097-69-1								
	PCB-1260	11096-82-5	60	111	24	60	111	24		
	DCB Decachlorobiphenyl (Surr)	2051-24-3							50	140
	Tetrachloro-m-xylene	877-09-8							47	150

Analysis Group Description	Method Description	Method Code								
Aqueous Analysis	Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography	8081A_8082A								
	Analyte Description	CAS Number	LCSREC Recovery Low %	LCSREC Recovery High %	LCSRPD Precision %	MSREC Recovery Low %	MSREC Recovery High %	MSRPD Precision %	SUREC Recovery Low %	SUREC Recovery High %
	4,4'-DDD	72-54-8	48	120	24	48	120	24		
	4,4'-DDE	72-55-9	47	120	20	47	120	20		
	4,4'-DDT	50-29-3	39	131	24	39	131	24		
	Aldrin	309-00-2	62	113	22	62	113	22		
	alpha-BHC	319-84-6	58	114	20	58	114	20		
	alpha-Chlordane	5103-71-9	59	114	21	59	114	21		
	beta-BHC	319-85-7	52	120	24	52	120	24		
	DCB Decachlorobiphenyl (Surr)	2051-24-3							56	122
	delta-BHC	319-86-8	10	137	26	10	137	26		
	Dieldrin	60-57-1	51	121	20	51	121	20		
	Endosulfan I	959-98-8	60	114	22	60	114	22		
	Endosulfan II	33213-65-9	58	112	21	58	112	21		
	Endosulfan sulfate	1031-07-8	42	122	21	42	122	21		
	Endrin	72-20-8	31	138	24	31	138	24		
	Endrin aldehyde	7421-93-4	52	110	25	52	110	25		
	Endrin ketone	53494-70-5	57	114	20	57	114	20		
	gamma-BHC (Lindane)	58-89-9	57	110	21	57	110	21		
	gamma-Chlordane	5103-74-2	60	114	21	60	114	21		
	Heptachlor	76-44-8	63	120	25	63	120	25		
	Heptachlor epoxide	1024-57-3	60	120	20	60	120	20		
	Methoxychlor	72-43-5	35	137	27	35	137	27		
	Tetrachloro-m-xylene	877-09-8							60	111
	Toxaphene	8001-35-2								

Analysis Group Description	Method Description	Method Code								
Soil Analysis	Automated Soxhlet Extraction	3541								
Aqueous Analysis	**Semivolatile Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)**	8270C								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	1,1'-Biphenyl	92-52-4	30	150	40	30	150	40		
	1,2,4,5-Tetrachlorobenzene	95-94-3	30	125	25	30	125	25		
	2,2'-oxybis[1-chloropropane]	108-60-1	36	101	41	36	101	41		
	2,3,4,6-Tetrachlorophenol	58-90-2	38	113	83	38	113	83		
	2,4,5-Trichlorophenol	95-95-4	48	108	44	48	108	44		
	2,4,6-Tribromophenol	118-79-6							35	124
	2,4,6-Trichlorophenol	88-06-2	50	106	42	50	106	42		
	2,4-Dichlorophenol	120-83-2	47	105	35	47	105	35		
	2,4-Dimethylphenol	105-67-9	44	105	49	44	105	49		
	2,4-Dinitrophenol	51-28-5	10	146	83	10	146	83		
	2,4-Dinitrotoluene	121-14-2	45	124	41	45	124	41		
	2,6-Dinitrotoluene	606-20-2	50	122	40	50	122	40		
	2-Chloronaphthalene	91-58-7	46	101	40	46	101	40		
	2-Chlorophenol	95-57-8	40	101	42	40	101	42		
	2-Fluorobiphenyl	321-60-8							35	105
	2-Fluorophenol	367-12-4							39	103
	2-Methylnaphthalene	91-57-6	45	100	40	45	100	40		
	2-Methylphenol	95-48-7	40	104	41	40	104	41		
	2-Nitroaniline	88-74-4	45	117	42	45	117	42		
	2-Nitrophenol	88-75-5	46	106	39	46	106	39		
	3,3'-Dichlorobenzidine	91-94-1	19	122	40	19	122	40		
	3-Nitroaniline	99-09-2	34	122	39	34	122	39		
	4,6-Dinitro-2-methylphenol	534-52-1	24	134	87	24	134	87		
	4-Bromophenyl phenyl ether	101-55-3	47	110	46	47	110	46		
	4-Chloro-3-methylphenol	59-50-7	47	109	36	47	109	36		

