BROWNFIELDS QUALITY ASSURANCE PROJECT PLAN (QAPP)

Former Federated Metals Site
300 Enterprise Avenue
Trenton, New Jersey

Prepared For:
The City of Trenton
319 East State Street
Trenton, New Jersey 08618

Prepared By:
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Brownfields QAPP Worksheet #1
U.S. EPA Region 2 Brownfields QAPP

Title: Former Federated Metals Site Quality Assurance Project Plan (QAPP)
Project Name/Property Name: Former Federated Metals Site
Property/Site Location: 300 Enterprise Avenue
Revision Number: 2
Revision Date:

Brownfields Cooperative Agreement Number:__BF97205312_____

The City of Trenton, New Jersey
Brownfields Recipient

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Feburary 20, 2014
Preparation Date (Day/Month/Year)

Brownfields Recipient Program Manager:

Signature

James Capasso/City of Trenton
Printed Name/Organization/Date

Environmental Consultant Quality Assurance Officer: (QAO)

Signature

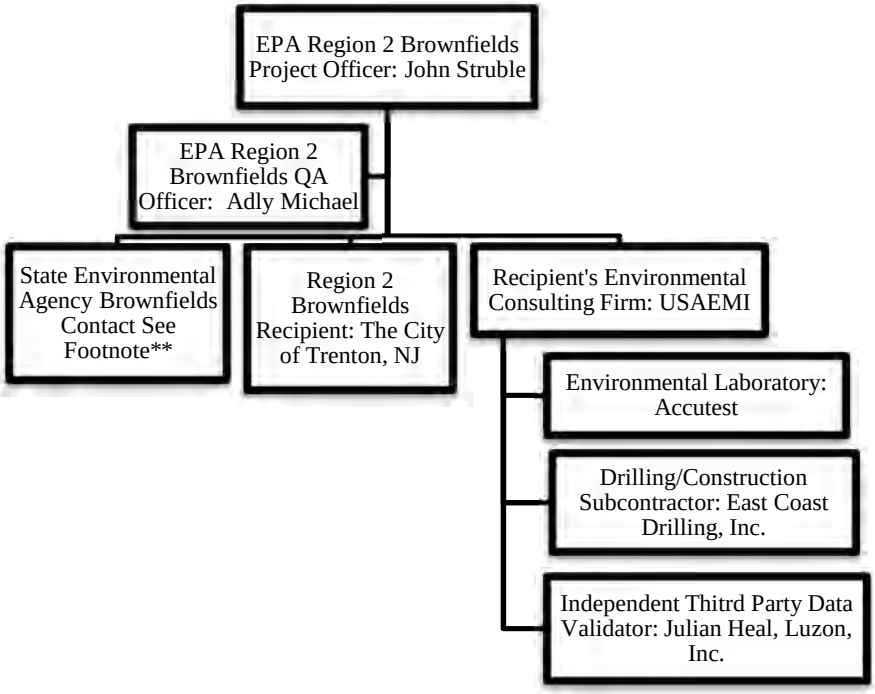
Jorge Gomez/USA Environmental Management, Inc.
Printed Name/Organization/Date

EPA Region 2 Brownfields Project Officer:

Signature

John Struble, USEPA
Printed Name/Organization/Date

Brownfields QAPP Worksheet #2a
Project Organizational Chart



*Data validation to be performed by third party – independent to project (can be within Environmental Consulting firm or subcontracted to a data validation firm).

** Environmental Assessment and remediation is proceeding under the oversight of a New Jersey Licensed Site Remediation Professional (LSRP); Ms. Carol S. Graff, CPG, LSRP

Brownfields QAPP Worksheet #2b
Personnel Responsibilities

Name	Title	Telephone Number	Organizational Affiliation	Responsibilities[1]
Jorge Gomez	Environmental Consultant Project Manager	609-656-8101	USA Environmental Management, Inc.	Project Manager, Sample Management Officer (SMO), Health & Safety Coordinator
Wayne Martin	Sampling Assistance(s)	609-656-8101	USA Environmental Management, Inc.	Contractor coordination and Sampling Operations
James Capasso	Brownfields Recipient Program Manager	609-989-3501	The City of Trenton	Task Manager
Carol S. Graff	State Brownfields Contact [3]	609-656-8101	USA Environmental Management, Inc.	LSRP Of Record
John Struble	EPA Brownfields Project Officer (BPO)		EPA Region 2	
Adly Michael	EPA Brownfields Quality Assurance Officer (QAO)	732-906-6161	EPA Region 2	
Matthew Cordova	Environmental Laboratory Contact	732-355-4550	Accutest, Inc	Client Manager
Julian Heal	Data Validator[2]	215-870-5092	Luzon, Inc.	QA/QC

[1] Resumes of project personnel are included Appendix B

2 Data validation to be performed by third party – independent to project (can be within Environmental Consulting firm or subcontracted to a data validation firm).

3 Environmental Assessment and remediation is proceeding under the oversight of a New Jersey Licensed Site Remediation Professional (LSRP); Ms. Carol S. Graff, CPG, LSRP

TBD – To be determined

Brownfields QAPP Worksheet #3a
Problem Definition/Project Description

PROBLEM DEFINITION

The purpose of this work is to investigate and remediate areas of concern (AOCs) previously identified at the site. The supplemental remedial investigations and remedial actions are required prior to the redevelopment of the site as a recreation area and greenway as part of the Assunpink Project.

The project includes the following: selective demolition and removal of concrete slab and suspected vault bottom(s) at petroleum-impacted areas; investigation of a former oil pump area and contingent removal of suspected underground storage tanks (USTs) and/or appurtenant piping; investigation of petroleum-impacted areas at locations of former heating oil USTs and contingent removal of suspected 20,000-gallon fuel oil UST; monitoring well installation and groundwater investigation; compliance with laws and regulations; and engineering oversight and report preparation.

PROJECT DESCRIPTION

Site Location and Description

The Former Federated Metals site is located at 300 Enterprise Ave., Trenton, NJ (Block 23102, Lot 9). The site is owned by the City of Trenton and consists of a 1-acre, vacant, triangular lot bordered to the southwest by an active railroad, to the northwest by Enterprise Avenue and to the east by a vacant, vegetated lot owned by the City of Trenton. The Assunpink Creek is located approximately 200 feet to the southeast of the property. A site location map is provided as Figure 1.

The remedial investigation and remedial actions will be conducted at the following AOCs:

AOC	Description
1	Former two 20,000-gallon oil USTs
4	Former 15,000-gallon oil UST
6	Former oil pump stand and tank
7	Former electrical transformers
8	Former four electrical transformers
10	Stormwater outfall
11	Historical metal refining activities (Site-wide)

USA Environmental Management, Inc (USAEMI) will collect post-excavation confirmatory samples from the excavations associated with former USTs and other AOCs. Post-excavation soil samples will also be collected following removal of UST and UST removals. The post-excavation samples will be collected at the limits and floor of the excavations in accordance with N.J.A.C.7:26E, subchapter 6.4 and the EPA soil sampling SOP. The number of post-excavation soil samples will be based on the size of the final excavation. It is anticipated that at least eight

(8) post-excavation samples will be collected from AOC 1 (former two 20,000-gallon oil USTs), eight (8) post-excavation samples will be collected from AOC 4 (former 15,000-gallon oil UST), six (6) post-excavation samples will be collected from AOC 6 (former location of an oil pump), and 10 post-excavation samples will be collected from AOC 7 and AOC 8 (former electrical transformers), and 20 post-excavation samples will be collected from AOC 10 (stormwater outfall) and AOC 11 (site-wide). The post-excavation samples will be analyzed as per the requirements 7:26E - Table 2-1: Analytical Requirements for Petroleum Storage and Discharge Areas, including polychlorinated biphenyls (PCBs) at PCB discharge areas.

At least five (5) monitoring wells will be installed in those areas with the highest concentrations of petroleum hydrocarbons or greatest evidence of contamination. Groundwater samples will be collected using the EPA Low Flow Sampling Method during two consecutive quarterly sampling events and analyzed for full target analyte list/target compound list plus 30 non-targeted organic compounds (TAL/TCL+30), which include volatile organic compounds (VOCs), semi-volatiles (Semi-VOCs), Pesticides, PCBs, and TAL Metals.

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Quality Assurance/Quality Control (QA/QC) samples will be collected during the sampling activities and included with the post-excavation soil samples and groundwater samples. All samples will be properly preserved and delivered to a NJDEP certified laboratory (Accutest Laboratories of Dayton, NJ) under chain of custody procedures.

Site History

The Site was utilized primarily by Federated Metals Corporation and American Smelting & Refining Company for the refining of secondary metals to produce metallic zinc dust from approximately 1925 until operations were ceased in August 1980. The buildings were demolished in April 1995 and the lot was subsequently used for the collection and storage of demolition and construction debris until 2002, after which the lot remained undeveloped and vacant. The Site is currently partially covered with a thick concrete slab (located approximately 1-ft below ground surface in the areas of the former main building) and is surrounded by a six foot chain link fence.

Contaminants of concern at the site include petroleum compounds, which were observed primarily in soil immediately above the water table (10 to 11 feet below ground surface) at location of former oil USTs (AOC 1, AOC 4, and AOC 6). PCB contamination with low concentrations was observed at location for former electrical transformers (AOCs 7 and 8). The previous site-wide investigation also revealed the presence of poly-aromatic hydrocarbons (PAHs) and metals. PCBs, PAHs, and some metals were detected at concentration exceeding the NJDEP Residential Direct Contact Soil Remediation Standards (RDCSRS) and Impact to Groundwater Soil Remediation Standards (IGWSRS).

The remedial actions for the site include excavation of impacted soils, pumping of impacted groundwater and liquid free product from excavation areas, and engineering controls (i.e., capping and/or fence) of impacted soils associated with the historic fill material at the site.

Brownfields QAPP Worksheet #3b
Project Quality Objectives/Systematic Planning Process Statements

Overall project objectives include:

- The objective of the project is to remediate contaminated soils observed during previous investigations and to evaluate the groundwater quality conditions at the site.

Who will use the data?
The data will be used by the City of Trenton to fulfill the NJDEP requirements for investigation and remediation of the site.

What will the data be used for?
Data will be used to meet the following project quality objectives (PQOs):

- Determine if there is an immediate threat to public health or the environment.
- Locate and identify potential sources of contamination.
- Characterize the extent of impact from contamination.
- Determine if there is a long-term risk from exposure to the site.
- Determine potential remediation and long-term stewardship strategies (if necessary).

What types of data are needed?

- Soil samples will be analyzed for extractable petroleum hydrocarbons (EPH) with contingency analysis for PAHs, 2-methyl naphthalene and naphthalene from heating oil UST areas. Soil samples will also be collected from electric transformer areas for PCB analysis. Soil samples will be collected site-wide for PAH and metal analysis. Groundwater samples will be analyzed for TAL/TCL+30.
- During the remedial actions, a photoionization detector (PID) will used to field screen the soils and to assist with the remediation of soils. Field parameters will obtained during the groundwater sampling events and will be recorded on sampling logs.
- Soil and groundwater samples will be collected in accordance with Technical Requirements for Site Remediation, N.J.A.C.7:26E and NJDEP Field Sampling Procedures Manual. Low-flow sampling will be employed during the collection of groundwater samples.

Brownfields QAPP Worksheet #4
Project Schedule/Timeline

List all project activities that will be performed during the course of the project. Include the anticipated start and completion dates.

Activities	Organization	Dates (MM/DD/YY)		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
Preparation of QAPP	USA Environmental Management, Inc.	01/20/14	01/31/14	QAPP	02/03/14
Review of QAPP	Names of EPA Region 2 BPO, QAO and Hydrogeologist	02/03/14	02/28/14	Approved QAPP by EPA Region BPO	03/03/14
Preparation of Health and Safety Plan	USA Environmental Management, Inc.	01/20/14	01/31/14	HASP	02/03/14
Procurement of Equipment	USA Environmental Management, Inc.	03/03/14	03/10/14	N/A	
Laboratory Request	USA Environmental Management, Inc.	03/03/14	03/10/14	N/A	
Field Reconnaissance/Access	USA Environmental Management, Inc.	03/10/14	03/10/14	N/A	N/A
Collection of Field Samples	USA Environmental Management, Inc.	03/17/14	03/31/14	N/A	N/A
Laboratory Package Received	USA Environmental Management, Inc.	04/21/14	04/28/14	Unvalidated data package	04/29/14
Validation of Laboratory Results	N/A	04/30/14	05/12/14	Validated data Packages	05/13/14
Data Evaluation/ Preparation of Final Report	USA Environmental Management, Inc.	05/13/14	06/13/14	Final Report	06/16/14

[1]Data validation to be performed by third party – independent to project (can be within Environmental Consulting firm or subcontracted to data validation firm).

Brownfields QAPP Worksheet #5a
Sampling Methods and Locations

List all site locations that will be sampled and include sample identification (ID) number. Specify matrix, and if applicable, depths at which samples will be taken. Only a short reference for the sampling location rationale is necessary for the table. The QAPP text should clearly identify the detailed rationale associated with each reference. Complete all required information, using additional templates if necessary.

Matrix	Sampling Location(s)	Depth (*units*)	Analytical Group	No. of Samples (*identify field duplicates*)	Sampling SOP Reference	Rationale for Sampling Location
Soil	A1-1 through A1-8	12 ft	EPH, 2-Methyl Naphthalene, Naphthalene, PAH	8	EPA Soil Sampling SOP; Worksheet #6	Post-excavation soil samples
Soil	A4-1 through A4-8	12 ft	EPH, 2-Methyl Naphthalene, Naphthalene, PAH	8	EPA Soil Sampling SOP; Worksheet #6	Post-excavation soil samples
Soil	A6-1 through A6-6	12 ft	EPH, 2-Methyl Naphthalene, Naphthalene, PAH	6	EPA Soil Sampling SOP; Worksheet #6	Post-excavation soil samples
Soil	A7-1 through A7-6	4 ft	PCBs	5	EPA Soil Sampling SOP; Worksheet #6	Post-excavation soil samples
Soil	A8-1 through A8-6	4 ft	PCBs	6	EPA Soil Sampling SOP; Worksheet #6	Post-excavation soil samples
Soil	A11-1 through A11-21	8 ft	Metals, Hexavalent Chromium, PAHs	21	EPA Soil Sampling SOP; Worksheet #6	Post-excavation soil samples
Groundwater	MW-1 through MW-5	20 ft	TCL/TAL+30[1]	6	EPA Low Flow Sampling SOP; Worksheet #6	Wells selected were chosen based on the direction of groundwater flow relative to the source.

[1] EPA Contract Laboratory program (CLP) Target Compound and Target Analyte Lists (TCL/TAL). Samples shall be analyzed for TCL VOCs, TCL SVOCs, TCL Pesticides, TCL PCBs, and for TAL Metals & Cyanide and up to 30 non-targeted organic compounds ("+ 30") as detected by gas chromatography/mass spectroscopy (GC/MS) analysis. A Target Compound List + 30 scan means the analysis of a sample for Target Compound List compounds and up to 10 non-targeted volatile organic compounds and up to 20 non-targeted semi-volatile organic compounds using GC/MS analytical methods. To achieve compliance with NJDEP's GWQS, TCL VOCs must also be analyzed by 8011 for Ethylene dibromide and 1,2-Dibromo-3- Chloropropane, and TCL BNs and or PAH must also be analyzed by 8270C SIM (Selected Ion Monitoring).

Brownfields QAPP Worksheet #5b
Analytical Methods and Requirements

Matrix	**Analytical Group**	**Concentration Level**[1]	**Analytical & Preparation Method/ SOP Reference**	**Sample Volume**	**Containers (*number, size, type*)**	**Preservation Requirements (*chemical, temperature, light protected)***	**Maximum Holding Time (*preparation/ analysis)***
Soil	EPH	Low	NJDEP Method Revision 3	300 grams	(1) 300 ml glass jar	Cool to 4°C	7 days
Soil	2-Methyl Naphthalene, Naphthalene, PAH	Low	SW-846 Method 8270D	300 grams	(1) 300 ml glass jar	Cool to 4°C	14 days
Soil	PCBs	Low	SW-846 Method 8082A	300 grams	(1) 300 ml glass jar	Cool to 4°C	14 days
Soil	TAL Metals	Low	SW-846 Method 6010C	300 grams	(1) 300 ml glass jar	Cool to 4°C	6 months
Soil	Hexavalent Chromium	Low	SW-846 Method 3060A	60 grams	(1) 60 ml glass jar	Cool to 4°C	6 months
Groundwater	VOCs+10	Low	SW-846 Method 8260B	120 ml	(3) 40 ml VOA vials w/Teflon lined septum	1:1 HCl to pH<2; cool to 4°C	14 days
Groundwater	Semi-VOCs+20	Low	SW-846 Method 8270D	2,000 ml	(2) 1,000 ml amber glass jars	cool to 6°C	7 days
Groundwater	Pesticides	Low	SW-846 Method 8081B	1,000 ml	(2) 1,000 ml amber glass jars	cool to 6°C	7 days
Groundwater	PCBs	Low	SW-846 Method 8082A	1,000 ml	(2) 1,000 ml amber glass jars	cool to 6°C	7 days
Groundwater	TAL Metals	Low	SW-846 Method 6010C	500 ml	(1) 500 ml plastic bottle	HNO3 to pH<2;	6 months
Groundwater	Total Cyanide	Low	SW-846 Method 9012B	50 ml	(1) 250 ml plastic bottle	NaOH to pH>12	14 days

[1]Concentration Level refers to Trace; Low; Medium; High of the sample.

Brownfields QAPP Worksheet #5c-1
Reference Limits and Evaluation Table

Complete this table for **each sample matrix**, analytical group and concentration level. Identify the target analytes/contaminants of concern, the applicable state regulatory criteria (project-required action limits), and the published achievable detection and reporting limits for each analyte.

Matrix *Soil*
Analytical Group PAHs
Concentration Level *Low*

Analyte	CAS Number	NJDEP Soil Remediation Standards (ug/kg)		Analytical Method	Achievable Laboratory Method[1]	
		RDCSRS	NRDCSRS		Detection Limit ug/kg	Reporting Limit ug/kg
Acenaphthene	83-32-9	3,400,000	37,000,000	SW-846 Method 8270D	9.7	33
Acenaphthylene	208-96-8	NS	300,000,000	SW-846 Method 8270D	11	33
Anthracene	120-12-7	17,000,000	30,000,000	SW-846 Method 8270D	12	33
Benzo(a)anthracene	56-55-3	600	2,000	SW-846 Method 8270D	11	33
Chrysene	218-01-9	62,000	230,000	SW-846 Method 8270D	11	33
Benzo(b)fluoranthene	205-99-2	62,000	230,000	SW-846 Method 8270D	11	33
Benzo(k)fluoranthene	207-08-9	6,000	23,000	SW-846 Method 8270D	13	33
Benzo(a)pyrene	50-32-8	200	200	SW-846 Method 8270D	10	33
Indeno(1,2,3-cd)pyrene	193-39-5	600	2,000	SW-846 Method 8270D	12	33
Dibenz(a,h)anthracene	53-70-3	200	200	SW-846 Method 8270D	11	33
Benzo(g,h,i)perylene	191-24-2	380,000,000	30,000,000	SW-846 Method 8270D	12	33
Fluoranthene	206-44-0	2,300,000	24,000,000	SW-846 Method 8270D	15	33
Fluorene	86-73-7	2,300,000	24,000,000	SW-846 Method 8270D	11	33
Naphthalene	91-20-3	6,000	17,000	SW-846 Method 8270D	9.1	33
Phenanthrene	85-01-8	NS	300,000,000	SW-846 Method 8270D	15	33
Pyrene	129-00-0	1,700,000	18,000,000	SW-846 Method 8270D	13	33

RDCSRS – NJDEP Residential Direct Contact Soil Remediation Standards
NRDCSRS – Non-Residential Direct Contact Soil Remediation Standards
[1]Method Detection Limits (MDLs) and Reporting Limits (RLs) are included with Compound List Reports in Appendix C
NS – No Standard

Brownfields QAPP Worksheet #5c-2
Reference Limits and Evaluation Table

Matrix *Soil*
Analytical Group PAHs and PCBs
Concentration Level *Low*

Analyte	CAS Number	NJDEP Soil Remediation Standards (ug/kg)		Analytical Method	Achievable Laboratory Method[1]	
		RDCSRS	NRDCSRS		Detection Limit ug/kg	Reporting Limit ug/kg
2-Methylnaphthalene	91-57-6	230,000	2,400,000	SW-846 Method 8270D	16	57
Aroclor 1016	12674-11-2	200	1,000	SW-846 Method 8082A	8.7	34
Aroclor 1221	11104-28-2	200	1,000	SW-846 Method 8082A	20	34
Aroclor 1232	11141-16-5	200	1,000	SW-846 Method 8082A	17	34
Aroclor 1242	53469-21-9	200	1,000	SW-846 Method 8082A	11	34
Aroclor 1248	12672-29-6	200	1,000	SW-846 Method 8082A	10	34
Aroclor 1254	11097-69-1	200	1,000	SW-846 Method 8082A	16	34
Aroclor 1260	11096-82-5	200	1,000	SW-846 Method 8082A	11	34

RDCSRS – NJDEP Residential Direct Contact Soil Remediation Standards

NRDCSRS – Non-Residential Direct Contact Soil Remediation Standards

[1]Method Detection Limits (MDLs) and Reporting Limits (RLs) are included with Compound List Reports in Appendix C

Brownfields QAPP Worksheet #5c-3
Reference Limits and Evaluation Table

Matrix *Soil*
Analytical Group Metals
Concentration Level *Low*

Analyte	CAS Number	NJDEP Soil Remediation Standards (mg/kg)		Analytical Method	Achievable Laboratory Method[1]	
		RDCSRS	NRDCSRS		Detection Limit mg/kg	Reporting Limit mg/kg
Aluminum	7429-90-5	78,000	NS	SW-846 6010C	1.474	50
Antimony	7440-36-0	31	450	SW-846 6010C	0.236	2
Arsenic	7440-38-2	19	19	SW-846 6010C	0.228	2
Barium	7440-39-3	16,000	59,000	SW-846 6010C	0.054	20
Beryllium	7440-41-7	16	140	SW-846 6010C	0.015	0.2
Cadmium	7440-43-9	78	78	SW-846 6010C	0.071	0.5
Calcium	7440-70-2	NS	NS	SW-846 6010C	8.374	500
Chromium	7440-47-3	NS	NS	SW-846 6010C	0.074	1
Cobalt	7440-48-4	1,600	590	SW-846 6010C	0.042	5
Copper	7440-50-8	3,100	45,000	SW-846 6010C	0.083	2.5
Iron	7439-89-6	NS	NS	SW-846 6010C	2.872	50
Lead	7439-92-1	400	800	SW-846 6010C	0.213	2
Magnesium	7439-95-4	NS	NS	SW-846 6010C	9.265	500
Manganese	7439-96-5	11,000	5,900	SW-846 6010C	0.054	1.5
Mercury	7439-97-6	23	65	SW-846 6010C	0.0043	0.034
Nickel	7440-02-0	1,600	23,000	SW-846 6010C	0.079	4
Potassium	7440-09-7	NS	NS	SW-846 6010C	6.107	1000
Selenium	7782-49-2	390	5,700	SW-846 6010C	0.259	2
Silver	7440-22-4	390	5,700	SW-846 6010C	0.101	0.5
Sodium	7440-23-5	NS	NS	SW-846 6010C	2.005	1000
Thallium	7440-28-0	5	79	SW-846 6010C	0.293	1
Vanadium	7440-62-2	78	1,100	SW-846 6010C	0.073	5
Zinc	7440-66-6	23,000	110,000	SW-846 6010C	0.234	2

RDCSRS – NJDEP Residential Direct Contact Soil Remediation Standards

NRDCSRS – Non-Residential Direct Contact Soil Remediation Standards

[1]Method Detection Limits (MDLs) and Reporting Limits (RLs) are included with Compound List Reports in Appendix C

NS – No Standard

Brownfields QAPP Worksheet #5c-4
Reference Limits and Evaluation Table

Matrix *Soil*
Analytical Group Hexavalent Chromium
Concentration Level *Low*

Analyte	CAS Number	NJDEP Soil Remediation Standards (mg/kg)		Analytical Method	Achievable Laboratory Method[1]	
		RDCSRS	NRDCSRS		Detection Limit mg/kg	Reporting Limit mg/kg
Hexavalent Chromium	18540-29-9	240	20	SW-846 Method 3060A	0.099	0.4

RDCSRS – NJDEP Residential Direct Contact Soil Remediation Standards
NRDCSRS – Non-Residential Direct Contact Soil Remediation Standards
[1]Method Detection Limits (MDLs) and Reporting Limits (RLs) are included with Compound List Reports in Appendix C

Brownfields QAPP Worksheet #5c-5
Reference Limits and Evaluation Table

Matrix *Groundwater*
Analytical Group *VOCs*
Concentration Level *Low*

Analyte	CAS Number	NJDEP Groundwater Quality Standards (ug/L)	Analytical Method	Achievable Laboratory Method[1]	
				Detection Limit ug/L	Reporting Limit ug/L
Acetone	67-64-1	6,000	SW-846 Method 8260B	3.3	10
Benzene	71-43-2	1	SW-846 Method 8260B	0.28	1
Bromochloromethane	74-97-5	NS	SW-846 Method 8260B	0.42	5
Bromodichloromethane	75-27-4	1	SW-846 Method 8260B	0.21	1
Bromoform	75-25-2	4	SW-846 Method 8260B	0.3	4
Bromomethane	74-83-9	10	SW-846 Method 8260B	0.56	2
2-Butanone (MEK)	78-93-3	NS	SW-846 Method 8260B	3.2	10
Carbon disulfide	75-15-0	700	SW-846 Method 8260B	0.18	2
Carbon tetrachloride	56-23-5	1	SW-846 Method 8260B	0.23	1
Chlorobenzene	108-90-7	50	SW-846 Method 8260B	0.35	1
Chloroethane	75-00-3	NS	SW-846 Method 8260B	0.39	1
Chloroform	67-66-3	70	SW-846 Method 8260B	0.25	1
Chloromethane	74-87-3	NS	SW-846 Method 8260B	0.36	1
Cyclohexane	110-82-7	NS	SW-846 Method 8260B	0.18	5
1,2-Dibromo-3-chloropropane	96-12-8	0.02	SW-846 Method 8011	0.014*	0.020*
Dibromochloromethane	124-48-1	1	SW-846 Method 8260B	0.19	1
1,2-Dibromoethane	106-93-4	NS	SW-846 Method 8260B	0.011*	0.020*
1,2-Dichlorobenzene	95-50-1	600	SW-846 Method 8260B	0.2	1
1,3-Dichlorobenzene	541-73-1	600	SW-846 Method 8260B	0.31	1
1,4-Dichlorobenzene	106-46-7	75	SW-846 Method 8260B	0.3	1
Dichlorodifluoromethane	75-71-8	1,000	SW-846 Method 8260B	0.63	5
1,1-Dichloroethane	75-34-3	50	SW-846 Method 8260B	0.26	1
1,2-Dichloroethane	107-06-2	2	SW-846 Method 8260B	0.22	1
1,1-Dichloroethene	75-35-4	1	SW-846 Method 8260B	0.34	1
cis-1,2-Dichloroethene	156-59-2	70	SW-846 Method 8260B	0.24	1

* The laboratory will achieve low MDLs and RLs for VOCs using SW-846 Method 8011

[1]Method Detection Limits (MDLs) and Reporting Limits (RLs) are included with Compound List Reports in Appendix C
NS – No Standard

Brownfields QAPP Worksheet #5c-5
Reference Limits and Evaluation Table

Matrix *Groundwater*
Analytical Group *VOCs*
Concentration Level *Low*

Analyte	CAS Number	NJDEP Groundwater Quality Standards (ug/L	Analytical Method	Achievable Laboratory Method[1]	
				Detection Limit ug/L	Reporting Limit ug/L
trans-1,2-Dichloroethene	156-60-5	100	SW-846 Method 8260B	0.38	1
1,2-Dichloropropane	78-87-5	1	SW-846 Method 8260B	0.28	1
cis-1,3-Dichloropropene	10061-01-5	1	SW-846 Method 8260B	0.15	1
trans-1,3-Dichloropropene	10061-02-6	1	SW-846 Method 8260B	0.21	1
Ethylbenzene	100-41-4	700	SW-846 Method 8260B	0.21	1
Freon 113	76-13-1	NS	SW-846 Method 8260B	0.77	5
2-Hexanone	591-78-6	NS	SW-846 Method 8260B	1.7	5
Isopropylbenzene	98-82-8	700	SW-846 Method 8260B	0.22	2
Methyl Acetate	79-20-9	7,000	SW-846 Method 8260B	1.5	5
Methylcyclohexane	108-87-2	NS	SW-846 Method 8260B	0.15	5
Methyl Tert Butyl Ether	1634-04-4	70	SW-846 Method 8260B	0.29	1
4-Methyl-2-pentanone(MIBK)	108-10-1	NS	SW-846 Method 8260B	1.5	5
Methylene chloride	75-09-2	3	SW-846 Method 8260B	0.86	2
Styrene	100-42-5	100	SW-846 Method 8260B	0.3	5
1,1,2,2-Tetrachloroethane	79-34-5	1	SW-846 Method 8260B	0.2	1
Tetrachloroethene	127-18-4	1	SW-846 Method 8260B	0.25	1
Toluene	108-88-3	600	SW-846 Method 8260B	0.44	1
1,2,3-Trichlorobenzene	87-61-6	NS	SW-846 Method 8260B	0.24	5
1,2,4-Trichlorobenzene	120-82-1	9	SW-846 Method 8260B	0.22	5
1,1,1-Trichloroethane	71-55-6	30	SW-846 Method 8260B	0.25	1
1,1,2-Trichloroethane	79-00-5	3	SW-846 Method 8260B	0.21	1
Trichloroethene	79-01-6	1	SW-846 Method 8260B	0.5	1
Trichlorofluoromethane	75-69-4	2,000	SW-846 Method 8260B	0.33	5
Vinyl chloride	75-01-4	1	SW-846 Method 8260B	0.41	1
m,p-Xylene		NS	SW-846 Method 8260B	0.4	1
o-Xylene	95-47-6	NS	SW-846 Method 8260B	0.19	1
Xylene (total)	1330-20-7	1,000	SW-846 Method 8260B	0.19	1

[1]Method Detection Limits (MDLs) and Reporting Limits (RLs) are included with Compound List Reports in Appendix C
NS – No Standard

Brownfields QAPP Worksheet #5c-6
Reference Limits and Evaluation Table

Matrix *Groundwater*
Analytical Group *Semi-VOCs*
Concentration Level *Low*

Analyte	CAS Number	NJDEP Groundwater Quality Standards (ug/L)	Analytical Method	Achievable Laboratory Method[1]	
				Detection Limit ug/L	Reporting Limit ug/L
2-Chlorophenol	95-57-8	40	SW-846 Method 8270D	0.97	5
4-Chloro-3-methyl phenol	59-50-7	NS	SW-846 Method 8270D	1.8	5
2,4-Dichlorophenol	120-83-2	20	SW-846 Method 8270D	1.2	2
2,4-Dimethylphenol	105-67-9	100	SW-846 Method 8270D	1.5	5
2,4-Dinitrophenol	51-28-5	40	SW-846 Method 8270D	17	20
4,6-Dinitro-o-cresol	534-52-1	NS	SW-846 Method 8270D	0.99	20
2-Methylphenol	95-48-7	NS	SW-846 Method 8270D	1	2
3&4-Methylphenol		NS	SW-846 Method 8270D	0.93	2
2-Nitrophenol	88-75-5	NS	SW-846 Method 8270D	1.5	5
4-Nitrophenol	100-02-7	NS	SW-846 Method 8270D	5.2	10
Pentachlorophenol	87-86-5	0.3	SW-846 Method 8270D SIM	0.1 **	0.3 **
Phenol	108-95-2	2,000	SW-846 Method 8270D	1.3	2
2,3,4,6-Tetrachlorophenol	58-90-2	200	SW-846 Method 8270D	0.94	5
2,4,5-Trichlorophenol	95-95-4	700	SW-846 Method 8270D	1.6	5
2,4,6-Trichlorophenol	88-06-2	20	SW-846 Method 8270D	1.3	5
Acenaphthene	83-32-9	400	SW-846 Method 8270D	0.26	1
Acenaphthylene	208-96-8	NS	SW-846 Method 8270D	0.23	1
Acetophenone	98-86-2	700	SW-846 Method 8270D	0.29	2
Anthracene	120-12-7	2,000	SW-846 Method 8270D	0.29	1
Atrazine	1912-24-9	3	SW-846 Method 8270D	0.49	2
Benzaldehyde	100-52-7	NS	SW-846 Method 8270D	3.3	5
Benzo(a)anthracene	56-55-3	0.1	SW-846 Method 8270D SIM	0.012 **	0.1 **
Benzo(a)pyrene	50-32-8	0.1	SW-846 Method 8270D SIM	0.012 **	0.1 **
Benzo(b)fluoranthene	205-99-2	0.2	SW-846 Method 8270D SIM	0.010 **	0.1 **
Benzo(g,h,i)perylene	191-24-2	NS	SW-846 Method 8270D SIM	0.016 **	0.1 **
Benzo(k)fluoranthene	207-08-9	0.5	SW-846 Method 8270D SIM	0.015 **	0.1 **
4-Bromophenyl phenyl ether	101-55-3	NS	SW-846 Method 8270D	0.36	2

** The laboratory will achieve low MDLs and RLs for Semi-VOCs using SW-846 Method 8270D SIM

[1]Method Detection Limits (MDLs) and Reporting Limits (RLs) are included with Compound List Reports in Appendix C

NS – No Standard

Brownfields QAPP Worksheet #5c-6
Reference Limits and Evaluation Table

Matrix *Groundwater*
Analytical Group *Semi-VOCs*
Concentration Level *Low*

Analyte	CAS Number	NJDEP Groundwater Quality Standards (ug/L	Analytical Method	Achievable Laboratory Method[1]	
				Detection Limit ug/L	Reporting Limit ug/L
Butyl benzyl phthalate	85-68-7	100	SW-846 Method 8270D	0.29	2
1,1'-Biphenyl	92-52-4	400	SW-846 Method 8270D	0.3	1
2-Chloronaphthalene	91-58-7	600	SW-846 Method 8270D	0.3	2
4-Chloroaniline	106-47-8	30	SW-846 Method 8270D	0.53	5
Carbazole	86-74-8	NS	SW-846 Method 8270D	0.36	1
Caprolactam	105-60-2	NS	SW-846 Method 8270D	0.69	2
Chrysene	218-01-9	5	SW-846 Method 8270D	0.29	1
bis(2-Chloroethoxy)methane	111-91-1	NS	SW-846 Method 8270D	0.31	2
bis(2-Chloroethyl)ether	111-44-4	7	SW-846 Method 8270D	0.31	2
bis(2-Chloroisopropyl)ether	108-60-1	300	SW-846 Method 8270D	0.45	2
4-Chlorophenyl phenyl ether	7005-72-3	NS	SW-846 Method 8270D	0.31	2
2,4-Dinitrotoluene	121-14-2	NS	SW-846 Method 8270D	0.43	1
2,6-Dinitrotoluene	606-20-2	NS	SW-846 Method 8270D	0.46	1
3,3'-Dichlorobenzidine	91-94-1	NS	SW-846 Method 8270D	0.36	2
1,4-Dioxane	123-91-1	NS	SW-846 Method 8270D	0.27	1
Dibenzo(a,h)anthracene	53-70-3	0.3	SW-846 Method 8270D SIM	0.017 **	0.1 **
Dibenzofuran	132-64-9	NS	SW-846 Method 8270D	0.27	5
Di-n-butyl phthalate	84-74-2	700	SW-846 Method 8270D	0.56	2
Di-n-octyl phthalate	117-84-0	100	SW-846 Method 8270D	0.31	2
Diethyl phthalate	84-66-2	6,000	SW-846 Method 8270D	0.33	2
Dimethyl phthalate	131-11-3	NS	SW-846 Method 8270D	0.28	2
bis(2-Ethylhexyl)phthalate	117-81-7	3	SW-846 Method 8270D	0.59	2
Fluoranthene	206-44-0	300	SW-846 Method 8270D	0.32	1
Fluorene	86-73-7	300	SW-846 Method 8270D	0.28	1
Hexachlorobenzene	118-74-1	0.02	SW-846 Method 8270D SIM	0.017 **	0.02 **
Hexachlorobutadiene	87-68-3	1	SW-846 Method 8270D	0.51	1
Hexachlorocyclopentadiene	77-47-4	40	SW-846 Method 8270D	7.1	10

** The laboratory will achieve low MDLs and RLs for Semi-VOCs using SW-846 Method 8270D SIM

[1]Method Detection Limits (MDLs) and Reporting Limits (RLs) are included with Compound List Reports in Appendix C
NS – No Standard

Brownfields QAPP Worksheet #5c-6
Reference Limits and Evaluation Table

Matrix *Groundwater*
Analytical Group *Semi-VOCs*
Concentration Level *Low*

Analyte	CAS Number	NJDEP Groundwater Quality Standards (ug/L	Analytical Method	Achievable Laboratory Method[1]	
				Detection Limit ug/L	Reporting Limit ug/L
Hexachloroethane	67-72-1	7	SW-846 Method 8270D	0.55	2
Indeno(1,2,3-cd)pyrene	193-39-5	0.2	SW-846 Method 8270D SIM	0.014 **	0.1 **
Isophorone	78-59-1	40	SW-846 Method 8270D	0.27	2
2-Methylnaphthalene	91-57-6	NS	SW-846 Method 8270D	0.38	1
2-Nitroaniline	88-74-4	NS	SW-846 Method 8270D	1.1	5
3-Nitroaniline	99-09-2	N	SW-846 Method 8270D	1.3	5
4-Nitroaniline	100-01-6	NS	SW-846 Method 8270D	1.7	5
Naphthalene	91-20-3	300	SW-846 Method 8270D	0.26	1
Nitrobenzene	98-95-3	6	SW-846 Method 8270D	0.42	2
N-Nitroso-di-n-propylamine	621-64-7	10	SW-846 Method 8270D	0.3	2
N-Nitrosodiphenylamine	86-30-6	10	SW-846 Method 8270D	0.31	5
Phenanthrene	85-01-8	NS	SW-846 Method 8270D	0.29	1
Pyrene	129-00-0	200	SW-846 Method 8270D	0.27	1
1,2,4,5-Tetrachlorobenzene	95-94-3	NS	SW-846 Method 8270D	0.31	2

** The laboratory will achieve low MDLs and RLs for Semi-VOCs using SW-846 Method 8270D SIM

[1]Method Detection Limits (MDLs) and Reporting Limits (RLs) are included with Compound List Reports in Appendix C

NS – No Standard

Brownfields QAPP Worksheet #5c-7
Reference Limits and Evaluation Table

Matrix *Groundwater*
Analytical Group *Pesticides*
Concentration Level *Low*

Analyte	CAS Number	NJDEP Groundwater Quality Standards (ug/L	Analytical Method	Achievable Laboratory Method[1]	
				Detection Limit ug/L	Reporting Limit ug/L
Aldrin	309-00-2	0.04	SW-846 Method 8081B	0.0079	0.01
alpha-BHC	319-84-6	0.02	SW-846 Method 8081B	0.0023	0.01
beta-BHC	319-85-7	0.04	SW-846 Method 8081B	0.0023	0.01
delta-BHC	319-86-8	NS	SW-846 Method 8081B	0.0019	0.01
gamma-BHC (Lindane)	58-89-9	0.03	SW-846 Method 8081B	0.0017	0.01
alpha-Chlordane	5103-71-9	NS	SW-846 Method 8081B	0.0029	0.01
gamma-Chlordane	5103-74-2	NS	SW-846 Method 8081B	0.0021	0.01
Dieldrin	60-57-1	0.03	SW-846 Method 8081B	0.0016	0.01
4,4'-DDD	72-54-8	0.01	SW-846 Method 8081B	0.0025	0.01
4,4'-DDE	72-55-9	0.01	SW-846 Method 8081B	0.0017	0.01
4,4'-DDT	50-29-3	0.01	SW-846 Method 8081B	0.0032	0.01
Endrin	72-20-8	2	SW-846 Method 8081B	0.002	0.01
Endosulfan sulfate	1031-07-8	40	SW-846 Method 8081B	0.0019	0.01
Endrin aldehyde	7421-93-4	NS	SW-846 Method 8081B	0.0037	0.01
Endrin ketone	53494-70-5	NS	SW-846 Method 8081B	0.0047	0.01
Endosulfan-I	959-98-8	40	SW-846 Method 8081B	0.0028	0.01
Endosulfan-II	33213-65-9	40	SW-846 Method 8081B	0.002	0.01
Heptachlor	76-44-8	0.05	SW-846 Method 8081B	0.0022	0.01
Heptachlor epoxide	1024-57-3	0.2	SW-846 Method 8081B	0.0026	0.01
Methoxychlor	72-43-5	40	SW-846 Method 8081B	0.0041	0.02
Toxaphene	8001-35-2	2	SW-846 Method 8081B	0.15	0.25

[1]Method Detection Limits (MDLs) and Reporting Limits (RLs) are included with Compound List Reports in Appendix C
NS – No Standard

Brownfields QAPP Worksheet #5c-8
Reference Limits and Evaluation Table

Matrix *Groundwater*
Analytical Group *PCBs*
Concentration Level *Low*

Analyte	CAS Number	NJDEP Groundwater Quality Standards (ug/L	Analytical Method	Achievable Laboratory Method[1]	
				Detection Limit ug/L	Reporting Limit ug/L
Aroclor 1016	12674-11-2	0.5	SW-846 Method 8082A	0.13	0.5
Aroclor 1221	11104-28-2	0.5	SW-846 Method 8082A	0.27	0.5
Aroclor 1232	11141-16-5	0.5	SW-846 Method 8082A	0.39	0.5
Aroclor 1242	53469-21-9	0.5	SW-846 Method 8082A	0.086	0.5
Aroclor 1248	12672-29-6	0.5	SW-846 Method 8082A	0.15	0.5
Aroclor 1254	11097-69-1	0.5	SW-846 Method 8082A	0.14	0.5
Aroclor 1260	11096-82-5	0.5	SW-846 Method 8082A	0.21	0.5
Aroclor 1268	11100-14-4	0.5	SW-846 Method 8082A	0.13	0.5
Aroclor 1262	37324-23-5	0.5	SW-846 Method 8082A	0.06	0.5

[1]Method Detection Limits (MDLs) and Reporting Limits (RLs) are included with Compound List Reports in Appendix C
NS – No Standard

Brownfields QAPP Worksheet #5c-9
Reference Limits and Evaluation Table

Matrix *Groundwater*
Analytical Group *Metals*
Concentration Level *Low*

Analyte	CAS Number	NJDEP Groundwater Quality Standards (ug/L	Analytical Method	Achievable Laboratory Method[1]	
				Detection Limit ug/L	Reporting Limit ug/L
Aluminum	7429-90-5	200	SW-846 Method 6010C	10.92	200.0
Antimony	7440-36-0	6	SW-846 Method 6010C	1.84	6.0
Arsenic	7440-38-2	3	SW-846 Method 6010C	1.48	3.0
Barium	7440-39-3	6,000	SW-846 Method 6010C	0.36	200.0
Beryllium	7440-41-7	1	SW-846 Method 6010C	0.17	1.0
Cadmium	7440-43-9	4	SW-846 Method 6010C	0.24	3.0
Calcium	7440-70-2	NS	SW-846 Method 6010C	55.21	5000.0
Chromium	7440-47-3	70	SW-846 Method 6010C	0.92	10.0
Cobalt	7440-48-4	NS	SW-846 Method 6010C	0.54	50.0
Copper	7440-50-8	1,300	SW-846 Method 6010C	1.02	10.0
Iron	7439-89-6	300	SW-846 Method 6010C	13.32	100.0
Lead	7439-92-1	5	SW-846 Method 6010C	2.42	3.0
Magnesium	7439-95-4	NS	SW-846 Method 6010C	22.82	5000.0
Manganese	7439-96-5	50	SW-846 Method 6010C	0.15	15.0
Mercury	7439-97-6	2	SW-846 Method 6010C	0.089	0.200
Nickel	7440-02-0	100	SW-846 Method 6010C	1.55	10.0
Potassium	7440-09-7	NS	SW-846 Method 6010C	41.11	10000.0
Selenium	7782-49-2	40	SW-846 Method 6010C	2.43	10.0
Silver	7440-22-4	40	SW-846 Method 6010C	1.45	10.0
Sodium	7440-23-5	50,000	SW-846 Method 6010C	57.88	10000.0
Thallium	7440-28-0	2	SW-846 Method 6010C	1.32	2.0
Vanadium	7440-62-2	60	SW-846 Method 6010C	0.72	50.0
Zinc	7440-66-6	2,000	SW-846 Method 6010C	4.36	20.0

[1]Method Detection Limits (MDLs) and Reporting Limits (RLs) are included with Compound List Reports in Appendix C
NS – No Standard

Brownfields QAPP Worksheet #5d-1

Analytical Laboratory Sensitivity and Project Criteria

Complete this template for **each matrix**, analytical group and concentration level. Define the data quality indicators performance criteria within the analytical method, and the associated QC sample(s) used to assess the specific performance criteria. Specify whether the QC sample(s) associated with sample and/or analysis.

Matrix Soil
Analytical Group Semi-VOCs
Concentration Level Low

Analytical Method/SOP	Data Quality Indicators[1]	Performance Criteria (related to analytical method)	QC Sample such as Duplicate, Matrix Spike, Surrogates etc.) Used To Assess Performance Criteria	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
EPA Method 8270D	Precision – Overall	RPD $\leq$ 50 when positive results for both samples are $\geq$ 2x QL RPD $\leq$ 50 when positive result for one sample is $\geq$ 2x QL and positive result for other sample is < 2x QL No situations where one result is detected at $\geq$ 2x QL and other result is not detected.	Field Duplicates	S & A
	Accuracy/Bias	Percent recoveries 40-140	Laboratory Control Sample	A
	Accuracy/Bias – Contamination	No target compounds $\geq$ QL (except phthalates must be $\leq$ 5 x QL)	Equipment Blanks and Method Blanks	S & A
	Accuracy/Bias	Cooler temperature 4ºC $\pm$ 2ºC	Cooler Temperature Blank	S
	Data Completeness	Field 90%, Laboratory 95%	Data Completeness Check	S & A

[1]Defined as Precision; Accuracy/Bias; Sensitivity/Quantitation Limits, Representativeness; Comparability, Completeness

Brownfields QAPP Worksheet #5d-2

Analytical Laboratory Sensitivity and Project Criteria

Matrix Soil
Analytical Group PCBs
Concentration Level Low

Analytical Method/SOP	**Data Quality Indicators**[1]	**Performance Criteria (related to analytical method)**	**QC Sample such as Duplicate, Matrix Spike, Surrogates etc.) Used To Assess Performance Criteria**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
EPA Method 8082A	Precision – Overall	RPD $\leq$ 50 when positive results for both samples are $\geq$ 2x QL RPD $\leq$ 50 when positive result for one sample is $\geq$ 2x QL and positive result for other sample is < 2x QL No situations where one result is detected at $\geq$ 2x QL and other result is not detected.	Field Duplicates	S & A
	Accuracy/Bias	Percent recoveries 40-140	Laboratory Control Sample	A
	Accuracy/Bias – Contamination	No target compounds $\geq$ QL	Equipment Blanks and Method Blanks	S & A
	Accuracy/Bias	Cooler temperature 4ºC $\pm$ 2ºC	Cooler Temperature Blank	S
	Data Completeness	Field 90%, Laboratory 95%	Data Completeness Check	S & A

[1]Defined as Precision; Accuracy/Bias; Sensitivity/Quantitation Limits, Representativeness; Comparability, Completeness

Brownfields QAPP Worksheet #5d-3

Analytical Laboratory Sensitivity and Project Criteria

Matrix Soil
Analytical Group Metals
Concentration Level Low

Analytical Method/SOP	Data Quality Indicators[1]	Performance Criteria (related to analytical method)	QC Sample such as Duplicate, Matrix Spike, Surrogates etc.) Used To Assess Performance Criteria	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
EPA Method 6010C	Precision – Overall	RPD $\leq$ 50 when positive results for both samples are $\geq$ 5x QL Absolute difference < 4x QL when positive results for both samples are < 5x QL *RPD $\leq$ 50 when positive result for one sample is $\geq$ 5x QL and positive result for other sample is < 5x QL No situations where one result is detected at $\geq$ 5x QL and other result is not detected.	Field Duplicates	S & A
	Accuracy/Bias	Percent recoveries 70 – 130%	Detection Limit Standard	A
	Accuracy/Bias	Percent recoveries 80 – 120%	Interference Check Sample	A
	Accuracy/Bias (ICP/MS only)	30-120% of IS in blank or calibration standard	Internal Standards	A
	Accuracy/Bias - Contamination	No target compounds $\geq$ QL	Initial Calibration Blanks, Continuing Calibration Blanks, Preparation Blanks, and Equipment Blanks	S & A
	Accuracy/Bias	Cooler temperature 4ºC $\pm$ 2ºC	Cooler Temperature Blank	S
	Data Completeness	Field 90%, Laboratory 95%	Data Completeness Check	S & A

[1]Defined as Precision; Accuracy/Bias; Sensitivity/Quantitation Limits, Representativeness; Comparability, Completeness

Brownfields QAPP Worksheet #5d-4

Analytical Laboratory Sensitivity and Project Criteria

Matrix Soil
Analytical Group Hexavalent Chromium
Concentration Level Low

Analytical Method/SOP	**Data Quality Indicators**[1]	**Performance Criteria (related to analytical method)**	**QC Sample such as Duplicate, Matrix Spike, Surrogates etc.) Used To Assess Performance Criteria**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
EPA Method 3060A	Precision – Overall	RPD $\leq$ 50 when positive results for both samples are $\geq$ 2x QL RPD $\leq$ 50 when positive result for one sample is $\geq$ 2x QL and positive result for other sample is < 2x QL No situations where one result is detected at $\geq$ 2x QL and other result is not detected.	Field Duplicates	S & A
	Accuracy/Bias	Percent recoveries 90-110%	Laboratory Control Sample	A
	Accuracy/Bias – Contamination	No target analytes > QL	Method Blanks	A
	Accuracy/Bias	Cooler temperature 4ºC $\pm$ 2ºC	Cooler Temperature Blank	S
	Data Completeness	Field 90%, Laboratory 95%	Data Completeness Check	S & A

[1]Defined as Precision; Accuracy/Bias; Sensitivity/Quantitation Limits, Representativeness; Comparability, Completeness

Brownfields QAPP Worksheet #5d-5

Analytical Laboratory Sensitivity and Project Criteria

Matrix Groundwater
Analytical Group VOCs
Concentration Level Low

Analytical Method/SOP	Data Quality Indicators[1]	Performance Criteria (related to analytical method)	QC Sample such as Duplicate, Matrix Spike, Surrogates etc.) Used To Assess Performance Criteria	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
EPA Method 8260B	Precision – Overall	RPD $\leq$ 30 when positive results for both samples are $\geq$ 2x QL RPD $\leq$ 30 when positive result for one sample is $\geq$ 2x QL and positive result for other sample is < 2x QL No situations where one result is detected at $\geq$ 2x QL and other result is not detected.	Field Duplicates	S & A
	Accuracy/Bias	Percent recoveries 70-130%	Laboratory Control Sample	A
	Accuracy/Bias – Contamination	No target compounds $\geq$ QL (except methylene chloride, acetone and 2-butanone < 2x QL)	Trip Blanks and Method Blanks	S & A
	Accuracy/Bias – Contamination	No target compounds $\geq$ QL	Instrument Blanks	A
	Accuracy/Bias	Cooler temperature 4ºC $\pm$ 2ºC	Cooler Temperature Blank	S
	Data Completeness	Field 90%; Laboratory 95%	Data Completeness Check	S & A

[1]Defined as Precision; Accuracy/Bias; Sensitivity/Quantitation Limits, Representativeness; Comparability, Completeness

Brownfields QAPP Worksheet #5d-6

Analytical Laboratory Sensitivity and Project Criteria

Matrix Groundwater
Analytical Group Semi-VOCs
Concentration Level Low

Analytical Method/SOP	Data Quality Indicators[1]	Performance Criteria (related to analytical method)	QC Sample such as Duplicate, Matrix Spike, Surrogates etc.) Used To Assess Performance Criteria	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
EPA Method 8270D	Precision – Overall	RPD $\leq$ 50 when positive results for both samples are $\geq$ 2x QL RPD $\leq$ 50 when positive result for one sample is $\geq$ 2x QL and positive result for other sample is < 2x QL No situations where one result is detected at $\geq$ 2x QL and other result is not detected.	Field Duplicates	S & A
	Accuracy/Bias	Percent recoveries 40-140	Laboratory Control Sample	A
	Accuracy/Bias – Contamination	No target compounds $\geq$ QL (except phthalates must be $\leq$ 5 x QL)	Equipment Blanks and Method Blanks	S & A
	Accuracy/Bias	Cooler temperature 4ºC $\pm$ 2ºC	Cooler Temperature Blank	S
	Data Completeness	Field 90%, Laboratory 95%	Data Completeness Check	S & A

[1]Defined as Precision; Accuracy/Bias; Sensitivity/Quantitation Limits, Representativeness; Comparability, Completeness

Brownfields QAPP Worksheet #5d-7

Analytical Laboratory Sensitivity and Project Criteria

Matrix Groundwater
Analytical Group Pesticides
Concentration Level Low

Analytical Method/SOP	**Data Quality Indicators**[1]	**Performance Criteria (related to analytical method)**	**QC Sample such as Duplicate, Matrix Spike, Surrogates etc.) Used To Assess Performance Criteria**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
EPA Method 8081B	Precision – Overall	RPD $\leq$ 50 when positive results for both samples are $\geq$ 2x QL RPD $\leq$ 50 when positive result for one sample is $\geq$ 2x QL and positive result for other sample is < 2x QL No situations where one result is detected at $\geq$ 2x QL and other result is not detected.	Field Duplicates	S & A
	Accuracy/Bias	Percent recoveries 40-140	Laboratory Control Sample	A
	Accuracy/Bias – Contamination	No target compounds $\geq$ QL (except phthalates must be $\leq$ 5 x QL)	Equipment Blanks and Method Blanks	S & A
	Accuracy/Bias	Cooler temperature 4ºC $\pm$ 2ºC	Cooler Temperature Blank	S
	Data Completeness	Field 90%, Laboratory 95%	Data Completeness Check	S & A

[1]Defined as Precision; Accuracy/Bias; Sensitivity/Quantitation Limits, Representativeness; Comparability, Completeness.