Analysis Group Description	Method Description	Method Code								
Soil Analysis	Automated Soxhlet Extraction	3541								
Aqueous Analysis	**Semivolatile Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)**	8270C								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	4-Chloroaniline	106-47-8	25	108	36	25	108	36		
	4-Chlorophenyl phenyl ether	7005-72-3	47	109	39	47	109	39		
	4-Nitroaniline	100-01-6	38	123	40	38	123	40		
	4-Nitrophenol	100-02-7	36	127	43	36	127	43		
	Acenaphthene	83-32-9	47	104	40	47	104	40		
	Acenaphthylene	208-96-8	49	114	38	49	114	38		
	Acetophenone	98-86-2	30	150	40	30	150	40		
	Anthracene	120-12-7	45	112	42	45	112	42		
	Atrazine	1912-24-9	30	150	40	30	150	40		
	Benzaldehyde	100-52-7	30	150	40	30	150	40		
	Benzo[a]anthracene	56-55-3	47	110	40	47	110	40		
	Benzo[a]pyrene	50-32-8	47	112	42	47	112	42		
	Benzo[b]fluoranthene	205-99-2	41	107	53	41	107	53		
	Benzo[g,h,i]perylene	191-24-2	38	126	43	38	126	43		
	Benzo[k]fluoranthene	207-08-9	44	115	44	44	115	44		
	Bis(2-chloroethoxy)methane	111-91-1	44	101	36	44	101	36		
	Bis(2-chloroethyl)ether	111-44-4	38	99	43	38	99	43		
	Bis(2-ethylhexyl) phthalate	117-81-7	40	122	41	40	122	41		
	Butyl benzyl phthalate	85-68-7	41	118	41	41	118	41		
	Caprolactam	105-60-2	30	150	40	30	150	40		
	Carbazole	86-74-8	45	114	36	45	114	36		
	Chrysene	218-01-9	46	111	39	46	111	39		
	Dibenz(a,h)anthracene	53-70-3	39	127	45	39	127	45		
	Dibenzofuran	132-64-9	46	104	38	46	104	38		
	Diethyl phthalate	84-66-2	47	115	38	47	115	38		

Analysis Group Description	Method Description	Method Code								
Soil Analysis	Automated Soxhlet Extraction	3541								
Aqueous Analysis	**Semivolatile Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)**	8270C								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	Dimethyl phthalate	131-11-3	49	111	37	49	111	37		
	Di-n-butyl phthalate	84-74-2	43	121	38	43	121	38		
	Di-n-octyl phthalate	117-84-0	33	129	41	33	129	41		
	Fluoranthene	206-44-0	40	120	36	40	120	36		
	Fluorene	86-73-7	46	109	40	46	109	40		
	Hexachlorobenzene	118-74-1	47	108	43	47	108	43		
	Hexachlorobutadiene	87-68-3	43	107	39	43	107	39		
	Hexachlorocyclopentadiene	77-47-4	23	129	49	23	129	49		
	Hexachloroethane	67-72-1	37	97	48	37	97	48		
	Indeno[1,2,3-cd]pyrene	193-39-5	41	125	47	41	125	47		
	Isophorone	78-59-1	47	110	37	47	110	37		
	Methylphenol, 3 & 4	106-44-5	42	105	43	42	105	43		
	Naphthalene	91-20-3	43	100	32	43	100	32		
	Nitrobenzene	98-95-3	43	104	33	43	104	33		
	Nitrobenzene-d5	4165-60-0							25	104
	N-Nitrosodi-n-propylamine	621-64-7	42	107	43	42	107	43		
	N-Nitrosodiphenylamine	86-30-6	44	111	40	44	111	40		
	Pentachlorophenol	87-86-5	17	122	52	17	122	52		
	Phenanthrene	85-01-8	43	108	39	43	108	39		
	Phenol	108-95-2	41	102	39	41	102	39		
	Phenol-d5	4165-62-2							25	105