Brownfields QAPP Worksheet #5d-8

Analytical Laboratory Sensitivity and Project Criteria

Matrix Groundwater
Analytical Group PCBs
Concentration Level Low

Analytical Method/SOP	**Data Quality Indicators**[1]	**Performance Criteria (related to analytical method)**	**QC Sample such as Duplicate, Matrix Spike, Surrogates etc.) Used To Assess Performance Criteria**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
EPA Method 8082A	Precision – Overall	*RPD $\leq$ 20 .	Field Duplicates	S & A
	Accuracy/Bias	Percent recoveries 40-140	Laboratory Control Sample	A
	Accuracy/Bias – Contamination	No target analytes $\geq$ ½ QL	Equipment Blanks and Method Blanks	S & A
	Accuracy/Bias	Cooler temperature 4ºC $\pm$ 2ºC	Cooler Temperature Blank	S
	Data Completeness	Field 90%, Laboratory 95%	Data Completeness Check	S & A

[1]Defined as Precision; Accuracy/Bias; Sensitivity/Quantitation Limits, Representativeness; Comparability, Completeness

Brownfields QAPP Worksheet #5d-9
Analytical Laboratory Sensitivity and Project Criteria

Matrix Groundwater
Analytical Group Metals
Concentration Level Low

Analytical Method/SOP	Data Quality Indicators[1]	Performance Criteria (related to analytical method)	QC Sample such as Duplicate, Matrix Spike, Surrogates etc.) Used To Assess Performance Criteria	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
EPA Method 6010C	Precision – Overall	RPD $\leq$ 30 when positive results for both samples are $\geq$ 5x QL Absolute difference < 2x QL when positive results for both samples are < 5x QL *RPD $\leq$ 30 when positive result for one sample is $\geq$ 5x QL and positive result for other sample is < 5x QL No situations where one result is detected at $\geq$ 5x QL and other result is not detected.	Field Duplicates	S & A
	Precision – Laboratory	RPD $\leq$ 20 if results are $\geq$ 5 x QL	Laboratory Duplicates	A
	Accuracy/Bias	Percent recoveries 80 – 120%	Laboratory Control Sample	A
	Accuracy/Bias	$\pm$ 10% of original result	Serial Dilution Analysis	A
	Accuracy/Bias	Percent recoveries 80 – 120%	Interference Check Sample	A
	Accuracy/Bias - Contamination	No target compounds $\geq$ QL	Initial Calibration Blanks, Continuing Calibration Blanks, and Preparation Blanks	A
	Accuracy/Bias	Cooler temperature 4ºC $\pm$ 2ºC	Cooler Temperature Blank	S
	Data Completeness	Field 90%, Laboratory 95%	Data Completeness Check	S & A

[1]Defined as Precision; Accuracy/Bias; Sensitivity/Quantitation Limits, Representativeness; Comparability, Completeness

Brownfields QAPP Template #5e
Secondary Data Criteria and Limitations Table

Identify all secondary data and information that will be used for the project, and their originating sources. Specify how the secondary data will be used, and the limitations on their use.

Secondary Data	Data Source (Originating Organization, Report Title, and Date)	Data Generator(s) (Originating Org., Data Types, Data Generation/ Collection Dates)	How Data Will Be Used	Limitations on Data Use
Previous Investigation Sampling Results	Site Investigation Report, prepared by EnviroSure, Inc., June 28, 2008	Soil samples were collected by EnviroSure, Inc in November 2007	The purpose of previous investigations was to evaluate the soil conditions and any impact from previous operations conducted at the site. The objective of the current study is to remediate impacted soils.	Additional sampling will be required to confirm that the remedial actions were completed and no soils remain at the site with concentrations above the applicable standards.

Brownfields QAPP Worksheet #6
Project Specific Method and Standard Operating Procedures (SOPs) Reference Table

List all field sampling SOPs, analytical method references (for preparation and analysis of the samples) and corresponding analytical laboratory SOPs that will be used for the Brownfields project. Include copies of the SOPs which can be provided on CD-ROM.

ANALYTICAL METHOD REFERENCE (*Include document title, method name/number, revision number, date)*
1a. Laboratory measurements will be performed by the selected laboratory according to the method requested, generally according to EPA Solid Waste Methods SW-846 specified container, preparation and analytical methods. Table 2 includes the analytical method references.
2a.
ANALYTICAL LABORATORY SOPs (*Include document title, date, revision number, and originator=s name)*
1b. Analytical laboratory SOP references listed in Table 2.
2b.
FIELD SAMPLING SOPs [1] (*Include document title, date, revision number, and originator=s name)*
1c. Low Flow Procedures for Collection of Groundwater Samples, July 30, 1996, revised on January 19, 2010, U.S EPA – Region 1
2c. Soil Sampling, February 18, 2000, U.S EPA Environmental Response Team
3c. Sampling Equipment Decontamination (SOP #2006), August 8, 1994, U.S EPA Environmental Response Team
4c. Sample Preservation, Storage, Handling, and Documentation, January 22, 2014, Revision 1, USAEMI
5c. Field Screening SOP, January 22, 2014, Revision 1, USAEMI
[1] Project Sampling SOPs include sample collection, sample preservation, equipment decontamination, preventive maintenance, etc.

Brownfields QAPP Worksheet #7
Field Equipment Calibration, Maintenance, Testing, and Inspection

Identify all equipment and instruments (other than analytical instrumentation) that require calibration, maintenance, testing or inspection and provide the SOP reference number for each type of equipment. In addition, document the frequency of activity, acceptance criteria and corrective action requirements on the template. Below (in italics) is an example of such information.

Field Equipment	Calibration Activity	Maintenance Activity	Testing/ Inspection Activity	Frequency	Acceptance Criteria		Corrective Action	SOP Reference
Horiba Meter or equivalent	Calibrate with standard solutions	NA	NA	Prior to day's activities; end of day's activities; anytime anomaly suspected	pH Meter	+/- 0.1 units	Clean probe, replace battery, replace membrane, replace probe	Table 2, F-2
					Dissolved Oxygen	± 3%		
					Specific Conductivity	± 1%		
					Temperature	± 0.1 °C		
					Turbidity	± 2 NTU		
PID	Calibrate with 100 ppmV isobutylene standard. Blank: zero air check	NA	NA	Daily- before use Calibration check – every 4 hours, at end of day, or if instrument gives erratic results	± 10% of true value		Recalibrate or service; rerun affected sample.	Table 2, F-1

Brownfields QAPP Worksheet #8-1
Analytical Laboratory Instrument and Equipment Maintenance, Testing, and Inspection

Identify all analytical instrumentation that requires maintenance, testing or inspection and provide the SOP reference for each. Document the frequency, acceptance criteria and corrective action requirements on the template.

Instrument/ Equipment	Maintenance Activity	Testing/Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	Analytical SOP Reference
GC/MS	VOC and SVOC Analysis (see L-1 and L-2)	Daily: Check connections, replace disposables, perform injection port maintenance, and clip column. Perform leak checks as needed	As per instrument manufacturer's recommendations	Acceptable recalibration; see analytical SOP (Appendix A)	Inspect the system, correct problem, recalibrate and/or reanalyze samples.	GC/MS Analysts: Accutest Laboratories	Table 2, L-1, L-2

Analytical Laboratory Instrument Calibration

Identify all analytical instrumentation that requires calibration and provide the SOP reference number for each. Document the frequency, acceptance criteria, and corrective action requirements on the template. **Below (in italics) is an example of such information.**

Instrument/ Equipment	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Responsible Person	Analytical SOP Reference
GC/MS	See laboratory SOPs (Appendix A; as per instrument manufacturer's recommended procedures	Initial: After instrument set up and when calibration verification fails; minimum 5 points Continuing: Daily prior to samples and every 12 hours	%RSD <30 for CCCs and minimum RF for SPCCs % D < 20 for CCCs and minimum RF for SPCCs	Perform necessary equipment maintenance and check calibration standards Perform necessary equipment maintenance and check calibration standards	GC/MS Analysts: Accutest Laboratories	Table 2, L-1, L-2

Brownfields QAPP Worksheet #8-2
Analytical Laboratory Instrument and Equipment Maintenance, Testing, and Inspection

Identify all analytical instrumentation that requires maintenance, testing or inspection and provide the SOP reference for each. Document the frequency, acceptance criteria and corrective action requirements on the template.

Instrument/ Equipment	Maintenance Activity	Testing/Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	Analytical SOP Reference
GC/ECD	Pesticide and PCB Aroclor Analysis (see L-3 and L-4)	Daily: Check connections, replace disposables, perform injection port maintenance, and clip column. Perform leak checks and clean detector as needed.	As per instrument manufacturer's recommendations	Acceptable recalibration; see analytical SOP (Appendix A)	Inspect the system, correct problem, recalibrate and/or reanalyze samples.	GC/ECD Analysts: Accutest Laboratories	Table 2, L-3, L-4

Analytical Laboratory Instrument Calibration

Identify all analytical instrumentation that requires calibration and provide the SOP reference number for each. Document the frequency, acceptance criteria, and corrective action requirements on the template.

Instrument/ Equipment	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Responsible Person	Analytical SOP Reference
GC/ECD	See laboratory SOPs (Appendix A; as per instrument manufacturer's recommended procedures	Initial: After instrument set up and when calibration verification fails; minimum 5 points or 6 points (non-linear) Continuing: Daily prior to samples and after every 10 samples or every 12 hours, whichever is more frequent	%RSD < 20 or r $\geq$ 0.995 %D $\leq$ 15;	Perform necessary equipment maintenance and check calibration standards Perform necessary equipment maintenance and check calibration standards	GC/ECD Analysts: Accutest Laboratories	Table 2, L-3, L-4

Brownfields QAPP Worksheet #8-3
Analytical Laboratory Instrument and Equipment Maintenance, Testing, and Inspection

Identify all analytical instrumentation that requires maintenance, testing or inspection and provide the SOP reference for each. Document the frequency, acceptance criteria and corrective action requirements on the template.

Instrument/ Equipment	Maintenance Activity	Testing/Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	Analytical SOP Reference
ICP-AES,	Metals Analysis (see L-5)	ICP: Check argon tank pressure, check tubing and nebulizer daily, clean plasma torch assembly as needed, clean filters as needed, check o-rings daily .	As per instrument manufacturer's recommendations	Acceptable recalibration; see analytical SOP (Appendix A)	Inspect the system, correct problem, recalibrate and/or reanalyze samples.	Metal Analysts: Accutest Laboratories	Table 2, L-5

Analytical Laboratory Instrument Calibration

Identify all analytical instrumentation that requires calibration and provide the SOP reference number for each. Document the frequency, acceptance criteria, and corrective action requirements on the template.

Instrument/ Equipment	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Responsible Person	Analytical SOP Reference
ICP-AES	See laboratory SOPs (Appendix A); as per instrument manufacturer's recommended procedures	Initial Calibration: ICP: One standard and a blank; daily prior to samples	None for ICP	Perform necessary equipment maintenance and check calibration standards	Metals Analyst: Accutest Laboratory	Table 2, L-5
		Initial Calibration Verification: Daily prior to samples	90-110% of true value	Perform necessary equipment maintenance and check calibration standards		
		Continuing Calibration Verification: Every 10 samples or 2 hours, whichever is more frequent, and at end of analytical run	90-110% of true value for ICP	Perform necessary equipment maintenance and check calibration standards		

Brownfields QAPP Worksheet #8-4
Analytical Laboratory Instrument and Equipment Maintenance, Testing, and Inspection

Identify all analytical instrumentation that requires maintenance, testing or inspection and provide the SOP reference for each. Document the frequency, acceptance criteria and corrective action requirements on the template.

Instrument/ Equipment	Maintenance Activity	Testing/Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	Analytical SOP Reference
Spectrophotometer	Hexavalent Chromium Analysis (see L-6)	Inspect outer and inner chamber for cleanliness daily, check tubing daily, check flow of reagents daily, calibrate by outside vendor annually.	As per instrument manufacturer's recommendations	Acceptable recalibration; see analytical SOP (Appendix A)	Inspect the system, correct problem, recalibrate and/or reanalyze samples.	Metal Analysts: Accutest Laboratories	Table 2, L-6

Analytical Laboratory Instrument Calibration

Identify all analytical instrumentation that requires calibration and provide the SOP reference number for each. Document the frequency, acceptance criteria, and corrective action requirements on the template.

Instrument/ Equipment	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Responsible Person	Analytical SOP Reference
Spectrophotometer	See laboratory SOPs (Appendix A); as per instrument manufacturer's recommended procedures	Initial: Prior to sample analysis	$r \geq 0.995$	Perform necessary equipment maintenance and check calibration standards	Metals Analyst: Accutest Laboratory	Table 2, L-6
		Continuing Calibration: After every 10 samples and at end of analytical run	80-120% of true value	Perform necessary equipment maintenance and check calibration standards		

Brownfields QAPP Worksheet #9a
Sample Handling System

Use this Template to identify components of the project-specific sample handling system. Record personnel and their organizational affiliations primarily responsible for ensuring proper handling, custody and storage of field samples from the time of collection, to laboratory delivery, to final sample disposal. Indicate the number of days field samples and their extracts/digestates will be archived prior to disposal.

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
Sample Collection (Personnel/Organization): Jorge Gomez/USAEMI
Sample Packaging (Personnel/Organization): Jorge Gomez/USAEMI
Coordination of Shipment (Personnel/Organization): Jorge Gomez/USAEMI
Type of Shipment/Carrier: Laboratory carrier.
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (Personnel/Organization): Matt Cordova/Accutest
Sample Custody and Storage (Personnel/Organization): Matt Cordova/Accutest
Sample Preparation (Personnel/Organization): Laboratory technicians/Accutest
Sample Determinative Analysis (Personnel/Organization): Accutest
SAMPLE ARCHIVING
Field Sample Storage (No. of days from sample collection): 60 days after delivery of data package
Sample Extract/Digestate Storage (No. of days from extraction/digestion): 60 days after delivery of data package.
SAMPLE DISPOSAL
Personnel/Organization: Laboratory technicians/Accutest
Number of Days from Analysis: 60 days after delivery of data package

Brownfields QAPP Worksheet #9b
Sample Custody Requirements

Describe the procedures that will be used to maintain sample custody and integrity for the site-specific project. Include examples of chain-of-custody forms, traffic reports, sample identification, custody seals, laboratory sample receipt forms, and laboratory sample transfer forms. Attach these items, or reference the applicable SOPs where these items can be found.

Sample Identification Procedures: All samples will be identified using a unique sample identification scheme suitable to the project and the sampling protocol. The numbering scheme to be used is presented in Worksheet #5a

Field Sample Custody/Tracking Procedures (sample collection, packaging, shipment, and delivery to laboratory): Refer to Worksheet #9a.

Laboratory Sample Custody/Tracking Procedures (receipt of samples, archiving, and disposal): Refer to Worksheet #9a.

Chain-of-Custody Procedures: The chain-of-custody procedures are initiated in the field immediately following sample collection. The procedures consist of: (1) preparing and attaching a unique sample label to each sample collected; (2) completing the chain-of-custody form; and (3) preparing and packing the samples for shipment.

Brownfields QAPP Worksheet #10-1
Field and Analytical Laboratory Quality Control Summary

Matrix	Soils					
Analytical Group	Semi-VOCs					
Concentration Level	Low					
Analytical Method/ SOP Reference	L-2					
Sampler's Name	TBD					
Field Sampling Organization	USAEMI					
Laboratory Name	Accutest Laboratories					
No. of Sample Locations	6					
Laboratory QC:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action (CA)**	**Person(s) Responsible for CA**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Method Blank	Each batch not to exceed 20 samples	Less than MDL	Reextract and reanalyze entire batch	Lab Analyst	Contamination	Less than MDL
Equipment Blank	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Storage Blank	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Instrument Blank	Daily	Less than MDL	Rerun	Lab Analyst	Contamination	Less than MDL
Laboratory Duplicate	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Matrix Spike	1 per 20 samples	See Compound List Report (SOP)	Investigate possible matrix effect. Record in case narrative.	Lab Analyst	Accuracy/Bias	See Compound List Report (SOP)
Matrix Spike Duplicates	1 per 20 samples	See Compound List Report (SOP)	Investigate possible matrix effect. Record in case narrative	Lab Analyst	Precision	See Compound List Report (SOP)
Surrogates	Every sample and QC	See Compound List Report (SOP)	Reextract and reanalyze sample	Lab Analyst	Accuracy/Bias	See Compound List Report (SOP)
LCS	Each batch not to exceed 20 samples	See Compound List Report (SOP)	Reextract and reanalyze entire batch	Lab Analyst	Accuracy/Bias	See Compound List Report (SOP)
Internal Standards (ISs)	Every sample and QC	50 - 200%	Reanalyze sample	Lab Analyst	Accuracy/Bias	50 - 200%
Cooler Temperature Blank	1 per cooler	< 6C	Inform client	Sample receiving	Preservation	< 6C

TBD = To Be Determined

Brownfields QAPP Worksheet #10-2
Field and Analytical Laboratory Quality Control Summary

Matrix	Soils					
Analytical Group	PCB Aroclors					
Concentration Level	Low					
Analytical Method/ SOP Reference	L-4					
Sampler's Name	TBD					
Field Sampling Organization	USAEMI					
Laboratory Name	Accutest Laboratories					
No. of Sample Locations	11 soil samples					
Laboratory QC:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action (CA)**	**Person(s) Responsible for CA**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Method Blank	1 per extraction batch	< MDL	Reanalyze/Reextract Batch	Laboratory Analyst	Contamination Bias	< MDL
Equipment Blank	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable
Storage Blank	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable
Instrument Blank	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable
Laboratory Duplicate	Not used, See MSD	Not used, See MSD	Not used, See MSD	Not used, See MSD	Not used, See MSD	Not used, See MSD
Matrix Spike	1 per 20 samples	See Compound List Report (SOP)	None if BS passed	Laboratory Analyst	Accuracy	See Compound List Report (SOP)
Matrix Spike Duplicates	1 per 20 samples	See Compound List Report (SOP)	None if BS Passed	Laboratory Analyst	Precision	See Compound List Report (SOP)
LCS	1 per extraction batch	See Compound List Report (SOP)	Reanalyze/ Reextract Batch	Laboratory Analyst	Accuracy	See Compound List Report (SOP)
Surrogates	1 per sample	See Compound List Report (SOP)	Reanalyze/Reextract Sample	Laboratory Analyst	Accuracy	See Compound List Report (SOP)
Internal Standards (ISs)	Every sample and QC	50 - 200%	Reanalyze sample	Lab Analyst	Accuracy/Bias	50 - 200%
Cooler Temperature Blank	1 per cooler	< 6C	Inform client	Sample receiving	Preservation	< 6C

TBD = To Be Determined

Brownfields QAPP Worksheet #10-3
Field and Analytical Laboratory Quality Control Summary

Matrix	Soil					
Analytical Group	Metals					
Concentration Level	Low					
Analytical Method/ SOP Reference	L-5					
Sampler's Name	TBD					
Field Sampling Organization	USAEMI					
Laboratory Name	Accutest Laboratories					
No. of Sample Locations	21					
Laboratory QC:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action (CA)**	**Person(s) Responsible for CA**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Method Blank	Each batch not to exceed 20 samples	< ½ RL	Re-digest and reanalyze entire batch	Lab Analyst	Contamination	< ½ RL
Reagent Blank**	Daily	< RL	Rerun	Lab Analyst	Contamination	<RL
Laboratory Duplicate	Not normally used, See MSD	RPD < 20% for duplicate values greater than or equal to 5 times the RL	Investigate possible matrix effect. Record in case narrative	Lab Analyst	Precision	RPD < 20% for duplicate values greater than or equal to 5 times the RL
Matrix Spike	Each batch not to exceed 20 samples	Recovery of 75-125%	Redigest and reanalyze entire batch	Lab Analyst	Accuracy/Bias	Recovery of 75-125%
Matrix Spike Duplicates	1 per 20 samples	RPD < 20% for duplicate values greater than or equal to 5 times the RL	Investigate possible matrix effect. Record in case narrative	Lab Analyst	Precision	RPD < 20% for duplicate values greater than or equal to 5 times the RL
LCS	Each batch not to exceed 20 samples	Recovery of 80-120%	Redigest and reanalyze entire batch	Lab Analyst	Accuracy/Bias	Recovery of 80-120%
Surrogates	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Other: Interference Check Sample	Beginning of run	80 – 120%	Regenerate interfering element correction factors, Reanalyze	Lab Analyst	Interference	80 – 120%
Other: Serial Dilution	1 per 20 samples	Within 10%	Record in case narrative	Lab Analyst	Accuracy/Bias	Within 10%
Other: QL Check Standard	Beginning and end of each run	Recovery of 70-130%	Reanalyze samples	Lab Analyst	Accuracy/Bias	Recovery of 70-130%
Internal Standards (ISs) (ICP/MS only)	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Cooler Temperature Blank	1 per cooler	< 6C	Inform client	Sample receiving	Preservation	< 6C

** Also referred to as initial and continuing calibration blanks.
TBD = To Be Determined

Brownfields QAPP Worksheet #10-4
Field and Analytical Laboratory Quality Control Summary

Matrix	Soil					
Analytical Group	Hexavalent Chromium					
Concentration Level	Low					
Analytical Method/ SOP Reference	L-6					
Sampler's Name	TBD					
Field Sampling Organization	USAEMI					
Laboratory Name	Accutest Laboratories					
No. of Sample Locations	21					
Laboratory QC:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action (CA)**	**Person(s) Responsible for CA**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Method Blank	1 per 20 samples	< QL	Rerun Batch	Laboratory Analyst	Contamination Bias	< QL
Equipment Blank	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable
Instrument Blank	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Laboratory Duplicate	1 per 20 samples	20% RSD	None	Laboratory Analyst	Accuracy	20% RSD
Matrix Spike	1 per 20 samples	85 – 115 % Rec	Dilute sample 1:5 and reanalyze	Laboratory Analyst	Accuracy	85 – 115 % Rec
Matrix Spike Duplicates	1 per 20 samples	20% RSD	None	Laboratory Analyst	Precision	20% RSD
LCS	1 per 20 samples	90– 110% Rec	Rerun batch	Laboratory Analyst	Accuracy	90– 110% Rec
Surrogates	Not Applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Cooler Temperature Blank	1 per cooler	< 6C	Inform client	Sample receiving	Preservation	< 6C

TBD = To Be Determined

Brownfields QAPP Worksheet #10-5
Field and Analytical Laboratory Quality Control Summary

Matrix	Groundwater					
Analytical Group	VOCs					
Concentration Level	Low					
Analytical Method/ SOP Reference	L-1					
Sampler's Name	TBD					
Field Sampling Organization	USAEMI					
Laboratory Name	Accutest Laboratories					
No. of Sample Locations	5					
Laboratory QC:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action (CA)**	**Person(s) Responsible for CA**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Method Blank	1 per 12 hours	< MDL	Reanalyze Batch	Laboratory Analyst	Contamination Bias	< MDL
Trip Blank	1 per sample batch	< MDL	Narrate in case narrative	Laboratory Analyst	Contamination Bias	< MDL
Storage Blank	Weekly	< MDL	Investigate cause of contamination	Organics Staff	Contamination/Bias	< MDL
Instrument Blank	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Laboratory Duplicate	Not used. See MSD	Not used. See MSD	Not used. See MSD	Not used. See MSD	Not used. See MSD	Not used. See MSD
Matrix Spike	1 per 20 samples	See Compound List Report (SOP)	Narrate in case narrative	Laboratory Analyst	Accuracy	See Compound List Report (SOP)
Matrix Spike Duplicates	1 per 20 samples	See Compound List Report (SOP)	Narrate in case narrative	Laboratory Analyst	Precision	See Compound List Report (SOP)
Surrogates	Every sample and QC	See Compound List Report (SOP)	Reanalyze Sample	Laboratory Analyst	Accuracy	See Compound List Report (SOP)
Internal Standards (ISs)	Every sample and QC	50 – 200%	Reanalyze Sample	Laboratory Analyst	Instrument Performance	50 – 200%
Laboratory Control Samples	1 per 12 hours	See Compound List Report (SOP)	Reanalyze Batch	Laboratory Analyst	Accuracy	See Compound List Report (SOP)
Cooler Temperature Blank	1 per cooler	< 6C	Inform client	Sample receiving	Preservation	< 6C

TBD = To Be Determined

Brownfields QAPP Worksheet #10-6
Field and Analytical Laboratory Quality Control Summary

Matrix	Groundwater					
Analytical Group	Semi-VOCs					
Concentration Level	Low					
Analytical Method/ SOP Reference	L-2					
Sampler's Name	TBD					
Field Sampling Organization	USAEMI					
Laboratory Name	Accutest Laboratories					
No. of Sample Locations	5					
Laboratory QC:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action (CA)**	**Person(s) Responsible for CA**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Method Blank	Each batch not to exceed 20 samples	Less than MDL	Reextract and reanalyze entire batch	Lab Analyst	Contamination	Less than MDL
Storage Blank	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Laboratory Duplicate	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Matrix Spike	1 per 20 samples	See Compound List Report (SOP)	Investigate possible matrix effect. Record in case narrative.	Lab Analyst	Accuracy/Bias	See Compound List Report (SOP)
Matrix Spike Duplicates	1 per 20 samples	See Compound List Report (SOP)	Investigate possible matrix effect. Record in case narrative	Lab Analyst	Precision	See Compound List Report (SOP)
Surrogates	Every sample and QC	See Compound List Report (SOP)	Reextract and reanalyze sample	Lab Analyst	Accuracy/Bias	See Compound List Report (SOP)
Internal Standards (ISs)	Each batch not to exceed 20 samples	See Compound List Report (SOP)	Reextract and reanalyze entire batch	Lab Analyst	Accuracy/Bias	See Compound List Report (SOP)
Laboratory Control Samples	Every sample and QC	50 - 200%	Reanalyze sample	Lab Analyst	Accuracy/Bias	50 - +200%
Cooler Temperature Blank	1 per cooler	< 6C	Inform client	Sample receiving	Preservation	< 6C

TBD = To Be Determined

Brownfields QAPP Worksheet #10-7
Field and Analytical Laboratory Quality Control Summary

Matrix	Groundwater					
Analytical Group	Pesticides					
Concentration Level	Low					
Analytical Method/ SOP Reference	L-3					
Sampler's Name	TBD					
Field Sampling Organization	USAEMI					
Laboratory Name	Accutest Laboratories					
No. of Sample Locations	5					
Laboratory QC:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action (CA)**	**Person(s) Responsible for CA**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Method Blank	1 per extraction batch	< MDL	Reanalyze/Reextract Batch	Laboratory Analyst	Contamination Bias	< MDL
Storage Blank	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable
Laboratory Duplicate	Not used, See MSD	Not used, See MSD	Not used, See MSD	Not used, See MSD	Not used, See MSD	Not used, See MSD
Matrix Spike	1 per 20 samples	See Compound List Report (SOP)	None if BS passed	Laboratory Analyst	Accuracy	See Compound List Report (SOP)
Matrix Spike Duplicates	1 per 20 samples	See Compound List Report (SOP)	None if BS Passed	Laboratory Analyst	Precision	See Compound List Report (SOP)
Surrogates	1 per extraction batch	See Compound List Report (SOP)	Reanalyze/ Reextract Batch	Laboratory Analyst	Accuracy	See Compound List Report (SOP)
Laboratory Control Samples	1 per sample	See Compound List Report (SOP)	Reanalyze/Reextract Sample	Laboratory Analyst	Accuracy	See Compound List Report (SOP)
Internal Standards (ISs)	Every sample and QC	50 - 200%	Reanalyze sample	Lab Analyst	Accuracy/Bias	50 - 200%
Cooler Temperature Blank	1 per cooler	< 6C	Inform client	Sample receiving	Preservation	< 6C

TBD = To Be Determined

Brownfields QAPP Worksheet #10-8
Field and Analytical Laboratory Quality Control Summary

Matrix	Groundwater					
Analytical Group	PCBs					
Concentration Level	Low					
Analytical Method/ SOP Reference	L-4					
Sampler's Name	TBD					
Field Sampling Organization	USAEMI					
Laboratory Name	Accutest Laboratories					
No. of Sample Locations	5					
Laboratory QC:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action (CA)**	**Person(s) Responsible for CA**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Method Blank	1 per extraction batch	< MDL	Reanalyze/Reextract Batch	Laboratory Analyst	Contamination Bias	< MDL
Storage Blank	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable
Laboratory Duplicate	Not used, See MSD	Not used, See MSD	Not used, See MSD	Not used, See MSD	Not used, See MSD	Not used, See MSD
Matrix Spike	1 per 20 samples	See Compound List Report (SOP)	None if BS passed	Laboratory Analyst	Accuracy	See Compound List Report (SOP)
Matrix Spike Duplicates	1 per 20 samples	See Compound List Report (SOP)	None if BS Passed	Laboratory Analyst	Precision	See Compound List Report (SOP)
Surrogates	1 per extraction batch	See Compound List Report (SOP)	Reanalyze/ Reextract Batch	Laboratory Analyst	Accuracy	See Compound List Report (SOP)
Laboratory Control Samples	1 per sample	See Compound List Report (SOP)	Reanalyze/Reextract Sample	Laboratory Analyst	Accuracy	See Compound List Report (SOP)
Internal Standards (ISs)	Every sample and QC	50 - 200%	Reanalyze sample	Lab Analyst	Accuracy/Bias	50 - 200%
Cooler Temperature Blank	1 per cooler	< 6C	Inform client	Sample receiving	Preservation	< 6C

TBD = To Be Determined

Brownfields QAPP Worksheet #10-9
Field and Analytical Laboratory Quality Control Summary

Matrix	Groundwater					
Analytical Group	Metals					
Concentration Level	Low					
Analytical Method/ SOP Reference	L-5					
Sampler's Name	TBD					
Field Sampling Organization	USAEMI					
Laboratory Name	Accutest Laboratories					
No. of Sample Locations	5					
Laboratory QC:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action (CA)**	**Person(s) Responsible for CA**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Method Blank	Each batch not to exceed 20 samples	< ½ RL	Re-digest and reanalyze entire batch	Lab Analyst	Contamination	< ½ RL
Reagent Blank**	Daily	< RL	Rerun	Lab Analyst	Contamination	<RL
Laboratory Duplicate	Not normally used, See MSD	RPD < 20% for duplicate values greater than or equal to 5 times the RL	Investigate possible matrix effect. Record in case narrative	Lab Analyst	Precision	RPD < 20% for duplicate values greater than or equal to 5 times the RL
Matrix Spike	Each batch not to exceed 20 samples	Recovery of 75-125%	Redigest and reanalyze entire batch	Lab Analyst	Accuracy/Bias	Recovery of 75-125%
Matrix Spike Duplicates	1 per 20 samples	RPD < 20% for duplicate values greater than or equal to 5 times the RL	Investigate possible matrix effect. Record in case narrative	Lab Analyst	Precision	RPD < 20% for duplicate values greater than or equal to 5 times the RL
LCS	Each batch not to exceed 20 samples	Recovery of 80-120%	Redigest and reanalyze entire batch	Lab Analyst	Accuracy/Bias	Recovery of 80-120%
Surrogates	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Other: Serial Dilution	Beginning of run	80 – 120%	Reanalyze check sample	Lab Analyst	Interference	80 – 120%
Other: QL Check Standard	1 per 20 samples	Within 10%	Record in case narrative	Lab Analyst	Accuracy/Bias	Within 10%
Other: Interference Check Sample	Beginning and end of each run	Recovery of 70-130%	Regenerate interfering element correction factors, Reanalyze	Lab Analyst	Accuracy/Bias	Recovery of 70-130%
Internal Standards (ISs) (ICP/MS only)	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Cooler Temperature Blank	1 per cooler	< 6C	Inform client	Sample receiving	Preservation	< 6C

** Also referred to as initial and continuing calibration blanks.
TBD = To Be Determined

Brownfields QAPP Worksheet #10-10
Field and Analytical Laboratory Quality Control Summary

Matrix	Groundwater					
Analytical Group	Hexavalent Chromium					
Concentration Level	Low					
Analytical Method/ SOP Reference	L-6					
Sampler's Name	TBD					
Field Sampling Organization	USAEMI					
Laboratory Name	Accutest Laboratories					
No. of Sample Locations	5					
Laboratory QC:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action (CA)**	**Person(s) Responsible for CA**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Method Blank	1 per 20 samples	< QL	Rerun Batch	Laboratory Analyst	Contamination Bias	< QL
Storage Blank	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable
Instrument Blank	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Laboratory Duplicate	1 per 20 samples	20% RSD	None	Laboratory Analyst	Accuracy	20% RSD
Matrix Spike	1 per 20 samples	85 – 115 % Rec	Dilute sample 1:5 and reanalyze	Laboratory Analyst	Accuracy	85 – 115 % Rec
Matrix Spike Duplicates	1 per 20 samples	20% RSD	None	Laboratory Analyst	Precision	20% RSD
LCS	1 per 20 samples	90– 110% Rec	Rerun batch	Laboratory Analyst	Accuracy	90– 110% Rec
Surrogates	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable
Cooler Temperature Blank	1 per cooler	< 6C	Inform client	Sample receiving	Preservation	< 6C

TBD = To Be Determined

Brownfields QAPP Worksheet #11a
Data Management and Documentation

Describe the documentation that will be generated for the project, and the data management procedures that will be used in handling that information. The three basic areas to cover are field data, laboratory data and data assessment (verification and validation of data) presented in the final report. Clearly specify what documentation will be provided in the final report and what documentation goes into the project files. Below is a list that includes but not limited to the types of documentation that may be routinely generated, collected and managed in a Brownfields project.

Field Sample Collection Documents and Records	Analytical Laboratory Documents and Records	Data Assessment Documents and Records	Project File
• Site and field logbooks • Boring logs • Well construction diagrams • Chain-of-Custody (COC) forms • Well Data Sheets • Field Data Sheets • Photographs	• Sample receipt logs • Internal and external COC forms • Equipment calibration logs • Sample preparation worksheets/logs • Sample analysis worksheets/run logs • Telephone/email logs • Corrective action documentation	• Data validation reports • Field inspection checklist(s) • Laboratory Audit checklist (if performed) • Review forms for electronic entry of data into database • Corrective action documentation	• The project file will be maintained and store for at least 10 years.

Brownfields QAPP Worksheet #11b
Project Reports

Identify the types of reports that will be routinely provided during the Brownfields project (e.g., status reports, final reports, etc.). Include the type of report, frequency of reporting, the project delivery dates, the personnel responsible for report preparation, and the report recipients.

Type of Report	**Frequency (Daily, weekly, monthly, quarterly, annually, etc.)**	**Projected Delivery Date(s)**	**Person(s) Responsible for Report Preparation (Title and Organizational Affiliation)**	**Report Recipient(s) (Title and Organizational Affiliation)**
Verbal or Written Status Report	As necessary	As necessary	Jorge Gomez, Project Manager, USAEMI	John Duggan, Project, Coordinator, USAEMI; Matthew Brener/JR Capasso, City of Trenton
Data Usability Assessment Report	One/ after data generated and validated	TBD	Jorge Gomez, Project Manager, USAEMI	John Duggan, Project, Coordinator, USAEMI; Matthew Brener/JR Capasso, City of Trenton
Final Project Report	One/ after sampling and risk assessment completed	TBD	Jorge Gomez, Project Manager and John Duggan, Project Coordinator, USAEMI	Matthew Brener/JR Capasso, City of Trenton & Remedial Project Manager, EPA

Brownfields QAPP Worksheet #12a
Planned Project Assessments Table

Identify the type, frequency, and responsible parties of planned assessment activities that will be performed for the project, if applicable. **This may be an optional activity for the project. If not applicable to the project, state as such in the QAPP. Do not complete the Template.**

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person(s) Responsible for Performing Assessment (Title and Organizational Affiliation)	Person(s) Responsible for Responding to Assessment Findings (Title and Organizational Affiliation)	Person(s) Responsible for Identifying and Implementing Corrective Actions (Title and Organizational Affiliation)	Person(s) Responsible for Monitoring Effectiveness of Corrective Actions (Title and Organizational Affiliation)
Laboratory Technical Systems/ Performance Audits	NA	NA	NA	NA	NA	NA	NA
Performance Evaluation Samples	NA	NA	NA	NA	NA	NA	NA
On-Site Field Inspection	NA	NA	NA	NA	NA	NA	NA

Brownfields QAPP Worksheet #12b
Assessment Findings and Corrective Action Responses

For each type of assessment, describe procedures for handling QAPP and project deviations encountered during the planned project assessments. **This may be an optional activity for the project. If not applicable to the project, state as such in the QAPP. Do not complete the Template.**

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings (Name, Title, Organization)	Timeframe of Notification	Nature of Corrective Action Response Documentation	Individual(s) Receiving Corrective Action Response (Name, Title, Org.)	Timeframe for Response
Project Readiness Review	NA	NA	NA	NA	NA	NA
Field Observations/ Deviations from Work Plan	NA	NA	NA	NA	NA	NA
Laboratory Technical Systems/ Performance Audits	NA	NA	NA	NA	NA	NA
On-Site Field Inspection	NA	NA	NA	NA	NA	NA
Performance Evaluation Samples	NA	NA	NA	NA	NA	NA

Brownfields QAPP Worksheet #13a
Project Data Verification Process (Step I) [1]

Describe the processes that will be followed to verify project data. Describe how each item will be verified, when the activity will occur, and what documentation is necessary, and identify the person responsible for verification.

Verification Input	Description	Internal/ External[2]	Responsible for Verification (Name, Organization)
Site/Field Logbooks	Field notes will be prepared daily by the Environmental Consultant Project Manager and will be complete, appropriate, legible and pertinent. Upon completion of field work, logbooks will be placed in the project files.	Internal	Jorge Gomez, USAEMI
Chains of custody	COC forms will be reviewed against the samples packed in the specific cooler prior to shipment. The reviewer will initial the form. An original COC will be sent with the samples to the laboratory, while copies are retained for (1) the Sampling Trip Report and (2) the project files.	Internal	Jorge Gomez, USAEMI
Laboratory analytical data package	Data packages will be reviewed/verified internally by the laboratory performing the work for completeness and technical accuracy prior to submittal.	Internal	Accutest
Laboratory analytical data package	Data packages will be reviewed as to content and sample information upon receipt by the Environmental Consultant Project Manager and the Third Party Data Validation Personnel.	Internal/External	Jorge Gomez, USAEMI; Julian Heal, Luzon, Inc.
Electronic Data Deliverables	EDDs will be used to import data into USAEMI's database. The imported data will be verified with the validated data for accuracy.	Internal	Jorge Gomez, USAEMI
Final Sample Report	The project data results will be compiled in a sample report for the project. Entries will be reviewed/verified against hardcopy information.	Internal	Jorge Gomez, USAEMI

[1]Step I – Completeness Check

[2]Internal or External is in relation to the data generator.

Brownfields QAPP Worksheet #13b
Project Data Validation Process (Steps IIa and IIb) [1]

Describe the processes that will be followed to validate project data. Describe how each item will be verified, when the activity will occur, and what documentation is necessary, and identify the person responsible. **Below (in italics) is an example of such information. See Table 1 for additional examples of data elements.**

Step IIa/IIb[1]	Validation Input	Description	Responsible for Validation (Name, Organization)
IIa	SOPs	Ensure that the sampling methods/procedures outlined in QAPP were followed, and that any deviations were noted/approved.	Jorge Gomez, USAEMI
IIb	SOPs	Determine potential impacts from noted/approved deviations, in regard to PQOs.	Jorge Gomez, USAEMI
IIa	Chains of custody	Examine COC forms against QAPP and laboratory contract requirements (e.g., analytical methods, sample identification, etc.).	Julian Heal, Luzon, Inc.
IIa	Laboratory data package	Examine packages against QAPP and laboratory contract requirements, and against COC forms (e.g., holding times, sample handling, analytical methods, sample identification, data qualifiers, QC samples, etc.).	Julian Heal, Luzon, Inc.
IIb	Laboratory data package	Determine potential impacts from noted/approved deviations, in regard to PQOs. Examples include PQLs and QC sample limits (precision/accuracy).	Jorge Gomez, USAEMI; Julian Heal, Luzon, Inc
IIb	Field duplicates	Compare results of field duplicate (or replicate) analyses with RPD criteria	Jorge Gomez, USAEMI: Julian Heal, Luzon, Inc.

[1]Step IIa – Compliance with Methods, Procedures, and Contracts

[1]Step IIb – Comparison with Performance Criteria in QAPP

Brownfields QAPP Worksheet #13c
Project Matrix and Analytical Validation (Steps IIa and IIb)[1] Summary

Identify the matrices, analytical groups, and concentration levels that each entity performing validation will be responsible for, as well as criteria that will be used to validate those data. **Below (in italics) is an example of such information. See Table 1 for additional examples of data elements.**

Step IIa/IIb[1]	Matrix	Analytical Group	Concentration Level	Validation Criteria	Data Validator (title and organizational affiliation)
IIa/IIb	Soil	Semi-VOCs	Low	(2), Worksheet #5d-1, 8-1, 10-1	Julian Heal, Luzon, Inc.
IIa/IIb	Soil	PCBs	Low	(4), Worksheet #5d-2, 8-2, 10-2	Julian Heal, Luzon, Inc.
IIa/IIb	Soil	Metals	Low	(5), Worksheet #5d-3, 8-3, 10-3	Julian Heal, Luzon, Inc.
IIa/IIb	Soil	Hexavalent Chromium	Low	(6), Worksheet #5d-4, 8-4, 10-4	Julian Heal, Luzon, Inc.
IIa/IIb	Aqueous	VOCs	Low	(1), Worksheet #5d-5, 8-1, 10-5	Julian Heal, Luzon, Inc.
IIa/IIb	Aqueous	Semi-VOCs	Low	(2), Worksheet #5d-6, 8-1, 10-6	Julian Heal, Luzon, Inc.
IIa/IIb	Aqueous	Pesticides	Low	(3), Worksheet #5d-7, 8-2, 10-7	Julian Heal, Luzon, Inc.
IIa/IIb	Aqueous	PCBs	Low	(4), Worksheet #5d-7, 8-2, 10-8	Julian Heal, Luzon, Inc.
IIa/IIb	Aqueous	Metals	Low	(5), Worksheet #5d-9, 8-3, 10-9	Julian Heal, Luzon, Inc.

[1]Step IIa – Compliance with Methods, Procedures, and Contracts
[1]Step IIb – Comparison with Performance Criteria in QAPP
NA - Not applicable
(1) - Validating Volatile Organic Compounds by SW-846 Method 8260B, HW-24, Revision 2, August 2008, Region 2.
(2) - Validating Semi-volatile Organic Compounds by SW-846 Method 8270, HW-22, Revision 4, August 2008, Region 2.
(3) - Data Validation SOP of Organochlorine Pesticides by Gas Chromatography SW-846 Method 8081B, HW-44, Revision 1, Oct 2006, Region 2.
(4) - Data Validation SOP of Organic Analysis of PCBs by Gas Chromatography SW-846 Method 8082A, HW-45, Rev. 1, Oct. 2006, Region 2.
(5) - Evaluation of Metals Data for the CLP Program, HW-2, Revision 13, September 2006, Region 2.
(6) - USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, EPA 540-R-04-004, October 2004.
* - Up to 25% of the soil, sediment, surface water, and/or tissue data will be subjected to validation.

Brownfields QAPP Worksheet #13d
Usability Assessment (Step III) [1]

Data Usability

The purpose of this section is to indicate the methods by which it will be ensured that the validated laboratory data collected for this investigation are consistent with the project quality objectives established for the investigation, to ensure the quality of data was sufficient for its intended use, and to identify trends, relationships, and anomalies in the data. Conclusions based on the data, limitations on the use of the data, and the determination if data gaps exist will be included in the data usability assessment. The data usability assessment will be performed by the USAEMI Project Manager, in conjunction with the USAEMI Project QA Manager and will be performed after the data validation has been completed.

Precision

The RPD between the matrix spike and matrix spike duplicate in the case of organic parameters, or sample and sample duplicate in the case of all parameters, is calculated to compare to precision objectives. MS/MSDs and laboratory duplicates will be used to assess analytical precision and the field duplicates will be used to assess project precision. The RPD will be calculated according to the following formula:

$$RPD = \frac{(Amount\ in\ Sample\ 1 - Amount\ in\ Sample\ 2)}{0.5\,(Amount\ in\ Sample\ 1 + Amount\ in\ Sample\ 2)}\ x\ 100$$

The impact of analytical imprecision, project imprecision, and overall imprecision (when both analytical and project precision tests show problems) on data usability will be assessed. If the precision results yield data which are not usable, the data usability assessment will identify how this problem will be resolved and the potential need for resampling will be discussed in the final project report.

Accuracy

If field or laboratory contamination exists, the impact on the data will be evaluated during the data usability assessment. The direction of bias for contamination will be identified.

In order to assure the accuracy of the analytical procedures, matrix spike samples will be utilized. The increase in concentration of the analyte observed in the spiked sample, due to the addition of a known quantity of the analyte, compared to the reported value of the same analyte in the unspiked sample, determines percent recovery (%R).

Accuracy is similarly assessed by determining %Rs for surrogate compounds added to each field and QC sample to be analyzed for organic parameters. Accuracy for all analyses will be further assessed through determination of %Rs for LCSs and calibration results, etc. If the Data Validation Reports indicate contamination and/or analytical biases, the impact on the data will be assessed.

%R for MS/MSD results will be determined according to the following equation:

$$\%R = \frac{(Amount\ in\ Spiked\ Sample - Amount\ in\ Sample)}{Known\ Amount\ Added} x\,100$$

%R for LCSs and surrogate compound results will be determined according to the following equation:

$$\%R = \frac{Experimental\ Concentration}{Known\ Amount\ Added} x\,100$$

Overall contamination and accuracy/bias will be reviewed for each matrix and analytical parameter. The data usability assessment will include any limitations on the use of the data, if it is limited to a particular matrix, data package, parameter, or laboratory. If the accuracy results yield data which are not usable, the data usability assessment will identify how this problem will be resolved and the potential need for resampling will be discussed in the final project report.