Analysis Group Description	Method Description	Method Code								
Aqueous Analysis	Purge and Trap	5030B								
Aqueous Analysis	**Volatile Organic Compounds (GC/MS)**	8260B								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	1,1,1,2-Tetrachloroethane	630-20-6	63	140	34	63	140	34		
	1,1,1-Trichloroethane	71-55-6	63	133	35	63	133	35		
	1,1,2,2-Tetrachloroethane	79-34-5	62	125	35	62	125	35		
	1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	46	148	35	46	148	35		
	1,1,2-Trichloroethane	79-00-5	77	127	35	77	127	35		
	1,1-Dichloroethane	75-34-3	73	126	35	73	126	35		
	1,1-Dichloroethene	75-35-4	65	136	35	65	136	35		
	1,1-Dichloropropene	563-58-6	74	123	35	74	123	35		
	1,2,3-Trichlorobenzene	87-61-6	59	127	35	59	127	35		
	1,2,3-Trichloropropane	96-18-4	66	125	35	66	125	35		
	1,2,4-Trichlorobenzene	120-82-1	60	127	35	60	127	35		
	1,2,4-Trimethylbenzene	95-63-6	71	122	30	71	122	30		
	1,2-Dibromo-3-Chloropropane	96-12-8	37	133	35	37	133	35		
	1,2-Dibromoethane (EDB)	106-93-4	74	123	35	74	123	35		
	1,2-Dichlorobenzene	95-50-1	77	120	24	77	120	24		
	1,2-Dichloroethane	107-06-2	68	132	32	68	132	32		
	1,2-Dichloroethane-d4 (Surr)	17060-07-0							64	135
	1,2-Dichloroethene, Total	540-59-0	71	124	35	71	124	35		
	1,2-Dichloropropane	78-87-5	76	124	34	76	124	34		
	1,3,5-Trichlorobenzene	108-70-3	58	132	35	58	132	35		
	1,3,5-Trimethylbenzene	108-67-8	70	126	33	70	126	33		
	1,3-Dichlorobenzene	541-73-1	76	120	24	76	120	24		
	1,3-Dichloropropane	142-28-9	76	124	36	76	124	36		
	1,4-Dichlorobenzene	106-46-7	77	120	24	77	120	24		
	1,4-Dichlorobenzene-d4	3855-82-1								

Analysis Group Description	Method Description	Method Code								
Aqueous Analysis	Purge and Trap	5030B								
Aqueous Analysis	**Volatile Organic Compounds (GC/MS)**	8260B								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	1,4-Dioxane	123-91-1	10	160	35	10	160	35		
	2,2-Dichloropropane	594-20-7	52	131	35	52	131	35		
	2,3- & 3,4- Dichlorotoluene	STL01556	66	122	30	66	122	30		
	2,3,6-Trichlorotoluene	2077-46-5	32	144	35	32	144	35		
	2,4- & 2,5- & 2,6-Dichlorotoluene	STL01557	66	126	26	66	126	26		
	2,4,5-Trichlorotoluene	6639-30-1	38	132	35	38	132	35		
	2,4-Dichlorobenzotrifluoride	320-60-5	69	129	32	69	129	32		
	2,5-Dichlorobenzotrifluoride	320-50-3	65	127	35	65	127	35		
	2-Butanone (MEK)	78-93-3	39	138	35	39	138	35		
	2-Chlorobenzotrifluoride	88-16-4	57	145	34	57	145	34		
	2-Chloroethyl vinyl ether	110-75-8	10	110	35	10	110	35		
	2-Chlorotoluene	95-49-8	69	122	33	69	122	33		
	2-Hexanone	591-78-6	25	132	35	25	132	35		
	3,4-Dichlorobenzotrifluoride	328-84-7	62	130	35	62	130	35		
	3-Chlorobenzotrifluoride	98-15-7	67	136	35	67	136	35		
	3-Chlorotoluene	108-41-8	70	130	35	70	130	35		
	4-Bromofluorobenzene (Surr)	460-00-4							70	118
	4-Chlorobenzotrifluoride	98-56-6	68	135	35	68	135	35		
	4-Chlorotoluene	106-43-4	73	120	30	73	120	30		
	4-Isopropyltoluene	99-87-6	56	131	35	56	131	35		
	4-Methyl-2-pentanone (MIBK)	108-10-1	45	145	35	45	145	35		
	Acetone	67-64-1	22	150	35	22	150	35		
	Acetonitrile	75-05-8	30	140	35	30	140	35		
	Acrolein	107-02-8	30	140	35	30	140	35		
	Acrylonitrile	107-13-1	30	140	35	30	140	35		