Representativeness

If field duplicates indicate spatial variability, the data usability assessment will evaluate the impact on the data. Overall sample representativeness will be evaluated for each matrix and analytical parameter by reviewing adherence to sampling procedures, QAPP requirements and audits, if performed. The data usability assessment will include any limitations on the use of the data, if limited to a particular matrix, data package, parameter, or laboratory. If the results of the evaluation of representativeness yield data which are not usable, the data usability assessment will identify how this problem will be resolved and the potential need for resampling will be discussed in the final project report.

Sensitivity and Quantitation Limits

Overall sensitivity will be reviewed for each matrix and analytical parameter. The impact on the lack of sensitivity or the reporting of higher quantitation limits by the laboratory will be assessed. The data usability assessment will include any limitations on the use of the data, if limited to a particular matrix, data package, parameter, or laboratory. If the results of the evaluation of sensitivity yield data which are not usable, the data usability assessment will identify how this problem will be resolved and the potential need for resampling will be discussed in the final project report.

Completeness

Completeness is the ratio of the number of valid sample results to the total number of samples analyzed or processed. Following completion of the testing, the percent completeness will be calculated by the following equation:

$$Completeness = \frac{(number\ of\ valid\ measurements)}{(number\ of\ measurements\ planned)} x 100$$

Overall completeness will be reviewed for each matrix and analytical parameter. The goals for field and laboratory completeness are 90% and 95%, respectively. The data usability assessment will include any limitations on the use of the data, if limited to a particular matrix, data package, parameter, or laboratory. If the results of the evaluation of completeness yield data which are not usable, the data usability assessment will identify how this problem will be resolved and the potential need for resampling will be discussed in the final project report.

Data Limitations and Actions

The field and laboratory data collected during this investigation will be used to achieve the objectives identified in Sections 6.0 and 8.0 of this QAPP. The QC results associated with each analytical parameter for each matrix will be compared to the objectives presented in this QAPP. 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. Limitations on the use of the data will be stated and explained, if necessary.

In addition, the data obtained will be both qualitatively and quantitatively assessed on a project-wide, matrix-specific, and parameter-specific basis. Results of the measurement error assessments will be applied against the site as a whole; any conclusions will be documented in the final report. Data generated in association with QC results not meeting the stated acceptance criteria may still be considered usable for decision-making purposes, depending on certain factors. This assessment will be performed by the TRC Project Manager, in conjunction with the TRC Project QA Manager, and the results presented and discussed in detail in the final report. 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 procedures proposed in the QAPP,
- Conformance to the EPA methods and laboratory SOPs cited in the QAPP,
- Adherence to proposed sampling strategy,
- Presence of elevated detection limits due to matrix interferences or contaminants present at high concentrations,
- Presence of analytes not expected to be present,
- Conformance to validation protocols included in the QAPP for both field and laboratory data,
- Unusable data sets (qualified as “R”) based on the data validation results,

- Data sets identified as usable for limited purposes (qualified as "J") based on the data validation results,
- Effect of qualifiers applied as a result of data validation on the ability to achieve the project objectives,
- Status of all issues requiring corrective action, as presented in the QA reports to management,
- Effect of nonconformance (procedures or requirements) on project objectives,
- Adequacy of the data as a whole in meeting the project objectives, and
- Identification of any remaining data gaps and need to reevaluate data needs.

Every reasonable attempt will be made to eliminate any sources of sampling and analytical error as early as possible in the program. An ongoing data assessment program throughout the program will also assist in the early detection and correction of problems, thereby ensuring that project objectives are met.

Reconciliation with the project objectives will have been considered to have been met if the measurement performance criteria from Section 6.0 are met. If the data usability indicates that the project quality objectives in Section 8.0 have not been met, then the project management team will meet to determine if additional work needs to be performed.

Table 1

Data Elements for Data Review Process				
Item	Step I - Data Verification	Step IIa - Data Validation Compliance	Step IIb - Data Validation Comparison	Step III - Data Usability
Planning Documents				
Evidence of approval of QAPP	X			Use outputs from previous steps
Identification of personnel	X			
Laboratory name	X			
Methods (sampling & analytical)	X	X	X	
Performance requirements (including QC criteria)	X	X		
Project quality objectives	X		X	
Reporting forms	X	X		
Sampling plans – locations, maps grids, sample ID numbers	X	X		
Site identification	X			
SOPs (sampling & analytical)	X	X		
Staff training & certification	X			
List of project-specific analytes	X	X		
Analytical Data Package				
Case narrative	X	X	X	Use outputs from previous steps
Internal lab chain of custody	X	X		
Sample condition upon receipt, & storage records	X	X		
Sample chronology (time of receipt, extraction/digestion, analysis)	X	X		
Identification of QC samples (sampling /lab)	X	X		
Associated PE sample results	X	X	X	
Communication Logs	X	X		
Copies of lab notebook, records, prep sheets	X	X		
Corrective action reports	X	X		
Definition of laboratory qualifiers	X	X	X	
Documentation of corrective action results	X	X	X	
Documentation of individual QC results (e.g., spike, duplicate, LCS)	X	X	X	
Documentation of laboratory method deviations	X	X	X	
Electronic data deliverables	X	X		
Instrument calibration reports	X	X	X	
Laboratory name	X	X		
Laboratory sample identification no.	X	X		
QC sample raw data	X	X	X	
QC summary report	X	X	X	

Data Elements for Data Review Process				
Raw data	X	X	X	Use outputs from previous steps
Reporting forms, completed with actual results	X	X	X	
Signatures for laboratory sign-off (e.g., laboratory QA manager)	X	X		
Standards traceability records (to trace standard source form NIST, for example)	X	X	X	
Sampling Documents				
Chain of custody	X	X		Use outputs from previous steps
Communication logs	X	X		
Corrective action reports	X	X	X	
Documentation of corrective action results	X	X	X	
Documentation of deviation from methods	X	X	X	
Documentation of internal QA review	X	X	X	
Electronic data deliverables	X	X		
Identification of QC samples	X	X	X	
Meteorological data from field (e.g., wind, temperature)	X	X	X	
Sampling instrument decontamination records	X	X		
Sampling instrument calibration logs	X	X		
Sampling location and plan	X	X	X	
Sampling notes & drilling logs	X	X	X	
Sampling report (from field team leader to project manager describing sampling activities)	X	X	X	
External Reports				
External audit report	X	X	X	Use outputs from previous steps
External PT sample results	X	X		
Laboratory assessment	X	X		
Laboratory QA plan	X	X		
MDL study information	X	X	X	
NELAP accreditation	X	X		

Table 2
Analytical SOP References

Reference Number	Title, Revision Date and/or Number[1]	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work Y or N
L-1	USEPA. Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry. SW846 Method 8260B, Revision 2. December 1996.	Definitive	VOCs	GC/MS	Accutest Laboratories	N
L-2	USEPA. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry. SW846 Method 8270D, Revision 4. February 2007. Preparation method: Soil: USEPA. Ultrasonic Extraction. SW846 Method 3550C, Revision 3, February 2007.	Definitive	SVOCs	GC/MS	Accutest Laboratories	N
L-3	USEPA. Organochlorine Pesticides by Gas Chromatography. SW846 Method 8081B, Revision 2, February 2007. Preparation method: Soil: USEPA. Pressurized Fluid Extraction (PFE). SW846 Method 3545A, Revision 1, February 2007.	Definitive	Pesticides	GC/ECD	Accutest Laboratories	N
L-4	USEPA. Polychlorinated Biphenyls (PCB) by Gas Chromatography. SW846 Method 8082A, Revision 1, February 2007. Preparation method: Soil: USEPA. Pressurized Fluid Extraction (PFE). SW846 Method 3545A, Revision 1, February 2007.	Definitive	PCB Aroclors	GC/ECD	Accutest Laboratories	N

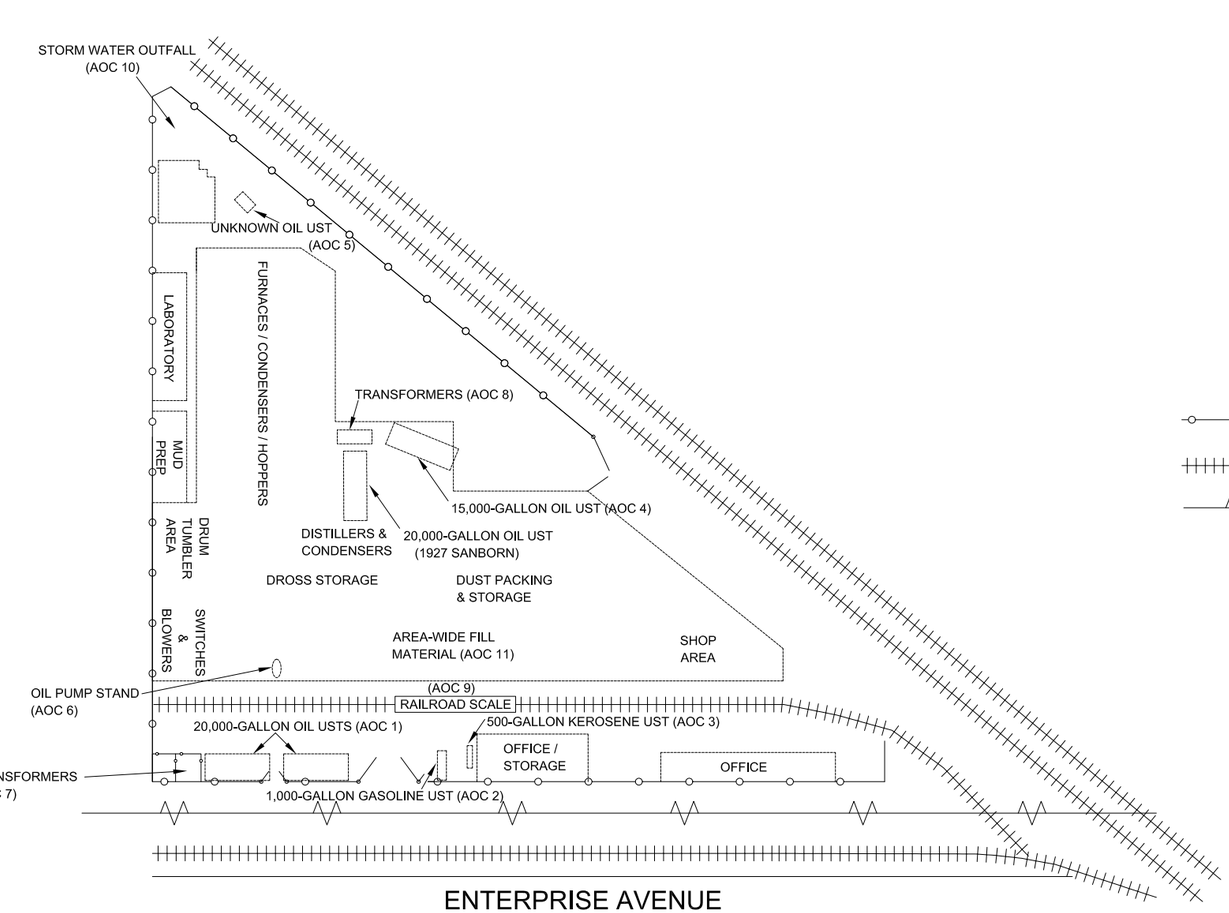
Table 2
Analytical SOP References

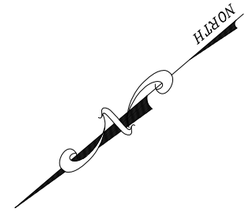
Reference Number	Title, Revision Date and/or Number[1]	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work Y or N
L-5	USEPA. Inductively Coupled Plasma-Atomic Emission Spectrometry. SW846 Method 6010C, Revision 3, February 2007. USEPA. Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique). SW846 Method 7471B, Revision 2. February 2007. USEPA. Mercury in Liquid Waste (Manual Cold-Vapor Technique). SW846 Method 7470A, Revision 1. September 1994. Preparation methods: Water: USEPA. Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy. SW846 Method 3010A, Revision 1. July 1992. Soil: USEPA. Acid Digestion of Sediments, Sludges, and Soils. SW846 Method 3050B, Revision 2. December 1996.	Definitive	Metals	ICP/AES, CVAA	Accutest Laboratories	N
L-6	USEPA. Chromium, Hexavalent (Colorimetric). SW846 Method 7196A, Revision 1. July 1992. Preparation method: water: Not applicable; included in SW846 Method 7196A Soil: USEPA. Alkaline Digestion for Hexavalent Chromium. SW846 Method 3060A, Revision 1. December 1996.	Definitive	Hexavalent Chromium	Spectrophotometer	Accutest Laboratories	N
F-1	NJDEP Manual	Screening	VOCs	PID or FID	USA Environmental Management, Inc.	N

Table 2
Analytical SOP References

Reference Number	Title, Revision Date and/or Number[1]	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work Y or N
F-2	NJDEP Manual	Definitive	pH, DO, temperature, specific conductance, ORP, turbidity, salinity	Horiba U-22 (or equivalent)	USA Environmental Management, Inc.	N

[1]Laboratory SOPs and Field Screening Procedures are included in Appendix A.
GC/MS – Gas Chromatograph/Mass Spectrometer; ICP/AES – Inductively Coupled Plasma/Atomic Emission Spectrometer; CVAA – Cold Vapor Atomic Absorption.
NA – Not Applicable





LEGEND

- METAL FENCE
- RAILROAD TRACKS
- OVERHEAD TELEPHONE AND ELECTRIC WIRES

NOTE:
Approximate location of historical site features based on Parcel A Facility Map from September 7, 2006 Ransom Environmental Phase I ESA Report and observations during November 2007 field work.
.

GRAPHIC SCALE

0 30 60
(IN FEET)
1 inch = 30 ft.

SITE LOCATION MAP
Former Federated Metals Site
300 Enterprise Avenue
Trenton, New Jersey

Figure 1

APPENDIX A

Laboratory SOPs

1,2-DIBROMOETHANE AND 1,2-DIBROMO-3-CHLOROPROPANE BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of the following compounds in drinking water and ground water:

Compound Name	CAS No.[a]
1,2-Dibromoethane (EDB)	106-93-4
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8

[a] Chemical Abstract Services Registry Number.

1.2 For compounds and matrices other than those listed in Section 1.1, the laboratory must demonstrate the usefulness of the method by collecting precision and accuracy data on actual samples and provide qualitative confirmation of results by gas chromatography/mass spectrometry (GC/MS).

1.3 The experimentally determined method detection limits (MDL) for EDB and DBCP were calculated to be 0.01 µg/L. The method has been shown to be useful for these analytes over a concentration range of approximately 0.03 to 200 µg/L. Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system, sample matrix, and calibration.

1.4 This method is restricted to use by or under the Supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

1.5 1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

2.0 SUMMARY OF METHOD

2.1 Thirty five mL of sample are extracted with 2 mL of hexane. Two µL of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and analysis. Aqueous matrix spikes are extracted and analyzed in an identical manner as the samples in order to compensate for possible extraction losses.

2.2 The extraction and analysis time is 30 to 50 minutes per sample depending upon the analytical conditions chosen. See Table 1 and Figure 1.

2.3 Confirmatory evidence is obtained using a different column (Table 1).

3.0 INTERFERENCES

3.1 Impurities contained in the extracting solvent (hexane) usually account for the majority of the analytical problems. Reagent blanks should be analyzed for each new bottle of hexane before use. Indirect daily checks on the hexane are obtained by monitoring the reagent blanks. Whenever an interference is noted in the method or instrument blank, the laboratory should reanalyze the hexane. Low level interferences generally can be removed by distillation or column chromatography, however, it is generally more economical to obtain a new source of hexane solvent. Interference-free hexane is defined as containing less than 0.01 µg/L of the analytes. Protect interference-free hexane by storing it in an area known to be free of organochlorine solvents.

3.2 Several instances of accidental sample contamination have been attributed to diffusion of volatile organics through the septum seal into the sample bottle during shipment and storage. Trip blanks must be used to monitor for this problem.

3.3 This liquid/liquid extraction technique extracts a wide boiling range of non-polar organic compounds and, in addition, extracts some polar organic compounds.

3.4 EDB at low concentrations may be masked by very high concentrations of dibromochloromethane (DBCM), a common chlorinated drinking water contaminant, when using the confirmation column.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringe - 10, 25, and 100 µL with a 2 in. x 0.006 in. needle (Hamilton 702N or equivalent).

4.2 Gas Chromatograph

4.2.1 The GC must be capable of temperature programming and should be equipped with a linearized electron capture detector and a capillary column splitless injector.

4.2.2 Columns

4.2.2.1 Column A - 0.32 mm ID x 30 m fused silica capillary with dimethyl silicone mixed phase (Durawax-DX 3, 0.25 µm film, or equivalent).

4.2.2.2 Column B (confirmation column) - 0.32 mm ID x 30 m fused silica capillary with methyl polysiloxane phase (DB-1, 0.25 µm film, or equivalent).

4.3 Volumetric flasks, Class A - 10 mL.

4.4 Glass bottles - 15 mL, with Teflon lined screw caps or crimp tops.

4.5 Analytical balance - 0.0001 g.

4.6 Graduated cylinder - 50 mL.

4.7 Transfer pipet.

5.0 REAGENTS

5.1 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 on 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.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Hexane, C_6H_{14} - UV grade (Burdick and Jackson #216 or equivalent).

5.4 Methyl alcohol, CH_3OH - Demonstrated to be free of analytes.

5.5 Sodium chloride, NaCl - Pulverize a batch of NaCl and place it in a muffle furnace at room temperature. Increase the temperature to 400°C for 30 minutes. Store in a capped bottle.

5.6 1,2-Dibromoethane (99%), $C_2H_4Br_2$, (Aldrich Chemical Company, or equivalent).

5.7 1,2-Dibromoe-3-chloropropane (99.4%), $C_3H_5Br_2C1$, (AMVAC Chemical Corporation, Los Angeles, California, or equivalent).

5.8 Stock standards - These solutions may be purchased as certified solutions or prepared from pure standards using the following procedures:

5.8.1 Place about 9.8 mL of methanol into a 10 mL ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes and weigh to the nearest 0.0001 g.

5.8.2 Use a 25 µL syringe and immediately add two or more drops (≈ 10 µL) of standard to the flask. Be sure that the standard falls directly into the alcohol without contacting the neck of the flask.

5.8.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

5.8.4 Store stock standards in 15 mL bottles equipped with Teflon lined screw-caps or crimp tops. Stock standards are stable for at least four weeks when stored at 4°C and away from light.

5.9 Intermediate standard - Use stock standards to prepare an intermediate standard that contains both analytes in methanol. The intermediate standard should be prepared at a concentration that can be easily diluted to prepare aqueous calibration standards that will bracket the working concentration range. Store the intermediate standard with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration standards. The storage time described for stock standards also applies to the intermediate standard.

5.10 Quality control (QC) reference sample - Prepare a QC reference sample concentrate at 0.25 mg/L of both analytes from standards from a different source than the standards used for the stock standard.

5.11 Check standard - Add an appropriate volume of the intermediate standard to an aliquot of organic-free reagent water in a volumetric flask. Do not add more than 20 µL of an alcoholic intermediate standard to the water or poor precision will result. Use a 25 µL microsyringe and rapidly inject the alcoholic intermediate standard into the expanded area of the almost filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask several times. Discard the contents contained in the neck of the flask. Aqueous calibration standards should be prepared every 8 hours.

6.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Recommended Chromatographic Conditions

Two gas chromatography columns are recommended. Column A is a highly efficient column that provides separations for EDB and DBCP without interferences from trihalomethanes. Column A should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column B is recommended for use as a confirmatory column when GC/MS confirmation is not available. Retention times for EDB and DBCP on these columns are presented in Table 1.

Column A:

Injector temperature:	200°C.
Detector temperature:	290°C.
Carrier gas (Helium)Linear velocity:	25 cm/sec.
Temperature program:	
Initial temperature:	40°C, hold for 4 min.
Program:	40°C to 190°C at 8°C/min.

Final temperature:	190°C, hold for 25 min., or until all expected analytes have eluted.

See Figure 1 for a sample chromatogram and Table 1 for retention data.

Column B:

Injector temperature:	200°C.
Detector temperature:	290°C.
Carrier gas (Helium)Linear velocity:	25 cm/sec.
Temperature program:	
Initial temperature:	40°C, hold for 4 min.
Program:	40°C to 270°C at 10°C/min.
Final temperature:	270°C, hold for 10 min., or until all expected analytes have eluted.

See Table 1 for retention data.

7.2 Calibration

7.2.1 Prepare at least five calibration standards. One should contain EDB and DBCP at a concentration near, but greater than, the method detection limit (Table 1) for each compound. The others should be at concentrations that bracket the range expected in the samples. For example, if the MDL is 0.01 µg/L, and a sample expected to contain approximately 0.10 µg/L is to be analyzed, aqueous calibration standards should be prepared at concentrations of 0.03 µg/L, 0.05 µg/L, 0.10 µg/L, 0.15 µg/L, and 0.20 µg/L.

7.2.2 Analyze each calibration standard and tabulate peak height or area response versus the concentration in the standard. Prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (< 10% relative standard deviation), linearity can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3 Sample preparation

7.3.1 Remove samples and standards from storage and allow them to reach room temperature.

7.3.2 For samples and field blanks contained in 40 mL bottles, remove the container cap. Discard a 5 mL volume using a 5 mL transfer pipet. Replace the container cap and weigh the container with contents to the nearest 0.1 g and record this weight for subsequent sample volume determination.

7.3.3 For calibration standards, check standards, QC reference samples, and blanks, measure a 35 mL volume using a 50 mL graduated cylinder and transfer it to a 40 mL sample container.

7.4 Extraction

7.4.1 Remove the container cap and add 7 g of NaCl to all samples.

7.4.2 Recap the sample container and dissolve the NaCl by shaking by hand for about 20 seconds.

7.4.3 Remove the cap and using a transfer pipet, add 2.0 mL of hexane. Recap and shake vigorously by hand for 1 minute. Allow the water and hexane phases to separate. If stored at this stage, keep the container upside down.

7.4.4 Remove the cap and carefully transfer a sufficient amount (0.5-1.0 mL) of the hexane layer into a vial using a disposable glass pipet.

7.4.5 Transfer the remaining hexane phase, being careful not to include any of the water phase, into a second vial. Reserve this second vial at 4°C for reanalysis if necessary.

7.5 Analysis

7.5.1 Transfer the first sample vial to an autosampler set up to inject 2.0 µL portions into the gas chromatograph for analysis. Alternately, 2 µL portions of samples, blanks and standards may be manually injected, using the solvent flush technique, although an auto sampler is strongly recommended.

7.6 Determination of sample volume

7.6.1 For samples and field blanks, remove the cap from the sample container. Discard the remaining sample/hexane mixture. Shake off the remaining few drops using short, brisk wrist movements. Reweigh the empty container with original cap and calculate the net weight of sample by difference to the nearest 0.1 g. This net weight is equivalent to the volume of water extracted.

7.7 Calculations

7.7.1 Identify EDB and DBCP in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards and the check standard.

7.7.2 Use the calibration curve or calibration factor to directly calculate the uncorrected concentration (C_i) of each analyte in the sample (e.g. calibration factor x response).

7.7.3 Calculate the sample volume (V_s) as equal to the net sample weight:

V_s (mL) = gross weight (grams) - bottle tare (grams)

7.7.4 Calculate the corrected sample concentration as:

$$\text{Concentration } (\mu g/L) = \frac{C_i \times 35}{V_s}$$

7.7.5 Report the results for the unknown samples in µg/L. Round the results to the nearest 0.01 µg/L or two significant figures.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality control program.

8.1.1 The laboratory must make an initial determination of the method detection limits and demonstrate the ability to generate acceptable accuracy and precision with this method. This is established as described in Section 8.2.

8.1.2 In recognition of laboratory advances that are occurring in chromatography, the laboratory is permitted certain options to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 7.1 and 8.2.

8.1.3 The laboratory must analyze a reagent and calibration blank to demonstrate that interferences from the analytical system are under control every twenty samples or per analytical batch, whichever is more frequent.

8.1.4 The laboratory must, on an ongoing basis, demonstrate through the analyses of QC reference samples and check standards that the operation of the measurement system is in control. The frequency of the check standard analyses is equivalent to 5% of all samples or every analytical batch, whichever is more frequent. On a weekly basis, the QC reference sample must be run.

8.2 To establish the ability to achieve low detection limits and generate acceptable accuracy and precision, the analyst must perform the following operations:

8.2.1 Prepare seven samples each at a concentration of 0.03 µg/L.

8.2.2 Analyze the samples according to the method beginning in Section 7.0.

8.2.3 Calculate the average concentration ($\bar{X}$) in µg/L and the standard deviation of the concentrations (s) in µg/L, for each analyte using the seven results. Then calculate the MDL at 99% confidence level for seven replicates as 3.143s.

8.2.4 For each analyte in an aqueous matrix sample, $\bar{X}$ must be between 60% and 140% of the true value. Additionally, the MDL may not exceed the 0.03 µg/L spiked concentration. If both analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If either analyte fails to meet a criterion, repeat the test. It is recommended that the laboratory repeat the MDL determination on a regular basis.

8.3 The laboratory must demonstrate on a frequency equivalent to 5% of the sample load or once per analytical batch, whichever is more frequent, that the measurement system is in control by analyzing a check standard of both analytes at 0.25 µg/L.

8.3.1 Prepare a check standard (0.25 µg/L) by diluting the intermediate standard with water to 0.25 µg/L.

8.3.2 Analyze the sample according to Section 7.0 and calculate the recovery for each analyte. The recovery must be between 60% and 140% of the expected value for aqueous matrices. For non-aqueous matrices, the U.S. EPA will set criteria after more interlaboratory data are gathered.

8.3.3 If the recovery for either analyte falls outside the designated range, the analyte fails the acceptance criteria. A second calibration verification standard containing each analyte that failed must be analyzed. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test.

8.4 On a weekly basis, the laboratory must demonstrate the ability to analyze a QC reference sample.

8.4.1 Prepare a QC reference sample at 0.10 µg/L by diluting the QC reference sample concentrate (Section 5.9).

8.4.2 For each analyte in an aqueous matrix, the recovery must be between 60% and 140% of the expected value. When either analyte fails the test, the analyst must repeat the test only for that analyte which failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system or faulty samples and/or standards. If this occurs, locate and correct the source of the problem and repeat the test. For non-aqueous matrices, the U.S. EPA will set criteria after more interlaboratory data are gathered.

8.5 Instrument performance - Check the performance of the entire analytical system daily using data gathered from analyses of blanks, standards, and replicate samples.

8.5.1 Peak tailing significantly in excess of that shown in the chromatogram (Figure 1) must be corrected. Tailing problems are generally traceable to active sites on the GC column or to the detector operation.

8.5.2 Check the precision between replicate analyses. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks, especially at the injection port.

9.0 METHOD PERFORMANCE

9.1 Method detection limits are presented in Table 1. Single laboratory accuracy and precision at several concentrations in tap water are presented in Table 2.

9.2 In a preservation study extending over a 4 week period, the average percent recoveries and relative standard deviations presented in Table 3 were observed for organic-free reagent water (acidified), tap water and ground water. The results for acidified and non-acidified samples were not significantly different.

10.0 REFERENCES

1. Optimization of Liquid-Liquid Extraction Methods for Analysis of Organics in Water, EPA-600/S4-83-052, 1984.

2. Henderson, J.E.; Peyton, G.R.; Glaze, W.H. Identification and Analysis of Organic Pollutants in Water; Keith, L.H., Ed; Ann Arbor Sci.: Ann Arbor, MI; 1976.

3. Richard J.J.; Junk, G.A. Journal AWWA 1977, 69, 62.

4. Budde, W.L.; Eichelberger, J.W. Organic Analyses Using Gas Chromatography-Mass Spectrometry; Ann Arbor Science: Ann Arbor, MI; 1978.

5. Glaser, J.A.; et al. Environmental Science and Technology 1981, 15, 1426.

6. Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH 1986.

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS (MDL) FOR 1,2-DIBROMOETHANE (EDB) AND 1,2-DIBROMO-3-CHLOROPROPANE (DBCP)

Analyte	Retention Time, Minutes		MDL (µg/L)
	Column A	Column B	
EDB	9.5	8.9	0.01
DBCP	17.3	15.0	0.01

Column A: Durawax-DX 3

Column B: DB-1

TABLE 2.
SINGLE LABORATORY ACCURACY AND PRECISION FOR EDB AND DBCP IN TAP WATER

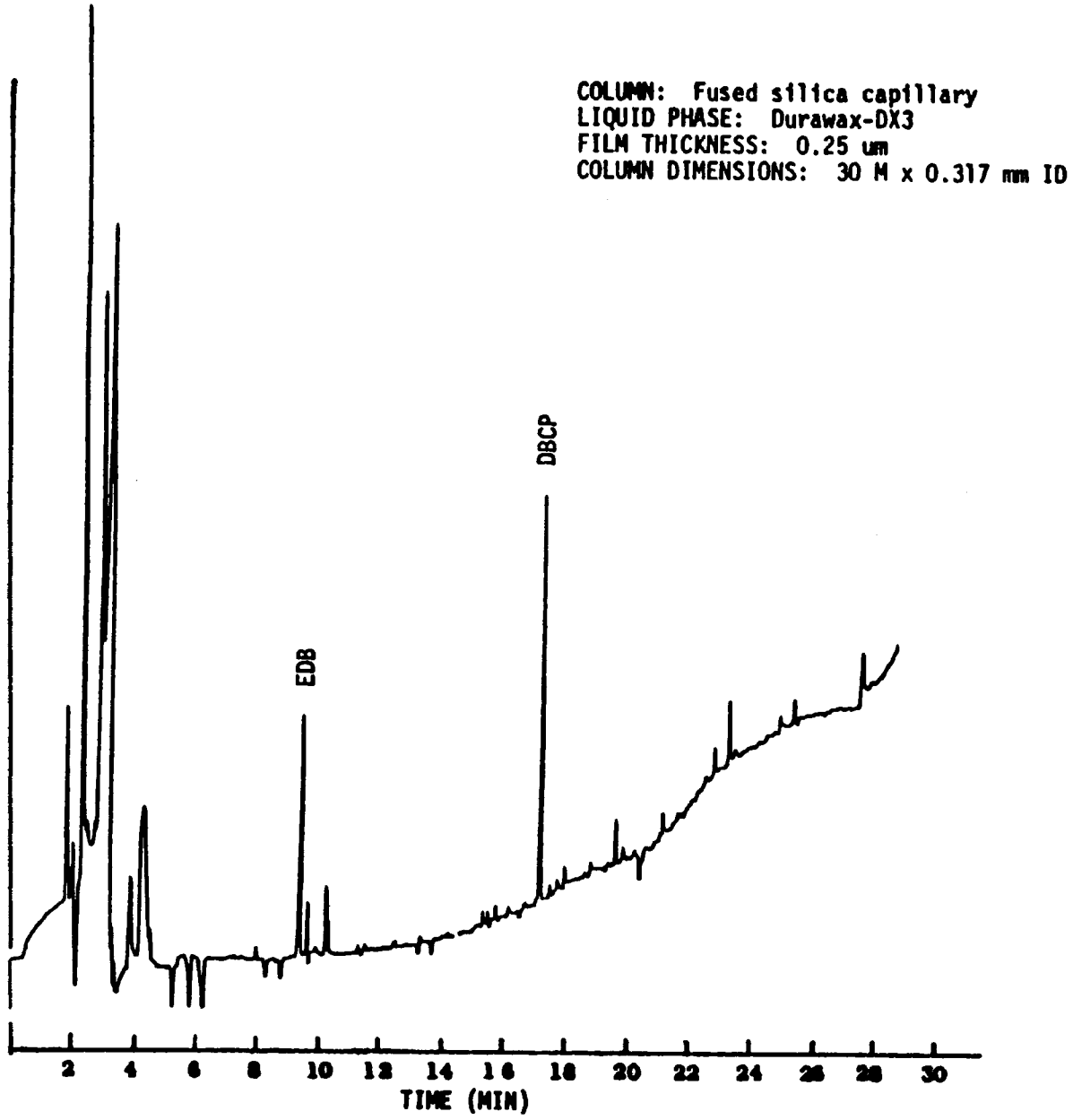
Analyte	Number of Samples	Spike Concentration (µg/L)	Average Recovery (%)	Relative Standard Deviation (%)
EDB	7	0.03	114	9.5
	7	0.24	98	11.8
	7	50.0	95	4.7
DBCP	7	0.03	90	11.4
	7	0.24	102	8.3
	7	50.0	94	4.8

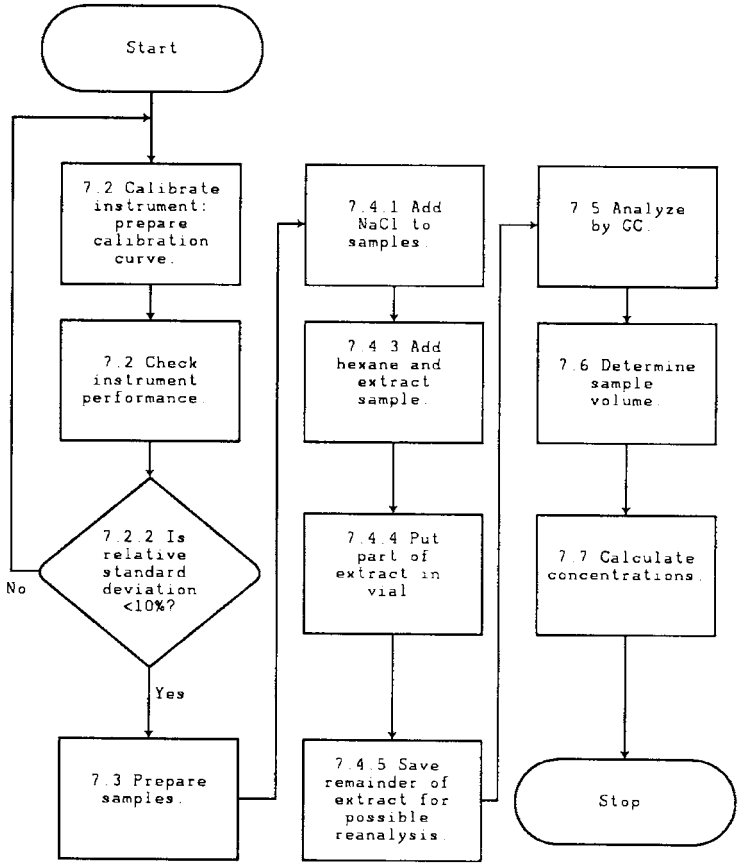
TABLE 3.
ACCURACY AND PRECISION AT 2.0 µg/L
OVER A 4-WEEK STUDY PERIOD

Analyte	Matrix[1]	Number of Samples	Average Accuracy (% Recovery)	Relative Std. Dev. (%)
EDB	RW-A	16	104	4.7
	GW	15	101	2.5
	GW-A	16	96	4.7
	TW	16	93	6.3
	TW-A	16	93	6.1
DBCP	RW-A	16	105	8.2
	GW	16	105	6.2
	GW-A	16	101	8.4
	TW	16	95	10.1
	TW-A	16	94	6.9

[1] RW-A = Organic-free reagent water at pH 2
GW = Ground water, ambient pH
GW-A = Ground water at pH 2
TW = Tap water, ambient pH
TW-A = Tap water at pH 2

FIGURE 1.
SAMPLE CHROMATOGRAM FOR EXTRACT OF WATER SPIKED
AT 0.114 µg/L WITH EDB AND DBCP




Start
7.2 Calibrate instrument: prepare calibration curve.
7.2 Check instrument performance.
7.2.2 Is relative standard deviation <10%?
No
Yes
7.3 Prepare samples.
7.4.1 Add NaCl to samples.
7.4.3 Add hexane and extract sample.
7.4.4 Put part of extract in vial
7.4.5 Save remainder of extract for possible reanalysis.
7.5 Analyze by GC.
7.6 Determine sample volume.
7.7 Calculate concentrations.
Stop

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager: Nancy Cole

QA Manager:

Effective Date: 5/29/13

TEST NAME: HEXAVALENT CHROMIUM IN SOILS BY ION CHROMATOGRAPHY

METHOD REFERENCE: SW846 Methods 3060A and 7199

Revised Sections: ***14.0 (all 14 renumbered), 17.1***

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of hexavalent chromium in soils, sludges, brick, concrete, and other solid matrices. The solid sample is digested in an alkaline digestion solution to solubilize both water soluble and water insoluble hexavalent chromium compounds. Magnesium chloride in a phosphate buffer is added to suppress oxidation of Cr(III). The hexavalent chromium is separated from the other sample constituents in the digestate by an ion exchange column and then determined in the sample by reaction with diphenylcarbazide in acid solution. The diphenylcarbazide complex produces a characteristic pink color that can be measured by a UV/VIS detector at 530 nm.

2.0 SUMMARY

2.1 This method uses an alkaline digestion to solubilize both water-insoluble (with the exception of partial solubility of barium chromate in some soil matrices), and water soluble Cr(VI) compounds in solid waste samples. The sample is digested using 0.28M Na_2CO_3 /0.5M NaOH solution and heating at 90- 95°C for 60 minutes to dissolve the Cr(VI) and stabilize it against reduction to Cr(III).The digestate is then buffered to a pH of 9.0 to 9.5 and then the dissolved hexavalent chromium is separated from interfering substances using an ion exchange column on an ion chromatograph. The separated sample is then reacted with diphenylcarbazide in acid solution to form a red-violet color. The intensity of this color is measured by a UV/VIS detector at a wavelength of 530 nm and is quantitated against a calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is dependent upon the instrument used for analysis. Analyses done on the DX500 or the ICS3000 have a normal reporting limit of 0.4 mg/kg, based on an instrument level of 0.010 mg/l, a final volume of 100 ml, and an initial weight of 2.5 g. Analyses done on the Metrohm have a normal reporting limit of 0.8 mg/kg as soil digestates must be analyzed at a 1:2 dilution on the Metrohm in order to obtain good chromatography. Note: The reporting limit must be based on a level greater than or equal to the low standard and higher than the calculated MDL.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound

compound that meets the method qualitative identification criteria. When multiple instruments are used for an analysis, a pooled MDL is reported.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. The calibration check standard must be run at a frequency of 10 percent. For most methods, the mid-level calibration check standard criteria is $\pm$ 10 percent of the true value. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the detection limit.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run with each calibration. The laboratory must assess laboratory performance of a check standard using the method defined control limits.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits must also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent must be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample must be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of $\pm$ 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results must be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and must be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent must be used.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{Matrix Spike Recovery}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). - The minimum concentration of a substance 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. MDLs must be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce

working standards which cover the working range of the instrument. Standards must be prepared at the frequency specified in the appropriate section. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: hexavalent chromium.

6.0 PRESERVATION & HOLDING TIME

6.1 Soil samples must be kept under refrigeration at 4^0 C until time of digestion.

6.2 All samples that are analyzed following this method must be analyzed within 30 days of sample collection. The alkaline digestate is stable for up to 168 hours after extraction from soil.

7.0 INTERFERENCES

7.1 Several types of interferences are possible with this method.

7.1.1 Contamination. Trace levels of Cr may sometimes be found in reagent salts. Reagent blanks must be analyzed to assess for potential Cr(VI) contamination.

7.1.2 Reduction of Cr(VI) to Cr(III) can occur in the presence of reducing species in an acidic medium. However, at a pH of 6.5 or greater, CrO_4^{2-}, which is less reactive than $HCRO_4^-$, is the predominant species.

7.1.3 Waste material suspected of containing soluble Cr(III) concentrations greater than 4 times the laboratory Cr(VI) reporting limit may have Cr(VI) results that are biased high due to method induced oxidation. Mg (II) salts, in a phosphate buffer, are added to suppress this oxidation.

7.1.4 Overloading of the analytical column capacity with high concentrations of anionic species can cause a loss of Cr(VI). This is particularly a problem with chloride and sulfate. The column

specified in this method can handle samples containing up to 5% of sodium sulfate or 2% of sodium chloride.

8.0 APPARATUS

8.1 Ion Chromatograph with a guard column, an analytical column, a post-column delivery system, a knitted reaction coil and a UV/Vis absorbance detector. Three instruments are available for this analysis; the Dionex ICS5000, the Dionex ICS3000, or the Metrohm 844 UV/Vis Compact IC.

8.2 Either the Dionex ICS3000 or the Dionex ICS5000 with the GP50 gradient pump and the AD25 absorbance detector, capable of reading the absorbance at 530 nm can be used with the specific parts listed below. Alternate columns may be used if all method requirements can be met.

8.2.1 Guard Column, IONPAC NG1-10um Guard column, 4 x 35 mm. Dionex part number 039567.

8.2.2 Analytical Column, IONPAC AS7 Analytical column, 4 x 250 mm. Dionex part number 035393.

8.2.3 PC10 Postcolumn Pneumatic Delivery Package, 4 mm. Dionex part number 050601 for the ICS3000 or additional pump for post-column delivery in the ICS5000.

8.2.4 Knitted Reaction Coil, 750ul, unpotted. Dionex part number 042631.

8.2.5 25 ul injection loop. A different size sample loop may be used if method verification is performed before running samples.

8.3 The Metrohm 844 UV/Vix Compact IC can be used with the specific parts lists below. Alternate columns may be used if all method requirements can be met.

8.3.1 Guard Discs (Metrohm part number 6.1011.120) and guard disc holder (Metrohm part number 6.1011.020)

8.3.2 Analytical Column, Metrosep A Supp 10 250/4.0, part number 6.1020.030.

8.3.3 Postcolumn pump, Metrohm 818 IC pump.

8.3.4 Post Column Reactor (Knitted Reaction Coil), Metrohm part number 6.2836.000.

8.3.5 40 ul injection loop. A different size sample loop may be used if method verification is performed before running samples.

8.4 Helium tank and regulator for Dionex ICS3000 system. Gas pressure must be at > 100 PSI for the injectors to work properly.

8.5 Volumetric flasks, class A.

8.6 Volumetric pipets, class A or autopipeters. Note: If autopipeters are used, make sure that the calibration is checked before use as specified in the autopipeter SOP.

8.7 0.45 um membrane filters, that can be attached to the end of the syringe or 0.45 um filters to use in the in-line filter system for the Metrohm system.

8.8 Disposable syringes.

8.9 pH meter. Orion pH/ISE Meter Model 710A or equivalent.

8.10 Four-place analytical balance.

8.11 One or two place balance. Ohaus Galaxy 4000 or equivalent.

8.12 50 and 250 ml glass beakers with watch glasses. All glassware must be washed with soap and tap water and then well rinsed with deionized water.

8.13 Filter paper, 0.45 um. Acceptable filter papers include the following: MSI cellulostic white grid filters, 0.45 um, 47 mm (catalog number E04WG047S1).

8.14 Filter pump and vacuum filtration apparatus.

8.15 Hot plate, capable of maintaining the digestion solutions at 90 to 95 C, with constant stirring ability.

8.16 Thermometer, calibrated to an NIST certified thermometer a minimum of once per year.

8.17 Graduated plastic beakers.

9.0 REAGENTS

9.1 All reagents must be made from ACS grade reagents unless otherwise noted. Deionized water must be used whenever water is needed. The expiration date for standards and reagents is the date supplied by the manufacturer or if no expiration date is given, a default of 6 months is used. For acid solutions (nitric, sulfuric, hydrochloric) the expiration date is 2 years from the date of preparation of the solution.

9.2 Nitric acid, HNO_3, concentrated, trace metals grade.

9.3 Nitric acid, HNO_3, 5.0 M, trace metals grade. Add 32 ml of concentrated nitric acid to approximately 50 ml of DI water. Dilute to a final volume of 100 ml with DI water and mix well. Store at 20-25°C in the dark. Do not use concentrated nitric acid to make up the 5.0 M solution if it has a yellow tinge. The yellow color is indicative of a photo reduction of nitrate to nitrite, a reducing agent for Cr(VI).

9.4 Sodium Carbonate, Na_2CO_3, anhydrous.

9.5 Sodium Hydroxide, NaOH.

9.6 Magnesium Chloride, $MgCl_2$ (anhydrous). Note: 392.18 mg of $MgCl_2$ is equivalent to 100 mg of Mg^{2+}.

9.7 Phosphate Buffer Solution (0.5 M K_2HPO_4/0.5 M KH_2PO_4 buffer at pH 7): Dissolve 87.09 g of K_2HPO_4 and 68.04 g of KH_2PO_4 into 700 ml of distilled deionized water. Transfer to a 1 liter volumetric flask and dilute to volume.

9.8 Digestion Solution: Dissolve 20.0 g of NaOH and 30.0 g of Na_2CO_3 in distilled deionized water in a one-liter volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle at 20 to 25°C and prepare fresh monthly. The pH of this digestion solution must be checked before using. If the pH is not greater than or equal to 11.5, then the digestion solution must be discarded and a new solution must be made up.

9.9 Insoluble hexavalent chromium spike, lead chromate, $PbCrO_4$. The insoluble matrix spike is prepared by adding 10 to 20 mg of $PbCrO_4$ to the insoluble matrix spike aliquot.

9.10 Soluble hexavalent chromium spiking solution stock. A 1000 mg/l stock solution of potassium dichromate can be used as the stock solution for the spiking solution. (Available as 1000 mg/l chromium solution, AAS grade from Fisher or equivalent).

9.11 Soluble hexavalent chromium spiking solution, 100 mg/l. Add 10.0 ml of the 1000 mg/l hexavalent chromium to a 100 ml volumetric flask and dilute to volume with DI water. Mix well. One (1.00) ml of this spiking solution can be used to spike the soluble matrix spike aliquot. The approximate level of the spike in the spiked sample will be 40 mg/kg.

9.12 Hexavalent Chromium Calibration Standard Solutions. The calibration standards must be prepared fresh daily or each time the analysis is run. For instrument calibration, prepare the standards from the stocks as shown below. Note that both calibration standards and continuing calibration verification standards are prepared in digestion solution.

9.12.1 Hexavalent Chromium 10.00 mg/L stock solution. Add 1.00 ml of 1000 mg/L hexavalent chromium to a 100 ml volumetric flask and dilute to volume with dilution water (section 9.16). Mix well.

9.12.2 Hexavalent Chromium 1.00 mg/L stock solution. Dilute 10.0 ml of the 10 mg/L stock solution to a final volume of 100 ml with dilution water (section 9.16) and mix well.

9.12.3 Daily Standards. Add the amount of stock specified below to the 100 ml volumetrics containing 50 ml of digestion solution(section 9.8). Adjust the pH to between 9.0 and 9.5 with nitric acid and bring to a final volume of 100 ml with deionized water.

Blank: No spike is added to the blank.
0.005 mg/L: Add 0.50 ml of 1.00 mg/L.
0.050 mg/L: Add 5.00 ml of 1.00 mg/L.
0.100 mg/L: Add 1.00 ml of 10.0 mg/L.
0.500 mg/L: Add 5.00 ml of 10.0 mg/L.

9.12.4 Hexavalent Chromium CCV (Continuing Calibration Verification) Solutions. The check standards must be prepared fresh daily or each time the analysis is run. Prepare the standards from the stocks as shown below. All check standards must go through the entire digestion process, starting at step 10.3. A minimum of 4 check standards must be made for a batch of 20 samples. Note: The check standards must be made from a different source than the calibration standards.

9.12.4.1 Hexavalent Chromium 5.0 mg/l stock solution. Add 1.00 ml of 1000 mg/l hexavalent chromium to a 200 ml volumetric flask and dilute to volume with DI water. Mix well.

9.12.4.2 For initial calibration curves that have the 0.500 mg/l standard as the upper limit, a calibration check at 0.250 mg/l must be used. Therefore, add the amount of stock solution specified below to 50 ml of digestion solution. Do not dilute to a final volume. This entire solution must be digested. After digestion and pH adjustment, the final volume will be 100 ml.

0.250 mg/L: Add 10.00 ml of 5.0 mg/L.

9.13 Eluent. Dissolve 33 g of ammonium sulfate in 500 ml of DI water and add 6.5 ml of ammonium hydroxide. Dilute to one liter with DI water. Filter the solution through a 0.45 um filter and then degas the solution with helium gas for 5 to 10 minutes before use.

9.14 Post-Column Reagent. Dissolve 0.5 g of 1,5 diphenylcarbazide in 100 ml of HPLC grade methanol in a 1000 ml volumetric flask. Make sure to dissolve all of the 1,5 diphenylcarbazide in methanol before proceeding. In a separate container, add 28 ml of concentrated sulfuric acid (96 to 98%) into 500 ml of DI water, mix and degas with helium gas for 5 to 10 minutes prior to adding the diphenylcarbazide solution. Dilute to volume with DI water. This reagent is stable for 4 to 5 days.

9.15 Buffer Solution. Dissolve 33 g of ammonium sulfate in 75 ml of DI water and add 6.5 ml of ammonium hydroxide. Dilute to 100 ml with DI water. Degas the solution with helium gas for 5 to 10 minutes before use.

9.16 Dilution Water. A batch of DI water must be prepared by adjusting the pH within the range of 9.0 to 9.5 using the buffer solution. Use this solution for diluting working standards and high level samples.

9.17 Digestate Dilution Solution A. If samples or quality control points are over the range of the calibration curve, they must be diluted with a solution containing a similar matrix to the digested samples. This digestion dilution solution is used if the original analysis is undiluted. Take 500 ml of digestion solution and adjust the pH to between 9.0 and 9.5 with nitric acid. Then dilute to a final volume of 1000 ml with deionized water.

9.18 Digestate Dilution Solution B. . If samples or quality control points are over the range of the calibration curve, they must be diluted with a solution containing a similar matrix to the digested samples. This digestion dilution solution is used if the original analysis is diluted by a factor of 2. Take 250 ml of digestion solution and adjust the pH to between 9.0 and 9.5 with nitric acid. Then dilute to a final volume of 1000 ml with deionized water.

9.19 Quality Control Sample (lab control sample). A solid quality control sample obtained and prepared from an independent source is required.

9.19.1 An NIST standard must be used if available. SRM 2701 is the only currently available NIST standard for use as the recommended quality control sample. The Certificate of Analyses provided with this SRM provides a certified value of 551.2 mg/kg +/- 34.5 as determined via EPA Method 6800, an alternately available method utilizing Speciated Isotope Dilution Mass Spectrometry. The observed range for EPA Method 7199 as referenced in the Certificate of Analysis is 270 mg/kg to 557 mg/kg. The Certificate of Analysis does not offer a certified range for this material.

9.19.1.1 When using an NIST standard without a certified range, such as NIST SRM 2701, a solid lead chromate lab control is also required.

9.19.2 If the NIST standard is not available (i.e. backordered or discontinued), then an alternate independent solid lab control must be used. A recommended source is ERA Catalog number 921, Hexavalent Chromium in soil. Solid lead chromate may also be used as an alternate solid lab control source.

10.0 DIGESTION PROCEDURE

Below is a step-by-step procedure for the digestion of samples for the determination of hexavalent chromium.

10.1 For each sample to be analyzed, weight out 2.5 $\pm$ 0.10 g of the sample into a clean, labeled glass beaker. A one or two place balance may be used for this weighing. The sample must be well mixed before the aliquot is removed as described below.

10.1.1 Mix each sample by turning the sample job end over end for 30 seconds. Then stir each sample for 30 seconds. If the sample jar is filled too full, it may be difficult to stir the sample in the jar. In that case, the sample must be transferred to a larger container and stirred.

10.1.2 For the sample that is to be used for the quality control sample, first follow the steps outlined in Then remove 20 grams of sample from the jar and place it in a beaker and mix well. Take the mixed soil and place it on a large piece of weighing paper. Divide the soil into 6 sections and weigh out a 2.5 $\pm$ 0.10 g aliquot from each section. One aliquot will be for the soluble Cr(VI) matrix spike, one aliquot will be for the insoluble Cr(VI) matrix spike, one aliquot will be for the original sample analysis, one aliquot will be for the duplicate sample analysis, and the remaining two aliquots will be used to complete the procedures required if the initial post-digest spike does not meet the $\pm$ 15 criteria.

10.2 Add the spikes to the matrix spikes and the spike blanks. Prepare the solid lab control.

10.2.1 Spike the soluble Cr(VI) matrix spike with 1.0 ml of the 100 mg/l Cr(VI) spiking solution. (Check with the area supervisor or manger before starting to see if an additional spike level will be needed.)

10.2.2 Spike the soluble Cr(VI) spike blank with 1.0 ml of the 100 mg/l Cr(VI) spiking solution.

10.2.3 Using an analytical balance, weigh out 0.010 to 0.020 g of $PbCrO_4$ onto a clean piece of weighing paper and carefully add the spike into the insoluble matrix spike sample. Make sure to record the weight used.

10.2.4 Using an analytical balance, weigh out 0.010 to 0.020 g of $PbCrO_4$ onto a clean piece of weighing paper and carefully add the spike into the insoluble blank spike. Make sure to record the weight used.

10.2.5 Weigh out an appropriate weight of the solid lab control. For NIST SRM 2701, normally weigh out from 0.450 to 0.550 g of sample. If a different solid lab control is used, then check with the area supervisory team for more information on appropriate weights to use.

10.3 Add 50 ml of digestion solution to each sample. Also add approximately 0.392 g of $MgCl_2$ (from 0.38 to 0.42 g) and 0.5 ml of the 1.0 M phosphate buffer. In addition to the samples, 3 extra beakers must be prepared for the method blank, the soluble Cr(VI) spike blank, and the insoluble Cr(VI) spike blank.

10.4 In addition to the samples, the CCV (continuing calibration check) standards must also be digested. Add the entire CCV solution (refer to step 9.12.4) into a clean, labeled glass beaker. Also add approximately 0.392 g of $MgCl_2$ (from 0.38 to 0.42 g) and 0.5 ml of the 1.0 M phosphate buffer.

10.5 Cover all samples and quality control (including the calibration check samples) with watch glasses. Add a stirring bar to each sample and stir the samples for at least 5 minutes without heating.

10.6 Place the samples on a stirring hot plate that has been preheated to 90 to 95°C. Heat the samples with constant stirring for 60 minutes, maintaining a temperature range of 90 to 95°C. The temperature must be measured by placing a calibrated thermometer in an extra beaker containing digestion reagent on the hot plate. The temperature must be recorded at 30 minutes and 60 minutes during the digestion process. Both the start and the stop time of the digestion must be recorded. A second analyst must sign off on the digestion worksheet to verify that all of the proper times and temperatures are documented.

10.7 Cool the samples to room temperature. Filter them through 0.45 um filter paper. Rinse the filter and filtration apparatus with DI water and transfer the filtrate into labeled graduated plastic beakers.

10.7.1 If the filters become clogged using the 0.45 um filter paper, a larger size filter paper (Whatman GFB or GFF) may be used to prefilter the samples. However, the final filtration must be through the 0.45 um filters. If a pre-filtration is required, it must be recorded on the digestion log.

10.7.2 The solids and the filter remaining after the filtration of the matrix spikes may need to be saved in a labeled plastic beaker and stored in the refrigerator. If low recoveries are obtained on the matrix spikes, these solids may be needed for additional analyses. Check with the area supervisor or manager for further instructions.

10.7.3 At this point, the digestates are stable and may be held for up to 168 hours before proceeding with step 10.8.

10.8 Before starting the analysis, the pH of the digestates must be adjusted.

10.8.1 Place a stirring bar in the sample and place it on a stirring plate. Adjust the pH of the solution between 9.00 and 9.50 by carefully adding 5.0 M nitric acid to the digestate while constantly measuring the pH. Do **not** let the pH of the solution go below 9.00. If the pH goes below 9.00, then the digestate must be discarded and a new digestate prepared. Make sure to record the final pH.

10.8.2 If the pH is changing too rapidly with 5.0 M nitric acid, then a more dilute solution of nitric acid may be used for the pH adjustment.

10.8.2.1 Carbon dioxide and nitric acid fumes will be evolved during this process. Therefore, this step must be performed in a hood or well ventilated area.

10.8.3 Quantitatively transfer the contents of the beaker to a 100 ml volumetric flask and adjust the sample volume to the mark with DI water. Mix well. At this point, a brief description of each sample (color, turbidity, etc.) can be added to the digestion log.

10.8.4 A second analyst must verify and sign off on the worksheet to verify that all pH adjustments are properly documented.

10.9 If a precipitate or turbidity is observed after filtration, then filter the sample a second time through a 0.45 um filter. Let the sample come to room temperature before analysis.

11.0 ION CHROMATOGRAPHY ANALYSIS PROCEDURE FOR THE DIONEX ICS3000.

11.1 Check to make sure that the helium tank pressure is > 100 PSI and the pressure gauge by the eluent bottles is set at 6 PSI.

11.2 Fill the eluent bottle(s) that are to be used with eluent. Make sure to close the corner knob before opening the eluent bottle. Note: It is recommended that 2 bottles be filled with eluent and 50% taken from each bottle during the analysis so that the eluent lasts longer. Fill the reagent delivery bottle with post-column reagent.

11.2.1 Note: The post-column reagent is off-line when it is set to valve A. It is on-line when it is set to valve B. When not running, set the valve to A.

11.2.2 The eluent must be filtered through a 0.45 um filter before use.

11.3 Set the GP50 (pump control) and the AD25 (detector control) to local control and direct read. Press local, direct, and enter).

11.4 Turn on the GP50 and go to the diagnostics menu and look at the pressure statistics. The pressure must be constant for 1 minute and the values for the left and right pressure points must be close. If the pressure is fluctuating or the left and right pressure points are far apart, then the pump must be primed.

11.5 Prime the pump using the procedure described below.

11.5.1 On the GP50 screen, change the pressure limit to 0. Set the instrument to use 100% of eluent A. Open up the pressure transducer on the pump. This is very important – the instrument may be damaged if the transducer head is not open when the pump is being primed.

11.5.2 Put the syringe in the priming valve, open the syringe port, and hit prime. Liquid will slowly be pushed out into the syringe. Let 10 ml of liquid collect in the syringe. Turn the prime off, tighten the syringe port, and close the transducer head. The pressure should climb back up.

11.5.3 Allow the instrument conditions to settle and then check the pressure statistics in the diagnostics menu again. If there is still a problem, the priming procedure may be repeated using isopropyl alcohol. If alcohol is used, push the IPA through the pump without the prime on and then turn the pump on and push the liquid out for several minutes. Make sure that the transducer is open so that the IPA does not go into the column and suppressor.

11.5.4 If using two eluent bottles, then repeat the above procedure using 100% of eluent B. Note: The pump must be primed for each eluent bottle used.

11.6 Set the flow rate of the eluent pump to 1.5 ml/min and adjust the pressure of the reagent delivery system so that the final flow rate from the detector is 2.0 ml/min. Normally the pressure required for this flow rate is approximately 40 psi. The flow must be checked from the wastelline that is downstream from the AD25 detector with a graduated cylinder and a stop watch after it is initially set and again after the instrument has warmed up for approximately 30 minutes. The flow rate must always be verified prior to calibration and sample analysis.

11.7 Once the pump is ready to go, set up a schedule in the software. Refer to the instrument manuals or help screens in the program for help in using the software. Note: a method is required for each analysis. If a new method is required, check with the area supervisor or manager for additional help. A new method is required each time the instrument is recalibrated as the calibration is stored in the method.

11.8 The digestates are normally analyzed undiluted on the DX500 and ICS3000 instrumentation, but some difficult matrices may require dilution before analysis. If dilution is required, it must be done with dilution water (Section 9.16) and the dilution factor must be entered into the autosampler tables.

11.8.1 Digestates which are black or viscous may need to be started on dilution. Check with supervisory staff for further guidance.

11.9 Load the autosampler and turn it on. The autosampler must then move to the first sample. A manual run log or a printout of the instrument schedule must be generated to show the order that the samples are loaded into the autosampler.

11.10 Load the schedule in the software and start the run. Make sure that all results are being printed so that the problems can be easily identified while the run is going.

11.10.1 Data files on the DX500 must be saved using the naming scheme of year, month, day, run number followed by the extension of .ic. For example, the second IC run on October 11, 2006 would be named 06101102.ic. This name must always be used in the workgroup description in the LIMS system. Data files on the ICS3000 must be saved using the naming scheme of instrument number, year, month, day, and run number followed by the extension of txt. For example, the second IC run on 4/24/07 on the ICS3000 (instrument 6), would be named 607042402.txt.

11.10.2 For this method, a daily calibration is required. The calibration must consist of a minimum of 3 standards and a blank and must not cover more than 2 orders of magnitude. Calibrations standards may be varied from the ones stated in this SOP depending on the levels of hexavalent chromium that are to be reported. A low standard must be at or below 0.010 mg/l for soil analysis for hexavalent chromium. (0.005 mg/l is the normal low standard). A correlation coefficient of 0.999 is required. If this correlation coefficient is not met, than the instrument must be recalibrated.

11.10.3 After the calibration, the continuing calibration verification check standard (CCV) and a continuing calibration blank (CCB) must be run. The CCV must be from a separate source than the calibration curve and must have recoveries within a range of 90 to 110 percent.

The CCB must have results of less than the reporting limit. If either of these QC points does not meet criteria, then all samples bracketed by this quality control must be reanalyzed. The exception is if there is a high bias in the CCV check and the associated sample results are less than the reporting limit.

11.10.4 After the CCV, CCB pair, then begin analyzing the samples and run QC. All samples as associated quality control (method blanks, spike blanks, matrix spikes, duplicate) must be analyzed in duplicate. The RSD between each duplicate must be checked and be within 20% or within ± reporting limit for hexavalent chromium. If this criteria is not met, then reanalyze the affected sample in duplicate.

11.10.4.1 Duplicate analyses are not required for the calibration curve or CCV and CCB checks.

11.10.4.2 Report the highest value from the two duplicate injections for each sample.

11.10.5 After every 10 samples (or every 20 injections of samples in duplicate) the CCV and CCB checks must be run. The continuing calibration checks must have recoveries in the range of 90 to 110 percent. If the CCV or CCB fails to meet criteria, then all samples bracketed by the out of compliant QC should be rerun if possible.

11.10.5.1 Note: If the hexavalent chromium samples are close to holding time, then a single injection of each sample may be run to meet holding time criteria. If single sample injections are done, then run a CCV, CCB after every 10 single injections. The duplicate injections for each sample are still required and must be run as soon as possible after the completion of the initial injections. This is not normally an issue for hexavalent chromium soil digests.

11.10.6 After the quality control sample analysis is completed, prepare a post-digest spike on this sample. The sample must be spiked at 2 times the concentration found in the original sample aliquot or 40 mg Cr(VI)/kg, whichever is greater.

11.10.6.1 The 40 mg/kg spike can be made by spiking a 20 ml aliquot of digestate containing 0.50 g of digested sample with 0.20 ml of 100 mg/l Cr(VI) standard (Section 9.10).

11.10.7 After the run is completed, review all of the chromatograms and check for interferences, dilutions, etc.

11.10.8 For large or overlapping peaks, make dilutions using the digestate dilution solution. If the samples were originally run undiluted, use digestion dilution solution A for dilutions. If the standards and samples were originally run with a factor of 2 dilution, then they must be diluted with digestion dilution solution B (section 9.17).

11.11 If no additional batches are to be analyzed on the instrument, then the instrument must be shut down by running the stop method, which switches the eluent over to DI water on the DX-500. On the ICS3000, the eluent must be switched to DI water manually. The lines must not be left filled with the alkaline eluent.

11.12 Review all data and update the appropriate tests in the LIMS system. A write-up including a run log,

a calibration summary, batch quality control summary, and copies of all chromatograms must be turned into the area supervisor for each batch.

11.12.1 If edits are needed in the calibration after the data has been calculated, the run can be reprocessed using the batch function in the software. Refer to the instrument manuals or on-screen help for addition information.

11.12.2 If manual integrations are needed for any reason, then all requirements from the manual integration SOP, EQA044, must be followed.

11.12.3 Calculations are done using the equations shown below. Sample concentration calculations are automated in the LIMS system. Sample values less than the MDL are treated as zero in all calculations

11.12.3.1 Calculation of the sample result (automated calculation).

$$\text{Conc. Cr(VI) in the sample in mg/kg} = \frac{(\text{conc. in digestate in ug/ml}) \times (\text{final volume in ml}) \times \text{DF}}{(\text{initial sample weight in g}) \times (\%\text{solids}/100)}$$

11.12.3.2 Calculation of amount spiked.

$$\text{Spike amount (SA) in mg/kg} = \frac{(\text{conc. of spiking solution, ug/ml}) \times (\text{vol. of spike, ml})}{(\text{initial sample weight in g}) \times (\%\text{solids}/100)}$$

11.12.3.3 Calculation of matrix spike recovery

$$\text{Percent recovery} = \frac{(SSR - SR) \times 100}{SA}$$

where SSR = Spiked sample result
SR = Sample result
SA = Spike added

11.12.3.4 Calculation of CCV recovery.

$$\text{Percent recovery} = \frac{\text{CCV result} \times 100}{\text{True Value}}$$

11.12.3.5 Calculation of RPD.

$$\text{Dup RPD.} = \frac{(SR - DR) \times 100}{\{(SR + DR)/2\}}$$

where SR = Sample result and

DR = Duplicate result.

12.0 ION CHROMATOGRAPHY ANALYSIS PROCEDURE FOR THE DIONEX ICS5000.

12.1 Fill the eluent bottle(s) that are to be used with eluent. Fill the reagent delivery bottle with post-column reagent.

12.1.1 The eluent must be filtered through a 0.45 um filter before use.

12.2 Prime the pump using the procedure described below.

12.2.1 Go to the instrument tab in Chromeleon and open the prime valves for both pump 1 and 2 and then hit the prime button. Do the eluent pump first and then the color pump

12.2.2 Allow the instrument conditions to settle and then check the pressure statistics in the diagnostics menu again. If there is still a problem, the priming procedure may be repeated. When completed, make sure to close the prime valves.

12.3 Set the flow rate of the eluent pump to 1.5 ml/min and set the flow for the color pump to 0.5 ml/min. The final flow rate from the detector is 2.0 ml/min. Make sure that the pressure is steady.

12.4 Once the pump is ready to go, set up a schedule in the software. Click on the data tab to go to the screen needed for the schedule. Refer to the instrument manuals or help screens in the program for help in using the software. Note: a method is required for each analysis. If a new method is required, check with the area supervisor or manager for additional help. A new method is required each time the instrument is recalibrated as the calibration is stored in the method.

12.5 The digestates are normally analyzed undiluted on the ICS5000 and ICS3000 instrumentation, but some difficult matrices may require dilution before analysis. If dilution is required, it must be done with dilution water (Section 9.16) and the dilution factor must be entered into the autosampler tables.

12.5.1 Digestates which are black or viscous may need to be started on dilution. Check with supervisory staff for further guidance.

12.6 Load the autosampler and turn it on. The autosampler must then move to the first sample. A manual run log or a printout of the instrument schedule must be generated to show the order that the samples are loaded into the autosampler.

12.7 Load the schedule in the software and start the run. .

12.7.1 Data files on the ICS5000 must be saved using the naming scheme of instrument number, year, month, day, and run number followed by the extension of txt. For example, the second IC run on 6/29/11 on the ICS5000 (instrument 8), would be named 811062902.txt. This name must always be used in the workgroup description in the LIMS system

12.7.2 For this method, a daily calibration is required. The calibration must consist of a minimum of 3 standards and a blank and must not cover more than 2 orders of magnitude. Calibrations standards may be varied from the ones stated in this SOP depending on the levels of

hexavalent chromium that are to be reported. A low standard must be at or below 0.010 mg/l for soil analysis for hexavalent chromium. (0.005 mg/l is the normal low standard.) A correlation coefficient of 0.999 is required. If this correlation coefficient is not met, than the instrument must be recalibrated.

12.7.3 After the calibration, the continuing calibration verification check standard (CCV) and a continuing calibration blank (CCB) must be run. The CCV must be from a separate source than the calibration curve and must have recoveries within a range of 90 to 110 percent. The CCB must have results of less than the reporting limit. If either of these QC points does not meet criteria, then all samples bracketed by this quality control must be reanalyzed. The exception is if there is a high bias in the CCV check and the associated sample results are less than the reporting limit.

12.7.3.1 Note: If the run will finish when there is no analyst present to monitor it, then it must be set up to run the smart standby. This is done by going to the instrument tab and under queue, select run smart standby.

12.7.4 After the CCV, CCB pair, then begin analyzing the samples and run QC. All samples as associated quality control (method blanks, spike blanks, matrix spikes, duplicate) must be analyzed in duplicate. The RSD between each duplicate must be checked and be within 20% or within $\pm$ reporting limit for hexavalent chromium. If this criteria is not met, then reanalyze the affected sample in duplicate.

12.7.4.1 Duplicate analyses are not required for the calibration curve or CCV and CCB checks.

12.7.4.2 Report the highest value from the two duplicate injections for each sample.

12.7.5 After every 10 samples (or every 20 injections of samples in duplicate) the CCV and CCB checks must be run. The continuing calibration checks must have recoveries in the range of 90 to 110 percent. If the CCV or CCB fails to meet criteria, then all samples bracketed by the out of compliant QC should be rerun if possible.

12.7.5.1 Note: If the hexavalent chromium samples are close to holding time, then a single injection of each sample may be run to meet holding time criteria. If single sample injections are done, then run a CCV, CCB after every 10 single injections. The duplicate injections for each sample are still required and must be run as soon as possible after the completion of the initial injections. This is not normally an issue for hexavalent chromium soil digests.

12.7.6 After the quality control sample analysis is completed, prepare a post-digest spike on this sample. The sample must be spiked at 2 times the concentration found in the original sample aliquot or 40 mg Cr(VI)/kg, whichever is greater.

12.7.6.1 The 40 mg/kg spike can be made by spiking a 20 ml aliquot of digestate containing 0.50 g of digested sample with 0.20 ml of 100 mg/l Cr(VI) standard (Section 9.10).

12.7.7 After the run is completed, review all of the chromatograms and check for interferences, dilutions, etc.

12.7.8 For large or overlapping peaks, make dilutions using the digestate dilution solution. If the samples were originally run undiluted, use digestion dilution solution A for dilutions. If the standards and samples were originally run with a factor of 2 dilution, then they must be diluted with digestion dilution solution B (section 9.17).

12.8 To shut down the instrument, manually switch the eluent to DI water and completely shut off the color pump. Change the eluent flow rate to 0.3 ml/min.

12.9 Review all data and update the appropriate tests in the LIMS system. A write-up including a run log, a calibration summary, batch quality control summary, and copies of all chromatograms must be turned into the area supervisor for each batch.

12.9.1 If edits are needed in the calibration after the data has been calculated, the run can be reprocessed using the batch function in the software. Refer to the instrument manuals or on-screen help for addition information.

12.9.2 If manual integrations are needed for any reason, then all requirements from the manual integration SOP, EQA044, must be followed.

12.9.3 Calculations are done using the equations shown below. Sample concentration calculations are automated in the LIMS system. Sample values less than the MDL are treated as zero in all calculations.

12.9.3.1 Calculation of the sample result (automated calculation).

$$\text{Conc. Cr(VI) in the sample in mg/kg} = \frac{(\text{conc. in digestate in ug/ml}) \times (\text{final volume in ml}) \times \text{DF}}{(\text{initial sample weight in g}) \times (\%\text{solids}/100)}$$

12.9.3.2 Calculation of amount spiked.

$$\text{Spike amount (SA) in mg/kg} = \frac{(\text{conc. of spiking solution, ug/ml}) \times (\text{vol. of spike, ml})}{(\text{initial sample weight in g}) \times (\%\text{solids}/100)}$$

12.9.3.3 Calculation of matrix spike recovery

$$\text{Percent recovery} = \frac{(SSR - SR) \times 100}{SA}$$

where SSR = Spiked sample result
SR = Sample result
SA = Spike added

12.9.3.4 Calculation of CCV recovery.

$$\text{Percent recovery} = \frac{\text{CCV result} \times 100}{\text{True Value}}$$

12.9.3.5 Calculation of RPD.

$$\text{Dup RPD.} = \frac{(SR - DR) \times 100}{\{(SR + DR)/2\}}$$

where SR = Sample result and
DR = Duplicate result.

13.0 ION CHROMATOGRAPHY ANALYSIS PROCEDURE FOR THE METROHM.

13.1 Fill the eluent bottle(s) that are to be used with degassed eluent. Attach drying tube and put on system. Fill the reagent delivery bottle with post-column reagent. Fill the large plastic bottles on the autosampler with DI water.

13.1.1 The eluent must be filtered through a 0.45 um filter before use.

13.1.2 Make sure that the in-line autosampler filter is changed approximately once per day or every 100 injections. If you are going to be running hold-time critical waters, then the filter must be changed before the calibration to prevent possible problems during the run.

13.1.3 The guard disc must normally be changed every 300 to 400 injections. Check and change the guard disc before starting up the instrument if necessary.

13.2 Start up the instrument by first opening the ICNET software.

13.2.1 Open the CR6 icon first and then, when the hardware window opens, you can change properties as needed by double clicking on each hardware picture.

13.2.2 Go to control and select “start-up hardware”. Then select “measure baseline from the dropdown window. The instrument hardware will start and the baseline measuring window will open. To view the pressure and temperature of the 844 (main) unit and the 818 (reagent addition) unit, double click on the monitor icon. The column temperature must be preset to 30 deg. C and the pressure must be approximately 2100 psi for the 844 unit and 160 psi for the 818 unit. The flow rate for the eluent pump must be 1.0 ml/min and the flow rate for the PCR pump must be 0.5 ml/min.

13.2.3 Let the system equilibrate for approximately 30 minutes.

13.3 If the instrument lines did not run dry, then priming the pump should not be needed. If the lines were dry, then prime the pump using the procedure described below.

13.3.1 Open up the pressure transducer knob which can be found on the box wall of the 844 box, right beneath the pump head and behind the column box. This is very important – the instrument may be damaged if the transducer head is not open when the pump is being primed.

13.3.2 Attach the syringe to the left port on outside (front) of the 844 unit. Pull air through the syringe until eluent starts flowing steadily into the syringe and then wait for several minutes.

13.3.3 Remove the syringe and close the knob on the pressure transducer.

13.4 If any system changes have been made in the start-up process, then the top (blue) line of the CR6 window will have an asterisk after "Cr6.smt". Go to "system" and choose "save" to save the new information.

13.5 Next open the MagIC Net Software. There will be 5 large icons on the left of the screen.

13.5.1 The "configuration" icon shows devices, columns, eluents, and solutions used. These are all preset.

13.5.2 The "manual" icon is for manual injections and will not normally be used.

13.5.3 The "method" icon contains the methods that have been developed to run soil and water matrices. New methods can also be set up using this icon, but this will not normally have to be done.

13.5.4 The "workplace" icon is where autosampler schedules can be set-up before starting a run.

13.5.5 The "database" icon is where the data processing and reporting is done.

13.6 Go to the "workplace" icon. Set up the schedule in the "run" window. When setting up the schedule, the following information must be entered: sample ID under IDENT, dilution factor, and autosampler position. Name the schedule using the naming convention of instrument number, year, month, day, and run number. For example, the second IC run on 4/24/07 on the Metrohm (instrument 7), would be named 707042402. Make sure to save the schedule after it is completed.

13.6.1 Note: when the in-line filter is being used, a separate autosampler tube will be needed for each injection.

13.6.2 The autosampler is random access so samples do not have to be set up in the order that they are going to be run in the schedule.

13.7 The digestion solution matrix in the samples and standards can cause salting and clogging in the instrumentation and, on this instrument, often results in poor peak shape. To minimize these problems, the initial analysis of the samples and standards must be done by diluting the standards and samples by a factor of 2 with dilution water (Section 8.16). This dilution will minimize interferences while retaining a low detection limit. Make sure to enter this dilution factor of 2 in the autosampler tables.

13.8 Load the autosampler and run the sample table test under the sample table option to make sure that the file is correct. Then start the run. A manual run log or a printout of the instrument schedule must be generated to show the order that the samples are loaded into the autosampler.

13.8.1 For this method, a daily calibration is required. The calibration must consist of a minimum of 3 standards and a blank and must not cover more than 2 orders of magnitude. Calibrations standards may be varied from the ones stated in this SOP depending on the levels of hexavalent chromium that are to be reported. A low standard must be at or below 0.010 mg/l for soil analysis for hexavalent chromium. (0.005 mg/l is the normal low standard). A correlation coefficient of 0.999 is required. If this correlation coefficient is not met, than the instrument must be recalibrated.

13.8.2 After the calibration, the continuing calibration verification check standard (CCV) and a continuing calibration blank (CCB) must be run. The CCV must be from a separate source than the calibration curve and must have recoveries within a range of 90 to 110 percent. The CCB must have results of less than the reporting limit. If either of these QC points does not meet criteria, then all samples bracketed by this quality control must be reanalyzed. The exception is if there is a high bias in the CCV check and the associated sample results are less than the reporting limit.

13.8.3 After the CCV, CCB pair, then begin analyzing the samples and run QC. All samples as associated quality control (method blanks, spike blanks, matrix spikes, duplicate) must be analyzed in duplicate. The RSD between each duplicate must be checked and be within 20% or within $\pm$ reporting limit for hexavalent chromium. If this criteria is not met, then reanalyze the affected sample in duplicate.

13.8.3.1 Duplicate analyses are not required for the calibration curve or CCV and CCB checks.

13.8.3.2 Report the highest value from the two duplicate injections for each sample.

13.8.4 After every 10 samples (or every 20 injections of samples in duplicate) the CCV and CCB checks must be run. The continuing calibration checks must have recoveries in the range of 90 to 110 percent. If the CCV or CCB fails to meet criteria, then all samples bracketed by the out of compliant QC should be rerun if possible.

13.8.4.1 Note: If the hexavalent chromium samples are close to holding time, then a single injection of each sample may be run to meet holding time criteria. If single sample injections are done, then run a CCV, CCB after every 10 single injections. The duplicate injections for each sample are still required and must be run as soon as possible after the completion of the initial injections. This is not normally an issue for hexavalent chromium soil digests.

13.8.5 After the quality control sample analysis is completed, prepare a post-digest spike on this sample. The sample must be spiked at 2 times the concentration found in the original sample aliquot or 40 mg Cr(VI)/kg, whichever is greater.

13.8.5.1 The 40 mg/kg spike can be made by spiking a 20 ml aliquot of digestate containing 0.50 g of digested sample with 0.20 ml of 100 mg/l Cr(VI) standard (Section 9.10).

13.8.6 After the run is completed, review all of the chromatograms and check for interferences, dilutions, etc.

13.8.7 For large or overlapping peaks, make dilutions using the digestate dilution solution. If the samples were originally run undiluted, use digestion dilution solution A for dilutions. If the standards and samples were originally run with a factor of 2 dilution, then they must be diluted with digestion dilution solution B (section 9.17).

13.9 If no additional batches are to be analyzed on the instrument, then the instrument must be switched over to DI Water. For short periods of time (< 1 week), the eluent may be left in the column. For longer periods of time, put a 1:10 dilution of eluent into the column and cap both ends. To switch all other lines in the instrument to DI water, change the connections so that the column is off line. Then fill the eluent and PCR bottles with DI waters and set the flow rate to 0.5 ml/min for the eluent. Pump DI water through the system for at least 15 minutes.

13.10 Review all data and update the appropriate tests in the LIMS system. A write-up including a run log, a calibration summary, batch quality control summary, and copies of all chromatograms must be turned into the area supervisor for each batch.

13.10.1 If edits are needed in the data, select the samples and go the reprocessing menu. Make the appropriate changes and then update and reprocess the data. Generate the export file as described below. Go to Tools, Template and SOEXPORT. Edit the file name to the correct name (as outlined in 12.6 above) and hit OK. Then go to Determinations, export, and SOEXPORT. The csv file will be saved on the general chemistry network drive under the Metrohm folder.

13.10.2 If manual integrations are needed for any reason, then all requirements from the manual integration SOP, EQA044, must be followed.

13.11 Calculations are done using the equations summarized in 11.12.3.

13.11.1 **The actual value for the NIST lab control must be manually corrected in LIMS for the % solids correction.**

14.0 INSTRUMENT MAINTENANCE FOR THE DIONEX ICS5000 and the DIONEX ICS2000.

14.1 The digestion solution can cause problems with clogging and leaking of the system. Putting a 100 mM HCl rinse through the system helps remove the alkaline salts. Fill the autosampler tubes with 100 mM HCl rinse and put the cap in the rinse position. After the rinse is complete, also run a DI water rinse. It is recommended that this rinse procedure be done after every run.

14.2 Periodically, due to the matrix of samples, both guard and analytical columns become degraded and cleaning them becomes necessary. This is evidenced in changing retention times, round-shaped peaks, tailing peaks and overall poor integration. Column clean-ups must be done on an as needed basis. There are 3 recommended cleanup solutions for the NG1 and AS7 columns.

14.2.1 Metal contamination column clean-up: Use 500 ml of 0.1M oxalic acid solution.

14.2.2 Low valency hydrophilic ionic contamination column clean-up. Use 500 ml of 10X eluent concentrate.

14.2.3 High valency hydrophobic ion 200 mM HCl in 5% acetonitrile: The acetonitrile solution is stored in a separate eluent bottle because acetonitrile slowly breaks down in acidic aqueous solutions. Prepare 2 bottles (E1 and E2) with the following 500-mL solutions: E1: 5% Acetonitrile and E2: 200 mM HCl using DI water.

14.2.4 Column Clean-up Procedure.

14.2.4.1 Prepare 500 mL solution of the appropriate cleanup solution from 12.1

14.2.4.2 Reverse the order of the guard and analytical column in the eluent flow path. Contaminants that have accumulated on the guard column can be eluted onto the analytical column and irreversibly damage it. If in doubt, clean each column separately. Double check that the eluent flows in the direction designated on each of the column labels.

14.2.4.3 Set the pump flow rate to 0.5 mL/min for an AS7 analytical and NG1 guard column.

14.2.4.4 Rinse the column for 15 minutes with DI water before pumping the chosen cleanup solution over the columns.

14.2.4.5 Pump the cleanup solution through the column for at least 60 minutes.

14.2.4.6 If using the 200 mM HCl in 5% acetonitrile, use a gradien to introduce the clean-up solution into the columns. (i.e. – gradually increase the concentration until you are at the full solution concentration. After clean-up, also gradually decrease the concentration.)

14.2.4.7 Rinse the column for 15 minutes with DI water before pumping eluent over the column.

14.2.4.8 Equilibrate the columns with eluent before resuming normal operation for at least 30 minutes.

14.2.4.9 Reconnect analytical and guard columns in the normal run configuration.

15.0INSTRUMENT MAINTENANCE FOR THE METROHM

15.1Change the in-line filter every 100 injections. If running holding time critical samples, make sure to change the filter before starting the run.

15.2Change the column guard frit every 300 to 400 injections

15.3Change the pump seals as needed, when leaking or pressure problems are observed.

15.4The digestion solution can cause problems with clogging and leaking of the system. Putting a 100 mM HCl rinse through the system helps remove the alkaline salts. Fill the autosampler tubes with 100 mM HCl rinse. Take the column and the guard frit off line and pump through the HCl rinse and a DI water rinse. It is recommended that this rinse procedure be done after every run.

15.5 Periodically, due to the matrix of samples, the analytical columns become degraded and cleaning them becomes necessary. This is evidenced in changing retention times, round-shaped peaks, tailing peaks and overall poor integration. Column clean-ups must be done on an as needed basis following the recommendations in the Metrohm column documentation. If the column cannot be adequately cleaned, then it may need to be replaced.

16.0 QC REQUIREMENTS

16.1 Analyze a new calibration curve, at a minimum, on each analysis day. The curve must be made up of a minimum of 3 points and a blank, but more standards may be run if needed. The calibration curve is required to have a correlation coefficient greater than or equal to 0.999.

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where r = correlation coefficient
x = amount of analyte
y = response of instrument
$\bar{x}$ = average of x values
$\bar{y}$ = average of y values

16.2 Initially analyze all samples either undiluted or at a low (normally a factor of 2) dilution. (This low dilution is done to minimize the impact of the digestion solution matrix on the system.) If the sample concentration is higher than the highest standard, then reanalyze the sample as a (larger) dilution. Prepare the dilution so that the sample is in the mid-range of the calibration curve. Each sample must be analyzed with at least two duplicate injections and the RSD between the two injections must be less than 20% or the results must be within a window of plus or minus the detection limit from each other. The duplicate injections should normally be run concurrently, but may be run sequentially if needed to meet holding time requirements. The higher of the two replicate injections must be reported. If the replicate injections do not meet the RSD criteria stated above, then analysis must be repeated with additional replicate injections.

16.3 One preparation blank is required for each set of 20 samples or less or with each batch. The preparation blank is required to contain all the reagents in the same volumes as used in the preparation of the samples. The preparation blank is required to be less than the RL. If it is over the RL, correct the problem and restart the analysis if this is possible within holding time. If it will be outside of holding time, then complete the initial analysis within holding time and check with the area supervisor for further instructions.

16.4 A soluble spike blank and a solid lab control sample must be prepared and analyzed for each set of 20 samples of a similar matrix or with each batch, whichever is smaller.

16.4.1 A spike blank prepared using soluble hexavalent chromium as the spike is required. If the spike blank is not within the acceptance range, then the entire batch must be redigested and reanalyzed. The acceptance range for the soluble spike blank is 80 to 120 percent recovery.

16.4.2 A solid lab control has been obtained from NIST; however an alternate commercial supplier may be utilized if not available from NIST. When using the NIST lab control, a solid lead chromate lab control must also be prepared.

16.4.2.1 For the NIST SRM 2701, the certified value is 551.2 mg/kg +/- 34, when corrected for %solids. The Certificate of Analysis for this SRM does not provide a certified acceptance range for EPA Method 7199; however Appendix A 2 references an observed range of 270 mg/kg to 557 mg/kg. Until such time that a certified range is available for this SRM for this method, the laboratory shall utilize in-house limits developed from a minimum of 20 data points. The in-house acceptance criteria must be equal to or tighter than the observed data referenced in Table A2 in the Certificate of Analysis for the SRM.

16.4.2.2 A solid lead chromate lab control is also required when running SRM 2701. The acceptance range for the solid lead chromate lab control is 80 to 120% of the true value.

16.4.2.3 If either the NIST SRM 2701 or the lead chromate lab control are outside of the ranges indicated in Section 15.4.2.1 and 15.4.2.2, then the entire batch must be redigested and reanalyzed.

16.5 After every 10 samples, every 20 readings (10 samples with duplicate injections) and at the end of the sample analysis sequence a mid-level calibration check (CCV) and a calibration blank (CCB) must be analyzed. Prepare the mid-point calibration check from a different stock than the calibration curve. This calibration check standard must also be analyzed at the beginning of the analysis immediately after the calibration curve. The acceptance criteria for the mid-range calibration check standard is 90 – 110% of the true value of the standard. If the CCV fails this criteria, correct the problem and then reanalyze all samples in the area bracketed by the non-compliant CCV. The acceptance criteria for the CCB is less than the reporting limit. If the CCB fails this criteria, correct the problem and then reanalyze all samples in the area bracketed by the non-compliant CCB.

16.6 A duplicate sample must be prepared and analyzed for each set of 20 samples of a similar matrix or with each batch, whichever is smaller. An acceptance criteria of 20 percent relative percent difference must be applied if the original and duplicate sample values are greater than or equal to 4 times the reporting detection limit. If the values are less than 4 times the reporting detection limit, then a control limit of $\pm$ the reporting detection limit must be applied.

16.7 Both a soluble and an insoluble hexavalent chromium matrix spike must be prepared and analyzed for each set of 20 samples of a similar matrix or with each batch, whichever is smaller. The acceptance range for matrix spike recoveries is 75 to 125 percent recovery. If the matrix spike recoveries for either the soluble or the insoluble spikes are not within these recovery limits, then the lab supervisor or manager must be immediately notified. The client services department will then be notified to contact

the client. The method requires additional testing as listed below, but the lab must not proceed with this testing until client approval is obtained and the testing is logged into the LIMS system.

16.7.1 All samples and quality control must be rehomogenized, redigested and reanalyzed to verify the original sample results.

16.7.2 Additional tests, such as oxidation-reduction potential, pH, sulfide, ferrous iron, etc., may be requested to help quantify the reducing nature of the sample. For some projects, eH and pH analysis may be specified for all samples at the start of the project.

16.7.3 A mass balance study for total chromium may be done, using the digested solids remaining after the alkaline digestion and filtration of the matrix spike and from an unspiked aliquot of the sample.

16.8 A post-digest spike must be prepared and analyzed for each set of 20 samples of a similar matrix or with each batch, whichever is smaller. The post-spike must be spiked at 40 mg/kg or twice the level in the sample, whichever is greater. The acceptance range for post digest spike recoveries is 85 to 115 percent recovery. No additional action is necessary if the post-digest spike is outside of this recovery range.

16.9 Retention Time Windows. Because the hexavalent chromium is separated in the column and then colorimetrically reacted before detection, retention time identification is not as critical as with other ion chromatographic methods. However, a significant shift in retention time may point to analytical problems. Therefore, the hexavalent chromium peak must be within a reasonable retention time window to be considered valid. A criterion of 5% is normally applied. However, sample concentration and matrix can greatly affect retention time and the experience of the analyst and reviewer must weigh heavily in the interpretation of a chromatogram. Values in a window of 10% can be accepted at the discretion of a senior reviewer. Values outside of the 10 % window cannot be reported unless that peak is confirmed with a post-digest spike.

17.0 DOCUMENTATION REQUIREMENTS

17.1 The analyst must document all relevant information, including all sample weights and volumes, digestion times and temperatures, all intermediate and final pH values, all times relevant to the pH adjustment process, all sample and background analysis results, and any relevant comments for any section of the digestion or analysis. Sample digestion and analysis sheets are provided. It is required that a second analyst sign off and verify that digestion times and temperatures and pH adjustment documentation is accurate and complete. All temperatures must be recorded with both the corrected and uncorrected values and the thermometer number used.

17.2 For the analysis, all reagent identification numbers must be recorded on the sample worksheets. In addition, all reagent information such as lot numbers must also be recorded in the reagent logbook.

18.0 DATA REVIEW AND REPORTING

18.1 All samples must be updated to GP and GN batches in the LIMS system. The analyst must calculate all matrix spike, duplicate, external, and CCV recoveries and review the results of all blanks. These calculations may be automated or manual.

18.2 All documentation must be completed, including reagent references and spike amounts and spiking solution references.

18.3 A data file must be exported to the LIMS system and the spike amounts must be entered into the file at the GNAPP process step.

18.4 A final data package, consisting of the prep and analysis raw data, the LIMS cover page, the reagent reference pages, and the QC summary pages must be turned into the area supervisor or other senior reviewer for review.

18.5 After review by the supervisor, the data is released in the LIMS for access to the clients.

18.6 Additional reviews are periodically done by the manager of the department for technical completeness. The raw data is then electronically filed in the report generation department.

19.0 POLLUTION PREVENTION & WASTE MANAGEMENT

19.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 18.2.

19.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

19.2.1 Non hazardous aqueous wastes

19.2.2 Hazardous aqueous wastes

19.2.3 Chlorinated organic solvents

19.2.4 Non-chlorinated organic solvents

19.2.5 Hazardous solid wastes

19.2.6 Non-hazardous solid wastes

20.0 ADDITIONAL REFERENCES

20.1 Refer to the DIONEX DX500 instrument manual or the DIONEX ICS3000 manual and the AS7 and NG1 column manuals.

20.2Refer to the Metrohm instrumentation manuals.

METHOD 9010C

TOTAL AND AMENABLE CYANIDE: DISTILLATION

1.0 SCOPE AND APPLICATION

1.1 This method is a reflux-distillation procedure used to extract soluble cyanide salts and many insoluble cyanide complexes from wastes and leachates. It is based on the decomposition of nearly all cyanides by a reflux distillation procedure using a strong acid and a magnesium catalyst. Cyanide, in the form of hydrocyanic acid (HCN) is purged from the sample and captured into an alkaline scrubber solution. The concentration of cyanide in the scrubber solution is then determined by Method 9014 or Method 9213. This method may be used as a reflux-distillation procedure for both total cyanide and cyanide amenable to chlorination. The "reactive" cyanide content of a waste is not determined by this method. Refer to 40 CFR 261.23 for information on the characteristic of reactivity.

1.2 This method was designed to address the problem of "trace" analyses (<1000 ppm). The method may also be used for "minor" (1000 ppm - 10,000 ppm) and "major" (>10,000 ppm) analyses by adapting the appropriate sample dilution. However, the amount of sodium hydroxide in the standards and the sample analyzed must be the same.

2.0 SUMMARY OF METHOD

2.1 The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide concentration in the absorbing solution is then determined colorimetrically or titrametrically by Method 9014 or by ion-selective electrode by Method 9213.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure. Chlorine and sulfide are interferences in Method 9010.

3.2 Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding an excess of sodium arsenite to the waste prior to preservation and storage of the sample to reduce the chlorine to chloride which does not interfere.

3.3 Sulfide interference can be removed by adding an excess of bismuth nitrate to the waste (to precipitate the sulfide) before distillation. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by the addition of bismuth nitrate.

3.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation. Nitrate and nitrite are interferences when present at levels higher than 10 mg/L and in conjunction with certain organic compounds.

3.5 Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/L were not found to interfere.

3.6 Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in high concentrations and may make the endpoint for the titrimetric determination difficult to detect. Refer to Sec. 6.7 for an extraction procedure to eliminate this interference.

4.0 APPARATUS AND MATERIALS

4.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of one liter size with inlet tube and provision for condenser. The gas scrubber may be a 270-mL Fisher-Milligan scrubber (Fisher, Part No. 07-513) or equivalent. The reflux apparatus may be a Wheaton 377160 distillation unit or equivalent.

4.2 Hot plate stirrer/heating mantle.

4.3 pH meter.

4.4 Amber light.

4.5 Vacuum source.

4.6 Refrigerator.

4.7 Erlenmeyer flask - 500 mL.

4.8 KI starch paper.

4.9 Class A volumetric flasks - 1000, 250, and 100 mL.

5.0 REAGENTS

5.1 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 on 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.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Reagents for sample collection, preservation, and handling

5.3.1 Sodium arsenite (0.1N), $NaAsO_2$. Dissolve 3.2 g of $NaAsO_2$ in 250 mL water.

5.3.2 Ascorbic acid, $C_6H_8O_6$.

5.3.3 Sodium hydroxide solution (50%), NaOH. Commercially available.

5.3.4 Acetic acid (1.6M) CH_3COOH. Dilute one part of concentrated acetic acid with 9 parts of water.

5.3.5 2,2,4-Trimethylpentane, C_8H_{18}.

5.3.6 Hexane, C_6H_{14}.

5.3.7 Chloroform, $CHCl_3$.

5.4 Reagents for cyanides amenable to chlorination

5.4.1 Calcium hypochlorite solution (0.35M), $Ca(OCl)_2$. Combine 5 g of calcium hypochlorite and 100 mL of water. Shake before using.

5.4.2 Sodium hydroxide solution (1.25N), NaOH. Dissolve 50 g of NaOH in 1 liter of water.

5.4.3 Sodium arsenite (O.1N). See Sec. 5.3.1.

5.4.4 Potassium iodide starch paper.

5.5 Reagents for distillation

5.5.1 Sodium hydroxide (1.25N). See Sec. 5.4.2.

5.5.2 Bismuth nitrate (0.062M), $Bi(NO)_3 \cdot 5H_2O$. Dissolve 30 g of $Bi(NO)_3 \cdot 5H_2O$ in 100 mL of water. While stirring, add 250 mL of glacial acetic acid, CH_3COOH. Stir until dissolved and dilute to 1 liter with water.

5.5.3 Sulfamic acid (0.4N), H_2NSO_3H. Dissolve 40 g of H_2NSO_3H in 1 liter of water.

5.5.4 Sulfuric acid (18N), H_2SO_4. Slowly and carefully add 500 mL of concentrated H_2SO_4 to 500 mL of water.

5.5.5 Magnesium chloride solution (2.5M), $MgCl_2 \cdot 6H_2O$. Dissolve 510 g of $MgCl_2 \cdot 6H_2O$ in 1 liter of water.

5.5.6 Lead acetate paper.

5.5.7 Stock potassium cyanide solutions -- Refer to Method 9014 for the preparation of stock cyanide solutions and calibration standards.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Samples should be collected in plastic or glass containers. All containers must be thoroughly cleaned and rinsed.

6.2 Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with potassium iodide-starch test paper. A blue color indicates the need for treatment. Add 0.1N sodium arsenite solution a few mL at a time until a drop of sample produces no color on the indicator paper. Add an additional 5 mL of sodium arsenite solution for each liter of sample. Ascorbic acid can be used

as an alternative although it is not as effective as arsenite. Add a few crystals of ascorbic acid at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

6.3 Aqueous samples must be preserved by adding 50% sodium hydroxide until the pH is greater than or equal to 12 at the time of collection.

6.4 Samples should be chilled to 4 EC.

6.5 When properly preserved, cyanide samples can be stored for up to 14 days prior to sample preparation steps.

6.6 Solid and oily wastes may be extracted prior to analysis by Method 9013. It uses a dilute NaOH solution (pH = 12) as the extractant. This yields extractable cyanide.

6.7 If fatty acids, detergents, and surfactants are a problem, they may be extracted using the following procedure. Acidify the sample with acetic acid (1.6M) to pH 6.0 to 7.0.

CAUTION: This procedure can produce lethal HCN gas.

Extract with isooctane, hexane, or chloroform (preference in order named) with solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the compounds below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with 50% NaOH solution.

7.0 PROCEDURE

7.1 Pretreatment for cyanides amenable to chlorination

7.1.1 This test must be performed under amber light. $K_3[Fe\text{-}(CN)_6]$ may decompose under UV light and hence will test positive for cyanide amenable to chlorination if exposed to fluorescent lighting or sunlight. Two identical sample aliquots are required to determine cyanides amenable to chlorination.

7.1.2 To one 500 mL sample or to a sample diluted to 500 mL, add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with 1.25N sodium hydroxide until an excess of chlorine is present as indicated by KI-starch paper turning blue. The sample will be subjected to alkaline chlorination by this step.

CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is necessary that this reaction be performed in a hood.

7.1.3 Test for excess chlorine with KI-starch paper and maintain this excess for one hour with continuous agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional calcium hypochlorite solution.

7.1.4 After one hour, add 1 mL portions of 0.1N sodium arsenite until KI-starch paper shows no residual chlorine. Add 5 mL of excess sodium arsenite to ensure the presence of excess reducing agent.

7.1.5 Analyze the total cyanide concentration of both the chlorinated and the unchlorinated samples by Method 9014 or 9213. The difference between the total cyanide concentration in the chlorinated and unchlorinated samples is equal to the cyanide amenable to chlorination.

7.2 Distillation procedure

7.2.1 Place 500 mL of sample, or sample diluted to 500 mL in the one liter boiling flask. Pipet 50 mL of 1.25N sodium hydroxide into the gas scrubber. If the apparatus in Figure 1 is used, add water until the spiral is covered. Connect the boiling flask, condenser, gas scrubber and vacuum trap.

7.2.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enter the boiling flask through the air inlet tube.

7.2.3 If samples are known or suspected to contain sulfide, add 50 mL of 0.062M bismuth nitrate solution through the air inlet tube. Mix for three minutes. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

7.2.4 If samples are known or suspected to contain nitrate or nitrite, or if bismuth nitrate was added to the sample, add 50 mL of 0.4N sulfamic acid solution through the air inlet tube. Mix for three minutes.

NOTE: Excessive use of sulfamic acid could create method bias.

7.2.5 Slowly add 50 mL of 18N sulfuric acid through the air inlet tube. Rinse the tube with water and allow the airflow to mix the flask contents for three minutes. Add 20 mL of 2.5M magnesium chloride through the air inlet and wash the inlet tube with a stream of water.

7.2.6 Heat the solution to boiling. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, and closing the vacuum source, disconnect the gas scrubber.

7.2.7 Transfer the solution from the scrubber into a 250-mL volumetric flask. Rinse the scrubber into the volumetric flask. Dilute to volume with water.

7.2.8 Proceed to the cyanide determinative methods given in Methods 9014 or 9213. If the distillates are not analyzed immediately, they should be stored at 4 EC in tightly sealed flasks.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one reagent blank per analytical batch or one in every 20 samples to determine if contamination or any memory effects are occurring.

8.3 Analyze check standards with every analytical batch of samples. If the standards are not within 15% of the expected value, then the samples must be reanalyzed.

8.4 Run one replicate sample for every 20 samples. A replicate sample is a sample brought through the entire sample preparation and analytical process. The CV of the replicates should be 20% or less. If this criterion is not met, the samples should be reanalyzed.

8.5 Run one matrix spiked sample every 20 samples to check the efficiency of sample distillation by adding cyanide from the working standard or intermediate standard to 500 mL of sample to ensure a concentration of approximately 40 µg/L. The matrix spiked sample is brought through the entire sample preparation and analytical process.