Analysis Group Description	Method Description	Method Code								
Aqueous Analysis	Purge and Trap	5030B								
Aqueous Analysis	**Volatile Organic Compounds (GC/MS)**	8260B								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	Allyl chloride	107-05-1			35			35		
	Benzene	71-43-2	80	120	32	80	120	32		
	Bromobenzene	108-86-1	77	120	29	77	120	29		
	Bromochloromethane	74-97-5	70	127	35	70	127	35		
	Bromodichloromethane	75-27-4	66	130	35	66	130	35		
	Bromoform	75-25-2	46	150	35	46	150	35		
	Bromomethane	74-83-9	33	150	35	33	150	35		
	Carbon disulfide	75-15-0	54	132	35	54	132	35		
	Carbon tetrachloride	56-23-5	55	150	35	55	150	35		
	Chlorobenzene	108-90-7	80	120	29	80	120	29		
	Chloroethane	75-00-3	36	142	35	36	142	35		
	Chloroform	67-66-3	72	127	35	72	127	35		
	Chloromethane	74-87-3	50	139	35	50	139	35		
	Chloroprene	126-99-8			35			35		
	cis-1,2-Dichloroethene	156-59-2	70	120	35	70	120	35		
	cis-1,3-Dichloropropene	10061-01-5	66	120	35	66	120	35		
	Cyclohexane	110-82-7	45	142	35	45	142	35		
	Dibromochloromethane	124-48-1	60	140	35	60	140	35		
	Dibromofluoromethane (Surr)	1868-53-7							70	128
	Dibromomethane	74-95-3	72	125	35	72	125	35		
	Dichlorodifluoromethane	75-71-8	13	150	35	13	150	35		
	Ethyl ether	60-29-7			35			35		
	Ethyl methacrylate	97-63-2			35			35		
	Ethylbenzene	100-41-4	72	126	33	72	126	33		
	Hexachlorobutadiene	87-68-3	38	147	35	38	147	35		
	Hexane	110-54-3			35			35		

Analysis Group Description	Method Description	Method Code								
Aqueous Analysis	Purge and Trap	5030B								
Aqueous Analysis	**Volatile Organic Compounds (GC/MS)**	8260B								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	Iodomethane	74-88-4			35			35		
	Isobutyl alcohol	78-83-1			35			35		
	Isopropylbenzene	98-82-8	58	130	35	58	130	35		
	Methacrylonitrile	126-98-7			35			35		
	Methyl acetate	79-20-9	47	142	35	47	142	35		
	Methyl methacrylate	80-62-6			35			35		
	Methyl tert-butyl ether	1634-04-4	64	123	35	64	123	35		
	Methylcyclohexane	108-87-2	45	145	35	45	145	35		
	Methylene Chloride	75-09-2	63	129	35	63	129	35		
	m-Xylene & p-Xylene	179601-23-1	73	130	32	73	130	32		
	Naphthalene	91-20-3	45	127	35	45	127	35		
	n-Butanol	71-36-3			35			35		
	n-Butylbenzene	104-51-8	49	134	34	49	134	34		
	n-Heptane	142-82-5								
	N-Propylbenzene	103-65-1	62	128	34	62	128	34		
	o-Xylene	95-47-6	72	124	33	72	124	33		
	Propionitrile	107-12-0			35			35		
	sec-Butylbenzene	135-98-8	55	132	33	55	132	33		
	Styrene	100-42-5	71	127	34	71	127	34		
	tert-Butyl alcohol	75-65-0			35			35		
	tert-Butylbenzene	98-06-6	55	128	35	55	128	35		
	Tetrachloroethene	127-18-4	70	135	35	70	135	35		
	Tetrahydrofuran	109-99-9			35			35		
	Toluene	108-88-3	80	123	35	80	123	35		
	Toluene-d8 (Surr)	2037-26-5							71	118
	trans-1,2-Dichloroethene	156-60-5	73	126	35	73	126	35		