8.6 It is recommended that at least two standards (a high and a low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within ± 10% of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

8.7 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences such as samples which contain sulfides.

9.0 METHOD PERFORMANCE

9.1 The titration procedure using silver nitrate is used for measuring concentrations of cyanide exceeding 0.1 mg/L. The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

9.2 EPA Method 335.2 (sample distillation with titration) reports that in a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.06 to 0.62 mg/L CN^-, the standard deviations for precision were ± 0.005 to ± 0.094, respectively. In a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/L CN^-, recoveries (accuracy) were 85% and 102%, respectively.

9.3 In two additional studies using surface water, ground water, and landfill leachate samples, the titration procedure was further evaluated. The concentration range used in these studies was 0.5 to 10 mg/L cyanide. The detection limit was found to be 0.2 mg/L for both total and amenable cyanide determinations. The precision (CV) was 6.9 and 2.6 for total cyanide determinations and 18.6 and 9.1 for amenable cyanide determinations. The mean recoveries were 94% and 98.9% for total cyanide, and 86.7% and 97.4% for amenable cyanide.

10.0 REFERENCES

1. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ATSM: Philadelphia, PA, 1985,; D1193-77.

2. 1982 Annual Book ASTM Standards, Part 19; "Standard Test Methods for Cyanide in Water"; ASTM: Philadelphia, PA, 1982; 2036-82.

3. Bark, L.S.; Higson, H.G. Talanta 1964, 2, 471-479.

4. Britton, P.; Winter, J.; Kroner, R.C. "EPA Method Study 12, Cyanide in Water"; final report to the U.S. Environmental Protection Agency. National Technical Information Service: Springfield, VA, 1984; PB80-196674.

5. Casey, J.P.; Bright, J.W.; Helms, B.D. "Nitrosation Interference in Distillation Tests for Cyanide"; Gulf Coast Waste Disposal Authority: Houston, Texas.

6. Egekeze, J.O.; Oehne, F.W. J. Anal. Toxicology 1979, 3, 119.

7. Elly, C.T. J. Water Pollution Control Federation 1968, 40, 848-856.

8. Fuller, W. Cyanide in the Environment; Van Zyl, D., Ed.; Proceedings of Symposium; December, 1984.

9. Gottfried, G.J. "Precision, Accuracy, and MDL Statements for EPA Methods 9010, 9030, 9060, 7520, 7521,7550, 7551, 7910, and 7911"; final report to the U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory. Biospheric: Cincinnati, OH, 1984.

10. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

11. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

12. Standard Methods for the Examination of Water and Wastewater, 18th ed.; Greenberg, A.E.; Clesceri, L.S.; Eaton, A.D.; Eds.; American Water Works Association, Water Pollution Control Federation, American Public Health Association: Washington, DC, 1992.

13. Umaña, M.; Beach, J.; Sheldon, L. "Revisions to Method 9010"; final report to the U.S. Environmental Protection Agency. Office of Solid Waste. Research Triangle Institute: Research Triangle Park, NC, 1986.

14. Umaña, M.; Sheldon, L. "Interim Report: Literature Review"; interim report to the U.S. Environmental Protection Agency. Office of Solid Waste. Research Triangle Institute: Research Triangle Park, NC, 1986.

FIGURE 1.
APPARATUS FOR CYANIDE DISTILLATION

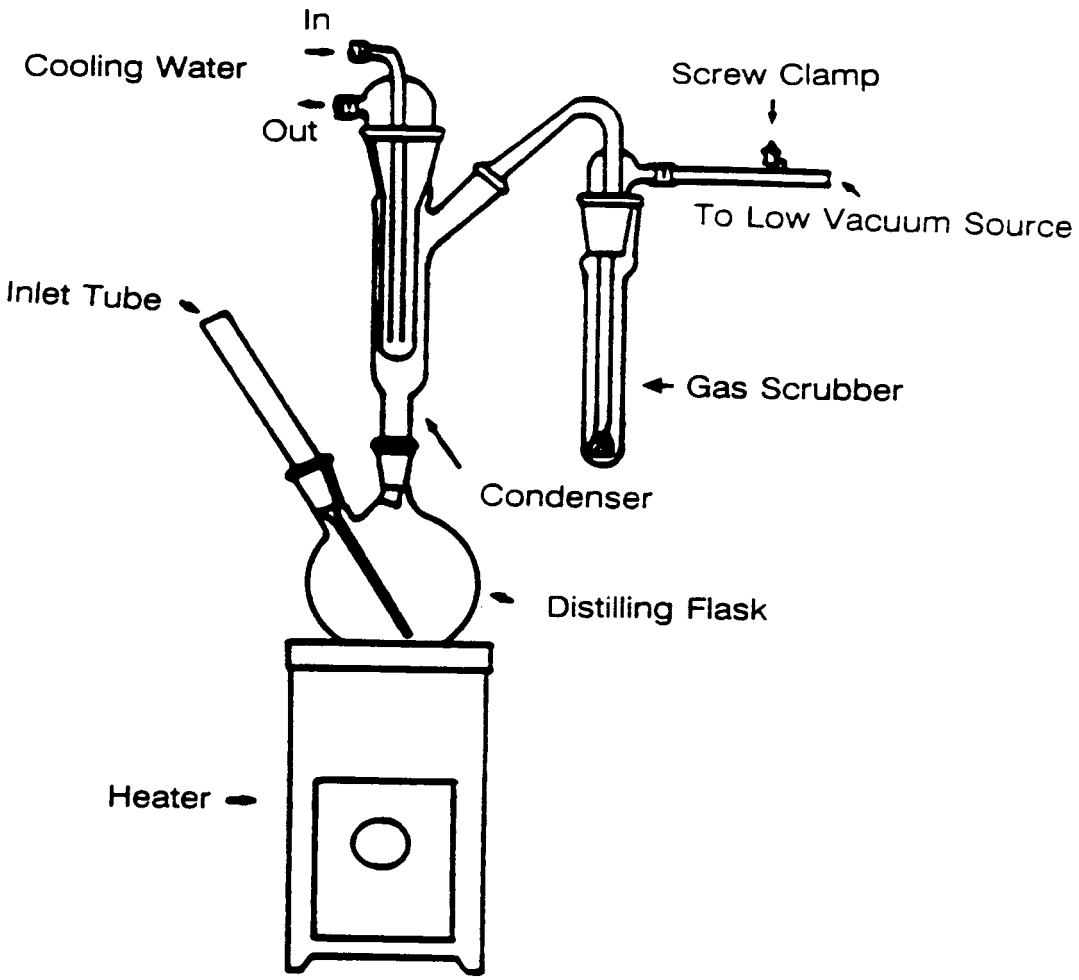
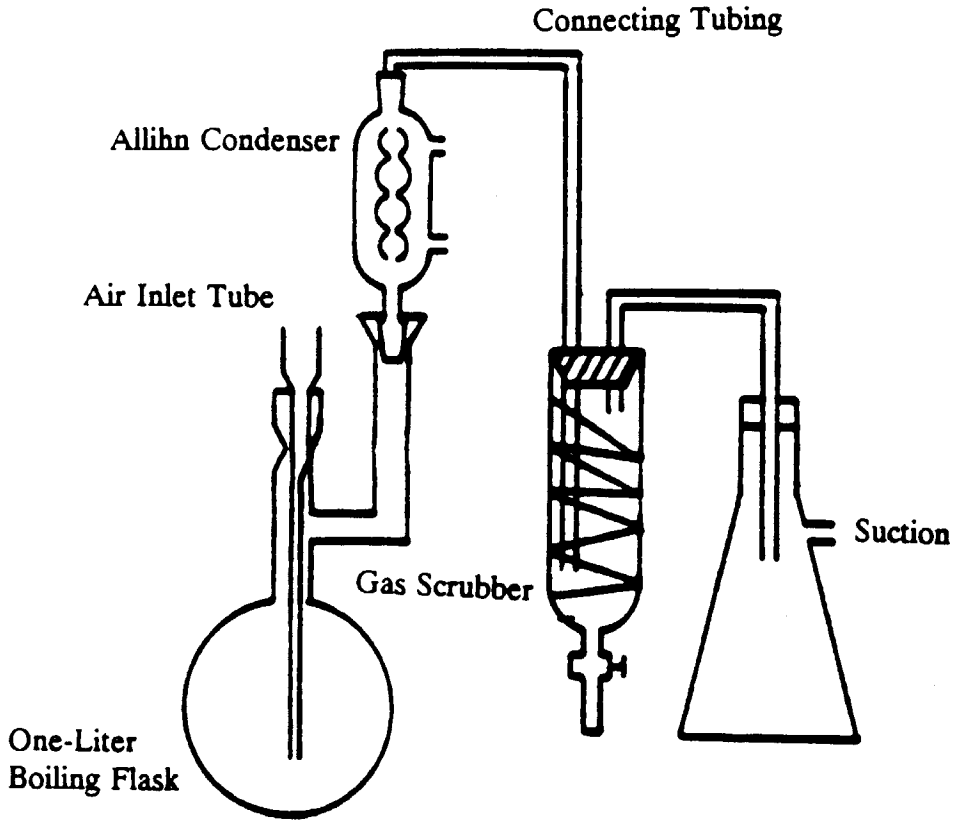
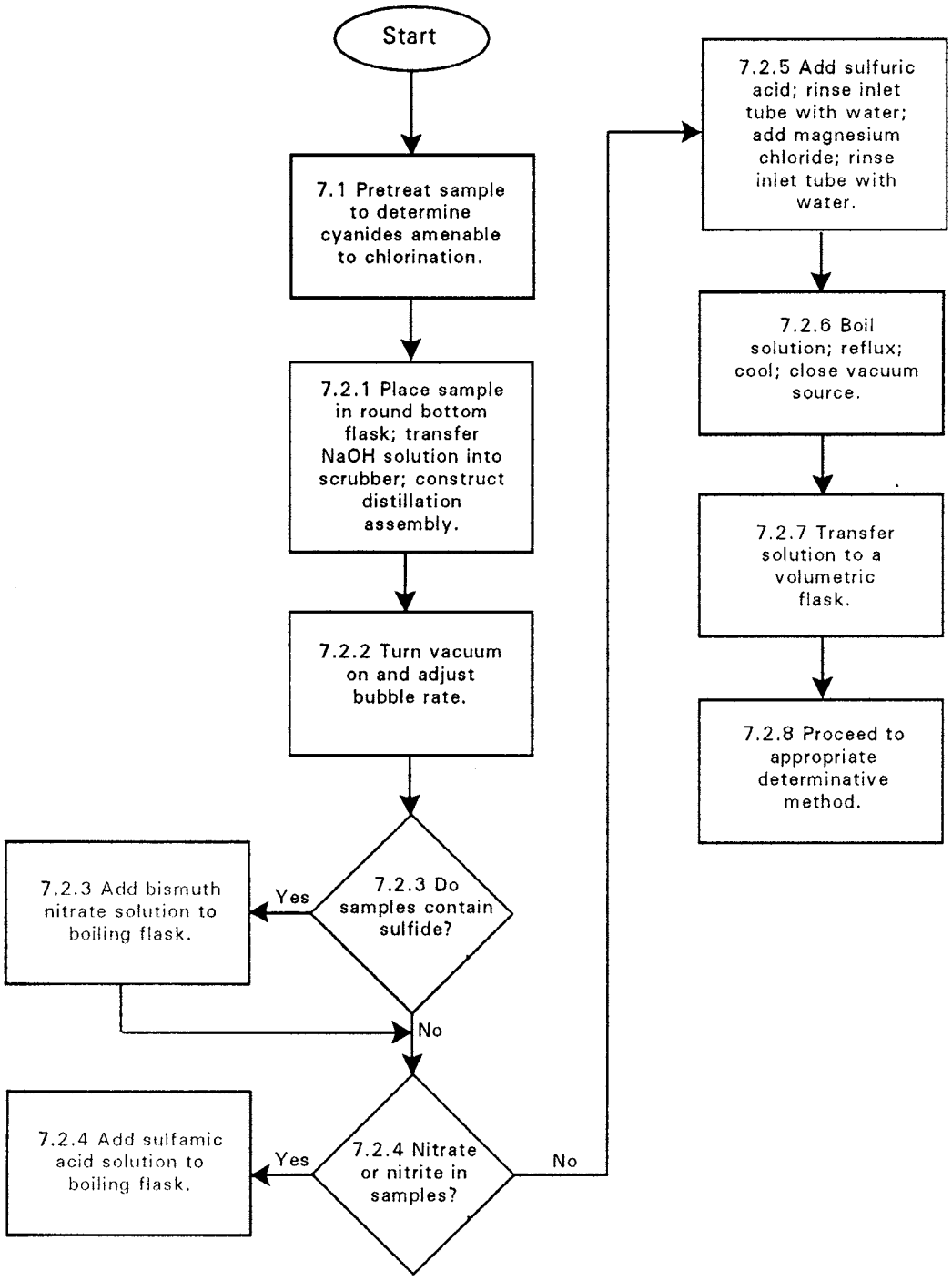


FIGURE 2.
APPARATUS FOR CYANIDE DISTILLATION



TOTAL AND AMENABLE CYANIDE: DISTILLATION



ACCUTEST LABORATORIES
Standard Operating Procedure

Lab Manager

QA Manager

Effective Date: 8/8/13

TEST NAME **DETERMINATION OF ORGANOCHLORINE PESTICIDES USING GC SYSTEM**

METHOD REFERENCE SW846 8081B (Revision 2, February 2007)

Revised sections: 2.1, 9.6.1, 9.8.1, 10.1.1, 12.1.1, 12.4.3, 13.1, changed should to must
Added Sections: 9.9, 13.5, renumbered 9.10 and 13.6 – 13.9

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the analytical procedures, which are utilized by Accutest to acquire samples for analysis of organochlorine pesticides and screening of polychlorinated biphenyls (PCBs) by gas chromatography with Electron Capture Detectors (ECD).

1.2 The method is applicable to extracts from solid and liquid matrices. The compounds listed in Table 1 are determined by a dual-column analysis system.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 15 g for solids) is extracted using the appropriate matrix-specific sample extraction technique. Liquid samples are extracted at neutral pH with methylene chloride using Method 3510 (separatory funnel). Solid samples are extracted using Method 3546 Microwave Extraction or Method 3550C, Sonication. A variety of cleanup steps may be applied to the extract, depending on the nature of the matrix interferences and the target analytes. Cleanups include Florisil (Method 3620), silica gel (Method 3630), gel permeation chromatography (Method 3640), and sulfur (Method 3660).

2.2 After cleanup, the extract is analyzed by injecting a 2-µL sample that is split between dual narrow-bore fused silica capillary columns that are mounted in a single gas chromatograph with electron capture detectors (GC/ECD).

2.3 The peaks detected are qualitatively identified by comparison to retention times specific to the known target list of compounds on two different column types (primary and confirmation).

2.4 If sensitivity permits, the positive hit should be confirmed by GC/MS method 8270D.

2.5 Once identified the compound is quantitated by external standard techniques with an average calibration factor generated from a calibration curve.

3.0 REPORTING LIMIT & METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. RL's may vary depending on matrix and sample volumes or weight and percent moisture. Refer to Table 1 for current reporting limits.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. The different types of blanks are Method Blank, Instrument Blank, Storage Blank, and Sulfur Blank.

FIELD BLANK – an analytical sample prepared from organic-free water and carried through the sampling handling protocol serves as a check for contamination.

CALIBRATION FACTOR (CF) - a measure of the gas chromatographic response of a target analyte to the mass injected. The calibration factor is analogous to the Relative Response Factor (RRF) used in the Volatile and Semivolatile fractions.

CONTINUING CALIBRATION - analytical standard run every 12 hours and at the end of analytical sequence to verify the initial calibration of the system.

CONTINUOUS LIQUID-LIQUID EXTRACTION - used herein synonymously with the term's continuous extraction, continuous liquid extraction, and liquid extraction. This extraction technique involves boiling the extraction solvent in a flask and condensing the solvent above the aqueous sample. The condensed solvent drips through the sample, extracting the compounds of interest from the aqueous phase.

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the electron capture detector to the target compounds.

MATRIX - the predominant material of which the sample to be analyzed is composed. A sample matrix is either water or soil/sediment. Matrix is <u>not</u> synonymous with phase (liquid or solid).

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.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents and surrogate standards that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) – The minimum concentration of a substance 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. MDLs must be determined approximately once per year for frequently analyzed parameters.

PERCENT DIFFERENCE (%D) - to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105^{o}C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105 ^{o}C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

REAGENT WATER - water in which an interferant is not observed at or above the minimum detection limit of the parameters of interest.

RELATIVE PERCENT DIFFERENCE (RPD) - to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the instrument response of an analyte. Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RETENTION TIME (RT) - the time required (in minutes) for a standard compound to elute from a chromatographic column.

SURROGATES - for semivolatiles and pesticides/Aroclors, compounds added to every blank, sample, matrix spike, matrix spike duplicate, and standard; used to evaluate analytical efficiency by measuring recoveries. Surrogate are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental media.

INSTRUMENT BLANK - a system evaluation sample containing lab reagent grade water with internal standards and/or surrogate standards added. An instrument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, and the BHCs. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/Mass approved toxic gas respirator must be worn when the analyst handles high concentrations of these toxic compounds.

6.0 INTERFERENCES

6.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

6.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other stages of sample processing. Refer to "The Preparation of Glassware for Extraction of Organic Contaminants" SOP for practices utilized in the extraction department.

6.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary from source to source. Interferences such as sulfur and phthalate are treated with copper and alumina by organics preparation respectively.

6.3.1 The presence of elemental sulfur will result in broad peaks that interfere with detection of early-eluting organochlorine pesticides. Method 3660 is suggested for removal of sulfur.

6.3.2 Avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination can best minimize interference from phthalate esters.

6.4 Waxes, lipids, and other high molecular weight materials can be removed by method-3640 (Gel Permeation Chromatography-GPC column cleanup).

6.5 To reduce carryover when high-concentration samples are sequentially analyzed, the syringe must be rinsed out between samples with solvent.

6.6 In the case where an unusually concentrated sample is encountered, it must be followed by the analysis of an instrument blank. An instrument blank is a sample containing hexane with surrogate standards added at 20 ppb. An instrument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

7.0 SAMPLE PRESERVATION AND HOLDING TIME

7.1 PRESERVATION

7.1.1 Water Samples

7.1.1.1 Collect samples in 1 liter glass amber bottles without preservatives.

7.1.1.2 A liter of an unpreserved sample is required for extraction. Additional sample volume is necessary for any samples used for matrix spike and matrix spike duplicates. Therefore, 3 liters of at least one sample in every group of 20 field samples are required for analysis to accommodate all quality control requirements.

7.1.2 Soil Samples

7.1.2.1 Samples are collected in a 300-ml amber glass sample bottle. No preservative is required.

7.1.3 Sample must be taken with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing possible phthalate contamination.

7.1.4 The samples must be protected from light and refrigerated at $\leq 6\ ^{0}C$ from the time of receipt until extraction and analysis.

7.2 HOLDING TIME

7.2.1 Aqueous sample must be extracted within 7 days of sampling.

7.2.2 Soil sample must be extracted within 14 days of sampling.

7.2.3 Extracts must be analyzed within 40 days following extraction.

8.0 APPARATUS AND MATERIALS

8.1 GAS CHROMATOGRAPH SYSTEM

8.1.1 Gas Chromatograph – Agilent or Hewlett Packard Models 6890 and 5890. The analytical system is completed with a temperature programmable gas chromatograph and all required accessories including syringes, capillary chromatographic columns, and gases. The capillary column is directly coupled to the source. The injection port is designed for splitless injection with capillary columns.

8.1.2 Columns

8.1.2.1 Column pair 1

8.1.2.1.1 30 m x 0.32 mm ID, 0.5 μm film thickness fused silica, DB-1701 narrow-bore capillary column or equivalent.

8.1.2.1.2 30 m x 0.32 mm ID, 0.5 μm film thickness fused silica, DB-5 narrow-bore capillary column.

8.1.2.2 Column pair 2

8.1.2.2.1 30 m x 0.32 mm ID, 0.5 μm film thickness fused silica, RTX CLPI narrow-bore capillary column or equivalent.

8.1.2.2.2 30 m x 0.32 mm ID, 0.25 μm film thickness fused silica, RTX CLPII narrow-bore capillary column or equivalent.

8.1.3 Detectors

8.1.3.1 Electron Capture Detectors (HP).

8.1.3.2 Micro Electron Capture Detectors (HP).

8.2 AUTOSAMPLER

8.2.1 Agilent or Hewlett Packard Model 7673A, 7683, 7643A capable of holding 100 of 2-ml crimp vials.

8.3 DATA SYSTEM

8.3.1 MSD iinterfaced to the gas chromatograph which allows the continuous acquisition and storage on machine-readable media (disc) of all chromatographic data obtained throughout the duration of the analysis.

8.3.2 The ENVIROQUANT (PC) data system is capable of quantitation using multipoint calibration.

8.3.3 Legato Networker with lookup database on 4mm DAT tape for long term, off line magnetic storage of data.

8.4 SYRINGES

8.4.1 Manually held ul graduated syringes, various volumes (Hamilton or equiv.).

8.4.2 10 μl graduated, auto sampler (Hamilton or equiv.).

8.5 VOLUMETRIC FLASKS, Class A.

9.0 REAGENTS AND STANDARDS

9.1 Refer to Accutest Sample Preparation SOPs EOP001 and EOP040A for reagents and standards used for sample extraction.

9.2 Solvents - Ultra pure, chromatography graded Hexane.

9.3 Stock Standard Solutions

9.3.1 Two separate sources of commercially prepared standards with traceability documentation are used.

9.3.1.1 Pesticides Mixtures containing one or more of the following compounds: alpha-BHC, beta-BHC, delta-BHC, gamma-BHC(Lindane), Heptachlor, Aldrin, Heptachlor Epoxide, Endosulfan I, Dieldrin, 4,4'-DDE, Endrin, Endosulfan II, 4,4'-DDD, Endosulfan sulfate, 4,4—DDT, Methoxychlor, Endrin ketone, Endrin Aldehyde, alpha-Chlordane & gamma-chlordane.

9.3.1.2 Individual standards containing Toxaphene, Chlordane and Mirex.

9.4 Working Solutions

9.4.1 Prepare working solutions, using stock solution, in hexane, as needed, that contain the compounds of interest, either singly or mixed together. Refer to Table 3 for details.

9.5 Calibration Standards

9.5.1 Initial Calibration Standards

9.5.1.1 Calibration standards are prepared at a minimum of five concentrations, including surrogates, from the above working solutions. Suggested levels and preparations are shown in Table 4A.

9.5.1.2 Separate calibration standards are required for each multi-component target analyte (i.e., Toxaphene and Chlordane). Unless otherwise necessary for a specific project, such as Ohio VAP or the Dept. of Defense (DoD), a single calibration standard near the mid-point of the expected calibration range of each multi-component analyte is employed. Refer to Table 4B and 4C for preparation scheme. Optional curves as shown on Table 4D and 4E may also be used for a multi-point calibration per project's specification.

9.5.2 Continuing Calibration Verification (CCV)

9.5.2.1 Continuing calibration checks containing all the single-component analytes are prepared at concentrations of 10 μg/l, 25 ug/l and 50 μg/l as described in Table 5. During analysis, these alternate concentrations are run to check the initial calibration.

9.5.2.2 In situations where only Toxaphene or Chlordane is of interest for a specific project and for Ohio VAP multi-level calibration checks of each multi-component analyte of interest may be prepared and analyzed throughout the analytical sequence.

9.6 Initial Calibration Verification (ICV) - Second Source Calibration Check Standard

9.6.1 Prepare the ICV standards from separate sources of stock standards from the calibration curve following the procedures in Tables 3 and 4.

9.6.2 The ICV must be analyzed immediately following the initial calibration.

9.7 Surrogates

9.7.1 Tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) are used as surrogate standards for this method.

9.7.2 A calibration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed with each calibration solution to define a range similar to the target compounds.

9.7.3 Surrogate compounds are also contained in continuing calibration checks, and second source calibration check standard.

9.7.4 Spike each sample, QC sample and blank with an appropriate amount of corresponding surrogate spiking solution, prior to extraction, for a final concentration in the extract of 40 μg/l of each surrogate compound.

9.8 Breakdown Evaluation Solution

9.8.1 The DDT and Endrin breakdown evaluation solution is prepared in hexane as outlined in Table 6.

9.9 Instrument Blank

9.9.1 An instrument blank is run after the DDT and Endrin breakdown check, and after each subsequent Continuing Calibration Check. Spike hexane with an appropriate amount of surrogate spiking solution for a final concentration of 40 μg/l of each surrogate compound.

9.10 Storage of Standards

9.10.1 Store unopened stock standard solutions according to the manufacturer's documented holding time and storage temperature recommendations. Protect from light.

9.10.2 Store all other working standard solutions in glass vials with Teflon lined screw caps at $\leq$ 6°C in the dark.

9.10.3 Opened stock standard solutions must be replaced after 6 months or sooner if manufacturer's expiration date comes first or comparison with quality control check samples indicates a problem.

9.10.4 All other standards must be replaced after six months or sooner if routine QC indicates a problem or manufacturer's expiration date comes first.

10.0 CALIBRATION

10.1 Initial Calibration

10.1.1 The calibration range covered for all single-component analytes employs at least five of the following standards: 1, 2, 5, 10, 25, 50, 75 and 100* μg/l (*this point may be dropped if it exceeds the linear range of the instrument). The method reporting limit is established by the concentration of the lowest standard analyzed during the initial

calibration. Lower concentration standard may be needed to meet the reporting limit requirements of state specific regulatory program. The linear range covered by this calibration is the highest concentration standard. Calibration is performed for both the primary and secondary columns.

10.1.2 A calibration range must be constructed for each surrogate compound. Accordingly, add appropriate amounts of each surrogate compound to the calibration solution to define a range similar to the target compounds.

10.1.3 Unless otherwise necessary for a specific project, the analysis of the multi-component analytes (such as: Toxaphene or Chlordane) employs a single-point calibration. This single calibration standard is included with the initial calibration of the single component analytes for pattern and retention time recognition. For Ohio VAP and Dept. of Defense (DoD) projects an initial 5 point calibration is required for these analytes if there are positive hits.

10.1.4 Aliquot proper amount of each calibration standard into a 2-ml crimp top vial.

10.1.5 Each analyte is quantitatively determined using the external standard technique. The Calibration Factor (CF) is defined in Section 14.1.

10.1.6 For the initial calibration to be valid, the percent relative standard deviation (% RSD) (see Section 14.2) must be less than 20 % for each analyte of interest on each column. If any analyte exceeds the 20% RSD acceptance limit for a given calibration other calibration options, such as linear calibration not through the origin may be used or corrective action must be taken.

10.1.6.1 If the problem is associated with a standard, reanalyze the standard and recalculate the RSD.

10.1.6.2 Alternatively, narrow the calibration range by replacing the low or the high calibration standard that cover a narrow range.

10.1.6.2.1 The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

10.2 Initial Calibration Verification (ICV) - Second Source Calibration Check Standard

10.2.1 The initial calibration is verified with a second source calibration check standard from an external source (Section 9.6). At a minimum, it must be performed right after the initial calibration.

10.2.2 The percent difference (%D) (Section 14.3) for this standard must meet the %D criteria of 20% used for calibration verification on each column.

10.2.2.1 If %D is greater than 20%, reanalyze the ICV second source check or re-prepare using a fresh ampoule and reanalyze the ICV second source check standard.

10.2.2.2 If the %D criteria cannot be achieved after re-injection of the second source check standard. a new calibration curve must be prepared by making fresh calibration standards using one of the two standard sources that match each other.

10.3 Continuing Calibration Verification (CCV)

10.3.1 Continuing calibration check standards (Section 9.5.2) must be acquired at the beginning of each 12 hour shift prior to analyzing samples, after every 10 injections not to exceed 12 hours and at the end of the analysis sequence. Analysts must alternate the use of the two different concentration mixtures for calibration verification depending on the range of the curve.

10.3.2 For the continuing calibration to be valid, the percent difference (%D) must be less than 20 % for each compound of interest on each column.

10.3.3 Each sample analysis must be bracketed by periodic analyses of acceptable calibration verification standards followed by an instrument blank, run after 10 injections or 12-hours, whichever is more frequent. If %D criteria fails during a mid sequence calibration check or at the end of the analysis sequence, a continuing calibration check is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed. In situations where the first check fails to meet the criteria, the instrument logbook must have clear documented notations as to what the problem was and what corrective action was implemented to enable the second check to pass.

10.3.4 When a calibration verification standard fails to meet the QC criteria all samples injected after the last standard that met the QC criteria must be evaluated to prevent misquantitations and possible false negative results. Re-injection of the sample extracts may be required.

10.3.4.1 If the analyte was not detected in the specific samples analyzed during the analytical shift or sequence, the extracts for those samples do not need to be reanalyzed when the calibration standard response is <u>above</u> the initial calibration response, i.e. >20%.

10.3.4.2 If the analyte was detected in the specific samples analyzed during the analytical shift, or the calibration standard response is below the initial calibration response, then the extracts for those samples need to be reanalyzed.

10.3.5 Each subsequent injection of a continuing calibration standard must be checked against the retention time windows established in Section 11.0. If any of these subsequent standards fall outside their absolute retention time windows, the GC system is not in control. Determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

11.0 RETENTION TIME WINDOWS

11.1 Retention time windows must be calculated for each analyte and surrogate on each GC column and whenever a new chromatographic column is installed, when a new initial calibration is analyzed or when there are significant changes in the operating conditions. The retention time windows must be reported with the analysis results in support of the identifications made.

11.2 Employ the following approach to establish retention time windows.

11.2.1 Make three injections of all single component standard mixture and multi-response products at approximately equal intervals during the 72-hr period.

11.2.2 Calculate the mean and standard deviation of the three absolute retention times-recording the retention time to three decimal places (e.g. 10.015 min) - for each single component pesticide.

11.2.3 For multi-response pesticides, choose five major peaks and calculate the mean and standard deviation of the three retention times for those peaks. The peak chosen should be fairly immune to losses due to degradation and weathering in the samples.

11.2.4 In those cases where the standard deviations of the retention time window for a particular pesticide is <0.01 minutes, the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes.

11.2.5 The width of the retention time window for each analyte and surrogate is defined as ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period. If the default standard deviation is employed, the width of the window will be 0.03 minutes.

11.2.6 Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

12.0 PROCEDURE

12.1 Sample Extraction

12.1.1 In general, water samples are extracted at a neutral pH with methylene chloride using a separate funnel (Method 3510) (Refer to SOP: EOP001). Solid samples are extracted using Method 3546 Microwave Extraction (Refer to SOP: EOP3546) or Method 3550C, Sonication (Refer to SOP: EOP003).

12.2 Sample Cleanup

12.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the

sample to be analyzed and the data quality objectives for the measurements. Refer to the appropriate SOPs for details.

12.2.1.1 If a sample is of biological origin, or contains high molecular weight materials, the use of Method 3640 (GPC cleanup - pesticide option) is recommended. Frequently, one of the adsorption chromatographic cleanups (alumina, silica gel, or florisil) may also be required following the GPC cleanup.

12.2.1.2 Method 3610 (alumina) may be used to remove phthalate esters.

12.2.1.3 Method 3620 (florisil) may be used to separate organochlorine pesticides from aliphatic compounds, aromatics, and nitrogen-containing compounds.

12.2.1.4 Method 3630 (silica gel) may be used to separate single component organochlorine pesticides from some interferants.

12.2.1.5 Elemental sulfur, which may be present in certain sediments and industrial wastes, interferes with the electron capture gas chromatography of certain pesticides. Sulfur must be removed by the technique described in Method 3660.

12.3 Instrument Conditions

12.3.1 Recommended instrument conditions are listed in Table 2. Modifications of parameters specified with an asterisk are allowed as long as criteria of calibration are met. Any modification must be approved by team leader/manager.

12.4 DDT and Endrin Breakdown Evaluation

12.4.1 DDT and Endrin are easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a standard containing only 4,4'-DDT and Endrin. Presence of 4,4'-DDE, 4,4'-DDD, Endrin ketone or Endrin aldehyde indicates breakdown.

12.4.2 Before the initial calibration and at the beginning of each 12-hour shift, inject 1 µl of an evaluation standard directly on column. (Refer to Section 9.8).

12.4.3 The percent breakdown for Endrin and DDT (Section 14.7) is calculated and the breakdown report is saved in the LIMS system.

12.4.4 If degradation of either DDT or Endrin exceeds 15**%**, injector maintenance must be completed before proceeding with calibration. Refer to EQA036-01 for GC system maintenance utilized in the lab.

12.5 Initial Calibration

12.5.1 See Section 10.1.

12.6 Initial Calibration Verification (ICV)

12.6.1 Refer to Section 10.2.

12.7 Continuing Calibration Verification (CCV)

12.7.1 Refer to Section 10.3.

12.8 Sample Analysis (Primary)

12.8.1 All samples and quality control samples are injected into the Gas Chromatograph using the autosampler. Program the sampler for an appropriate number of syringe rinses and a 1ul or 2 μl injection size. A splitless injection technology is used.

12.8.2 Sample concentrations are calculated by comparing sample responses with the initial calibration of the system (Section 14.4). If sample response exceeds the limits of the initial calibration range, dilute the extract and reanalyze. Extracts must be diluted so that all peaks are on scale, as overlapping peaks are not always evident when peaks are off scale.

12.8.3 Sample injections may continue for as long as the calibration verification standards meet instrument QC requirements. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

12.8.4 If chromatographic peaks are masked by the presence of interferences, further sample cleanup is necessary. Refer to Section 12.2 for extract cleanup alternatives.

12.8.4.1 If extract cleanup is required, all QC samples must also be processed through the cleanup method.

12.9 Confirmation Analysis

12.9.1 Confirmation analysis is to confirm the presence of all compounds tentatively identified in the primary analysis.

12.9.1.1 All instrument performance quality control criteria for calibration and retention times must be satisfied on the confirmation analysis.

12.9.2 Each tentative identification must be confirmed using either a second GC column of dissimilar stationary phase or using another technique such as GC/MS.

12.9.2.1 The primary and secondary analysis is conducted simultaneously in the dual-column analysis.

12.9.2.2 GC/MS confirmation may be used in conjunction with dual-column analysis if the concentration is sufficient for detection in GC/MS**,** normally a concentration of approximately 10 ng/μl in the final extract for each single component compound is required. Method 8270 is recommended as a confirmation technique when sensitivity permits.

12.9.3 Once the identification has been confirmed, the agreement between the quantitative results on both columns must be checked.

12.10 Sample Dilution

12.10.1 Establish dilution of sample in order to fall within calibration range or to minimize the matrix interference.

- Utilize screen data (specific project only).
- Utilize acquired sample data.
- Utilize the history program or approval from client/project.
- Sample characteristics (appearance).

12.10.2 If no lower dilution has been reported, the dilution factor chosen must keep the response of the largest peak for a target analyte in the upper half of the initial calibration range of the instrument.

12.10.3 Preparing Dilutions.

12.10.3.1 Prepare sample dilutions quantitatively. Dilute a stored sample extract, if available with hexane using logical volume to volume ratios, i.e., 1:5, 1:10, 1:50, etc.

12.10.3.2 Syringe dilutions. – Refer to Table 8 for dilutions. A calibrated 1ml syringe must be used to prepare dilutions. Gently shake to disperse the extract throughout the solvent prior to loading on the auto-sampler tray for further analysis.

12.10.3.3 Volumetric Flask Dilutions - Dilutions can also be made with a Class A volumetric flask. Measure the appropriate sample extract volume in a calibrated syringe and bring to final volume with dilution solvent in a Class A volumetric flask. Gently shake to disperse the extract throughout the solvent and transfer to auto-sampler vial for analysis.

12.11 Data interpretation

12.11.1 Qualitative identification

12.11.1.1 Analyst shall identify the targeted compounds with competent knowledge interpreting retention time and/or chromatographic pattern by comparison of the sample to the standard of the suspected compound. The criteria required for a positive identification are:

12.11.1.1.1 The sample component must elute at the absolute retention time window (Refer to Section 11.0) for both primary and confirmation run.

12.11.1.1.2 For the multi-response pesticides, at least five major peaks are selected. The retention time window for each peak is determined from the initial calibration analysis. Identification of a multi-component analyte in the sample is based on pattern recognition in conjunction

with the elution of these five peaks within the retention time windows of the corresponding peaks of the standard on both GC columns.

12.11.1.1.3 Be aware of matrix interfering effects on peak shape and relative peak ratios that could distort the pattern. Interpretation of these phenomena may require a highly experienced chromatographer or at least a second opinion.

12.11.2 Quantitative analysis

12.11.2.1 When a target compound has been identified, concentration (see section 14.4) will be based on the integrated area/or height of the peak and calculated by external standard technique. Proper quantitation requires the appropriate selection of a baseline from which the peak area or height can be determined.

12.11.2.2 For multi-response pesticides, usually the areas of 5 peaks are used for quantitation to calculate the calibration factors for those peaks, but fewer may be used depending on the extent of matrix interferences. These calibration factors are then used to calculate the concentration of each corresponding peak in the sample chromatogram and the resulting concentrations are averaged to provide the final result for the sample.

12.11.2.3 When sample results are confirmed using two dissimilar columns or with two dissimilar detectors, the agreement between the quantitative results must be evaluated after the identification has been confirmed. Calculate the relative percent difference (RPD) between the two results using the formula in Section 14.6. Report the lower result.

12.11.2.3.1 A program to perform the RPD calculation had been developed and incorporated into ENVIROQUANT software.

12.11.2.3.2 If one result is significantly higher (e.g., >40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instrument data system (or operator) during peak integration.

12.11.2.3.3 If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the lower result with the footnote (remark) indicating “More than 40% RPD for detected concentrations between two GC columns”.

13.0 QUALITY CONTROL

13.1 QC Requirements Summary

DDT and Endrin Breakdown Evaluation	Every 12-hour shift
ICV -Second Source Calibration	Following initial calibration
Continuing Calibration Checks	Every 12-hour shift or 10 injections (whichever is more frequent) and at the end of analysis sequence

Instrument Blank	After DDT/Endrin Breakdown check, and after each subsequent CCV
Method Blank	One per extraction batch* or per day for a running batch
Blank Spike	One per extraction batch* or per day for a running batch
Matrix Spike	One per extraction batch*
Matrix Spike Duplicate	One per extraction batch*
Surrogate	Every sample and standard

*The maximum number of samples per batch is twenty or per project specification.

13.2 DDT and Endrin Breakdown Evaluation

13.2.1 Refer to Section 12.4.

13.3 Initial Calibration Verification (ICV) - Second Source Calibration Check

13.3.1 Refer to Section 10.2.

13.4 Continuing Calibration Verification (CCV)

13.4.1 Refer to Section 10.3.

13.5 Instrument Blank

13.5.1 If the instrument blank contains a target analyte above its MDL, the source of the contamination must be identified and corrected before proceeding with the analysis.

13.6 Method Blank

13.6.1 The method blank is either DI water or sodium sulfate (depending upon the sample matrix) which must be extracted with each set of 20 or less samples. For a running batch, a new method blank is required for each different extraction day. The method blank are then extracted and run through any clean-up procedures along with the other samples in that batch.

13.6.2 If the method blank contains a target analyte above its MDL, the entire batch must be re-extracted and re-analyzed.

13.6.3 Surrogate compounds are added to the method blank prior to extraction and analysis. If the surrogate accuracy in the blank does not meet criteria, the entire batch must be re-extracted and re-analyzed.

13.7 Blank Spike

13.7.1 A blank spike must be extracted with each set of 20 or less samples. For a running batch, a new blank spike is required for each different extraction day. The blank spike consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. A separate blank spike may be needed if the

sample requires Chlordane and/or Toxaphene. It is spiked with the same analytes at the same concentrations as the matrix spike/matrix spike duplicate.

13.7.1.1 For single-component analytes, the blank spike is prepared at 0.25 μg/l or 8.33 μg/kg on a dry weight basis.

13.7.1.2 For Toxaphene only analysis or per project specification, the blank spike is prepared at 5 μg/l or 167 μg/kg on a dry weight basis.

13.7.1.3 For Chlordane only analysis or per project specification, the blank spike is prepared at 4 μg/l or 133 μg/kg on a dry weight basis.

13.7.2 The blank spike recoveries must be assessed using in house limits..

13.7.3 If a blank spike is out of control, the following corrective actions must be taken. In the case where the blank spike recovery is high and no hits reported in associated samples and QC batch the sample results can be reported with footnote (remark) and no further action is required.

13.7.3.1 Check to be sure that there are no errors in the calculations, or spike solutions. If errors are found, recalculate the data accordingly.

13.7.3.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample batch.

13.7.3.3 If no problem is found, re-extract and reanalyze the sample batch.

13.8 Matrix Spike (MS)/Matrix Spike Duplicate (MSD)

13.8.1 One sample is randomly selected from each extraction batch of similar matrix types and spiked in duplicate to determine whether the sample matrix contributes bias to the analytical results.

13.8.2 A separate matrix spike and matrix spike duplicate set may be needed if the sample requires Chlordane and/or Toxaphene. Matrix spikes are prepared by spiking an actual sample for a concentration of 0.25 μg/l or 8.33 μg/kg on a dry weight basis for pesticides, 5 μg/l or 167 μg/kg for Toxaphene, 4 μg/l or 133 μg/kg for Chlordane.

13.8.3 Assess the matrix spike recoveries and relative percent difference (RPD) against the in house control limits.

13.8.4 If the matrix spike accuracy of any individual compound is out of control, the accuracy for the compound in the blank spike must be within control. Matrix interference is assumed and the data is reportable. No further corrective action is required.

13.9 Surrogates

13.9.1 Tetrachloro-m-xylene (TCMX) and Decachlorobiphenyl (DCB) are used as surrogate standards. All blanks, samples, QC samples, and calibration standards contain

surrogate compounds which are used to monitor performance of the extraction, cleanup (when used), and analytical system.

13.9.2 The recoveries (refer to Section 14.5) of the surrogates must be evaluated versus the surrogate control limits developed by the laboratory.

13.9.3 If surrogate recovery is not within established control limits, corrective action must be performed if surrogate recoveries indicate that a procedural error may have occurred during the analysis of the sample.

13.9.3.1 Check the surrogate calculations for calculation or integration errors and perform corrections if detected.

13.9.3.2 Re-analyze the extract if calculation errors are not detected. If the surrogate recoveries for the re-analyzed extract are in control, report data from the re-analysis only.

13.9.3.3 If data from the reanalysis is also out of control, re-extract and reanalyze the sample.

13.9.3.4 If, upon reanalysis, the surrogate recoveries are acceptable, report the reanalysis data. If the holding time has expired prior to the reanalysis, report both the original and reanalysis results and note the holding time problem.

13.9.3.5 If the recovery is again not within limits, the problem is considered to be matrix interference. Submit both data sets with the original analysis being reported.

13.9.4 The retention time shift for surrogate must be evaluated after the analysis of each sample. The sample must be reanalyzed when the retention time of any surrogate compound is outside the retention window.

13.9.4.1 Reanalysis may not be required for samples having visible matrix interference, defined as excessive signal levels from target or non-target interfering peaks. This judgment must be approved by team leader or supervisor.

13.10 Refer to Project Specific Bench Notes (GC8081) for additional program or client specific QC requirements.

14.0 CALCULATION

14.1 Calibration Factor (CF).

$$CF = \frac{A_S}{C_S}$$

where:
A_S = Area of the peak for the compound being measured.

C_s = Concentration of the compound being measured (µg/l).

14.2 Percent Relative Standard Deviation (% RSD).

$$\%RSD = \frac{SD}{CF_{av}} \times 100$$

where:
SD = Standard Deviation.
CF_{av} = Average calibration factor from initial calibration.

14.3 Percent Difference (% D).

$$\% D = \frac{|CF_{av} - CF_c|}{CF_{av}} X 100$$

where:
CF_c = CF from continuing calibration (CBCHK).

14.4 Concentration (Conc.).

14.4.1 <u>For water:</u>

$$\text{Conc. (µg/l)} = \frac{A_c \times M}{CF_{av}}$$

$$M = \frac{V_f \times D}{V_i}$$

14.4.2 <u>For soil/sediment</u> (on a dry weight basis, see EGN007):

$$\text{Conc. (µg/kg)} = \frac{A_c \times M}{CF_{av}}$$

$$M = \frac{V_f \times D}{W_s \times S}$$

where:
A_c = Area of peak for compound being measured.
V_f = Final Volume of total extract (ml).
D = Secondary dilution factor.
V_i = Initial volume of water extracted (ml).

W_s = Weight of sample extracted (g).
S = (100 - % moisture in sample) / 100 or % solid/100.
M = Multiplier.

14.5 Percent Recovery (% R).

$$\% R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

14.6 Relative Percent Difference (RPD).

$$RPD = \frac{|C_1 - C_2|}{(1/2)(C_1 + C_2)} \times 100$$

where:
C_1 = Matrix Spike Concentration or the result on column 1.
C_2 = Matrix Spike Duplicate Concentration or the result on column 2.

14.7 Percent Breakdown.

$$\% \text{ Breakdown for DDT} = \frac{\text{Total DDT degradation peak area}}{\text{Total DDT peak area}} \times 100$$

where:
Total DDT degradation peak area = DDE + DDD
Total DDT peak area = DDT + DDE + DDD

$$\% \text{ Breakdown for Endrin} = \frac{\text{Total Endrin degradation peak area}}{\text{Total Endrin peak area}} \times 100$$

where:
Total Endrin degradation peak area = Endrin aldehyde + Endrin ketone.
Total Endrin peak area = Endrin + Endrin aldehyde + Endrin ketone.

15.0 DOCUMENTATION

15.1 The Analytical Logbook is a record of the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

15.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in this log. For consistency, if surrogates are high or low indicate it as (↑) for high and (↓) for low.

15.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed, the page must be signed and dated by the respective person.

15.2.1 The Accutest Lot Number must be cross-referenced on the standard vial.

15.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument has a separate log.

15.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

15.5 Unused blocks of any form must be x'ed or z'ed by the analyst before submitting the data for review.

15.6 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information must also be verified during this review.

16.0 DATA REVIEW AND REPORTING

16.1 Initial and continuing calibration check. Verify that all calibration and continuing calibration criteria have been achieved. If the criteria had not been achieved, corrective action must be performed to bring the system in control before analyzing any samples.

16.1.1 If samples had been analyzed under non-compliant calibration criteria, all sample extracts must be re-analyzed once the system is brought into control.

16.2 Quality Control Data Review. Review all QC data. If QC criteria were not achieved, perform corrective action before proceeding with analysis.

16.2.1 In some situation, corrective action may demand that the entire sample batch be re-extracted and re-analyzed before processing data.

16.3 Chromatogram Review. The chromatogram of each sample is evaluated for target compounds.

16.3.1 Check specific retention time windows for each target compound for the presence of the target compound in each chromatogram.

16.3.1.1 Each sample may require the reporting of different target compounds. Review the login to assure that the correct target compounds are identified.

16.3.2 The compound must be identified on the primary and confirmatory column before assigning a qualitative identification.

16.3.3 Manual integration of chromatographic peaks must be identified by the analysts by initialing and dating the changes made to the report.

16.4 Transfer to LIMS. Following the initial screen review, transfer the processed data to the LIMS.

17.0 POLLUTION PREVENTION & WASTE MANAGEMENT

17.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 17.2.

17.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

17.2.1 Non hazardous aqueous wastes.

17.2.2 Hazardous aqueous wastes

17.2.3 Chlorinated organic solvents

17.2.4 Non-chlorinated organic solvents

17.2.5 Hazardous solid wastes

17.2.6 Non-hazardous solid wastes

Table 1. Target Compound List and Reporting Limits			
Compound	**CAS No.**	**Water (µg/l)**	**Soil (µg/kg)**
alpha-BHC	319-84-6	0.01	0.67
beta-BHC	319-85-7	0.01	0.67
delta-BHC	319-86-8	0.01	0.67
Gamma-BHC (Lindane)	58-89-9	0.01	0.67
Heptachlor	76-44-8	0.01	0.67
Aldrin	309-00-2	0.01	0.67
Heptachlor epoxide	1024-57-3	0.01	0.67
Endosu1fan I	959-98-8	0.01	0.67
Dieldrin	60-57-1	0.01	0.67
4,4'-DDE	72-55-9	0.01	0.67
Endrin	72-20-8	0.01	0.67
Endosulfan II	33213-65-9	0.01	0.67
4,4'-DDD	72-54-8	0.01	0.67
Endosulfan sulfate	1031-07-8	0.01	0.67
4,4'-DDT	50-29-3	0.01	0.67
Methoxychlor	72-43-5	0.02	1.3
Endrin ketone	53494-70-5	0.01	1.3
Endrin aldehyde	7421-93-4	0.01	0.67
α-Chlordane	5103-71-9	0.01	0.67
γ-Chlordane	5103-74-2	0.01	0.67
Mirex	2385-85-5	0.02	0.67
Chlordane (technical)	12789-03-6	0.50	34
Toxaphene	8001-35-2	0.25	17

Table 2. RECOMMENDED OPERATING CONDITION	
Gas Chromatograph/Electron Capture Detectors	
Carrier Gas	Helium
Make-up gas	5 % Methane/ 95 % Argon
Make-up gas flow	*40 ml/min
Injection port temperature	*280°C
Injection type	Splitless
Detector temperature	*320°C
Column flow	2 ml/min
Gas Chromatograph Temperature Program*	
Initial temperature	*160°C
Time 1	*2 minutes
Column temperature rate 1	*45 degrees/min
Temperature 1	*200°C
Column temperature rate 2	*7 degrees/min
Temperature 2	*260°C
Column temperature rate 3	*50 degrees/min
Final temperature	*305°C
Time 3	*0.8 minutes
Total run time	10-20 minutes

*Parameter modification allowed for performance optimization as long as QC criteria are achieved.

Table 3. Pesticides and Surrogates Working Solution	
Stock Solution	**Volume Added**
Pesticides Mixture (1,000 μg/ml)	0.1 ml
Pesticides Surrogate Std Spiking Solution (200 μg/ml)	0.5ml
Mirex (1000ug/ml) (optional)	0.1ml
Hexane	9.4 ml (or 9.3 ml with Mirex)
Total	10.0 ml

Pesticides Mixture (10 μg/ml) and Surrogates (10 μg/ml) Working Solution: Prepared by measuring 0.1 ml of 1,000 μg/ml of pesticides mixture, 0.5ml of 200 μg/ml pesticides surrogate std spiking solution and bringing to 10 ml with hexane. Note larger or smaller volumes of standards may be prepared, as needed using the same ratios. ICV is prepared in the same way, but a second source is used.