Analysis Group Description	Method Description	Method Code								
Aqueous Analysis	Purge and Trap	5030B								
Aqueous Analysis	**Volatile Organic Compounds (GC/MS)**	8260B								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	trans-1,3-Dichloropropene	10061-02-6	65	125	35	65	125	35		
	trans-1,4-Dichloro-2-butene	110-57-6	40	100	30	40	100	30		
	Trichloroethene	79-01-6	73	120	35	73	120	35		
	Trichlorofluoromethane	75-69-4	44	150	35	44	150	35		
	Vinyl acetate	108-05-4	44	150	35	44	150	35		
	Vinyl chloride	75-01-4	53	138	35	53	138	35		
	Xylenes, Total	1330-20-7	76	128	32	76	128	32		

Analysis Group Description	Method Description	Method Code								
Aqueous Analysis	Liquid-Liquid Extraction	3520C								
Aqueous Analysis	**Semivolatile Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Low Level**	8270C								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	1,1'-Biphenyl	92-52-4	30	150	35	30	150	35		
	1,2,4,5-Tetrachlorobenzene	95-94-3	30	125	25	30	125	25		
	1,2,4-Trichlorobenzene	120-82-1	34	96	45	34	96	45		
	1,2-Dichlorobenzene	95-50-1	34	95	38	34	95	38		
	1,2-Diphenylhydrazine(as Azobenzene)	122-66-7	31	107	41	31	107	41		
	1,3-Dichlorobenzene	541-73-1	33	93	38	33	93	38		
	1,3-Dinitrobenzene	99-65-0	30	125	25	30	125	25		
	1,4-Dichlorobenzene	106-46-7	34	93	41	34	93	41		
	1,4-Dioxane	123-91-1	23	88	20	23	88	20		
	1-Methylnaphthalene	90-12-0	10	140	30	10	140	30		
	2,2'-oxybis[1-chloropropane]	108-60-1	30	99	42	30	99	42		
	2,3,4,6-Tetrachlorophenol	58-90-2	36	103	40	36	103	40		
	2,3,5,6-Tetrachlorophenol	935-95-5	31	107	38	31	107	38		
	2,4,5-Trichlorophenol	95-95-4	34	104	39	34	104	39		
	2,4,6-Tribromophenol	118-79-6							16	122
	2,4,6-Trichlorophenol	88-06-2	36	103	39	36	103	39		
	2,4-Dichlorophenol	120-83-2	34	104	41	34	104	41		
	2,4-Dimethylphenol	105-67-9	33	97	40	33	97	40		
	2,4-Dinitrophenol	51-28-5	10	130	53	10	130	53		
	2,4-Dinitrotoluene	121-14-2	37	115	39	37	115	39		
	2,5-Dichlorophenol	583-78-8								
	2,6-Dichlorophenol	87-65-0	30	125	25	30	125	25		
	2,6-Dinitrotoluene	606-20-2	39	113	40	39	113	40		
	2-Chloronaphthalene	91-58-7	34	96	39	34	96	39		