Table 4A. Pesticides Calibration Standard Solutions					
Solution	**Working Solution**	**Concentration (μg/ml)**	**Volume Added (μl)**	**Final Volume in Hexane (ml)**	**Final Concentration(μg/l)**
Standard A	Pesticides Mixture	10	500	50	100
	Surrogates	10			100
Standard B	Pesticides Mixture	10	250	50	50
	Surrogates	10			50
Standard C	Pesticides Mixture	10	125	50	25
	Surrogates	10			25
Standard D	Pesticides Mixture	10	50	50	10
	Surrogates	10			10
Standard E	Pesticides Mixture	10	25	50	5
	Surrogates	10			5
Standard F	Pesticides Mixture	10	10	50	2
	Surrogates	10			2
Standard G	Pesticides Mixture	10	5	50	1
	Surrogates	10			1
Standard H	Pesticides Mixture	10	375	50	75
	Surrogates	10			75

Standard A: Prepared by measuring 500 μl of Pesticides Mixture (10 μg/ml) and Surrogates (10 μg/ml) Working Solution and bringing to 50 ml with hexane.

Standard B: Prepared by measuring 250 μl of Pesticides Mixture (10 μg/ml) and Surrogates (10 μg/ml) Working Solution and bringing to 50 ml with hexane.

Standard C: Prepared by measuring 125 μl of Pesticides Mixture (10 μg/ml) and Surrogates (10 μg/ml) Working Solution and bringing to 50 ml with hexane.

Standard D: Prepared by measuring 50 μl of Pesticides Mixture (10 μg/ml) and Surrogates (10 μg/ml) Working Solution and bringing to 50 ml with hexane.

Standard E: Prepared by measuring 25 μl of Pesticides Mixture (10 μg/ml) and Surrogates (10 μg/ml) Working Solution and bringing to 50 ml with hexane.

Standard F: Prepared by measuring 10 μl of Pesticides Mixture (10 μg/ml) and Surrogates (10 μg/ml) Working Solution and bringing to 50 ml with hexane.

Standard G: Prepared by measuring 5 μl of Pesticides Mixture (10 μg/ml) and Surrogates (10 μg/ml) Working Solution and bringing to 50 ml with hexane.

Standard H: Prepared by measuring 375 μl of Pesticides Mixture (10 μg/ml) and Surrogates (10 μg/ml) Working Solution and bringing to 50 ml with hexane.

Table 4B. Toxaphene Calibration Standard Solution (20ug/ml)	
Stock Solution	**Volume Added (µl)**
Toxaphene stock (4000 µg/ml)	125
Pesticides Surrogate Std Spiking Solution (200 µg/ml)	100
Hexane	24775
Total	25000

Toxaphene (20 µg/ml) and Surrogates (0.80 µg/l) Calibration Solution: Prepared by measuring 125 µl of 4000 µg/ml of Toxaphene stock solution, 100 µl of 200 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 4C. Chlordane Calibration Standard Solution (20 µg/ml)	
Stock Solution	**Volume Added (µl)**
Chlordane stock (2000 µg/ml)	250
Pesticides Surrogate Std Spiking Solution (200 µg/ml)	100
Hexane	24650
Total	25000

Chlordane (20 µg/ml) and Surrogates (0.80 µg/ml) Calibration Solution: Prepared by measuring 250 µl of 2000 µg/ml of Chlordane stock solution, 100 µl of 200 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 4D. Multi-point Toxaphene Calibration Standards (optional)					
Solution	**Stock Solution**	**Concentration (µg/ml)**	**Volume Added (µl)**	**Final Volume in Hexane (ml)**	**Final Concentration(µg/l)**
Standard A	Toxaphene	20	3750	25	3000
	Surrogate Spiking	0.8	3750		120
Standard B	Toxaphene	20	2500	25	2000
	Surrogate Spiking	0.8	2500		80
Standard C	Toxaphene	20	1250	25	1000
	Surrogate Spiking	0.8	1250		40
Standard D	Toxaphene	20	625	25	500
	Surrogate Spiking	0.8	625		20
Standard E	Toxaphene	20	312.5	25	250
	Surrogate Spiking	0.8	312.5		10
Standard F	Toxaphene	20	62.5	25	50
	Surrogate Spiking	0.8	62.5		2

Standard A: Prepared by measuring 3750 µl of 20 µg/ml of Toxaphene stock solution, 3750 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard B: Prepared by measuring 2500 µl of 20 µg/ml of Toxaphene stock solution, 2500 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard C: Prepared by measuring 1000 µl of 20 µg/ml of Toxaphene stock solution, 1000 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard D: Prepared by measuring 625 µl of 20 µg/ml of Toxaphene stock solution, 625 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard E: Prepared by measuring 312.5 µl of 20 µg/ml of Toxaphene stock solution, 312.5 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard F: Prepared by measuring 62.5 µl of 20 µg/ml of Toxaphene stock solution, 32.5 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 4E. Multi-point Chlordane Calibration Standards (optional)					
Solution	**Stock Solution**	**Concentration (µg/ml)**	**Volume Added (µl)**	**Final Volume in Hexane (ml)**	**Final Concentration(µg/l)**
Standard A	Chlordane	20	3750	25	3000
	Surrogate Spiking	0.8	3750		120
Standard B	Chlordane	20	2500	25	2000
	Surrogate Spiking	0.8	2500		80
Standard C	Chlordane	20	1250	25	1000
	Surrogate Spiking	0.8	1250		40
Standard D	Chlordane	20	625	25	500
	Surrogate Spiking	0.8	625		20
Standard E	Chlordane	20	312.5	25	250
	Surrogate Spiking	0.8	312.5		10
Standard F	Chlordane	20	62.5	25	50
	Surrogate Spiking	0.8	62.5		2

Standard A: Prepared by measuring 3750 µl of 20 µg/ml of Chlordane stock solution, 3750 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard B: Prepared by measuring 2500 µl of 20 µg/ml of Chlordane stock solution, 2500 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard C: Prepared by measuring 1000 µl of 20 µg/ml of Chlordane stock solution, 1000 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard D: Prepared by measuring 625 µl of 20 µg/ml of Chlordane stock solution, 625 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard E: Prepared by measuring 312.5 µl of 20 µg/ml of Chlordane stock solution, 312.5 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard F: Prepared by measuring 62.5 µl of 20 µg/ml of Chlordane stock solution, 32.5 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 5. Continuing Calibration Check Solutions					
Checks	**Working Solution**	**Concentration (μg/ml)**	**Volume Added (μl)**	**Final Volume in Hexane (ml)**	**Final Concentration(μg/l)**
Solution 1	Pesticides Mixture	10	250	50	50
	Surrogates	10			50
Solution 2	Pesticides Mixture	10	50	50	10
	Surrogates	10			10
Solution 3	Pesticides Mixture	10	125	50	25
	Surrogates	10			25

Solution 1: Prepared by measuring 250 μl of Pesticides Mixture (10 μg/ml) and Surrogates (10 μg/ml) Working Solution and bringing to 50 ml with hexane.

Solution 2: Prepared by measuring 50 μl of Pesticides Mixture (10 μg/ml) and Surrogates (10 μg/ml) Working Solution and bringing to 50 ml with hexane.

Solution 3: Prepared by measuring 125 μl of Pesticides Mixture (10 μg/ml) and Surrogates (10 μg/ml) Working Solution and bringing to 50 ml with hexane.

Table 6. DDT and Endrin Breakdown Evaluation Standard	
Stock Solution	**Volume Added (μl)**
Pesticides Performance Evaluation Mixture (10-250 μg/ml)	50
Hexane	49950
Total	50000

DDT and Endrin Breakdown Evaluation Standard (10-250 μg/l): Prepared by measuring 50 μl of Pesticides Performance Evaluation Mixture (10-250 μg/ml) and diluting to 50 ml with hexane.

Table 7
Sample Dilution Table

All dilutions must be made using a 1ml calibrated syringe.

Dilution	*Intact Sample*	*Solvent*
1:2	500ul	500ul
1:5	200ul	800ul
1:10	100ul	900ul
1:20	50ul	950ul
1:25	40ul	960ul
1:50	20ul	980ul

Two Step dilution

Dilution	**Step 1**		**Step 2**	
	Intact Sample	*Solvent*	*Sample Aliquot from Step 1*	*Solvent*
1:100	100ul	900ul	100ul	900ul
1:200	100ul	900ul	50ul	950ul
1:250	100ul	900ul	40ul	960ul
1:500	100ul	900ul	20ul	980ul

Three Step Dilution

Dilution	**Step 1**		**Step 2**		**Step 3**	
	Intact Sample	*Solvent*	*Sample Aliquot from Step 1*	*Solvent*	*Sample Aliquot from Step 2*	*Solvent*
1:1000	100ul	900ul	100ul	900ul	100ul	900ul
1:2000	100ul	900ul	100ul	900ul	50ul	950ul
1:2500	100ul	900ul	100ul	900ul	40ul	960ul
1:5000	100ul	900ul	100ul	900ul	20ul	980ul

Four Step Dilution

Dilution	**Step 1**		**Step 2**		**Step 3**		**Step 4**	
	Intact Sample	*Solvent*	*Sample Aliquot from Step 1*	*Solvent*	*Sample Aliquot from Step 2*	*Solvent*	*Sample Aliquot from Step 3*	*Solvent*
1:10,000	100ul	900ul	100ul	900ul	100ul	900ul	100ul	900ul
1:20,000	100ul	900ul	100ul	900ul	100ul	900ul	50ul	950ul
1:25,000	100ul	900ul	100ul	900ul	100ul	900ul	40ul	960ul
1:50,000	100ul	900ul	100ul	900ul	100ul	900ul	20ul	980ul

ACCUTEST LABORATORIES
Standard Operating Procedures

Lab Manager Nancy Cole

QA Manager Gregory Tarbell Jr.

Effective Date: 6/8/13

TEST NAME SW846 8082A: DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY

METHOD REFERENCE SW846 8082A (Revision 1, February 2007)

Revised Sections: ***2.1, 12.1.1, 13.1, Table 1, changed should to must***
Added Sections ***9.8, 13.5 renumbered sections 9.9 and 13.6-13.10***

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the analytical procedures, which are utilized by Accutest to acquire samples for analysis of polychlorinated biphenyls (PCBs) as Aroclors, using dual open-tubular, capillary columns with electron capture detectors (ECD).

1.2 This gas chromatographic (GC) method applicable to the determination of the PCB Aroclors listed in Table 1 in extracts from solid and aqueous matrices.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 15 g for solids) is extracted using the appropriate matrix-specific sample extraction technique. Petroleum Products and organic wastes are diluted with an organic solvent and follow SW 846 Method 3580A. Aqueous samples are extracted at neutral pH with methylene chloride using Method 3510 (separatory funnel). Solid samples are extracted with using Method 3546, Microwave Extraction.

2.2 Extracts for PCB analysis may be subjected to a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for these analytes. This cleanup technique will remove (destroy) many single component organochlorine or organophosphorus pesticides.

2.3 After cleanup, the extract is analyzed by injecting a 1 or 2-µL aliquot into a gas chromatograph with dual narrow bore fused silica capillary columns and electron capture detectors (GC/ECD). The chromatographic data may be used to determine the seven Aroclors in Table 1.

2.4 The peaks detected are qualitatively identified by comparison to retention times specific to the known target list of PCBs on two different column types (primary and confirmation).

2.5 Once identified, the Aroclor is quantitated by external standard techniques with an average calibration factor generated from a calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. RL's may vary depending on matrix difficulties and sample volumes or weight and percent moisture. Refer to Table 1 for current reporting limits.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. The types of blanks are Method Blank; Instrument Blank, Storage Blank, and Sulfur Blank.

CALIBRATION FACTOR (CF) - a measure of the gas chromatographic response of a target analyte to the mass injected. The calibration factor is analogous to the Relative Response Factor (RRF) used in the Volatile and Semivolatile fractions.

CONTINUING CALIBRATION - analytical standard run every 12 hours and at the end of analytical sequence to verify the initial calibration of the system.

CONTINUOUS LIQUID-LIQUID EXTRACTION - used herein synonymously with the terms continuous extraction, continuous liquid extraction, and liquid extraction. This extraction technique involves boiling the extraction solvent in a flask and condensing the solvent above the aqueous sample. The condensed solvent drips through the sample, extracting the compounds of interest from the aqueous phase.

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the electron capture detector to the target compounds.

MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

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.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards and surrogate standards (or SMCs for VOA), that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) - The minimum concentration of a substance 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. MDLs must be determined approximately once per year for frequently analyzed parameters.

PERCENT DIFFERENCE (%D) - As used in this SOP and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105^{o}C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105 ^{o}C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

REAGENT WATER - water in which an interferant is not observed at or above the minimum detection limit of the parameters of interest.

RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOP and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the instrument response of an analyte. Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RETENTION TIME (RT) - the time required (in minutes) for a standard compound to elute from a chromatographic column.

SURROGATES - for semivolatiles and pesticides/Aroclors, compounds added to every blank, sample, matrix spike, matrix spike duplicate, and standard; used to evaluate analytical efficiency by measuring recoveries. Surrogate are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental media.

INSTRUMENT BLANK - a system evaluation sample containing solvent and surrogate standards added. An instrument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of

the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 Polychlorinated biphenyls have been classified as known or suspected human or mammalian carcinogens. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/Mass approved toxic gas respirator must be worn when the analyst handles high concentrations of these toxic compounds.

6.0 INTERFERENCES

6.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

6.2 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Glassware must be scrupulously cleaned. Refer to "The Preparation of Glassware for Extraction of organic contaminants" SOP for practices utilized in the extraction department.

6.3 Interferences may be caused by contaminants that are co-extracted from the sample. The extent of the interferences will vary from source to source, which can be grouped into three broad categories.

6.3.1 Contaminated solvents, reagents, or sample processing hardware.

6.3.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

6.3.3 Compounds extracted from the sample matrix to which the detector will respond**.**

6.4 Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determination.

6.4.1 Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination can best minimize interference from phthalate esters.

6.4.2 Exhaustive cleanup of solvents, reagent and glassware may be required to eliminate background phthalate ester contamination.

6.4.3 These materials can be removed through the use of Method 3665 (sulfuric acid/permanganate cleanup).

6.5 Elemental sulfur is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Method 3660 is suggested for removal of sulfur.

6.6 To reduce carryover when high-concentration samples are sequentially analyzed, the syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of an instrument blank to check for cross contamination.

7.0 SAMPLE PRESERVATION AND HOLDING TIME

7.1 PRESERVATION

7.1.1 Water Samples

7.1.1.1 Collect samples in 1 liter glass amber bottles without preservatives.

7.1.1.2 A liter of an unpreserved sample is required for extraction. Additional sample volume is necessary for any samples used for matrix spike and matrix spike duplicates. Therefore, 3 liters of at least one sample in every group of 20 field samples are required for analysis to accommodate all quality control requirements.

7.1.2 Soil Samples

7.1.2.1 Samples are collected in a 300-ml amber glass sample bottle. No preservative is required.

7.1.3 Sample must be taken with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing possible phthalate contamination.

7.1.4 The samples must be protected from light and refrigerated at $\leq$ 6 °C from the time of receipt until extraction and analysis.

7.2 HOLDING TIME

7.2.1 Aqueous sample must be extracted within 1 year of sampling.

7.2.2 Soil sample must be extracted within 1 year of sampling.

7.2.3 Extracts must be analyzed within 40 days following extraction.

8.0 APPARATUS AND MATERIALS

8.1 GAS CHROMATOGRAPH SYSTEM

8.1.1 Gas Chromatograph-Agilent or Hewlett Packard Model 5890 and 6890. The analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port is designed for splitless injection with capillary columns. The capillary columns are directly coupled to the detectors.

8.1.2 Columns

8.1.2.1 Column pair 1

8.1.2.1.1 30 m x 0.32 mm fused silica (0.5 μm film thickness) DB-1701 narrow-bore capillary column or equivalent.

8.1.2.1.2 30 m x 0.32 mm fused silica (0,5 μm film thickness) DB-5 narrow-bore capillary column or equivalent.

8.1.2.2 Column pair 2

8.1.2.2.1 30 m x 0.32 mm fused silica (0.5 μm film thickness) RTX CLPI narrow-bore capillary column or equivalent.

8.1.2.2.2 30 m x 0.32 mm fused silica (0.25 μm film thickness) RTX CLPII narrow-bore capillary column or equivalent.

8.1.3 Detectors

8.1.3.1 Electron Capture Detectors (HP).

8.1.3.2 Micro Electron Capture Detectors (HP).

8.2 AUTOSAMPLER

8.2.1 Agilent or Hewlett Packard Model 7673A, 7683, 7643A capable of holding 100 of 2-ml crimp vials.

8.3 DATA SYSTEM

8.3.1 MSD interfaced to the gas chromatograph which allows the continuous acquisition and storage on machine readable media (disc) of all chromatographic data obtained throughout the duration of the analysis.

8.3.2 The ENVIROQUANT data system is capable of quantitation using multi-point calibration.

8.3.3 Lagato Networker with lookup database on 4mm DAT tape for long term, off line magnetic storage of data.

8.4 SYRINGE

8.4.1 Manually held ul-syringes, various volumes (Hamilton or equiv.).

8.4.2 10 μl graduated, auto sampler (Hamilton or equiv.).

9.0 REAGENTS AND STANDARDS

9.1 Refer to Accutest Sample Preparation SOPs EOP001 and EOP040A for reagents and standards used for sample extraction.

9.2 Solvents - Ultra pure, chromatography grade Hexane.

9.3 Stock standard solutions.

9.3.1 Two separate sources of commercially prepared standards with traceability documentation are used. The standards contain Aroclors 1016, 1221, 1232, 1242, 1248, 1254 and 1260.

9.4 Working Solutions

9.4.1 Prepare working solutions, using stock solution, in hexane, as needed, that contain the compounds of interest, either singly or mixed together. Refer to Table 3A, 3B for details.

9.5 Calibration Standards

9.5.1 Initial Calibration Standards

9.5.1.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks in the other five Aroclor mixtures. As a result, a multi-point calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing initial calibration for each of the seven Aroclors. Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260, including surrogates, by dilution of the above working solutions (Section 9.4) with hexane. Suggested levels and preparations are shown in Table 4A.

9.5.1.2 Separate calibration standards are required for the other five Aroclors. Unless otherwise necessary for a specific project, a single calibration standard near the mid-point of the expected calibration range of each remaining Aroclor is employed to determine its calibration factor and for pattern recognition. Refer to Table 4B for preparation scheme. Optional curves as shown on Table 4C may also be used for a multi-point calibration per project's specification.

9.5.2 Continuing Calibration Verification (CCV)

9.5.2.1 For Aroclor analyses, the continuing calibration checks must be a mixture of Aroclor 1016 and Aroclor 1260. Two standards at 500 μg/l and 1,000 μg/l are prepared as described in Table 5A. During the analysis, these two solutions are alternated to check the initial calibration.

9.5.2.2 In situations where only a few Aroclors are of interest for a specific project, the calibration checks of each Aroclor of interest may be prepared (Table 5B) and analyzed as the 1016/1260 mixture throughout the analytical sequence.

9.6 Initial Calibration Verification (ICV) - Second Source Calibration Check Standard

9.6.1 Prepare the ICV check standards from separate sources of stock standards from the calibration curve following the procedures in Table 6A, and 6B.

9.6.2 The ICV is prepared at 1,000 μg/l for each Aroclor and is analyzed immediately after and initial calibration.

9.7 Surrogates

9.7.1 Tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) are used as surrogate standards for this method.

9.7.2 A calibration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed with each calibration solution to define a range similar to the target compounds.

9.7.3 Surrogate compounds are also contained in continuing calibration checks, and second source calibration check standard.

9.7.4 Spike each sample, QC sample and blank with an appropriate amount of corresponding surrogate spiking solution, prior to extraction, for a final concentration in the extract of 40 μg/l of each surrogate compound.

9.8 Instrument Blank

9.8.1 An instrument blank is run after each Continuing Calibration Check. Spike hexane with an appropriate amount of surrogate spiking solution for a final concentration of 40 μg/l of each surrogate compound.

9.9 Storage of Standards

9.9.1 Store unopened stock standard solutions according to the manufacturer's documented holding time and storage temperature recommendations. Protect from light.

9.9.2 Store all other working standard solutions in glass vials with Teflon lined screw caps at $\leq$ 6°C in the dark.

9.9.3 Opened stock standard solutions must be replaced after 6 monts or sooner if manufacturer's expiration date comes first or comparison with quality control check samples indicates a problem.

9.9.4 All other standards must be replaced after six months or sooner if routine QC indicates a problem or manufacturer's expiration date comes first.

10.0 CALIBRATION

10.1 Initial Calibration

10.1.1 The method reporting limit is established by the concentration of the lowest standard analyzed during the initial calibration. Lower concentration standard may be needed to meet the reporting limit requirements of state specific regulatory program. The linear range covered by this calibration is the highest concentration standard.

10.1.2 The initial calibration for this method consists of two parts, described below.

10.1.2.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detectors and that a

sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. The calibration range covered for Aroclor 1016 and Aroclor 1260 employs standards of 50, 250, 500, 1,000, 2,000, and 3,000 μg/l.

10.1.2.2 Standards of the other five Aroclors are necessary for pattern recognition. These standards are also used to determine a single-point calibration factor for each Aroclor, assuming that the Aroclor 1016/1260 mixture in Section 10.1.2.1 has been used to describe the detector response. The concentration of each Aroclor standard is near the mid-point of the linear range of the detector, usually at 1,000 μg/l. The standards for these five Aroclors must be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of those 1016/1260 standards.

10.1.2.3 In situations where only a few Aroclors are of interest for a specific project, an initial calibration of a minimum of five standards of each Aroclors of interest instead of the 1016/1260 mixture may be performed.

10.1.3 A calibration range must be constructed for each surrogate compound. Accordingly, add appropriate amounts of each surrogate compound to the calibration solution to define a range similar to the target compounds.

10.1.4 Aliquot proper amount of each calibration standard into a 2 ml crimp top vial.

10.1.5 PCBs are quantitatively determined as Aroclors by the external standard technique. The Calibration Factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards is calculated using the equation in Section 14.1.

10.1.5.1 Use at least five peaks for the Aroclor 1016/1260 mixture, none of which are found in both of these Aroclors. At least five sets of calibration factors will be generated, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture.

10.1.5.2 A minimum of 3 characteristic peaks must be chosen for each of the other Aroclors, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Thus, each single standard will generate at least three calibration factors, one for each selected peak.

10.1.5.3 Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 6 peaks must include at least one peak that is unique to that Aroclor.

10.1.5.4 The calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration. When the Aroclor 1016/1260 mixture is used to demonstrate the detector response, the calibration model chosen for this mixture must be applied to the other five Aroclors for which only single standards are analyzed. If multi-point calibration is performed for individual Aroclors, use the calibration factors from those standards to evaluate linearity.

10.1.6 For the initial calibration to be valid, the percent relative standard deviation (% RSD) (see Section 14.2) must be less than 20 % for each Aroclor of interest on each column. If any

analyte exceeds the 20% acceptance limit for a given calibration, corrective action must be taken.

10.1.6.1 If the problem is associated with specific standards, reanalyze the standard and recalculate the RSD.

10.1.6.2 Alternatively, narrow the calibration range by replacing one or more of the calibration standards that cover a narrow range.

10.1.6.2.1 The changes to the upper end of the calibration range will affect the need to dilute samples above the range. If the instrument response indicates signs of detector saturation, the concentration of the standard at the upper limit will be reduced. The changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

10.2 Initial Calibration Verification (ICV) - Second Source Calibration Check Standard

10.2.1 The initial calibration is verified with an ICV, a second source calibration check standard from an external source (Section 9.6). It must be performed right after the initial calibration.

10.2.2 The percent difference (%D) (Section 14.3) for this standard must meet the %D criteria of 20% used for calibration verification on each column.

10.2.2.1 If %D is greater than 20%, reanalyze the second source check. If the limit cannot be met upon re-injection, re-prepare the second source solution using a fresh ampoule and repeat the process.

10.2.2.2 If the %D criteria cannot be achieved after re-preparation of the second source, prepare a third source and repeat the process. Make fresh calibration standards using one of the two standard sources that match each other.

10.3 Continuing Calibration Verification (CCV)

10.3.1 Continuing calibration verificatiion (CCV) standards (Section 9.5.2) must be acquired at the beginning of each 12-hour shift, after every 10 injections not to exceed 12 hours and at the end of the analysis sequence. The 500 μg/l check standard is alternated with 1,000 μg/l standard for calibration verification.

10.3.2 For Aroclor analyses, the calibration verification standard must be a mixture of Aroclor 1016 and Aroclor 1260. The calibration verification process does not require analysis of the other Aroclor standards used for pattern recognition, but the analyst may wish to include a standard for one of these Aroclors after the 1016/1260 mixture used for calibration verification throughout the analytical sequence.

10.3.3 The percent difference (%D) (see section 14.3) must be less than 20**%** for each Aroclor of interest on each column.

10.3.4 Each sample analysis must be bracketed by periodic analyses of acceptable calibration verification standards every 10 injections not to exceed 12 hours. If %D criteria fails

during a mid sequence calibration check or at the end of the analysis sequence, a continuing calibration check is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed. In situations where the first check fails to meet the criteria, the instrument logbook must have clear documented notations as to what the problem was and what corrective action was implemented to enable the second check to pass.

10.3.5 A continuing calibration standard is analyzed whenever the analyst suspects that the analytical system is out of calibration. If the calibration cannot be verified, corrective action is performed to bring the system into control. Analysis may not continue until the system is under control.

10.3.6 When a calibration verification standard fails to meet the QC criteria at the end of the analysis sequence, all samples injected after the last standard that met the QC criteria must be evaluated to prevent mis-quantitations, and re-injection of the sample extracts may be required.

10.3.6.1 If the analyte was not detected in the specific samples analyzed during the analytical shift or sequence, the extracts for those samples do not need to be reanalyzed when the calibration standard response is <u>above</u> the initial calibration response.

10.3.6.2 If the analyte was detected in the specific samples analyzed during the analytical shift or sequence, or the calibration standard response is below the initial calibration response, then the extracts for those samples need to be reanalyzed.

10.3.7 Each subsequent injection of a continuing calibration standard during the 12-hour analytical shift must be checked against the retention time windows established in Section 11.0. If any of these subsequent standards fall outside their absolute retention time windows, the GC system is out of control. Determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

11.0 RETENTION TIME WINDOWS

11.1 Absolute retention times are used for the identification of PCBs as Aroclors. Retention time windows must be calculated for each surrogate and at least 3 to 5 characteristic peaks of each Aroclor on each GC column, when a new initial calibration is run and whenever a new chromatographic column is installed, or when there are significant changes in the operating conditions. The retention time windows must be reported with the analysis results in support of the identifications made.

11.2 Employ the following approach to establish retention time windows:

11.2.1 Make three injections of each Aroclor at approximately equal intervals during the 72-hr period.

11.2.2 For each Aroclor, choose three or five major peaks and calculate the mean and standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in the samples. Record the retention time to three decimal places (e.g. 10.015 min) for each Aroclor.

11.2.3 In those cases where the standard deviations of the retention time window for a particular Aroclor is 0.01 minutes or less, the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes.

11.2.4 Apply plus or minus three times the standard deviations to retention time of each Aroclor standard (continuing calibration or middle level of initial calibration). This will be used to define the retention time window for the sample.

11.2.4.1 If default standard deviation of 0.01 minutes is employed, the width of the window will be 0.03 minutes.

11.2.5 Establish the center of the retention time window for each Aroclor and surrogate by using the absolute retention time for each Aroclor and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

11.2.6 When retention time windows are to be determined, analyze a standard containing DDT analogs to ensure that they do not elute at the same retention time as the last major Aroclor 1254 peak. The analyst must either adjust the GC conditions for better resolution, or choose another peak that is characteristic of the Aroclor and which does not elute at the same time as of the DDT analogs.

12.0 PROCEDURE

12.1 Sample Extraction

12.1.1 In general, water samples are extracted at a neutral pH with methylene chloride using a separate funnel (Method 3510) (Refer to SOP: EOP001). Solid samples are extracted using Method 3546, Microwave Extraction (Refer to SOP: EOP3546).

12.2 Sample Cleanup

12.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. Refer to appropriate SOPs for details.

12.2.1.1 Interferences by phthalate esters can be removed through the use of a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for PCBs. This method must be used whenever elevated baselines or overly complex chromatograms prevent accurate quantitation of PCBs.

12.2.1.2 Element sulfur, which may be present in certain sediments and industrial wastes, interfere with the electron capture gas chromatography of certain Aroclors. Sulfur must be removed by the technique described in Method 3660.

12.3 Instrument conditions.

12.3.1 Recommended instrument conditions are listed in Table 2. Modifications of parameters specified with an asterisk are allowed as long as criteria of calibration are met. Any modification must be approved by team leader/manager.

12.4 Initial calibration

12.4.1 Refer to Section 10.1.

12.5 Initial calibration Verification (ICV) -Second source calibration check standard

12.5.1 Refer to Section 10.2.

12.6 Continuing calibration Verifications (CCV)

12.6.1 Refer to Section 10.3.

12.7 Sample analysis (Primary)

12.7.1 All samples and quality control samples are injected into the Gas Chromatograph using the autosampler. Program the sampler for an appropriate number of syringe rinses and a 1ul or 2 μl injection size. A splitless injection technology is used.

12.7.2 Sample concentrations are calculated by comparing sample responses with the initial calibration of the system (Section 14.4). If sample response exceeds the limits of the initial calibration range, dilute the extract and reanalyze. Extracts must be diluted so that all peaks are on scale, as overlapping peaks are not always evident when peaks are off scale.

12.7.3 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the sample meet instrument QC requirements. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

12.7.4 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst must consult with the source of the sample to determine whether further concentration of the sample is warranted.

12.7.5 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement of the capillary column or detector is warranted. Rerun the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix.

12.8 Confirmation analysis.

12.8.1 Confirmation analysis is to confirm the presence of Aroclors tentatively identified in the primary analysis.

12.8.1.1 All instrument performance quality control criteria for calibration and retention time must be satisfied on the confirmation analysis.

12.8.2 Each tentative identification must be confirmed: using a second GC column of dissimilar stationary phase (as in the dual-column analysis), based on a clearly identifiable Aroclor pattern, or using another technique such as GC/MS.

12.8.2.1 The primary and secondary analysis is conducted simultaneously in the dual-column analysis.

12.8.2.2 GC/MS confirmation may be used in conjunction with dual-column analysis if the concentration is sufficient for detection in GC/MS, normally a concentration of approximately 10 ng/µl in the final extract for each Aroclor is required. Method 8270 is recommended as a confirmation technique when sensitivity permits.

12.8.3 Once the identification has been confirmed, the agreement between the quantitative results on both columns must be checked.

12.9 Sample Dilution

12.9.1 Establish dilution of sample in order to fall within calibration range or to minimize the matrix interference.

- Utilize screen data (specific project only).
- Utilize acquired sample data.
- Utilize the history program or approval from client/project.
- Sample characteristics (appearance, odor).

12.9.2 If no lower dilution has been reported, the dilution factor chosen must keep the response of the largest peak for a target analyte in the upper half of the initial calibration range of the instrument.

12.9.3 Preparing Dilutions.

12.9.3.1 Prepare sample dilutions quantitatively. Dilute the stored sample extract if available with hexane using logical volume to volume ratios, i.e., 1:5, 1:10, 1:50, etc.

12.9.3.2 Syringe Dilutions - A calibrated 1ml syringe must be used to prepare dilutions. Gently shake to disperse the extract throughout the solvent prior to loading on the auto-sampler tray for further analysis.

12.9.3.3 Volumetric Flask Dilutions – Dilutions can also be made with a Class A volumetric flask. Measure appropriate sample extract volume in a calibrated syringe and bring to a final volume with dilution solvent in a Class A volumetric flask. Gently shake to disperse the extract throughout the solvent prior to loading on the auto-sampler tray for further analysis.

12.10 Data interpretation

12.10.1 Qualitative identification

12.10.1.1 Analyst shall identify the target analytes with competent knowledge interpreting retention time and/or chromatographic pattern by comparison of the sample to the standard of the suspected Aroclor. The criteria required for a positive identification are:

12.10.1.1.1 The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

12.10.1.1.2 The target analytes must elute within the daily absolute retention time window on both primary and confirmation column.

12.10.1.1.3 For PCBs, at least five major peaks are selected. The retention time window for each peak is determined from the initial calibration analysis. This identification of PCBs as Aroclors is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of multi-component target analytes. Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte.

12.10.1.1.4 Be aware of matrix interfering effects on peak shape and relative peak ratios which could distort the pattern. Interpretation of this phenomenon may require a highly experienced chromatographer or at least a second opinion.

12.10.2 Quantitative analysis

12.10.2.1 Once the Aroclor pattern has been identified, compare the responses of at least 3 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each corresponding peak and the linear calibration established from the multi-point calibration of the 1016/1260 mixture. A concentration (see section 14.4) based on the integrated area/or height of each of the characteristic peaks is determined and then those resulting concentrations are averaged to provide the final result for the sample.

12.10.2.2 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. The quantitation may then be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times must be subtracted from the total area. When quantitation is performed in this manner,

the problems must be fully described for the data user and the specific procedures employed by the analyst must be thoroughly documented.

12.10.2.3 When sample results are confirmed using two dissimilar columns or with two dissimilar detectors, the agreement between the quantitative results must be evaluated after the identification has been confirmed. Calculate the relative percent difference (RPD) between the two results using the formula in Section 14.6. The lower result is reported.

12.10.2.3.1 If one result is significantly higher (e.g., >40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instrument data system (or operator) during peak integration.

12.10.2.3.2 If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the lower result with the footnote (remark) indicating "More than 40% RPD for detected concentrations between two GC columns".

13.0 QUALITY CONTROL

13.1 QC Requirements Summary

Initial Calibration	Whenever needed
Initial Calibration Verification (ICV)	Following initial calibration
Continuing Calibration Verifications (CCV)	Every 12-hour shift , after every 10 samples and at the end of analysis sequence
Instrument Blank	After each CCV
Method blank	One per extraction batch*
Blank Spike	one per extraction batch*
Matrix Spike	one per extraction batch*
Matrix Spike Duplicate	one per extraction batch*
Surrogates	every sample and standard

*The maximum number of samples per batch is twenty or per project specification.

13.2 Initial Calibration.

13.2.1 Refer to Section 10.1.

13.3 Initial Calibration Verification (ICV) -Second Source Calibration Check.

13.3.1 Refer to Section 10.2.

13.4 Continuing Calibration Verifications (CCV)

13.4.1 Refer to Section 10.3.

13.5 Instrument Blank

13.5.1 If the instrument blank contains a target analyte above its MDL, the source of the

contamination must be identified and corrected before proceeding with the analysis.

13.6 Method Blank.

13.6.1 The method blank is either DI water or sodium sulfate (depending upon the sample matrix) which must be extracted with each set of 20 or less samples. For a running batch, a new method blank is required for each different extraction day. The method blank must be carried through all stages of the sample preparation and measurement.

13.6.2 If the method blank contains a target analyte above its MDL established by the laboratory, the entire batch must be re-extracted and reanalyzed.

13.6.3 Surrogate compounds are added to the method blank prior to extraction and analysis. If the surrogate accuracy in the blank does not meet criteria established by the laboratory, the entire batch must be re-extracted and reanalyzed.

13.7 Blank Spike (Laboratory Control Sample)

13.7.1 A blank spike must be extracted with each set of 20 or less samples. For a running batch, a new blank spike is required for each different day. The blank spike consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. It is spiked with the same analyte at the same concentration as matrix spike. When the presence of specific Aroclors is not anticipated, the Aroclor 1016/1260 mixture may be appropriate choice for spiking. In situations where the other Aroclors are of interest for a specific project, the analyst may employ different spiking mixtures. The blank spike is prepared at a concentration of 2 μg/l or 66.7 μg/kg (on a dry weight basis) for each Aroclor.

13.7.2 The blank spike recoveries must be assessed using in house limits established by the laboratory.

13.7.3 If a blank spike is out of control, the following corrective actions must be taken. In the case where the blank spike recovery is high and no hits reported in associated samples and QC batch the sample results can be reported with footnote (remark) and no further action is required.

13.7.3.1 Check to be sure that there are no errors in the calculations, or spike solutions. If errors are found, recalculate the data accordingly.

13.7.3.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample batch.

13.7.3.3 If no problem is found, re-extract and reanalyze the sample batch.

13.8 Matrix Spike (MS) / Matrix Spike Duplicate (MSD).

13.8.1 One sample is randomly selected from each extraction batch and spiked in duplicate with select Aroclors to assess the performance of the method as applied to a particular matrix and to provide information on the homogeneity of the matrix. Both the MS and MSD are carried through the complete sample preparation, cleanup, and determinative procedures.

13.8.2 The MS and MSD must be spiked with the Aroclors of interest. If samples are not expected to contain target analytes, a matrix spike and matrix spike duplicate pair must be spiked with Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclor must be used for spiking.

13.8.3 Matrix spikes are prepared by spiking an actual sample at a concentration 2 μg/l or 66.7μg/kg on a dry weight basis.

13.8.4 Assess the matrix spike recoveries and relative percent difference (RPD) against the control limits established by the laboratory.

13.8.5 If the matrix spike accuracy of any individual Aroclor is out of control, the accuracy for that Aroclor in the blank spike must be within control. Matrix interference is assumed and the data is reportable. No further corrective action is required.

13.9 Surrogates.

13.9.1 Tetrachloro-m-xylene (TCMX) and Decachlrobiphenyl (DCB) are used as surrogate standards. All blanks, samples, matrix spikes, and calibration standards contain surrogate compounds which are used to monitor performance of the extraction, cleanup (when used), and analytical system.

13.9.2 The recoveries (Section 14.5) of the surrogates must be evaluated versus the surrogate control limits developed by the laboratory annually.

13.9.3 If surrogate recoveries are not within established control limits, corrective action must be performed if surrogate recoveries indicate that a procedural error may have occurred during the analysis of the sample.

13.9.3.1 Check the surrogate calculations for calculation or integration errors and perform corrections if detected.

13.9.3.2 Reanalyze the extract if no calculation errors are detected. If the surrogate recoveries for the reanalyzed extract are in control, report the data from the reanalysis only.

13.9.3.3 If the data from the reanalysis is also out of control, re-extract and reanalyze the sample.

13.9.3.4 If, upon reanalysis, the surrogate recoveries are acceptable, report the reanalysis data. If the holding time has expired prior to the reanalysis, report both the original and reanalysis results and note the holding time problem.

13.9.3.5 If the recovery is again not within limits, the problem is considered to be matrix interference. Submit both data sets with the original analysis being reported.

13.9.4 The retention time shift for surrogate must be evaluated after the analysis of each sample. The sample must be reanalyzed when the retention times for both surrogates are outside the retention time window.

13.9.4.1 Reanalyses are not required for samples having visible matrix interference, defined as excessive signal levels from target or non-target interfering peaks. This judgment must be approved by a team leader or supervisor.

13.10 Refer to Project Specific Bench Notes(GC8082) for additional program or client specific QC requirements.

14.0 CALCULATION

14.1 Calibration Factor (CF).

$$CF = \frac{A_s}{C_s}$$

where:
A_s = Area of the peak for the compound being measured.
C_s = Concentration of the compound being measured (μg/l).

14.2 Percent Relative Standard Deviation (% RSD).

$$\%RSD = \frac{SD}{CF_{av}} \times 100$$

where:
SD = Standard Deviation.
CF_{av} = Average calibration factor from initial calibration.

14.3 Percent Difference (% D).

$$\% D = \frac{|CF_{av} - CF_c|}{CF_{av}} \times 100$$

where:
CF_c = CF from continuing calibration (CBCHK).

14.4 Concentration (Conc.).

For water:

$$\text{Conc. } (\mu g/l) = \frac{A_c \times M}{CF_{av}}$$

$$M = \frac{V_f \times D}{V_i}$$

For soil/sediment (on a dry weight basis, see SOP EGN007):

$$\text{Conc. } (\mu g/kg) = \frac{A_c \times M}{CF_{av}}$$

$$M = \frac{V_f \times D}{W_s \times S}$$

where:
A_c = Area of peak for compound being measured.
V_f = Final Volume of total extract (ml).
D = Secondary dilution factor.
V_i = Initial volume of water extracted (ml).
W_s = Weight of sample extracted (g).
S = (100 - % moisture in sample) / 100 or % solid/100.
M = Multiplier.

14.5 Percent Recovery (% R).

$$\% R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

14.6 Relative Percent Difference (RPD).

$$RPD = \frac{|C_1 - C_2|}{(1/2)(C_1 + C_2)} \times 100$$

where:
C_1 = Matrix Spike Concentration or the result on column 1.
C_2 = Matrix Spike Duplicate Concentration or the result on column 2.

15.0 DOCUMENTATION

15.1 The Analytical Logbook is a record of the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

15.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in this log. For consistency, if surrogates are high or low indicate it as (↑) for high and (↓) for low.

15.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed, the page must be signed and dated by the respective person.

15.2.1 The Accutest Lot Number must be cross-reference on the standard vial.

15.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument will have a separate log.

15.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

15.5 Unused blocks of any form must be x'ed and z'ed by the analyst before submitting the data for review.

15.6 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information must also be verified during this review.

16.0 DATA REVIEW AND REPORTING

16.1 Initial and continuing calibration check. Verify that all calibration and continuing calibration criteria have been achieved. If the criteria had not been achieved, corrective action must be performed to bring the system in control before analyzing any samples.

16.1.1 If samples had been analyzed under non-compliant calibration criteria, all sample extracts must be re-analyzed once the system is brought into control.

16.2 Quality Control Data Review. Review all QC data. If QC criteria were not achieved, perform corrective action before proceeding with analysis.

16.2.1 In some situation, corrective action may demand that the entire sample batch be re-extracted and re-analyzed before processing data.

16.3 Chromatogram Review. The chromatogram of each sample is evaluated for target analytes.

16.3.1 Check specific retention time windows for each target compound for the presence of the target compound in each chromatogram.

16.3.1.1 Each sample may require the reporting of different target analytes. Review the login to assure that the correct target compounds are identified.

16.3.2 The Aroclor must be identified on the primary and confirmatory column before assigning a qualitative identification.

16.3.3 Manual integration of chromatographic peaks must be identified by the analysts. An electronic signature is applied upon data review.

16.4 Transfer to LIMS. Following the initial screen review, transfer the processed data to the LIMS.

17.0 POLLUTION PREVENTION & WASTE MANAGEMENT

17.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All

safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 17.2.

17.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

17.2.1 Non hazardous aqueous wastes.

17.2.2 Hazardous aqueous wastes

17.2.3 Chlorinated organic solvents

17.2.4 Non-chlorinated organic solvents

17.2.5 Hazardous solid wastes

17.2.6 Non-hazardous solid wastes

Table 1. PCB Aroclors and Reporting Limits				
Compound	**CAS Number**	**Water (μg/l)**	**Soil (μg/kg)**	**Oil (μg/kg)**
Arochlor – 1016	12674-11-2	0.5	30	2500
Arochlor – 1221	11104-28-2	0.5	30	2500
Arochlor – 1232	11141-16-5	0.5	30	2500
Arochlor – 1242	53469-21-9	0.5	30	2500
Arochlor – 1248	12672-29-6	0.5	30	2500
Arochlor – 1254	11097-69-1	0.5	30	2500
Arochlor – 1260	11096-82-5	0.5	30	2500

Table 2. RECOMMENDED OPERATING CONDITION	
Gas Chromatograph/Electron Capture Detectors	
Carrier Gas	Helium
Make-up gas	5 % Methane/ 95 % Argon
Make-up gas flow	*30 ml/min
Injection port temperature	*235 °C
Injection type	Splitless
Detector temperature	*320 °C
Column flow	*5 ml/min
Gas Chromatograph Temperature Program*	
Initial temperature	*170 °C
Time 1	*2 min
Column temperature rate 1	*30 degrees/min
Temperature 1	*180 °C
Column temperature rate 2	*3.5 degrees/min
Temperature 2	*240 °C
Column temperature rate 3	*10 degrees/min
Final temperature	*280 °C
Time 3	*5 min
Total run time	30-40 min

* Parameter modification allowed for performance optimization as long as QC criteria are achieved.

Table 3A. Aroclors 1016/1260 Mixture and Surrogates Working Solution	
Stock Solution	**Volume Added**
Aroclor 1016/1260 (1,000 μg/ml)	500 μl
Pesticides Surrogate Std Spiking Solution (200 μg/ml)	100 μl
Hexane	fill to volume
Total	25.0 ml

- Aroclors 1016/1260 (20 μg/ml) and Surrogates (0.8 μg/ml) Working Solution: Prepared by measuring 500 μl of 1,000 μg/ml Aroclor 101/1260 and 100μ of 200 μg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 3B. Individual Aroclor* and Surrogates Working Solution	
Stock Solution	**Volume Added**
Individual Aroclor* (1,000 μg/ml)	500 μl
Pesticides Surrogate Std Spiking Solution (200 μg/ml)	100 μl
Hexane	24.4 ml
Total	25 ml

*Aroclor: 1221, 1232, 1242, 1248, 1254, 1262 & 1268

- Individual Aroclor (20 μg/ml) and Surrogates (0.8 μg/ml) Working Solution: Prepared by measuring 500 μl of 1,000 μg/ml each individual Aroclor, 100 μl of 200 μg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 4A. Aroclors 1016/1260 Calibration Standard Solutions					
Standard	**Working Solution**	**Concentration (μg/ml)**	**Volume Added (μl)**	**Final Volume in Hexane (ml)**	**Final Concentration(μg/l)**
Standard A	Aroclors 1016/1260	20	62.5	25	50
	Surrogates	0.8			2
Standard B	Aroclors 1016/1260	20	312.5	25	250
	Surrogates	0.8			10
Standard C	Aroclors 1016/1260	20	625	25	500
	Surrogates	0.8			20
Standard D	Aroclors 1016/1260	20	1250	25	1,000
	Surrogates	0.8			40
Standard E	Aroclors 1016/1260	20	2,500	25	2,000
	Surrogates	0.8			80
Standard F	Aroclors 1016/1260	20	3,750	25	3,000
	Surrogates	0.8			120

- Standard A: Prepared by measuring 62.5 μl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.
- Standard B: Prepared by measuring 312.5 μl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.
- Standard C: Prepared by measuring 625 μl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.
- Standard D: Prepared by measuring 1,250 μl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.
- Standard E: Prepared by measuring 2,500 μl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.
- Standard F: Prepared by measuring 3,750 μl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.

Table 4B. Single-Point Calibration Standard (1,000 µg/l) for Individual Aroclor*	
Stock Solution	**Volume Added**
Individual Aroclor*/Surrogate Working Solution (20 µg/ml/0.80µg/ml) (Table 3B)	1,250 µl
Hexane	23.75 ml
Total	25 ml

* Aroclor: 1221, 1232, 1242, 1248, 1254, 1262, & 1268.

- Individual Aroclor Calibration Standard (1,000 µg/l) and Surrogates (40 µg/l) Solution: Prepared by measuring 1,250 µl of individual Aroclor and surrogates working solution, containing 20 µg/ml of each corresponding Aroclor and 0.80 µg/ml of both surrogate compounds, and bringing to 25 ml with hexane.

Table 4C. Multi-point Calibration Standards for Individual Aroclor* (optional)					
Standard	**Stock Solution**	**Concentration (µg/ml)**	**Volume Added (µl)**	**Final Volume in Hexane (ml)**	**Final Concentration(µg/l)**
Standard A	Aroclor*	20	62.5	25	50
	Surrogates	0.8			2
Standard B	Aroclor*	20	312.5	25	250
	Surrogates	0.8			10
Standard C	Aroclor*	20	625	25	500
	Surrogates	0.8			20
Standard D	Aroclor*	20	1250	25	1,000
	Surrogates	0.8			40
Standard E	Aroclor*	20	2,500	25	2,000
	Surrogates	0.8			80
Standard F	Aroclor*	20	3,750	25	3,000
	Surrogates	0.8			120

*Aroclor: 1221, 1232, 1242, 1248, 1254, 1262, & 1268.

- Standard A: Prepared by measuring 62.5 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

- Standard B: Prepared by measuring 312.5 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

- Standard C: Prepared by measuring 625 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

- Standard D: Prepared by measuring 1,250 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

- Standard E: Prepared by measuring 2,500 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

- Standard F: Prepared by measuring 3,750 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

Table 5A. Continuing Calibration Check Solutions for Aroclors 1016/1260					
Checks	**Working Solution**	**Concentration (µg/ml)**	**Volume Added (µl)**	**Final Volume in Hexane (ml)**	**Final Concentration (µg/l)**
Solution 1	Aroclors 1016/1260	20	625	25	500
	Surrogates	0.8			20
Solution 2	Aroclors 1016/1260	20	1250	25	1,000
	Surrogates	0.8			40

- Solution 1: Prepared by measuring 625 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.

- Solution 2: Prepared by measuring 1,250 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.

Table 5B. Continuing Calibration Check Solutions for Individual Aroclor*					
Checks	**Working Solution**	**Concentration (µg/ml)**	**Volume Added (µl)**	**Final Volume in Hexane (ml)**	**Final Concentration (µg/l)**
Solution 1	Aroclor*	20	625	25	500
	Surrogates	0.8			20
Solution 2	Aroclor*	20	1250	25	1,000
	Surrogates	0.8			40

* Aroclor: 1221, 1232, 1242, 1248, 12541262, & 1268

- Solution 1: Prepared by measuring 625 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

- Solution 2: Prepared by measuring 1,250 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

Table 6A. Second Source Calibration Check Standard for Aroclors 1016/1260 (1,000 µg/l)	
Stock Solution	**Volume Added**
Aroclors 1016/1260 (25 µg/ml) and Surrogates (2.5 µg/ml) Working Solution	1,000 µl
Hexane	24 ml
Total	25 ml

- Aroclors 1016/1260 (25 µg/ml) and Surrogates (2.5 µg/ml) Working Solution: Prepared by measuring 250 µl of 1,000 µg/ml Aroclors 1016/1260 mix solution (2nd source), 125 µl of 200 µg/ml pesticides surrogate std spiking solution and bringing to 10 ml with hexane.