Analysis Group Description	Method Description	Method Code								
Aqueous Analysis	Liquid-Liquid Extraction	3520C								
Aqueous Analysis	**Semivolatile Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Low Level**	8270C								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	2-Chlorophenol	95-57-8	31	99	39	31	99	39		
	2-Fluorobiphenyl	321-60-8							19	107
	2-Fluorophenol	367-12-4							10	111
	2-Methylnaphthalene	91-57-6	34	98	42	34	98	42		
	2-Methylphenol	95-48-7	33	98	38	33	98	38		
	2-Naphthylamine	91-59-8	25	135	30	25	135	30		
	2-Nitroaniline	88-74-4	29	112	65	29	112	65		
	2-Nitrophenol	88-75-5	34	107	41	34	107	41		
	3,3'-Dichlorobenzidine	91-94-1	10	89	56	10	89	56		
	3-Nitroaniline	99-09-2	11	104	48	11	104	48		
	4,6-Dinitro-2-methylphenol	534-52-1	24	124	41	24	124	41		
	4-Bromophenyl phenyl ether	101-55-3	37	104	40	37	104	40		
	4-Chloro-3-methylphenol	59-50-7	35	104	42	35	104	42		
	4-Chloroaniline	106-47-8	10	99	39	10	99	39		
	4-Chlorophenyl phenyl ether	7005-72-3	34	103	38	34	103	38		
	4-Nitroaniline	100-01-6	20	124	45	20	124	45		
	4-Nitrophenol	100-02-7	29	115	42	29	115	42		
	7,12-Dimethylbenz(a)anthracene	57-97-6	10	140	30	10	140	30		
	Acenaphthene	83-32-9	35	99	41	35	99	41		
	Acenaphthylene	208-96-8	37	107	40	37	107	40		
	Acetophenone	98-86-2	30	150	35	30	150	35		
	Aniline	62-53-3	21	86	20	21	86	20		
	Anthracene	120-12-7	35	105	37	35	105	37		
	Atrazine	1912-24-9	30	150	35	30	150	35		

Analysis Group Description	Method Description	Method Code								
Aqueous Analysis	Liquid-Liquid Extraction	3520C								
Aqueous Analysis	**Semivolatile Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Low Level**	8270C								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	Benzaldehyde	100-52-7	30	150	35	30	150	35		
	Benzidine	92-87-5	10	150	30	10	150	30		
	Benzo[a]anthracene	56-55-3	38	101	36	38	101	36		
	Benzo[a]pyrene	50-32-8	26	108	40	26	108	40		
	Benzo[b]fluoranthene	205-99-2	29	98	46	29	98	46		
	Benzo[g,h,i]perylene	191-24-2	20	115	44	20	115	44		
	Benzo[k]fluoranthene	207-08-9	28	107	31	28	107	31		
	Benzoic acid	65-85-0	10	114	59	10	114	59		
	Benzyl alcohol	100-51-6	10	68	20	10	68	20		
	Bis(2-chloroethoxy)methane	111-91-1	33	98	46	33	98	46		
	Bis(2-chloroethyl)ether	111-44-4	33	95	38	33	95	38		
	Bis(2-ethylhexyl) phthalate	117-81-7	20	116	40	20	116	40		
	Butyl benzyl phthalate	85-68-7	36	108	40	36	108	40		
	Caprolactam	105-60-2	30	150	35	30	150	35		
	Carbazole	86-74-8	29	112	35	29	112	35		
	Chlorophene	120-32-1	40	150	30	40	150	30		
	Chrysene	218-01-9	37	99	42	37	99	42		
	Cresols, Total	1319-77-3	29	144	33	29	144	33		
	Dibenz(a,h)anthracene	53-70-3	19	118	44	19	118	44		
	Dibenz[a,h]acridine	226-36-8	51	115	35	51	115	35		
	Dibenzofuran	132-64-9	34	101	39	34	101	39		
	Dibromoacetonitrile	3252-43-5								
	Diethyl phthalate	84-66-2	36	109	39	36	109	39		
	Dimethyl phthalate	131-11-3	37	106	42	37	106	42		
	Di-n-butyl phthalate	84-74-2	37	111	38	37	111	38		