- Aroclors 1016/1260 (1,000 µg/l) and Surrogates (100 µg/l) Solution: Prepared by measuring 1,000 µl of Aroclors 1016/1260 (25 µg/ml) and surrogates (2.5 µg/ml) working solution and bringing to 25 ml with hexane.

Table 6B. Second Source Calibration Check Standard for Individual Aroclor* (1,000 μg/l)	
Stock Solution	**Volume Added**
Individual Aroclor* (25 μg/ml) and Surrogates (2.5 μg/ml) Working Solution	1,000 μl
Hexane	24 ml
Total	25 ml

*Aroclor: 1221, 1232, 1242, 1248, 1254, 1262 & 1268

- Individual Aroclor (25 μg/ml) and Surrogates (2.5 μg/ml) Working Solution: Prepared by measuring 250 μl of 1,000 μg/ml each individual Aroclor stock solution (2nd source), 125 μl of 200 μg/ml pesticides surrogate std spiking solution and bringing to 10 ml with hexane.

- Individual Aroclor (1,000 μg/l) and Surrogates (100 μg/l) Solution: Prepared by measuring 1,000 μl of each individual Aroclor (25 μg/ml) and surrogates (2.5 μg/ml) working solution and bringing to 25 ml with hexane.

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager:

QA Manager:

Effective Date: 11/14/13

TITLE: CYANIDE (LACHAT AUTOANALYZER).

METHOD REFERENCE: EPA 335.4 for non-potable and potable waters
SW846 9012B modified for soils or aqueous wastes

Revised Sections: ***1.3, 15.3***

1.0 SCOPE AND APPLICATION

1.1 The purpose of this method is to determine the amount of total cyanide in any given sample by automated UV colorimetry following distillation to remove interferences.

1.2 The modification from SW846 9012B is reduced volumes for the micro distillation procedure and a modification of the sulfide pre-treatment procedure.

1.3 Additional QC requirements for DOD QSM 5.0 are also included in this SOP.

2.0 SUMMARY OF METHOD

2.1 The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by automated UV colorimetry. The distilled cyanide is reacted with chloramine-T at a pH of less than 8 to form cyanogen chloride. The cyanogen chloride is then reacted with pyridine-barbituric acid reagent to form a red-blue dye. The intensity of the dye is measured by recording the absorbance at 570 nm.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. For waters, the reporting limit for this method is established at the lowest concentration standard in the calibration curve which is normally 0.010 mg/l. For soils, the reporting limit is based on an instrument value of 0.020 mg/l, multiplied by the final volume and divided by the sample weight and %solids used. For a 0.5 g sample aliquot with 100% solids, the standard reporting limit is 0.24 mg/kg. Detected concentrations below this concentration cannot be reported without qualification.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's) For most methods, the mid-level calibration check standard criteria is ± 10 percent of the true value.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. For cyanide, method specific limits are defined. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK SAMPLE. Digest and analyze a high and a low standard with each batch of samples. These standards must have a recovery of 90 to 110 %. If the spike blank is outside of the control limits for a parameter, all samples must be redistilled and reanalyzed for that parameter. The exception is if the spike blank recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

LAB CONTROL SAMPLE. A solid lab control sample from an external source may be distilled with a batch, depending on individual client requirements. The solid lab control is evaluated using manufacturer's limits. If the lab control is outside of the control limits for a parameter, all samples must be redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are

within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples for EPA 335.4 or 1 in 20 samples for SW846 methods. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). - The minimum concentration of a substance 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. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 Cyanide is very toxic. Samples must be kept basic until the time of distillation to prevent the formation of HCN. Make sure that the distillation flasks are tightly closed and leak free during the distillation process.

5.3 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 All water samples should be preserved with NaOH to a pH of $\geq$ 12 and stored in a refrigerator at 4^{o}C. Ascorbic acid should be added to prevent decomposition of the cyanides by oxidizing agents such as chlorine. Ascorbic acid is normally added during the field with the initial sample preservation. Soil samples should be cooled to 4°C at the time of collection.

6.2 All cyanides should be analyzed within 14 days of the date of collection.

7.0 INTERFERENCES

7.1 Many of the interferences in this method can be reduced or eliminated by the distillation step. All samples should be distilled before analysis. Sulfides can cause interferences but these can be removed by treatment of the distillate with cadmium

carbonate solution. High results may also be obtained due to interferences from nitrate or nitrite. These interferences can be eliminated by pretreatment of the sample with sulfamic acid during the distillation step. Oxidizing agents interfere by decomposing most of the cyanide. Ascorbic acid, added to the sample at the time of collection, will minimize the effect of these oxidizing agents.

7.2 Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/kg were not found to interfere.

7.3 Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in high concentrations. This interference can be minimized by using a smaller sample size or by following a special extraction procedure. Check with the lab manager or supervisor for additional information.

8.0 APPARATUS

8.1 Automated continuous flow analyzer designed to deliver and react sample and reagents in the required order and ratios. Currently, two Lachat QuikChem 8000 Automated Ion Analyzers are being used.

8.1.1 Autosampler

8.1.2 Multichannel pump

8.1.3 Reaction manifold.

8.1.4 Colorimetric detector

8.1.5 Real time data acquisition device (either electronic or hard copies.)

8.2 Balance. Analytical balance capable of accurately weighing to the nearest 0.0001 g.

8.3 Volumetric glassware. Class A volumetric pipets and flasks as required. Note: All glassware should be washed with soap and tap water and then well rinsed with distilled, deionized water

9.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water should be used whenever water is required. The expiration date for standards and reagents is the date supplied by the manufacturer. If no expiration date is given by the manufacturer, then a default of 6 months is used. For acid solutions (nitric, sulfuric, hydrochloric) the expiration date is 2 years from the date of preparation of the solution.

9.1 Carrier solution, 0.25 M Sodium Hydroxide. Dissolve 10.0g of sodium hydroxide in a 1liter volumetric flask containing approximately 800 ml of DI water. Dilute to a final volume of 1 liter and mix well.

9.2 1.25 N Sodium Hydroxide Solution (for preparation of standards). Dissolve 10.0 g of sodium hydroxide in a 200 ml volumetric flask containing approximately 160 ml of DI water. Dilute to a final volume of 200 ml and mix well.

9.3 Phosphate Buffer Solution, 1.0 M. Dissolve 138 g of sodium phosphate monobasic (NAH_2PO_4 H_2O) in approximately 800 ml of DI water, add 0.5 ml of brij-35, dilute to a final volume of 1 liter and mix well.

9.4 Chloramine-T Solution. Add 2.0 g of chloramine-T to a 500ml volumetric flask containing approximately 250 ml of DI water. Dilute to a final volume of 500 ml with DI water and mix well. Note: This reagent works best when prepared fresh daily, but should be prepared fresh at least weekly.

9.5 Pyridine-Barbituric Acid Reagent. Note: Prepare this reagent in a hood. Weigh 15.0 g of barbituric acid in 1 liter volumetric flask. Add 100.0 ml of water, rinsing down the sides of the flask to wet the barbituric acid. Add 75 ml of pyridine with stirring and mix until the barbituric acid dissolves. Then add 15 ml of concentrated hydrochloric acid and mix. Dilute to a final volume of 1 liter with DI water and mix well.

9.6 Cyanide Stock Solution, 1000 mg/l. Dissolve 2.51 g of KCN and 2.0 g of KOH in approximately 900 ml of DI water in a 1 liter volumetric flask. Dilute to a final volume of 1 liter. Standardize weekly with silver nitrate solution.

9.7 Standard Silver Nitrate Solution, 0.0192 N. Crush approximately 5 g of silver nitrate crystals and dry to constant weight at 40 °C. Weigh out 3.2647 g of dried silver nitrate into a 1 liter flask containing approximately 800 ml of DI water. Dilute to a final volume of 1 liter with DI water and mix well.

9.8 Intermediate Cyanide Solution, 20.0 mg/l. (Normally used for external preparation only). Pipet 10.0 ml of 1000 mg/l stock solution of CN into a 500 ml volumetric flask containing approximately 400 ml of DI water. Dilute to a final volume of 500 ml and mix well. Note: These volumes may need to be adjusted to obtain the final concentration of 20.0 mg/l based on the standardized value of the cyanide stock. This intermediate may be used for a maximum of one week or until the expiration date of the weekly stock standardization, whichever is sooner.

9.9 Intermediate Cyanide Solution, 5.0 mg/l. Pipet 1.00 mL of 1000 mg/l cyanide solution into a 200 ml volumetric flask containing approximately 80 ml of DI water. Dilute to a final volume of 200 ml and mix well. Note: These volumes may need to be adjusted to obtain the final concentration of 5.0 mg/l based on the standardized value of the cyanide stock. This intermediate may be used for a maximum of one week or until the expiration date of the weekly stock standardization, whichever is sooner.

9.10 Intermediate Cyanide Solution for Distilled Check Standard, 1.0 mg/l. Pipet 0.20 ml of 1000 mg/l cyanide solution into a 200 ml volumetric flask containing approximately 80 ml of DI water. Dilute to a final volume of 200 ml and mix well. Note: These volumes may need to be adjusted to obtain the final concentration of 1.0 mg/l based on the standardized value of the cyanide stock. This intermediate

may be used for a maximum of one week or until the expiration date of the weekly stock standardization, whichever is sooner.

9.11 Cyanide Standard Solutions. Suggested standard concentrations are shown below. All standards are made up using the above intermediate solutions as outlined in the table below. Alternate standard concentrations may be used as long as all method requirements are met. Standards should have a final concentration of 0.25 N NaOH. This NaOH concentration can be obtained by adding 20 ml of 1.25 N NaOH to each of the standards. These standards should be made fresh daily before distillation or analysis. A blank must be included with each calibration curve.

ml of 5.0 mg/l CN	Final Volume	Concentration (mg/l)
16.0 ml	100 ml	0.80 mg/l
12.0 ml	100 ml	0.60 mg/l
8.0 ml	100 ml	0.40 mg/l
2.0 ml	100 ml	0.10 mg/l
0.40 ml	100 ml	0.020 mg/l
0.20 ml	100 ml	0.010 mg/l

9.12 Benzalrhodanine indicator. Dissolve 20 mg (0.02 gms) p-dimethylaminobenzalrhodanine in 100 ml acetone.

10.0 PROCEDURE

10.1 Below is a step-by-step procedure for the analysis of samples for the determination of cyanide. At the end of this SOP is a short summary outlining the overall procedure.

10.2 If the cyanide stock solution has not been standardized within a week, then the stock must be standardized before proceeding further with the analysis. The standardization can be done following the procedure outlined below.

10.2.1 Volumetrically measure out 25.0 ml of the 1000 mg/l cyanide stock solution into a graduated plastic beaker. Add 10 to 12 drops of benzalrhodanine indicator to the solution. Place a stir bar in the beaker.

10.2.2 Fill a buret with 0.0192 N silver nitrate solution. Titrate the sample with continuous stirring until the color changes from yellow to a brownish-pink. Approximately 25 ml of silver nitrate solution should be needed to reach this endpoint. Also analyze a method blank that has been brought to pH > 12 with KOH following this procedure.

10.2.3 Calculate the concentration of the stock cyanide solution using the equation shown below.

$$CN, mg/l = \frac{(A - B) \times 1000}{25 \text{ ml}}$$

Where A = the volume of $AgNO_3$ used to titrate the sample.

B = the volume of $AgNO_3$ used to titrate the blank.

Make sure to modify the volumes used in the preparation of the intermediate cyanide stocks based on the result of this standardization.

10.3 Install the cyanide reaction manifold. Check all tubing and change any tubing that is flat, dirty, etc. Install the appropriate sample loop and the appropriate filter. Place the tubing in the bottles for the pyridine/barbituric acid, the chloramine-T, the phosphate buffer, and the 0.25 M NaOH carrier. Also make sure that the waste container is in place. Refer to the manufacturer's instructions for additional information.

10.4 Start pumping reagents through the system.

10.5 Use the following commands for running the newer QuikChem software.

10.5.1 Select the "CN" icon from Windows. Click on Window and Tile to open. The run worksheet, run properties, and channel CN windows.

10.5.2 Type in the calibration standards and the ICV and ICB. Also type in the CCV/CCB pairs to run at the beginning, at the end, and after every 10 samples.

10.5.3 To insert sample lines, click on the gray box to the left of the sample line. Right click on the box and choose "append many" and enter the corresponding number of sample lines. Then type in the sample identification numbers. Next change the cup numbers to correspond with the correct position on the autosampler tray.

10.5.4 Load the autosampler tray and the click on the start icon to start the tray running.

10.5.5 After the calibration standards have finished running, click on the last icon in the channel 1 window to view the curve. If the calibration does not meet the criteria, then the instrument must be recalibrated. If the calibration meets criteria, then proceed with the samples and continuing quality control.

10.5.5.1 While the tray is running, you will see a stop sign on the tool bar. To suspend the tray, click on the stop sign and select the appropriate option.

10.5.6 When the run is complete when the stop sign goes away. Prepare a customized report by clicking on "tools" and choosing the custom report option. Click on "report" and choose "open format" and then choose "Accutest".

10.5.7 At the end of the run, rinse out the remainder of the system with DI water.

10.6 Calculations may be either done manually, using the Lachat software, or using the Accutest LIMS system. Check with the lab supervisor or manager for more instructions.

10.6.1 <u>For water samples</u>, the following calculations should be used.

original sample conc. of cyanide in mg/l =

$$\frac{\text{Calculated value in mg/l} * \text{dilution factor} * \text{final distillation volume in ml}}{\text{Initial distillation volume in ml}}$$

10.6.2 For soil samples, the following calculations should be used

original sample conc. of cyanide in mg/kg =

$$\frac{\text{Calculated value in mg/l} * \text{dilution factor} * \text{final distillation volume in ml}}{\text{Initial distillation weight in g} \times (\%\text{sol}/100)}$$

10.7 Review data and assemble a data package including the following items:

- Results report, showing dilution and weight correction factors.
- Daily standards prep sheet.
- Printout of peaks.
- Autosampler tray numbering sheet
- Distillation logs
- Reagent sheets
- Computer workgroup sheets

11.0 QUALITY CONTROL

11.1 Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

11.2 Method Detection Limits (MDLs). MDLs should be established using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

11.3 Limit of Detection (LOD) and Limit of Quantitation (LOQ). For samples run following the DOD QSM 4.1, LOD and LOQ samples must be analyzed quarterly following the specifications outlined in Box D-13 and D-14.

11.4 Linear Dynamic Range (LDR).). For each instrument, the upper limit of the linear dynamic range must be established. This must be done on initial use and every 6 months, or when instrument conditions change appreciably. A linear calibration should be prepared from 3 standards, one of which is close to the upper limit of the linear range. The LDR is determined by analyzing succeedingly higher standard concentrations of an analyte until the observed analyte concentration is no more

than 10 percent below the true value of the standard. Note: The normal cyanide calibration curve can be used to verify the linear dynamic range.

11.5 Quality Control Sample (also referred to as Initial Calibration Verification Standard, (ICV)). For the EPA methods, a standard from a different source than the calibration standard must be analyzed a minimum of once per quarter. For SW846 9012, an external must be analyzed with each calibration. Normally this is analyzed at the beginning of the run. For both EPA methods, the ICV should be within 10 percent of the true value. For the SW846 methods, the ICV should be within 15 percent of the true value. It is recommended that this check be run with all EPA and SW846 runs.

11.6 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. The method blank must contain the analyte at less that the reporting limit. If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

11.6.1 For DOD QSM 4.1, the method blank must be < ½ of the RL or less than 1/10th of the regulatory limit or of the sample concentration.

11.7 Spike Blank.

11.7.1 For samples prepared on the micro distillation unit where all standards are distilled, only one blank spike is required per batch on each day that a standard curve is distilled. This standard must have a recovery of 90 to 110%. It is recommended that this standard be prepared from the same source as the calibration standards.

11.7.1.1 On days that a standard curve is not distilled and for all DOD QSM4.1 work, two additional distilled standards must be prepared and analyzed. One standard must be near the low end of the curve, and the second must be near the high end of the curve. Recommended levels are 0.020 mg/l for the low distilled standard and 0.5 mg/l for the high distilled standard.

11.7.1.1.1 For EPA 335.4 and SW846 9012B M, the distilled standards must agree within + 10% of the true value.

11.7.1.1.2 For samples following DOD QSM 4.1, the standards must agree within 15% of the true value.

11.7.2 If the blank spike does not meet the recovery limits, then the associated samples must be redistilled and reanalyzed. The exception to this rule, for non-DOD samples, is if the blank spike recovery is high and the results of

the samples to be reported are less than the reporting limit, then the sample results can be reported with no flag.

11.8 Calibration Curve. Each day a calibration curve consisting of a minimum of 5 points and a blank must be run. The calibration curve should have a correlation coefficient of at least 0.995 and the concentration intercept must be less than the reporting limit for the method. If the calibration curve fails then the problem must be resolved and the curve reanalyzed before any samples can be analyzed.

11.8.1 For samples that are distilled using the micro distillation unit, all standards must be distilled.

11.8.2 For DOD QSM 4.1, a minimum of 6 points and a blank must be run. If the samples are pretreated for sulfide, the associated standards must also be pretreated and distilled for sulfide.

11.8.3 The calculation to be used for the calibration curve is shown below.

Correlation Coefficient

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where r = correlation coefficient
x = amount of analyte
y = response of instrument
$\bar{x}$ = average of x values
$\bar{y}$ = average of y values

11.9 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples for all water samples run by EPA methods. The laboratory must add a know amount of each analyte to a minimum of 1 in 20 samples for all soil samples and for all samples distilled and analyzed by SW846 methods.

11.9.1 For all water samples run by EPA methods, the spike recovery must be assessed against limits of 90 to 110 percent. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

11.9.2 For all samples analyzed using SW846 methods, the spike recovery should be assessed using in house limits. Until these limits can be generated, then default limits of 75 to 125 percent recovery should be applied. If a matrix

spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

11.9.3 For all work for DOD QSM 4.1, the matrix spike should be evaluated using the same criteria as the blank spike or lab control. DOD QSM 4.1 specifies 10% for distilled standards, but 15% for external checks. For matrix spikes, the 15% criteria will be applied.

11.9.4 The matrix spike recovery should be calculated as shown below.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{MS Recovery}$$

11.10 Matrix Duplicate. The laboratory must digest a duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the duplicate and the sample should be assessed. The duplicate rpd is calculated as shown below.

11.10.1 The duplicate RPD should be assessed using in house limits. Until these limits can be generated, then default limits of 20 percent RPD should be applied. If a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

11.10.2 The duplicate RPD should be calculated as shown below.

$$\frac{\text{(Sample Result - Duplicate Result)} \times 100}{\text{(Sample Result + Duplicate Result)} \times 0.5} = \%\ \text{RPD}$$

11.11 Continuing Calibration Verification. (Also known as the instrument performance check solution.) Analyze the continuing calibration verification solution and the continuing calibration blank after the initial calibration, after every tenth sample, and at the end of the sample run. If the CCV solution is not within 10 percent of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high (110% to 150%) and the samples are less than the reporting limit. In that case, the samples can be reported with no flag.) The CCV concentration should be at or near the mid-range of the calibration curve.

11.12 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after the initial calibration, after every tenth sample, and at the end of the sample run. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by the failing CCB.

11.13 Summary of major QC requirements. The table below shows a summary of the major QC requirements for cyanide.

QC Description	Frequency	Method and limits

ICV (external)	Every run	SW846 9012 ± 15% DOD QSM 4.1 ± 15% EPA 335.3/.4 ± 10%
CCV	Every 10 samples	All methods ± 10%
CCB	Every 10 samples	All methods < RL
Distilled Std (spike blank)	For micro distillation, a spike blank with each batch on each day. If standards are not distilled that day, then a low and a high check are required.	All methods ± 10%
Method Blank (≤ 20 samples)	Every day	SW846 9012B M and EPA 335.4 < RL. DOD QSM 4.1 < ½ RL or < 1/10th regulatory limit.
Matrix Spike (≤ 20 samples)	Spike one sample for every 10 samples in a batch for EPA methods. Two matrix spikes required for a 20 sample batch for EPA methods. Spike one sample in 20 for SW846 methods.	SW846 9012 ± 25% EPA 335.4 for wastewaters ± 25% EPA 335.4 for drinking water ± 10% DOD QSM 4.1 ± 15%
Duplicate (≤ 20 samples)	Every distillation batch	All methods ± 20%

12.0 DOCUMENTATION REQUIREMENTS

12.1 Each analyst should review all data and assemble a data package consisting of the following information.

- Results report, showing dilution and weight correction factors.
- Printout of peaks.
- Distillation or digestion log.
- Computer workgroup sheets.
- Standards prep sheet.
- Autosampler tray numbering sheet

12.2 In addition, all reagent information such as lot numbers should also be recorded in the reagent log book. Any unusual characteristics of the samples should be noted in the final results section of the final data report. Make sure that all sample ID's and dilutions are labeled on the data.

13.0 POLLUTION PREVENTION & WASTE MANAGEMENT

13.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts

specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 13.2.

13.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

13.2.1 Non hazardous aqueous wastes.

13.2.2 Hazardous aqueous wastes

13.2.3 Chlorinated organic solvents

13.2.4 Non-chlorinated organic solvents

13.2.5 Hazardous solid wastes

13.2.6 Non-hazardous solid wastes

14.0 PROCEDURE SUMMARY

14.1 The procedure outlined below is a summary for quick reference purposes only. Make sure to read and understand the entire SOP before starting an analysis.

a. Prepare reagents. Standardize CN stock.
b. Insert the reaction module, connect all reagents, and start the instrument.
c. Pour the calibration standards and start calibrating.
d. Enter sample information into autosampler table. (Make sure to save this and print this.)
e. Approve calibration.
f. Submit autosampler tray for analysis.
g. Print out peaks and results.
h. Review results and copy to the network and review on-line.
i. Turn in reviewed data to general chemistry supervisor.

15.0 ADDITIONAL REFERENCES

15.1 Lachat QuikChem 8000 Autoanalyzer manuals.

15.2 Lachat QuickChem Method 10-204-00-1-X

15.3 DOD QSM 5.0

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager: Wendy Mc

QA Manager: [signature]

Effective Date: 9/25/13

TITLE: COLD VAPOR ANALYSIS OF MERCURY FOR WATER SAMPLES

REFERENCE: EPA 245.1, revision 3.0 (1994) and SW846 7470A (modified)

Revised Sections: ***11.8, 12.10.1, 12.12.***

1.0 SCOPE AND APPLICATION

1.1 This method can be applied for the analysis of mercury for all potable and non-potable water samples. This SOP is based on the May 1994 revision of EPA method 245.1. The reporting limit for mercury water samples based on the procedures outlined in this SOP, is 0.0002 mg/l.

1.2 Aqueous wastewater may also be analyzed following method 7470A. The modification to this method are a direct scale-down of the reagents and the use of an automated analyzer.

2.0 SUMMARY

2.1 Cold vapor mercury is a flameless AA procedure based on the absorption of radiation at 253.7 by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state 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. Results are quantitated by comparison to a daily calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. Detected concentrations below this concentration cannot be reported without qualification.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the

testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. The calibration check standard must be run at a frequency of 10 percent or less. The mid-level calibration check standard criteria is either ± 10 percent of the true value.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should

be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

$$\frac{(|\text{MS Result - MSD Result}|) \times 100}{\text{(MS Result + MSD Result)/2}} = \text{MSD RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance 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. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the

definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 After the mercury digestate is reduced to Hg vapor, it must be handled in a closed system or in a hood to prevent inhalation of the toxic vapor. Make sure that the Hg instrument is vented directly to a hood.

6.0 PRESERVATION AND HOLDING TIME

6.1 All water samples must be preserved by acidification with nitric acid to a pH of 2 or lower and stored in a polyethylene or glass container.

6.2 All samples must be analyzed within 28 days of the date of collection.

7.0 INTERFERENCES

7.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations of sulfide as sodium sulfide as high as 20 mg/l do not interfere with mercury recoveries when following this method. High copper concentrations (> 10 mg/l) may also interfere with mercury recoveries.

7.2 Samples that are high in chloride such as seawater, brine, and industrial effluent may require as much as 25 ml of additional permanganate. NOTE: When chloride

concentrations are high, hydroxylamine sulfate and stannous sulfate should be used in place of the corresponding chlorides.

7.3 Finally, certain volatile organic materials will also absorb at this wavelength and can interfere. It can be determined if this type of interference is present by doing a preliminary run without reagents.

8.0 APPARATUS

8.1 Three Leeman instruments are available for analysis. **They are Leeman Hydra II** automated analyzers. Refer to the instrument manuals for further details on this instrumentation, including proper venting and safety requirements. Instrument maintenance is outlined below.

8.1.1 Change the sample tubing as needed.

8.1.2 Change the drying tubing as needed.

8.1.3 Clean the exterior of the instrument as needed.

8.1.4 Adjust the Hg lamp as needed. This can be done in the software on both instruments.

8.1.5 Complete any other maintenance required to maintain the instrument in good running order including, but not limited to, cleaning the cell, changing other tubing, changing the Hg lamp, etc.

8.2 Heating Equipment.

8.2.1 Graphite heating block. Capable of heating at 95 °C for 2 hours.

8.3 Digestion Bottles. Disposable plastic digestion tubes are used with the graphite heating block.

8.3.1 Disposable plastic digestion tubes (65 ml volume) with tops for graphite heating block.

8.4 Class A, to deliver, volumetric cylinders for measuring initial sample volumes and for calibrating glass tubes as outlined above.

8.5 Automatic pipettor bottles. Refer to EQA063 for calibration information.

9.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water should be used whenever water is required. All solutions listed below may be scaled up or down proportionally as needed.

9.1 Sulfuric acid, concentrated.

9.2 Nitric acid, concentrated. This acid must have a low mercury content.

9.3 Dilution acid. To approximately 400 ml of DI water, add 33.4 ml of concentrated sulfuric and 16.6 ml of concentrated nitric. Dilute to a final volume of 1000 ml. This dilution acid is used for making dilutions of digested samples.

9.4 Stannous chloride. Add 25 ml of concentrated hydrochloric acid to approximately 400 ml of DI water. Dilute to 500 ml with DI water and mix well. Add 50 g of stannous chloride dihydrate or 42 g of stannous chloride anhydrous and dissolve. Make sure that this solution is dissolved while in use.

9.4.1 Stannous sulfate may be used in place of stannous chloride.

9.5 Sodium chloride-Hydroxylamine hydrochloride. Add 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride to 2000 ml of water. Mix well. Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

9.6 Potassium Permanganate, 5 percent solution, w/v. Add 50 g of potassium permanganate to 1000 ml of water and mix well. **Caution** - Potassium permanganate is a strong oxidizing agent. Handle with care.

9.7 Potassium Persulfate, 5 percent solution, w/v. Dissolve 50.0 g of potassium persulfate in 1000 ml of water and mix well. **Caution** - Potassium persulfate is a strong oxidizing agent. Handle with care.

9.8 Mercury standard solutions.

9.8.1 10 ppm Hg solution. Using a 1.00 ml volumetric pipet or autopipet, add 1.00 ml of 1000 ppm stock (to be purchased from a vendor such as Fisher) to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with water and mix well. This standard may be held for up to 28 days.

9.8.1.1 The 10 ppm external source should be made up following the directions in 9.8.1.

9.8.2 **30.0** ppb Hg solution. Using an autopipet, add **0.300** ml of 10 ppm Hg solution to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

9.8.2.1 The 30.0 ppb external source should be made up following the directions in 9.8.2.

9.8.3 **3** ppb Hg solution. Using volumetric pipets or autopipets, add 10.0 ml of **30.0** ppb Hg solution to a 100 ml volumetric flask containing approximately 75 ml of DI water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

10.0 WATER DIGESTION FOR GRAPHITE HEATING BLOCK

Below is a step-by-step procedure for the digestion and analysis of water samples for mercury.

10.1 If necessary, acid rinse disposable digestion tubes with 10% nitric acid and deionized water before use.

10.2 Make up a standard curve consisting of 5 standards and a blank. Suggested concentrations are shown below. All standards are made up to a final volume of **30** ml. Different concentrations may also be used, as long as all of the method requirements are met. Make sure to clearly label each bottle. Calibration standards must be prepared fresh with each digestion batch.

ml of 3 ppb Hg solution	**ml of 30 ppb Hg solution**	**Ml of DI water**	**Total ug of Hg**	**ug/L of Hg**
0.000	0.000	**30**	0.000	0.000
2.00	0.000	**28.0**	**0.006**	0.20
5.00	0.000	**25.0**	**0.015**	0.50
0.00	1.00	**29.0**	**0.030**	1.00
0.00	2.50	**27.5**	**0.075**	2.50
0.00	5.00	**25.0**	**0.150**	5.00

10.3 Samples. For each sample, homogenize the sample well and pour out a representative aliquot of the sample into the digestion tube to the 30 ml mark. The digestion tubes are purchased from independent vendor and they are certified for the 50ml only. Accutest calibrates the 30ml volume for the 10% of the total tubes of any lot. The calibration results must be recorded in a log book with a QC/QA controlled book number. A smaller volume may be used if there are matrix problems or high levels of mercury in the sample using a class A, to deliver, graduated cylinder.

10.4 Make up additional quality control samples as shown below, using a final volume of **30** ml for each check standard. (Note: if a different standard curve is run, then the levels of the CCV and ICV standards should be adjusted accordingly in accordance with the requirements in the methods) Make sure to clearly label each bottle. Make sure to prepare enough CCV checks for the entire run. The ICV check must be from an alternate source of standards than the calibration curve. The CCV must be made from the same source as the calibration curve. A low check standard at the level of the CRDL (0.20 ug/l) is also required. This 0.20 ug/l check can be made up as outlined for the standard curve.

Sample ID	**ml of** 30 **ppb Hg solution**	**ml of DI water**	**Total ug of Hg**
CCV Check(s)	2.5	27.5	**0.075**
MB	0.0	30	**0.0**
MS	2.0	(a)	**0.06 (b)**
MSD	2.0	(a)	**0.06 (b)**
ICV	3.0	**27.0**	**0.09**
LCS	2.0	**28.0**	**0.06**

(a) **30** ml of sample
(b) plus the level of Hg in the sample.

10.5 To all samples, QC, and standards add the reagents listed below, swirling the samples well after each addition of reagent. Allow the samples to stand for at least 15 minutes after the addition of the permanganate. If the sample decolorizes, add additional permanganate until the purple color persists.

- **1.5** ml of conc. sulfuric acid.
- **0.75** ml of conc. nitric acid.
- **4.0** ml of 5% permanganate solution.

Wait 15 minutes, then

- **2.4** ml of potassium persulfate solution.

10.5.1 All of the additions shown can be done with a bottle pipettor which must be accurate to within a range of 90 to 110%.

10.6 Cap the samples and place them in the graphite heating block and heat for 2 hours at **90 to** 95 °C. Record the digestion times and temperature.

10.7 Enter the prep data into the LIMS system, double checking all volumes and spike amounts. After the prep data is checked, it can be approved and is available for use in the final calculations.

11.0 COLD VAPOR ANALYSIS PROCEDURE HYDRA II

11.1 While the samples are digesting, begin setting up the Leeman analyzer following the steps outlined below. Additional instructions are available in the instrument operators' manual.

11.1.1 Turn on the nitrogen and adjust to 60 to 90 psi. Turn on the instrument power if it is not already on.

11.1.2 Check the pump tubing and make sure that it is not flattened. Change if appropriate. Put the tubing in the clamps on the pump. Check the drying line and make sure that it is clean. Put fresh stannous chloride solution in the stannous chloride bottle. Fill the rinse bath or rinse bottle with fresh 10% nitric acid. The bath should be filled no more than ¾ full. Place the autosampler line and the stannous chloride line in the rinse container.

11.1.3 Turn on the analyzer and allow it to warm up.

11.1.3.1 For the Hydra AA II, open the Envoy software. Go to Method and click Instrument Control. On the Instrument Control page, click the startup icon. This will turn on the lamp, gas, and pump. You may also turn on/off the lamp, gas and pump individually on the Instrument Control Page.

11.1.4 Tighten the pump clamps until the flow is coming evenly through the lines. Do not overtighten.

11.1.4.1 Go to the Instrument control tab and pick the gas control test option. The input should be approximately 0.25 LPM. If the pressures are not correct, check with the area supervisor or manager before proceeding.

11.1.5 Start a batch to save your data.

11.1.5.1 Create a new chapter (Data File) by clicking Analysis. The batch should normally be named H5 followed by the month date and year, followed by the matrix designation for the batch, following by the run number. For example, the first water batch on instrument for 3/24/03 would be named H5032411w1. The realtime print option can also be turned on from this tab.

11.1.5.2 Set up autosampler racks containing the samples that are going to be run.

11.1.5.3 Create a new sequence by clicking sequence-new. Type the sequence name. After typing the samples in to sequence page make sure to click update and save. CCV and CCB checks can be entered in the macro column of the sequence page.

11.1.6 Set up the calibration.

11.1.6.1 Go to the Method menu, enter or verify the standard concentration by clicking on the standard tab. Also select number of replicates to be run for each standard. Normally one replicate is run per standard. The check standard concentrations and acceptance ranges are also defined under this standard info tab. Make sure to always click apply when any changes are made in a tab.

11.2 Add hydroxylamine hydrochloride to all samples and standards as outlined below.

12.2.1 Add **1.8** ml of hydroxylamine hydrochloride solution to each standard and sample and swirl until the solution has been completely decolorized. Transfer to a calibrated glass cylinder and dilute to a final volume of **50** ml and swirl to mix.

12.2.2 They hydroxylamine hydrochloride can be added using a bottle pipettor which is accurate in a range of 90 to 110%.

11.3 Measure out aliquots of the digested standards and samples into the autosampler cups. Work from the prep log and double check all transfers. Let all samples sit uncovered in the open autosampler vials for a minimum of one minute. Place the racks in the autosampler. Move the stannous chloride line into the stannous chloride bottle.

11.4 Start the calibration.

12.4.1 Click run sequence. The instrument will run the calibration and then pause. Click stop. Go to the Calibration page. Accept the calibration and then print the calibration. Click the Document icon, then choose HG5-PDF. Rename the file as MA*****_cal.

11.5 After the calibration has been accepted, start to run the samples.

12.5.1 For the Hydra AA II, go to the Sequence page. Right click on the first sample (ie. ICV) and click start from here.

11.6 Review the data. Any samples that are over the range of the curve should be diluted with the dilution acid (see Section 9.3) and reanalyzed. It is recommended that any sample analyzed after a sample with a value over the curve be reanalyzed for confirmation. Make sure to bracket every 10 samples with CCV and CCB checks.

11.7 Both paper and electronic reports can be generated using the report option. Never delete any samples from the reports. Electronic reports should be transferred into the LIMS system where the final calculations are done.

12.7.1 Go to analysis-Click result-Click chapter. Then go to report and select report spec. The normal report spec is "ACCUTEST". Click OK. Click on chapter in order to select all samples. Then click report output and then csv.file. Save as MA*****.csv. To print, select printer output and then type the report title (i.e. MA*****) and enter OK.

11.8 The calculations are done in the LIMS as described below. A final volume of 30.0 ml is used for calculation purposes for graphite heating block digestions. (The volume of 50.0 ml is factored out since all standards and samples are brought up to the same final volume and standard concentrations are calculated based on 30.0 ml.)

Final sample concentration in mg/L =

$$\frac{\text{concentration in the digestate in ug/l x final volume in ml}}{\text{Initial volume in ml}}$$

11.9 Review the data in the LIMS, adding comments and accepting results as appropriate.

11.10 Shut down the instruments.

12.10.2 To shut down the Hydra AA II, move the stannous chloride line from the stannous chloride bottle to the 10% HNO3 rinse bottle. Let the system rinse with 10% HNO3 for several minutes. Then switch the line to DI water bottle and let rinse for several more minutes. Let the pump and gas run until the lines are completely dry. Then go to instrument control menu and click off icon for Lamp, Gas and Pump.

12.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

12.1 Instrument Detection Limits (IDLs). The instrument detection limits must be done a minimum of once per year or when instrument conditions change significantly. The IDL is generated by running 10 replicates of a digested blank. The IDL is then defined as 3 times the standard deviation of the 10 replicates of the blank.

12.2 Method Detection Limits (MDLs). MDLs should be established using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.143, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

12.3 Instrument Calibration. The instrument must be calibrated daily or at a minimum of once every 24 hours and each time the instrument is set up. Calibration standards should be prepared fresh with each preparation batch. A minimum of a blank and 5 standards are required. The correlation coefficient of the curve must be a minimum of 0.995. No samples should be analyzed until all of the calibration criteria are met. Resloping is acceptable as long as it is immediately preceded and immediately followed by a complaint CCV and CCB.

12.4 Linear Dynamic Range (LDR). For each instrument, the upper limit of the linear dynamic range must be established. A linear calibration should be prepared from 3 standards, one of which is close to the upper limit of the linear range. The LDR is determined by analyzing succeedingly higher standard concentrations of mercury until the observed analyte concentration is no more than 10 percent below the true value of the standard. Sample concentrations that are greater than 90% of the determined upper LDR limit must be analyzed using dilutions. The LDR should be verified annually or whenever there is a significant change in the instruments analytical performance.

12.5 Quality Control Sample (also referred to as Initial Calibration Verification Standard (ICV)). At a minimum of once per quarter, a standard from a different source than the calibration standard must be analyzed. Normally this is analyzed at the beginning of the run <u>after</u> the CCV and CCB checks. The ICV must be within 10 percent of the true value. It is recommended that this standard be analyzed with each run so that it is included with all client reports. For SW846 7470A, this standard should be at a concentration near the midpoint of the calibration curve. If the ICV is outside of the acceptance limits, then the problem must be corrected and the ICV reanalyzed and shown to be within QC limits before any samples can be reported. All reported samples must be bracketed by an ICV which meets acceptance criteria.

12.5.1 If the ICV is biased high and all sample results are < RL, then, at the discretion of the data reviewer, data may be reported.

12.6 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. The method blank must contain mercury at less that the reporting limit. If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

12.7 Lab Control Sample. The laboratory must digest and analyze a laboratory control sample (spike blank) with each set of samples. A minimum of one lab control sample is required for every 20 samples. For a running batch, a new lab control sample is required for each different digestion day. For method 245.1, the laboratory must assess laboratory performance of an aqueous lab control against recovery limits of 85 to 115 percent. For method 7470A, the laboratory must assess laboratory performance of an aqueous lab control against recovery limits of 80 to 120 percent. In either case, if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit, then the sample results can be reported with no flag. If the lab control recovery is low or there are samples above the reporting limit, then all affected samples must be redigested and reanalyzed.

12.8 Matrix Spike.

12.8.1 For method 245.1, the laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples. The spike recovery should be within the limits of 70 to 130. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

12.8.2 For method 7470A, the laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The laboratory should assess the matrix spike recovery against limits of 75 to 125. (In house control limits are also generated on an annual basis and are used to support the default limits.) An exception to this rule occurs where the sample concentration exceeds the spike concentration by a factor of 4 or more. If the matrix spike fails this criterion, then the sample should be flagged as showing possible matrix interferences.

12.8.3 Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero. Refer to the calculation shown below.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{MS Recovery}$$

12.9 Matrix Spike Duplicate or Matrix Duplicate. The laboratory must digest a matrix spike duplicate or a duplicate sample for a minimum of 1 in 20 samples. Matrix spike

duplicates are normally used unless otherwise specified by client requirements. The relative percent difference (rpd) between the matrix spike duplicate and the matrix spike or between the duplicate and the sample should be assessed. The calculations for both rpds are shown below.

12.9.1 For method 245.1, the control limits for the matrix spike duplicates or the duplicates are calculated on an annual basis and are used to assess whether a matrix spike duplicate or a duplicate is in control. If it is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

12.9.2 For method 7470A, the duplicate or matrix spike duplicate RPD must be assessed against a limit of 20% RPD. (In house control limits are also generated on an annual basis and are used to support the default limits.) If it is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

12.9.3 Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero. Refer to the calculations shown below.

$$\frac{(\text{Sample Result} - \text{Duplicate Result}) \times 100}{(\text{Sample Result} + \text{Duplicate Result}) \times 0.5} = \%\ \text{RPD}$$

or

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

12.10 Continuing Calibration Verification. (Also known as the instrument performance check solution.) The CCV must be from the same source as the calibration curve.

12.10.1 Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCV solution is not within a method specified range of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.) The CCV concentration should be at or near the mid-range of the calibration curve.

12.10.1.1 For methods 245.1 and 7470A, the CCV must be within 10 percent of the true value.

12.10.2 The ICCV check must also be analyzed at the beginning of the run, immediately after the instrument is calibrated. For method 245.1, this first

check must be within 5 percent of the true value. If it is not and there is not a problem with the standard solution, the instrument should be recalibrated and rechecked.

13.10.2.1 This check is not required for method SW846 7470A.

12.11 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by the failing CCB.

12.12 CRA (Low) Check. For all runs, a low check at the level of the CRDL (0.20 ug/l) or reporting limit must be analyzed at the beginning of the run before analyzing any samples, but not before the ICV. No specific acceptance criteria are listed in any of the methods for this standard at this time. The method criteria of 70-130% recovery is applied to this low check standard. If this criterion is not met, then all samples associated with this CRA check must be reanalyzed along with a compliant CRA check.

12.12.1 If the CRA is biased high and there is no mercury found in the samples, then the sample results may be reported for mercury. If the CRA is biased high and there is mercury found in the samples, then the samples with Hg at levels ranging from the CCV to the high standard may be reported. Samples with levels of mercury between the CRA and the CCV standard may be biased high and cannot be reported.

12.12.2 Some client may require additional bracketing low checks to be analyzed. Client specific limits may also be required. Check with the area supervisor or manager for more information.

13.0 DOCUMENTATION REQUIREMENTS

Refer to the laboratory Quality Assurance Manual for additional documentation requirements.

13.1 Sample Worksheets. Digestion data sheets for the Hg water samples must show all digestion information including the sample ID's, sample volumes, bottle numbers, start times, end times, and pressure or temperature, as appropriate for all digestions. The digestion method (i.e digestion block) must be indicated on the digestion sheet. All sample information should be clearly entered on these sheets. In addition, any unusual characteristics of the samples or the digestion procedure should be noted in the Comments sections. Make sure also that all dilutions are clearly documented.

13.2 Standards and Reagents. All stocks and reagents must be recorded in the reagent logbook. All standards should be recorded on the digestion log with the samples.

13.3 Any run comments should be written on the raw data for the analysis and on the run log in the LIMS.

13.4 Annual bottle calibration verifications must be documented in the Mercury Bottle

calibration log.

14.0 DATA REVIEW AND REPORTING

14.1 All samples should be updated to QC batches in the LIMS system. The analyst is responsible for reviewing all data for compliance with the QC outlined in this SOP. They are responsible for making sure that the raw data is fully documented and it is loaded into the LIMS system. They are responsible for submitting samples for redigestion and reanalysis, when appropriate.

14.2 After the analyst review is completed, the supervisor or a designated reviewer shall review the run for technical compliance to the SOP. The reviewer is also responsible for making sure that the QC calculations are done correctly and that appropriate flags are added.

14.3 After the reviewer completes their review, the data is released for client access in the LIMS. The raw data and the run log are submitted to the area manager. The manager periodically does an additional review on data for technical completeness. Any hardcopy raw data is transferred to the report generation department for scanning and storage. Instrument data is transferred electronically.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS 004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes.

15.2.2 Hazardous aqueous wastes.

15.2.3 Chlorinated organic solvents.

15.2.4 Non-chlorinated organic solvents.

15.2.5 Hazardous solid wastes.

15.2.6 Non hazardous aqueous wastes.

16.0 ADDITIONAL REFERENCES

16.1 Leeman Hydra II instrument manual.

Lab Manager Wendy Jones

QA Manager Ad Ale

Effective Date: 8/7/13

TEST NAME: METALS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP) USING SOLID STATE ICP.

METHOD REF: SW846 6010C

Revised Sections: ***Section 9.5.3, 12.17, should to must***
Additions: ***10.7.2.1.1***

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the determination of metals in water, wipes, sludges, sediments, and soils. Sample matrices are pretreated following SW846 methods for digestion of soil, sediment, sludge, wipe or water samples. Refer to specific digestion SOP's for more information on digestion techniques.

1.2 A variety of metals can be analyzed by ICAP. These include, but are not limited to, Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, S, Se, Si, Ag, Na, Sr, Tl, Sn, Ti, Pd, V, W, Zn, and Zr.

2.0 SUMMARY

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This SOP describes operation of the ICAP 6500 Spectrometer following method SW846 6010C.

2.2.1 This inductively coupled argon plasma optical emission spectrometers (ICP-OES) uses an Echelle optical design and a Charge Injection Device (CID) solid-state detector to provide elemental analysis. Control of the spectrometer is provided by PC based iTEVA software.

2.2.2 In the instrument, samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a spectrometer, and the intensities of the emission lines are monitored the solid state detector.

2.2.3 Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples 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. In one mode of analysis the position used should be as free as possible from spectral interference and should 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. Interferences which cannot be addressed with background correction must be corrected using the appropriate interelement correction factors.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The normal reporting limits for this method have been established at the concentrations listed in Table 1. Reporting limits may vary depending on client needs and lab protocols, but the reporting limits must always be verified with a low check which meets the criteria outlined in this SOP. In addition, the reporting limits must always be greater than the MDL. Refer to the scheduling sheets and check with the metals supervisor for further information.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent during an analysis run, whichever is more frequent, and at the end of the analysis sequence. For this method, the mid-level calibration check standard criteria is $\pm$ 10 percent of the true value and the relative standard deviation for the replicates that are greater than 5 times the reporting limit is less than 5 percent. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the reporting limit.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run with each calibration. For this method, the external check standard criteria is $\pm$ 10 percent of the true value and the replicates that are greater than 5 times the reporting limit must have a relative standard deviation of less than 5 percent. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. For a running batch, a new lab control sample or spike blank is required for each different digestion day. Assess laboratory performance against the control limits of 80 to 120 percent. In house limits must also be generated once sufficient data (usually a minimum of 20 to 30 analyses) is available to support the default limits. For solid lab controls, the elements must be within the range given by the lab control supplier. If the lab control or spike blank

is outside of the control limits for a parameter, all samples must be redigested and reanalyzed for that parameter. The exception is if the lab control or spike blank recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX SPIKE DUPLICATE: A matrix spike duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the matrix spike duplicate and the matrix spike must be assessed. A duplicate may be used in place of the matrix spike duplicate on client request. The matrix spike duplicate RPD is calculated as shown below. The control limit for the duplicate is 20% rpd. If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

$$\frac{(|\text{Matrix Spike Result} - \text{Matrix SpikeDuplicate Result}|) \times 100}{(\text{Matrix Spike Result} + \text{Matrix Spike Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the default limits of 75 to 125 percent. If a matrix spike is out of control, then the results must be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and must be footnoted to that effect.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result}) \times 100}{(\text{Amount Spiked})} = \text{Matrix Spike Recovery}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less than ½ of the reporting limit for that parameter. If the method blank contains levels over this level, then the samples must be redigested and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance 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. MDLs must be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent

blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards must be prepared at the frequency specified in the appropriate section. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analysis.

LOW LEVEL CALIBRATION VERIFICATION (CRI or LLCCV). The LLCCV or CRI standard is a check standard containing the elements of interest at (or below) the reporting level for each element. For this method, the CRI (LLCV) must be analyzed at the beginning and end of each calibration (analysis) batch. The acceptance criterion for the CRI check is 70 to 130% recovery. If an element does not meet this criterion, then all bracketed samples for that element in the concentration range between the CRI and the CCV must be reanalyzed. Samples containing concentrations higher than the CCV may be reported as long as CCV criteria are met.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 All water samples should be preserved with nitric acid to a pH of 2 or less. All solid samples must be stored in a refrigerator at 4 degrees C.

6.2 All samples should be analyzed within 6 months of the date of collection.

7.0 INTERFERENCES

7.1 Several types of interferences can cause inaccuracies in trace metals determinations by ICP. These interferences are discussed below.

7.2 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, and background contribution from stray light from the line emission of high concentration elements. Corrections for these interferences can be made by using interfering element corrections, by choosing an alternate analytical line, and/or by applying background correction points.

7.3 Physical interferences can be caused by changes in sample viscosity or surface tension, by high acid content in a sample, or by high dissolved solids in a sample. These interferences can be reduced by using an internal standard, by making sample dilutions or by analyzing a sample using the method of standard additions.

7.4 Chemical interferences are not pronounced with ICAP due to the high temperature of the plasma, however if they are present, they can be reduced by optimizing the analytical conditions (i.e. power level, torch height, etc.).

8.0 EQUIPMENT AND SUPPLIES

8.1 Currently there are four solid state ICPs available for use in the lab. All are Thermo 6500 ICP units. These units have been optimized to obtain low detection limits for a wide range of elements. Since they are solid state systems, different lines may be included for elements to obtain the best analytical results. However, the lines which are normally included in the normal analysis program are shown in Table 2.

8.2 Instrument auto-samplers. For random access during sample analysis.

8.3 Class A volumetric glassware and pipets.

8.3.1 All glassware must be washed with soap and tap water and then soaked in a 10% nitric acid bath for a minimum of 2 hours. It must then be rinsed at least 3 times with deionized water.

8.4 Glass autosampler tubes

8.4.1 Autosampler tubes must be washed with soap and tap water and then soaked in a 10% nitric acid bath for a minimum of 2 hours. They must then be rinsed at least 3 times with deionized water.

8.5 Autopipeters with tips. These must be calibrated and checked as outlined in the autopipeter SOP, EQA004.

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water must be used whenever water is required. The expiration date for standards and reagents is the date supplied by the manufacturer or if no expiration date is given, a default of 6 months is used. For

acid solutions (nitric, sulfuric, hydrochloric) the expiration date is 2 years from the date of preparation of the solution.

9.2 Hydrochloric acid, trace metals grade.

9.3 Nitric Acid, Baker instra-analyzed or equivalent.

9.4 Standard stock solutions available from Absolute, Inorganic Ventures, MV Laboratories, Ultra Scientific or equivalent. Note: All standards must be ICP quality standards.

9.5 Calibration Standards. These can be made up by diluting the stock solutions to the appropriate concentrations . It is recommended that fresh calibration standards must be prepared a minimum of every two weeks. They must be monitored on a daily basis by comparison to an ICV. Standards which are going to be stored for several days must be transferred to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for long term storage.