Analysis Group Description	Method Description	Method Code								
Aqueous Analysis	Liquid-Liquid Extraction	3520C								
Aqueous Analysis	**Semivolatile Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Low Level**	8270C								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	Di-n-octyl phthalate	117-84-0	11	127	44	11	127	44		
	Diphenamid	957-51-7	30	140	30	30	140	30		
	Fluorene	86-73-7	34	104	40	34	104	40		
	Hexachlorobenzene	118-74-1	35	102	35	35	102	35		
	Hexachlorobutadiene	87-68-3	35	100	41	35	100	41		
	Hexachlorocyclopentadiene	77-47-4	36	115	47	36	115	47		
	Hexachloroethane	67-72-1	32	94	39	32	94	39		
	Indene	95-13-6	10	140	30	10	140	30		
	Indeno[1,2,3-cd]pyrene	193-39-5	22	115	54	22	115	54		
	Isophorone	78-59-1	38	102	43	38	102	43		
	Methylphenol, 3 & 4	106-44-5	32	100	41	32	100	41		
	Naphthalene	91-20-3	35	97	43	35	97	43		
	Nitrobenzene	98-95-3	37	100	42	37	100	42		
	Nitrobenzene-d5	4165-60-0							23	112
	N-Nitrosodiethylamine	55-18-5	31	107	40	31	107	40		
	N-Nitrosodimethylamine	62-75-9	10	150	35	10	150	35		
	N-Nitrosodi-n-butylamine	924-16-3	34	101	43	34	101	43		
	N-Nitrosodi-n-propylamine	621-64-7	32	102	36	32	102	36		
	N-Nitrosopiperidine	100-75-4	10	140	30	10	140	30		
	Pentachlorophenol	87-86-5	15	111	42	15	111	42		
	Phenanthrene	85-01-8	32	104	36	32	104	36		
	Phenol-d5	4165-62-2							15	112
	Phenol	108-95-2	32	95	39	32	95	39		
	Pyrene	129-00-0	35	106	42	35	106	42		
	Pyridine	110-86-1	26	96	46	26	96	46		

Analysis Group Description	Method Description	Method Code								
Aqueous Analysis	Liquid-Liquid Extraction	3520C								
Aqueous Analysis	**Semivolatile Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Low Level**	8270C								
	Analyte Description	**CAS Number**	**LCSREC Recovery Low %**	**LCSREC Recovery High %**	**LCSRPD Precision %**	**MSREC Recovery Low %**	**MSREC Recovery High %**	**MSRPD Precision %**	**SUREC Recovery Low %**	**SUREC Recovery High %**
	Terphenyl-d14	1718-51-0							10	132

Analysis Group Description	Method Description	Method Code								
Aqueous/Soil Analysis	PCB-Congeners by HRGC/HRMS	1668A								
	Analyte Description	IUPAC Number	LCSREC Recovery Low %	LCSREC Recovery High %	LCSRPD Precision %	MSREC Recovery Low %	MSREC Recovery High %	MSRPD Precision %	SUREC *Recovery Low %	SUREC *Recovery High %
	2-MoCB	1	50	150	NA	NA	NA	NA	30	140
	4-MoCB	3	50	150	NA	NA	NA	NA	30	140
	2,2'-DiCB	4	50	150	NA	NA	NA	NA	30	140
	4,4'-DiCB	15	50	150	NA	NA	NA	NA	30	140
	2,2',6-TrCB	19	50	150	NA	NA	NA	NA	30	140
	3,4,4'-TrCB	37	50	150	NA	NA	NA	NA	30	140
	2,2',6,6'-TeCB	54	50	150	NA	NA	NA	NA	30	140
	3,3',4,4'-TeCB3,6	77	50	150	NA	NA	NA	NA	30	140
	3,4,4',5-TeCB6	81	50	150	NA	NA	NA	NA	30	140
	2,2',4,6,6'-PeCB	104	50	150	NA	NA	NA	NA	30	140
	2,3,3',4,4'-PeCB3,6	105	50	150	NA	NA	NA	NA	30	140
	2,3,4,4',5-PeCB6	114	50	150	NA	NA	NA	NA	30	140
	2,3',4,4',5-PeCB3,6	118	50	150	NA	NA	NA	NA	30	140
	2',3,4,4',5-PeCB6	123	50	150	NA	NA	NA	NA	30	140
	3,3',4,4',5-PeCB3,6	126	50	150	NA	NA	NA	NA	30	140
	2,2',4,4',6,6'-HxCB	155	50	150	NA	NA	NA	NA	30	140
	2,3,3',4,4',5-HxCB6	156	50	150	NA	NA	NA	NA	30	140
	2,3,3',4,4',5'-HxCB6	157	50	150	NA	NA	NA	NA	30	140
	2,3',4,4',5,5'-HxCB6	167	50	150	NA	NA	NA	NA	30	140
	3,3',4,4',5,5'-HxCB3,6	169	50	150	NA	NA	NA	NA	30	140
	2,2',3,3',4,4',5-HpCB3	170	50	150	NA	NA	NA	NA	30	140
	2,2',3,4',5,6,6'-HpCB	188	50	150	NA	NA	NA	NA	30	140
	2,3,3',4,4',5,5'-HpCB6	189	50	150	NA	NA	NA	NA	30	140
	2,2',3,3',5,5',6,6'-OcCB	202	50	150	NA	NA	NA	NA	30	140
	2,3,3',4,4',5,5',6-OcCB	205	50	150	NA	NA	NA	NA	30	140
	2,2',3,3',4,4',5,5',6-NoCB3	206	50	150	NA	NA	NA	NA	30	140
	2,2',3,3',4,5,5',6,6'-NoCB	208	50	150	NA	NA	NA	NA	30	140
	DeCB3	209	50	150	NA	NA	NA	NA	30	140

Analysis Group Description	Method Description	Method Code								
Aqueous/Soil Analysis	PCDD/PCDFs by HRGC/HRMS	8290A								
	Analyte Description	CAS Number	LCSREC Recovery Low %	LCSREC Recovery High %	LCSRPD Precision %	MSREC Recovery Low %	MSREC Recovery High %	MSRPD Precision %	SUREC *Recovery Low %	SUREC *Recovery High %
	1,2,3,4,6,7,8-HPCDD	35822-46-9	50	150	NA	NA	NA	NA	30	140
	1,2,3,4,6,7,8-HPCDF	67562-39-4	50	150	NA	NA	NA	NA	30	140
	1,2,3,4,7,8-HxCDD	39227-28-6	50	150	NA	NA	NA	NA	30	140
	1,2,3,4,7,8-HXCDF	70648-26-9	50	150	NA	NA	NA	NA	30	140
	1,2,3,4,7,8,9-HPCDF	55673-89-7	50	150	NA	NA	NA	NA	30	140
	1,2,3,6,7,8-HxCDD	57653-85-7	50	150	NA	NA	NA	NA	30	140
	1,2,3,6,7,8-HXCDF	57117-44-9	50	150	NA	NA	NA	NA	30	140
	1,2,3,7,8,9-HxCDD	19408-74-3	50	150	NA	NA	NA	NA	30	140
	1,2,3,7,8,9-HXCDF	72918-21-9	50	150	NA	NA	NA	NA	30	140
	1,2,3,7,8-PeCDD	40321-76-4	50	150	NA	NA	NA	NA	30	140
	1,2,3,7,8-PECDF	57117-41-6	50	150	NA	NA	NA	NA	30	140
	2,3,4,6,7,8-HXCDF	60851-34-5	50	150	NA	NA	NA	NA	30	140
	2,3,4,7,8-PECDF	57117-31-4	50	150	NA	NA	NA	NA	30	140
	2,3,7,8-TCDD	1746-01-6	50	150	NA	NA	NA	NA	30	140
	2,3,7,8-TCDF	51207-31-9	50	150	NA	NA	NA	NA	30	140
	OCDD	3268-87-9	50	150	NA	NA	NA	NA	30	140
	OCDF	39001-02-0	50	150	NA	NA	NA	NA	30	140

Note all limits are subject to change based on final laboratory selection and required annual laboratory detection limit updates