9.5.1 Standards must be approximately matrix matched to the samples. For most samples, a 5 percent nitric acid and 5 percent hydrochloric acid will approximate the acid matrix of the sample and limit nebulization problems. If it is known that the samples contain a significantly different acid matrix, then the matrix of the standards must be modified or the samples must be diluted so that they are in a similar matrix to the curve.

9.5.2 Standards must be prepared so that there is minimal spectral interference between analytes.

9.5.3 Refer to the standards book for the make-up and concentrations of standards and stock solutions being used to calibrate the ICP. The standard curve consists of a blank and 1 non-zero standards at the levels shown in Table 3.

9.6 Calibration/Rinse Blank. The calibration blank is prepared by diluting a mixture of 50 ml of concentrated nitric acid and 50 ml of concentrated hydrochloric acid to a final volume of 1 liter with deionized water.

9.7 Analytical Quality Control Solutions. All of the solutions below are prepared by adding either mixed or single element metals solutions to a solution containing 5 percent nitric acid and 5 percent hydrochloric acid and diluting to a fixed final volume with this acid mixture. All of these solutions must be placed in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for long term storage.

9.7.1 Initial Calibration Verification solution. This standard solution must be made from a different source than the calibration curve. The values for each element must be near the midpoint of the calibration curve. This solution is used to verify the accuracy of the initial calibration. See Table 4 for suggested ICV concentrations.

9.7.2 Continuing Calibration Verification solution. The metals concentrations for this standard must be at approximately the mid-point of the calibration curve for each element. This standard must be prepared from the same source that is used for the calibration curve. See Table 4 for suggested CCV concentrations.

9.7.3 Interference Element Check Solutions. These solutions must be used on a periodic basis to check the interfering element corrections on the instruments. Note: If

interferences from different elements than those listed below are a problem, the interfering element solutions may be modified. Two acceptable solutions are outlined below.

9.7.1.1 ICSA Solution. The ICSA solution contains only the interfering elements. The recommended concentrations are shown below. If the linear ranges on a given instrument are lower than these levels, the concentrations may be set near the top of the linear range for those elements.

Al	500 mg/L
Ca	400 mg/L
Fe	200 mg/L
Mg	500 mg/L

9.7.1.2 ICSAB Solution. The ICSAB solution contains both the interferents and the analytes of interest. The recommended concentrations are shown below. If the linear ranges on a given instrument are lower than these levels, the concentrations may be set near the top of the linear range for those elements

Ag	1.0 mg/L	Zn	1.0 mg/L
Ba	0.50 mg/L	As	1.0 mg/L
Be	0.50 mg/L	Se	1.0 mg/L
Cd	1.0 mg/L	Sb	1.0 mg/L
Co	0.50 mg/L	Tl	1.0 mg/L
Cr	0.50 mg/L	Mo	0.5 mg/L
Cu	0.50 mg/L	Pd	0.5 mg/L
Mn	0.50 mg/L	Al	500 mg/L
Ni	1.0 mg/L	Ca	400 mg/L
Pb	1.0 mg/L	Fe	200 mg/L
V	0.50 mg/L	Mg	500 mg/L
W	0.50 mg/L	Zr	0.50 mg/L
Li	0.50 mg/l	Sr	0.5 mg/l
Bi	0.50 mg/l	Ti	0.5 mg/l
B	0.50 mg/l	S	0.5 mg/l
Sn	0.50 mg/l	Si	0.5 mg/l

9.7.2 CRI Standards (also referred to as LLCCV). The CRI standard must contain the elements of interest at (or below) the reporting limit for each element. The CRI level is at the reporting limit as shown in Table 1. This must be prepared by diluting calibration standard(s) to the reporting limit level for each element. They must be made in the same matrix as the calibration standards. Note: The CRI must be verified at the RL before any dilutions are applied

9.8 Matrix Spike and Spike Blank Solution (For soil samples). The final concentrations suggested for the matrix spike and spike blank solutions are shown in Table 5. The spiking solution is prepared by adding either mixed or single element metals solutions to a solution containing 2 percent nitric acid and diluting to a fixed final volume with this acid mixture. Two mls of this stock solution must be added to the spike blank and the matrix spike before they are digested and brought to a final volume of 100 ml.

9.9 Matrix Spike and Lab Control Solution (For aqueous samples and TCLP leachates).

9.9.1 The final concentrations suggested for the matrix spike are shown in Table 5. Two spiking solutions, which are used for aqueous samples and TCLP leachates respectively, are prepared by adding either mixed or single element metals solution to solutions containing 2 percent nitric acid and diluting to a fixed final volume with this acid mixture. 0.5 ml of the resulting stock solution is added to the matrix spike sample before they are digested.

9.9.2 A lab control sample must be digested and analyzed for every batch of 20 samples or less. The LCS is prepared by adding either mixed or single element metals solutions to DI water and bringing up to a fixed final volume. For TCLP samples, the lab control must be made using blank leachate solution rather than DI water. 50 ml of this solution is digested and brought to a final volume of 50 ml. In situations where any odd elements, such as B, Si, Sr, Sn, and Pd, is of interest for a specific project, besides a lab control, a spike blank is also digested.

9.10 Liquid Argon or Argon Gas. Argon is provided by Air Products in the large outdoor tank. No lab monitoring of the tank is normally necessary

9.11 Internal Standard Solution (with matrix modifier). To a 1 liter flask containing approximately 800 ml of DI water, add 20.0 ml of 10,000 mg/l Cesium solution, 5.0 ml of 10000 mg/l indium, and 1.000 ml of 10000 mg/l yttrium. Add 50 ml concentrated nitric acid and 50 ml concentrated hydrochloric acid and bring to a final volume of 1000 ml and mix well. This solution is added to all samples and standards as the instrument is running using a split line on the peristallic pump

10.0 PROCEDURE

10.1 General procedure on how to operate the SS Trace1 is described below. Refer to the Thermo 6500 operation manual for further details.

10.2 Before bringing up the instrument, make sure that the lines, the torch, the nebulizer, and the spray chamber are clean, the dehumidifier is filled with DI water up to the level between Minimum and Maximum, and that there are no leaks in the torch area.

10.3 Turn on the recirculating cooler. Verify that the liquid argon is turned on.

10.4 Set up the pump tubing and engage the peristaltic pump.

10.5 Put a new solution of acid rinse into the rinse reservoir. (Note: the composition of the rinse solution may be periodically changed to minimize sample introduction problems and sample carryover.) If internal standard is being used, make sure that sufficient internal standard solution is prepared.

10.6 Start up the instrument following the sequence shown below.

10.6.1 Double click the **iTEVA Control Center** Icon on desktop. Type ***admin*** in User Name field, and then click OK.

10.6.2 Once the iTEVA Control Center window is opened, click on **Plasma** Icon at status bar area. Then click on **Instrument Status** to check the interlock indicators (torch compartment, purge gas supply, plasma gas supply, water flow and exhaust must be in green; drain flow and busy must be in gray) and the Optics Temperature. (It should be around 38°C.) Click on the Close box.

10.6.3 Click **Plasma On**. When the plasma is on, click close. Let the instrument warm up for 15 to 20 minutes before starting the analysis. New tubing may take an hour to stabilize .

10.7 Torch Alignment and Auto Peak

10.7.1 If the torch has been cleaned, then it has to be realligned after it is replaced

10.7.1.1 Open the method and then click on **Sequence** tab, then click on List View Icon until you reach rack display.

10.7.1.2 Go to S-6 position (you can assign any position in the rack for torch alignment), then right click to select Go to empty sample S:6. (Now, the autosampler tip moves from Rinse to this position)

10.7.1.3 Click on **Analysis** tab, then select **Torch Alignment** from **Instrument** drop down menu. There will be a pop up dialog box present. Click RUN. Then there will be another dialog box pop up (This is a reminder for Torch Alignment Solution (2 ppm Zn)), click Ok. Now, the instrument is initiating an automated torch alignment. It takes about 7 minutes to complete this step. Progress is indicated in the progress bar.

10.7.1.4 After Torch Alignment is done, click Close. Click on **Sequence** tab, then follow by **List View** Icon.

10.7.1.5 Go to Rinse position at rack display, right click to select Go to rinse and let it rinse for 2 minutes.

10.7.2 Perform Auto Peak.

10.7.2.1 It is recommended that the Auto Peak Adjust procedure be performed monthly or whenever the peak shape has shifted for any element. A standard that contains all of the lines of interest is used and the system automatically makes the appropriate fine adjustment. (CCV solution is used for this process.)

10.7.2.1.1 A shift in peak shape can be defined as when the peak is no longer in the middle of the defined viewing window. The window must be set so that the peak is approximately centered and there is a sufficient area measured so that reproducible, consistent data can be obtained at reporting limit levels. This is done as part of the automatic process, but the window size can be adjusted manually in the method based on the shape of the peak to obtain the best fit for the peak. A wider peak may need a broader integration window for

the best analysis. In general, the window should cover at least the top 1/3 of the peak.

10.7.2.2 Click **Sequence** tab, then click on **List View** Icon till the rack is displayed.

10.7.2.3 Go to S-5 position (you can assign any position in the rack for auto peak adjust), then right click to select Go to empty sample S:5. (Now, the autosampler tip moves from Rinse to this position). Click on **Analysis** tab. All elements' result is showed in the display area. From **Instrument** drop down menu, select **Perform Auto Peak**. There will be a pop up dialog box present. Highlight _All Elements_, then click RUN. Then there will be another dialog box pop up (This is a reminder for Perform Auto Peak Solution), click Ok. Now, the instrument is performing auto peak adjust. It takes about 5 minutes to complete this process. The Auto Peak dialog box will show a green " √" in front of All Elements, which indicates Auto Peak is completed.

10.8 Open the method and start up the run.

10.8.1 Click on **Analyst** Icon at the workspace. Go the Method and choose Open from the drop down menu. Select the method with a Revision (usually select the last revision used).

10.8.2 Go to **Method** tab at the bottom of left-hand corner to click on **Automated Output** at the workspace area. Type a filename in Filename field in the data display area (i.e.: SA073107M1: starts with SA, then follow by MM-DD, then M1; M1 indicates the first analytical run for that day, then follow by M2, M3 and so on for the second and third runs).

10.8.3 Click on **Sequence** tab at the bottom of left-hand corner. From **Auto-Session** drop down menu bar, click on **New Autosampler** to create a sequence. This will pop up a dialog box , then click on **New** and fill number of samples (i.e.: 100) in the Number of Samples field and the sample ID (usually leave this field empty) in Sample Name field. Type a sequence name (i.e.: SEQ073107M1: starts with SEQ, then MM-DD-YY, then M1; M1 indicates the first analytical run for that day, then follow by M2, M3 and so on for the second and third runs) in the Sequence Name field. Click OK, then put in "0" on Settle Time Between Sequences box, click OK.

10.8.4 Right click on **Untitled** (CETAC ASX-520 Enviro 5 Named Rack is the rack that currently using) at the workspace area, click on **Auto-Locate ALL** to locate all samples.

10.8.5 Double click on **Untitled** again, then click on the sequence name (i.e.: SEQ073107M1), on the data display area, type the sequence in Samplename column, dilution factor (if needed) in CorrFact column, check the box in front of Check column, and select an appropriate check table.

10.8.6 Once done with creating sequence, go to **Method** drop down menu and save all changes as **Save As**. There will be a Save a Method dialog box present, go to Save

Option to check on "Overwrite Method and bump revision number" box, then click OK.

10.8.7 Go to **Sequence** tab, click on **List View** Icon from tool bar, then click on **Connect Autosampler to PC and Initialize** Icon. (Now, the autosampler tip is up and sits on the top of the rinse cup.)

10.8.8 The sequence includes the calibration and run quality control.

10.8.8.1 Calibrate the instrument as outlined below using the standards shown in Table 3. This calibration procedure is done a minimum of once every 24 hours. The calibration standards may be included in the autosampler program or they may be run separately.

10.8.8.2 Analyze ICV and ICB after the calibration is completed and before any samples are analyzed. An ICB may be run following the ICV, but is not required.)

10.8.8.2.1 For mixed runs (EPA 200.7 and SW846 6010C), the first CCV is designated the ICCV. For samples and quality control, insert the list pointer after a space after the sample. Check with the metals supervisors for additional information on the use of listpointers. In general, listpointer 2 refers to the SW846 6010 method and listpointer 1 refers to EPA 200.7 method.

10.8.8.3 Low Level Calibration Verification (Low checks or LLCCV)- Run low checks at reporting limits levels after ICCV and CCB. The low checks are named as CRI (or CRIB for DOD run), CRID and CRIA. The levels for each low check are listed in Table 8, Table 9 and Table 10.

10.8.8.3.1 Muti-level low check solutions must be analyzed for default reporting limits and special client reporting limits.

10.8.8.3.2 Low checks (LLCCV) must be analyzed at the end of each calibration (analysis) batch. The acceptance criterion for the CRI check is 70 to 130% recovery. If an element does not meet this criterion, then all samples for that element in the concentration range between the low checks and the CCV must be reanalyzed. Samples containing concentrations higher than the CCV may be reported as long as CCV criteria are met.

10.8.8.3.3 More frequent CRI (LCCV) checks may be analyzed during the course of the run if system stability at the low end of the calibration is questionable or if the lab wants to ensure that fewer samples will have to be submitted for reanalysis if there is a failed CRI at the end of a run.

10.8.8.3.4 It is recommended that the CRI check be run bracketing every 4 to 8 hour period of analysis. It may be run as frequently as every 10 samples if the supervisory staff deems that this is necessary

10.8.8.3.5 Method limits of 70 to 130% are applied to the low check standard, but tighter criteria may be needed in some client or project specific situations.

10.8.8.3.6 CRIB is only used for DOD runs and the limits are 80 to 120%.

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10.8.8.4 Before analyzing any real samples, an interference check solution must be checked. For all spiked elements, the analyzed results must be within 20 percent of the true results. For unspiked elements, the interfering element solutions must contain less than two times the absolute value of the reporting limit for each element.

10.8.8.5 If the interfering element solution is not within specifications and that element must be reported, then new interfering element correction (IEC) factors will need to be generated following the procedure outlined in Section 11 below. If new IEC's are generated, then the run must be restarted from the ICSA, ICSAB quality control samples and new CCV checks must be run before any samples can be reported.

10.8.8.6 After the initial analytical quality control has been analyzed, the samples and the preparation batch quality control must be analyzed. Each sample analysis must be a minimum of 2 readings using at least a 5 second integration time. For samples containing levels of elements greater than approximately 5 times the reporting limits, the relative standard deviations for the replicates must be less than 5%. If not, reanalyze the sample. If, upon reanalysis, the RSDs are acceptable, then report the data from the reanalysis. If RSD's are not acceptable on reanalysis, then the results for that element must be evaluated by the data reviewer and footnoted if necessary. In some cases, an additional dilution analysis may be needed. Check with the area supervisor or manager for additional information.

10.8.8.7 Between each sample, flush the nebulizer and solution uptake system with a blank rinse solution for the required period of time to ensure that analyte memory effects are not occurring. A time of 120 seconds is recommended for most analyses with the current autosampler set-up.

10.8.8.8 Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth samples during an analysis run, whichever is more frequent, and at the end of the sample run.

10.8.8.9 If the CCV solution is not within 10 percent of the true value, no samples can be reported in the area bracketed by the failing CCV for the failing element. Additionally, for the elements with a CCV greater than 5 times the reporting limit, the relative standard deviation for the replicates must be less than 5 percent.

10.8.8.10 The CCB results must be less than the reporting limit or limit of quantitation for each desired target analyte. If this criterion is not met, then no samples

can be reported in the area bracketed by the failing CCB for the failing element and all samples must be submitted for reanalysis.

10.8.8.10.1 However, if the samples are high relative to the CCB (> 10 X the CCB level) and a higher reporting limit is acceptable for the final end use of the data, then the samples may be evaluated using a higher reporting limit to meet the CCB criteria. This must be clearly documented on the run if a higher reporting limit is applied.

10.8.8.10.2 In addition, at the reviewer's discretion, samples that are < RL may be reported when the CCB is biased high. Analysts must assume that samples bracketed by a failing CCB must be reanalyzed unless instructed otherwise.

10.8.8.10.3 If a CCB fails, if possible, the analyst must stop the run and run a new CCV, CCB pair before proceeding with the analysis of any additional samples.

10.8.8.11 For one sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, a serial dilution must be prepared. Normally the sample used for the serial dilution is the sample that is used for the matrix spike and matrix spike duplicate. For the serial dilution, a 1:5 dilution must be made on the sample. The results of the 1:5 dilution must agree within 10 percent of the true value as long as the sample is greater than 50 times the reporting limit for that element before dilution (or 10 times the reporting limit after dilution) and the sample results are within the linear range. If not, an interference effect must be suspected and the serial dilution result for the element with the suspected interference must be footnoted. The serial dilution is calculated as shown below

10.8.8.12 If the matrix spike or matrix spike duplicate is out of acceptable limits, then it is recommended that post-digest spikes be prepared to determine potential interferences. For the post-spike, the sample must be spiked with approximately 2 times the sample level or two times the reporting limits, whichever is greater. Limits of 80 to 120 percent are applied. The serial dilution is used to confirm any matrix effects. The post-digest spike recovery must be footnoted on the matrix spike recovery or otherwise noted in the quality control summary report.

10.8.8.13 For any readings that exceed the linear range for a given element, a dilution is required. After a high reading, the sample following the high one must be examined for possible carryover. A verification may be necessary by rinsing the lines with an acid solution and then rereading the sample. A limit check table may be built into the autosampler file so that samples exceeding the linear range are flagged on the raw data.

10.8.8.14 For the interelement spectral interference corrections to remain valid during sample analysis, the interferent concentration must not exceed its linear range. If the interferent exceeds its linear range or its correction factor is big enough to affect the element of interest even at a lower concentration, sample dilution with reagent blank and reanalysis is required. In these

circumstance analyte detection limits are raised. Check with metals supervisor for more information.

10.8.8.15 Anytime that the interference is large relative to the sample, dilution may be required. Check with the metals supervisor for more information.

10.8.8.16 For any readings where the internal standard is outside of the range of 70 to 130% of the internal standard level in the calibration blank, then the sample must be diluted until the internal standard is within that range.

10.8.9 This method does not require the analysis of an interfering element check solution at the end of the run. However, this may be required to meet other method and/or client requirements. Run the ICSA and ICSAB solutions as instructed by the metals lab supervisor or manager or as noted in the program code instructions.

10.8.10 After the instrument is optimized, click **Run Auto-Session** Icon to start the run.

10.8.11 If you need to add or delete samples once the run is started, follow the steps shown below.

10.8.11.1 Adding Samples.

10.8.11.1.1 Click on **Sequence** tab, then click on **List View** Icon at the tool bar. There is the sequence table on the data display area.

10.8.11.1.2 Click on **Add Samples** Icon. This will pop up the dialog box, then fill number of samples that need to add in field. Click OK. By doing this, samples will be added at the end of sequence without a location the rack.

10.8.11.1.3 Go to the added samples, on the to position ID column, assign a number for each sample. This number will be the position in the rack. On the Samplename column, type in sample IDs, fill in Corr Fact (if needed) and Check Table.

10.8.11.1.4 The added samples will be analyzed at the end of the original sequence run order unless you assign them to run under different order.

10.8.11.2 Deleting Samples.

10.8.11.2.1 Click on **Sequence** tab, then click on **List View** Icon under the sequence display area.

10.8.11.2.2 To the sample that need to be deleted, on the to position ID column, change the number to "0". By doing this, that sample will be unlocated in the rack and the autosampler tip will go to the next sample.

10.9 When the analysis is completed export the data to LIMS following the procedure outlined below.

10.9.1 Double click on **ePrint** Icon on desktop. There will be a LEADTOOLS ePRINT dialog box pop up, then click **Finish Jobs** and **OK** boxes.

10.9.2 Double click the **PDF** Icon on desktop, the PDF file will present as Document_#. Right click on that file, select **Rename** to change the file name to an assigned analytical run ID. (i.e.: MA8324). This is the raw data for MA8324.

10.9.3 Drop the raw data to Lims.

10.9.4 By completing above steps, the raw data (i.e: MA8324) can be pulled up in the Raw Data Search function.

10.10 The data must be reviewed in the LIMS as outlined in the inorganic data review SOP, EQA034. Calculations for water samples are done automatically in the LIMS using the equation shown below.

original sample concentration of metal (μg/l) =

$$\frac{\text{(conc. in the digestate (μg/l)) x (final digestate volume (ml))}}{\text{(Initial sample volume (ml))}}$$

10.11 Aft the end of the analysis day, the ICP must be brought down using the following sequence:

10.11.1 Place the autosampler tip in rinse cup and rinse in a mixed solution of 5% nitric acid and 5% hydrochloric acid for 10 minutes and in DI water for 20 minutes. **Note**: A stronger acid may be needed depending on the matrix of the samples that were analyzed.

10.11.2 Turn off the plasma by click on the **Plasma** Icon and click on **Plasma Off**.

10.11.3 Close all iTEVA programs/ windows.

10.11.4 Release the tension on the sample pump platen.

10.11.5 Switch off recirculating chiller.

11.0 PROCEDURE FOR GENERATION OF INTERFERING ELEMENT CORRECTION FACTORS

11.1 All IEC's must be verified and updated a minimum of once every 6 months or whenever instrument conditions change significantly. It is recommended that elements with frequent high concentrations or with large IEC's should be checked more frequently.

11.2 Calculate the IEC correction factors and enter them into the method. Verify that the recalculated sample results are within QC limits. Calculate the correction factor using the equation shown below. This correction factor must be added to the correction factor already in place in the method for a given element.

$$IEC = \frac{\text{Concentration Result of the element with the interference}}{\text{Concentration result of the interfering element}}$$

11.3 Analyze the ICSA/ICSAB solutions and/or SIE solutions and verify that the combined standards are within QC limits. If they are not, make additional changes to the IEC factors and then re-verify both the individual and combined solution values.

11.4 Save and update the method.

11.5 Interfering element correction factors saved as raw data along with the run printouts on a daily basis so that the IEC's for a given run are traceable.

12.0 QC REQUIREMENTS

12.1 This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements for method SW846 6010C.

12.2 Method Detection Limits (MDLs). MDLs must be established for all analytes, using a solution spiked at approximately 3 to 5 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs must be determined approximately once per year or whenever there is a significant change in the background or instrument response.

12.3 Instrument Detection Limits (IDLs). Instrument Dection Limits (IDLs). It is required that IDL's be completed a minimum of every 3 months for all analytes or whenever instrument conditions have significantly changed. The Instrument Detection Limits (in ug/L) are determined by analyzing 7 replicates of a reagent blank solution on 3 non-consecutive days. The IDL is defined as 3 times the average of the standard deviations of the 3 days. For the IDL, each measurement shall be performed as though it were a separate analytical sample (i.e., each measurement shall be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs shall be determined and reported for each wavelength used in the analysis of the samples.

12.4 Linear Calibration ranges. The upper limit of the linear calibration ranges must be established for each analyte by determining the signal responses from a minimum of three concentration standards, one of which is close to the upper limit of the linear range. The linear calibration range which may be used for the analysis of samples must be judged by the analyst from the resulting data. Linear calibration ranges must be determined whenever there is a significant change in instrument response and every six months for those analytes that periodically approach their linear limit.

12.4.1 For work following the Army Corp of Engineers Shell document, the linear range cannot exceed the level of the high calibration standard on that run. All elements to be reported that exceed the high standard must be reanalyzed on dilution and the results reported from the dilution.

12.5 Initial Calibration Verification (ICV) and Initial Calibration Blank (ICB). After every new calibration, an ICV must be analyzed. The analysis of the ICV may be followed by the analysis of the ICB, although this is not required by the method.

12.5.1 For the ICV, all elements to be reported must be within 10 percent of the true value and the replicates that exceed 5 times the reporting limit must have a relative standard deviation of less than 5 percent. The ICV must be from a different source than the calibration standards and must be near the mid-point of the calibration curve. If the ICV does not meet criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard and showing that it meets QC criteria.

12.5.2 If an ICB is analyzed, than all elements to be reported must be less than the RL (LLOQ). If the ICB is outside of criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard and showing that it meets QC criteria. Analysis of a CCB before running any reportable samples can be used to verify that the system meets calibration blank requirements.

12.6 Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB). Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run.

12.6.1 For the CCV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit must have a relative standard deviation of less than 5 percent. The CCV must be made from the same source as the calibration standards at a concentration near the mid-level of the calibration curve. If an element does not meet the recovery criteria of the CCV (90 to 110%), than no samples can be reported for that element in the area bracketed by the CCV.

12.6.1.1 If the replicate rsd is high, but all replicates are within the recovery limits, then the results can be accepted at the discretion of the reviewer.

12.6.2 For the CCB, all elements to be reported must be less than the reporting limit (LLOQ). If an element does not meet this criteria, then no samples can be reported for that element in the area bracketed by the CCB.

12.7 Interference Check Standard. An interference check standard must be analyzed at the beginning of each analytical run. For all spiked elements, the analyzed results must be within 20 percent of the true values. For unspiked elements, the interfering element solutions must contain less than the absolute value of two times the reporting limit for each element. If this criteria is not met, then no samples containing the elements in question can be reported in the area bracketed by this QC unless the samples contain no significant interferents. This method does not require the analysis of an interfering element check solution at the end of the run. However, this may be required due to meet other method and/or client requirements. Run the ICSA and ICSAB as instructed by the metals lab supervisor or manager or as noted in the program code requirements.

12.8 Low Level Calibration Verification (CRI, CRIB, CRID, CRIA or LLCCV). These are the low level calibration verification standards containing the elements of interest at (or below) the reporting level for each element. A low level check standard at or below the RL/LOQ must be analyzed at the beginning and end of each calibration (analysis) batch. The acceptance criterion for these checks is 70 to 130% recovery for non-DOD work. For DOD, the acceptance criterion for this is 80 to 120%. If an element does not meet this criterion, then all bracketed samples for that element in the concentration range between the low level calibration verification check and the CCV must be reanalyzed. Samples containing concentrations higher than the CCV may be reported as long as CCV criteria are met. The CRI, CRIB, CRID and CRIA nomenclature is used to address different reporting limits for different methods. CRIB is normally used for the DOD LOQ check.

12.8.1 More frequent LCCV checks may be analyzed during the course of the run if system stability at the low end of the calibration is questionable or if the lab wants to ensure that fewer samples will have to be submitted for reanalysis if there is a failed low check at the end of a run.

12.8.2 It is recommended that the CRI check be run bracketing every 4 to 8 hour period of analysis. It may be run as frequently as every 10 samples if the supervisory staff deems that this is necessary.

12.9 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 sample batch. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank is considered acceptable.

12.9.1 The default SOP limit for the method blank is that is must be less than one half of the reporting limit.

12.9.2 In addition, the blank is considered acceptable if it is less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater.

12.9.3 If the method blank does not meet criteria, then it can be reanalyzed along with any associated samples. If it is still unacceptable, then all associated samples must be redigested and reanalyzed along with the other appropriate batch QC samples

12.10 Lab Control Sample or Spike Blank. The laboratory must digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 sample batch. The laboratory must assess laboratory performance of the lab control and spike blank against recovery limits of 80 to 120 percent. In house lab control and spike blank limits may also be generated to support these default limits. If the lab control or spike blank is outside of the control limits for a given element, all samples must be redigested and reanalyzed for that element.

12.10.1 If solid lab controls are used, then the manufacturer's limits must be applied.

12.11 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Recoveries must be assessed against default limits of 75 to 125 percent. In house limits may be generated for this method for informational purposes only. If a matrix spike is out of control, then the results must be flagged with the appropriate footnote and it is recommended that a post-digest spike be analyzed for the out of control element(s). If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and must be footnoted to that effect. Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

((Spiked Sample Result - Sample Result) / Amount Spiked) x 100 = matrix spike recovery

12.11.1 If a post-digest spike is required, the sample must be spiked with approximately 2 times the sample level or two times the reporting limits, whichever is greater. Limits of 80 to 120 percent are applied. The serial dilution is used to confirm any matrix effects. The post-digest spike recovery must be footnoted on the matrix spike recovery or otherwise noted in the quality control summary report. If the post-spike recoveries are out of the range of 80 to 120%, then the matrix spike results must be footnoted with a comment that the post-digest spike recovery indicates possible matrix interference.

12.12 Matrix Spike Duplicate (MSD) or Matrix duplicate (DUP). The laboratory must digest a matrix spike duplicate or matrix duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the MSD and the MS or between the DUP and the sample must be assessed. The rpd is calculated as shown below. The control limit for the duplicate rpd is method defined as 20%. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control. Note: Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

12.12.1 If a MSD or duplicate is out of control, then the data must be checked carefully to confirm that the high rpd for a given element is not a result of an analytical problem. If an analytical problem is suspected, the MSD or duplicate must be reanalyzed for confirmation. If the initial and reanalysis are in agreement (within 20%), then the high rpd is a result of preparation or sample issues and further analysis of the initial preparation is not required. If the initial and reanalysis are not in agreement due to an analytical problem, then any affected samples in the associated batch must also be reanalyzed for that element.

12.12.2 If more than 50% of the elements in a sample (that have levels of at least 5 times the reporting limit) have a high RPD, then the MSD or duplicate must be redigested for confirmation, unless the sample matrix is such that the non-homogeneity of the sample is visually apparent. If the results confirm, the results from the original MSD or duplicate must be flagged as indicative of possible sample non-homogeneity. If the results do not confirm, then the whole batch must be digested and reanalyzed.

12.12.3 If 50% or less of the elements in a sample (that have levels of at least 5 times the reporting limit) have a high rpd, then the high rpd(s) must be footnoted as indicating possible sample non-homogeneity unless other problems are suspected. If problems are suspected, the reviewer will initiate redigestion and reanalysis of the batch.

12.12.4 The calculations used to calculate RPD are shown below.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

12.13 Serial Dilution. A serial dilution is required on a frequency of one in 20 samples. For one sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, a serial dilution must be prepared. Normally the sample used for the serial dilution is the sample that is used for the matrix spike and matrix spike duplicate. For the serial dilution, a 1:5 dilution must be made on the sample. The results of the 1:5 dilution must agree within 10 percent of the true value as long as the sample is greater than 50 times the reporting limit for that element before dilution (or 10 times the reporting limit after dilution) and the sample results are within the linear range. If not, an interference effect must be suspected and the serial dilution result for the element with the suspected interference must be footnoted. The serial dilution is calculated as shown below.

$$\frac{100 \times ((\text{Sample result} - \text{Serial dilution result}))}{\text{Sample result}} = \text{Serial dilution percent difference}$$

12.14 Post Digestion Spike Addition. Post-digest spikes may also be used to determine potential interferences. Check with the metals supervisor for further information on when a post-digest spike must be performed. Recovery limits of 80 to 120 percent must be used to assess post-digest spikes.

12.15 IEC Correction Factor Generation. All interfering element correction factors (IEC's), must be verified and updated a minimum of once every 6 months or whenever instrument conditions change significantly.

12.16 Lower Limit of Quantitation check sample (LLQC). The LLQC is a sample at the reporting limit that is taken through the entire preparation and analytical process. This standard must be analyzed when reporting limits are initial established and on an as needed basis after that. The LLQC is equivalent to the LOQ (Limit of quantitation) standard which must be analyzed quarterly for the DOD QSM 4.1 program. The limits of quantitation are verified when all analytes in the LLQC sample are detected within 30% of their true value. If the limits cannot be verified at the spiked level, then the quantitation limit must be adjusted to a level where verification is successful.

12.17 Calibration Curve. The calibration curve must be prepared daily using a minimum of a calibration blank and one non-zero. The calibration must be verified with LLCCV/CRI and an ICV before any samples can be analyzed. If the curve is not verified as described in section 12.5 or 12.8, then no results can be reported for those elements which did not meet quality control criteria.

13.0 CALCULATIONS

13.1 For water samples, the following calculations must be used. Refer to the QC section for the calculations to be used for the QC samples.

original sample concentration of metal (μg/l) =

$$\frac{\text{(conc. in the digestate (μg/l)) x (final digestate volume (ml))}}{\text{(Initial sample volume (ml))}}$$

13.2 For soil samples, the following calculations must be used.

concentration of the metal in the dry sample (mg/kg) =

$$\frac{\text{(conc. in the digestate (mg/l) x final digestate volume(L))}}{\text{(sample wt. (kg)) x (\% solids/100)}}$$

14.0 DOCUMENTATION REQUIREMENTS

14.1 If any samples or QC checks require reanalysis, a brief explanation of the reason must be documented in the raw data. All instrument data must be exported to the LIMS system and a copy of the run log must be included in the logbook by the instrument.

14.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed. The Accutest Lot Number must be cross-referenced on the standard vial.

14.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. A copy of any outside maintenance reports must also be kept in the log. In addition to the maintenance, the maintenance log must also contain daily information on such items as the profile intensity. Each instrument has a separate log.

14.4 Any corrections to laboratory data must be done using a single line through the error and a reason for the correction. The initials of the person and date of correction must appear next to the correction.

14.5 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information must also be verified during this review.

15.0 INSTRUMENT MAINTENANCE

15.1 Recommended periodic maintenance includes the items outlined below.

15.1.1 Change the pump tubing weekly or as needed.

15.1.2 Clean the filter on the recirculating pump approximately once a month and dust off the power supply vents every one to two weeks.

15.1.3 Clean the radial view quartz surface weekly or more often if needed.

15.1.4 Clean the nebulizer, torch, and injector tube every two to four weeks or more often as needed.

15.1.5 Change the sampler tip as needed (every one to two months).

15.1.6 Clean the recirculating pump lines every 3 months or more often if needed.

15.1.7 Clean the slides on the autosampler with methanol and wipe them with a KimWipe saturated with Teflon spray a minimum of once per day.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non hazardous aqueous wastes.

16.2.2 Hazardous aqueous wastes

16.2.3 Chlorinated organic solvents

16.2.4 Non-chlorinated organic solvents

16.2.5 Hazardous solid wastes

16.2.6 Non-hazardous solid wastes

17.0 ADDITIONAL REFERENCES

17.1 Refer to other SOP's for ICP analysis (CLP, and EPA 200.7 for both DW and WW).

TABLE 1: NORMAL REPORTING LIMITS BY ELEMENT			
Analyte	**Water & Wipe Reporting Limit (µg/l)**	**Soil Reporting Limit (mg/kg)**	**TCLP Reporting Limit (mg/l)**
Aluminum	200	50	
Antimony	6	2	
Arsenic	3	2	0.50
Barium	200	20	1.0
Beryllium	1	0.2	
Cadmium	3	0.5	0.005
Calcium	5000	500	
Chromium	10	1	0.010
Cobalt	50	5	
Copper	10	2.5	
Iron	100	50	
Lead	3	2	0.50
Magnesium	5000	500	
Manganese	15	1.5	
Nickel	10	4.0	
Potassium	10000	1000	
Selenium	10	2	0.50
Silver	10	0.5	0.010
Sodium	10000	1000	
Thallium	2	1	
Vanadium	50	5	
Zinc	20	2	
Boron	100	10	
Molybdenum	20	1	
Palladium	50	5.0	
Sulfur	50	NA	
Silicon	200	20	
Strontium	10	1	
Tin	10	5	
Titanium	10	1	
Tungsten	50	5	
Zirconium	10	2	

TABLE 2: ANALYTICAL LINES ON THE SSTRACE1 AND SSTRACE2	
Element	**Wavelength**
Al	396.1
As	189.0
Ca	317.9
Fe	259.9
Mg	279.0
Mn	257.610
Pb	220.3
Se	196.0
Tl	190.8
V	292.4
Ag	328.0
Ba	455.4
Be	313.0
Cd	228.8
Co	228.6
Cr	267.7
Cu	324.7
K	766.4
Na	589.5
Ni	231.6
Sb	206.8
Zn	206.2
B	208.9
Mo	202.0
Pd	340.4
S	182.0
Sr	407.7
Sn	189.9
Ti	334.9
Si	212.4
W	207.9
Zr	339.1

TABLE 3: CALIBRATION STANDARD LEVELS in ug/l		
Element	**STD A (Blank)**	**STD B**
Ba	0	4000
Be	0	4000
Cd	0	4000
Cr	0	4000
As	0	4000
Se	0	4000
Pb	0	4000
Tl	0	4000
Mn	0	4000
Co	0	4000
Zn	0	4000
Cu	0	4000
Ni	0	4000
Sb	0	4000
Mo	0	4000
B	0	4000
Sn	0	4000
Ti	0	4000
Ag	0	500
V	0	4000
Sr	0	4000
Si	0	10000
Pd	0	4000
W	0	4000
Zr	0	4000
S	0	4000
Al	0	80000
Ca	0	80000
Fe	0	80000
Mg	0	80000
K	0	80000
Na	0	80000

TABLE 4: ICV, and CCV LEVELS		
Element	**ICV Suggested Level in ug/l**	**CCV Suggested Level in ug/l**
Al	40000	40000
As	2000	2000
Ca	40000	40000
Fe	40000	40000
Mg	40000	40000
Mn	2000	2000
Pb	2000	2000
Se	2000	2000
Tl	2000	2000
V	2000	2000
Ag	250	250
Ba	2000	2000
Be	2000	2000
Cd	2000	2000
Co	2000	2000
Cr	2000	2000
Cu	2000	2000
K	40000	40000
Na	40000	40000
Ni	2000	2000
Sb	2000	2000
Zn	2000	2000
B	2000	2000
Mo	2000	2000
Pd	2000	2000
Sr	2000	2000
Sn	2000	2000
Ti	2000	2000
Si	5000	5000
W	2000	2000
Zr	2000	2000
S	2000	2000

TABLE 5: SUGGESTED CONCENTRATIONS OF METALS IN THE MATRIX SPIKE AND SPIKE BLANK			
Element	**Soils Final Concentration in mg/kg**	**Aqueous Final Concentration in μg/l**	**TCLP Leachates Final Concentration in mg/l**
Ag	10	50	0.05
Al	5400	2000	
As	400	2000	2.0
B	100	2000	
Ba	400	2000	10.0
Be	10	50	
Ca	1250	25000	
Cd	10	50	0.05
Co	100	500	
Cr	40	200	0.20
Cu	50	250	
Fe	5200	1000	
K	1250	25000	
Mg	1250	25000	
Mn	100	500	
Mo	100	2000	
Na	1250	25000	
Ni	100	500	
Pb	100	500	2.0
Sb	100	500	
Se	400	2000	2.0
Tl	400	2000	
V	100	500	
Zn	100	500	
S	100	2000	
Sn	100	2000	
Sr	100	2000	
Ti	100	2000	
Si	200	4000	
Pd	100	2000	
W	100	2000	
Zr	100	2000	

TABLE 8: SUGGESTED CONCENTRATIONS OF METALS IN THE QUALITY CONTROL SAMPLE LOW CHECK (CRI or CRIB) SOLUTION	
Element	**Final Concentration in µg/l**
Sb	6
As	8
Ba	200
Be	2
Cd	3
Cr	10
Co	50
Cu	10
Pb	3
Mn	15
Ni	10
Se	10
Tl	10
V	50
Zn	20
B	100
Bi	20
Li	20
Mo	20
Pd	50
Sr	10
S	50
Sn	10
Ti	10
W	50
Zr	10
Ag	5
Si	200
Al	200
Ca	5000
Fe	100
Mg	5000
K	5000
Na	5000

TABLE 9: SUGGESTED CONCENTRATIONS OF METALS IN THE QUALITY CONTROL SAMPLE LOW CHECK (CRID) SOLUTION	
Element	**Final Concentration in µg/l**
Sb	3
As	3
Ba	4
Be	1
Cd	1
Cr	2
Co	3
Cu	2
Pb	2.5
Mn	3
Ni	4
Se	5
Tl	2
V	2
Zn	10
B	10
Bi	
Li	
Mo	
Pd	
Sr	
S	
Sn	
Ti	
W	
Zr	
Ag	1
Si	
Al	100
Ca	1
Fe	
Mg	100
K	2000
Na	1000

TABLE 10: SUGGESTED CONCENTRATIONS OF METALS IN THE QUALITY CONTROL SAMPLE LOW CHECK (CRIA) SOLUTION	
Element	**Final Concentration in µg/l**
Sb	20
As	20
Ba	
Be	
Cd	
Cr	
Co	
Cu	
Pb	20
Mn	
Ni	
Se	20
Tl	
V	
Zn	
B	
Bi	
Li	
Mo	
Pd	
Sr	
S	
Sn	
Ti	
W	
Zr	
Ag	
Si	
Al	500
Ca	
Fe	500
Mg	
K	
Na	

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager Nancy Cole

QA Manager

Effective Date: 7/02/13

TITLE: COLD VAPOR ANALYSIS OF MERCURY FOR SOIL SAMPLES

REFERENCES: SW846 7471B

Revised Sections: ***7.1, 7.4, 7.4.2, 7.4.4.1, 7.4.5, 8.1.4, Delete section 11.***

1.0 SCOPE AND APPLICATION

1.1 This method can be applied for the analysis of mercury in soils, sediments, bottom deposits, and sludge type materials. The reporting limit for mercury soil samples, based on a 0.6 g sample size, is 0.033 mg/kg.

2.0 SUMMARY

2.1 Cold vapor mercury is a flameless AA procedure based on the absorption of radiation at 253.7 by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state 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. Results are quantitated by comparison to a daily calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. Detected concentrations below this concentration cannot be reported without qualification.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. Recovery requirements vary by method. For this method a recovery from

80 to 120% is required. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's)

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of $\pm$ 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result}) \times 100}{(\text{Amount Spiked})} = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance 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. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation.

LOWER LIMIT OF QUANTITATION CHECK (also referred to as CRI, CRA, or LLQC). For all runs, a low check at the level of the reporting limit must be analyzed at the beginning of the run before analyzing any samples, but not before the ICV. A method criterion of 50 to 150% recovery is applied to this low check standard. If this criterion is not met, then all samples associated with this CRA check must be reanalyzed along with a compliant CRA check.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 After the mercury digestate is reduced to Hg vapor, it must be handled in a closed system or in a hood to prevent inhalation of the toxic vapor. Make sure that the Hg instrument is vented directly to a hood.

6.0 PRESERVATION AND HOLDING TIME

6.1 All solid samples should be stored at 4 $\pm$ 2ºC until the time of digestion.

6.2 All samples should be analyzed within 28 days of the date of sampling.

7.0 APPARATUS

7.1 Leeman Hydra II AA automated analyzers. Refer to the instrument manuals for further details on this instrumentation, including proper venting and safety requirements. Instrument maintenance is outlined below.

7.1.1 Change the sample tubing as needed.

7.1.2 Change the drying tubing as needed.

7.1.3 Clean the exterior of the instrument as needed.

7.1.4 Adjust the Hg lamp as needed. This can be done in the software on both instruments.

7.1.5 Complete any other maintenance required to maintain the instrument in good running order including, but not limited to, cleaning the cell, changing other tubing, changing the Hg lamp, etc.

7.2 Graphite heating block. Capable of heating at 95 ± 3 °C for 2 hours.

7.3 Digestion Bottles . Disposable plastic digestion tubes (65 ml volume) with tops for graphite heating block.

7.4 Calibrated glass tubes with verified 100.0 ml final volume calibration mark for bringing graphite heating block digestates to their final volume.

7.4.1 At a minimum of once per year, the calibration of these bottles must be verified and documented in the Hg Bottle calibration log following the procedure outlined below.

7.4.2 Carefully measure 100.0 ml of room temperature (20 to 25 deg. C) deionized water with a class A to deliver volumetric cylinder and pour into the calibrated Hg bottle.

7.4.3 If the bottom of the meniscus is on the calibration line, then the bottle passes calibration and can be used.

7.4.4 If the bottom of the meniscus is not on the line, then the bottle should be removed from service and replaced with a newly calibrated bottle. New bottles are calibrated following the same procedure as above, except that a line must be etched into the bottle at the bottom of the meniscus of the 60 ml of DI water.

7.5 Class A , to deliver, volumetric cylinders for measuring initial sample volumes and for calibrating glass tubes as outlined above.

7.6 Analytical Balance, 4 place. Calibration must be verified daily before use with NIST traceable weights.

7.7 Automatic pipettor bottles. The calibration on these bottles must be verified as outlined in EQA063.

7.8 Volumetric pipets, class A.

8.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water should be used whenever water is required. All solutions listed below may be scaled up or down proportionally as needed. Different reagents are required for the different heating techniques.

8.1 Digestion Block Reagents.

8.1.1 Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated nitric.

8.1.1.1 Make sure to only prepare the amount of acid that will be needed for the prep and analysis.

8.1.1.2 This preparation must be done in a hood.

8.1.2 Dilution Acid: To approximately 800 ml of DI water, add 37.5 ml of concentrated HCl and 12.5 ml of concentrated nitric acid. Dilute to 1000 ml with DI water and mix well. This dilution acid is used for making dilutions of digested samples from the digestion block digestion procedures.

8.1.3 Potassium permanganate, 5% solution: Dissolve 50 g of potassium permanganate in 1000 ml of DI water. **Caution** - Potassium permanganate is a strong oxidizing agent. Handle with care.

8.1.4 Stannous chloride. Add 7.5 ml of concentrated sulfuric acid to approximately 400 ml of DI water. Dilute to 500 ml with DI water and mix well. Add 50 g of stannous chloride di-hydrate or 42 g stannous chloride anhydrous and dissolve. Make sure that this solution is dissolved while in use.

8.1.4.1 Stannous sulfate may be used in place of stannous chloride.

8.1.4.2 If clogging occurs during analysis using the automated analyzer, then a less concentrated solution may be used.

8.1.5 Sodium chloride-Hydroxylamine hydrochloride or Sodium chloride-Hydroxylamine hydrosulfate. Add 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride to 2000 ml of water. Mix well. Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

8.2 Mercury standard solutions.

8.2.1 10 ppm Hg solution. Using a 1.00 ml volumetric pipette, add 1.00 ml of 1000 ppm stock (to be purchased from a vendor such as Fisher) to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with water and mix well. This standard may be held for up to 28 days.

8.2.1.1 The 10 ppm external source should be made up using a different mercury stock, and following the directions in 8.2.1.

8.2.2 100 ppb Hg solution. Using a 1.00 ml volumetric pipette, add 1.00 ml of 10 ppm Hg solution to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

8.2.2.1 The 100 ppb external source should be made up following the directions in 8.2.2.

8.2.3 10 ppb Hg solution. Using a 10.0 ml volumetric pipette, add 10.0 ml of 100 ppb Hg solution to a 100 ml volumetric flask containing approximately 75 ml of DI water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

9.0 INTERFERENCES

9.1 Potassium permanganate is added to eliminate possible sulfide interferences. Concentrations as high as 20 mg/kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water. High copper concentrations (> 10 mg/kg) may also interfere with mercury recoveries.

9.2 Samples that are high in chlorides may require additional permanganate because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 254 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and analyzed. This may be accomplished by using an excess of the hydroxylamine hydrosulfate.

9.3 Certain volatile organics may also absorb at this wavelength and can interfere.

10.0 GRAPHITE DIGESTION BLOCK PROCEDURE FOR SOIL DIGESTION

10.1 Make up a standard curve consisting of 5 standards and a blank. Suggested concentrations are shown below. Different concentrations may also be used, as long as all of the method requirements are met. Make sure to clearly label each digestion tube. Calibration standards must be prepared fresh each day. Add 5 ml of DI water to each standard before digestion. The final concentration of Hg is calculated in the final digestate.

Ml of 10 ppb Hg solution	ml of 100 ppb Hg solution	Total ug of Hg	ug/L of Hg
0.000	0.000	0.000	0.000
2.00	0.000	0.020	0.20
5.00	0.000	0.050	0.50
0.00	1.00	0.100	1.00
0.00	2.50	0.250	2.50
0.00	5.00	0.500	5.00

10.2 Samples. For each sample, homogenize the sample well and weigh out a 0.5 to 0.6 g aliquot of the sample into one labeled digestion tube. A solid lab control should be prepared in the same manner.

10.3 Make up additional quality control samples as shown below. (Note: if a different standard curve is run, then the levels of the CCV and ICV standards should be adjusted accordingly in accordance with the requirements in the method.) Make sure to clearly label each digestion tube. Make sure to prepare enough CCV checks for the entire run. The ICV check must be from an alternate source of standards than the calibration curve and at a different level than the CCV or the calibration standards. A low check standard is also required. This 0.20 ug/l check can be made up as outlined for the standard curve.

Sample ID	ml of 100 ppb Hg solution	ml of DIwater	µg/l of Hg
CCV Check(s)	2.5	7.5	2.5
MB	0.0	10.0	0.0
MS	2.0	0.0	2.0
MSD	2.0	0.0	2.0
Duplicate*	0.0	0.0	0.0
ICV	3.0	7.0	3.0

*Per project specification.

10.4 To all samples, QC, and standards add 5 ml of DI water and 5 ml of aqua regia and then heat for 2 minutes in a digestion block at 95 ± 3 °C. These reagents can be added with a bottle pipettor that is accurate to within 90 to 110%.

10.5 Cool the samples and then add 25 ml of DI water and 15 ml of potassium permanganate solution to each sample and mix thoroughly. Allow the samples to stand for at least 15 minutes

after the addition of the permanganate. If the sample decolorizes, add additional permanganate until the purple color persists.

10.5.1 These reagents can be added with a bottle pipettor that is accurate to within 90 to 110%.

10.5.2 For samples containing a mixture of solvent and water, take a sample aliquot of approximately 20 g (lower for higher solvent samples) of sample and add the reagents listed above. Pour the sample in a beaker and heat on a hot plate at 95 ± 3 °C until no solvent layer is visible. Then transfer the digestate to a digestion tube and proceed as outlined below. A method blank and spike blank must also be taken through this entire procedure.

10.6 Cap the samples and place them in the graphite digestion block for 30 minutes at 95 ± 3 °C. Record the temperature and time for each digestion batch on the analysis sheet. Remove and cool.

10.7 Enter the prep data into the LIMS system, double checking all weights and spike amounts. After the prep data is checked, it can be approved and is available for use in the final calculation.

11.0 MERCURY ANALYSIS PROCEDURE HYDRA AA II

11.1 While the samples are digesting, begin setting up the Leeman analyzer following the steps outlined below. Additional instructions are available in the instrument operators manual.

11.1.1 Turn on the nitrogen and adjust to 60 to 90 psi. Turn on the instrument power if it is not already on.

11.1.2 Check the pump tubing and make sure that it is not flattened. Change if appropriate. Put the tubing in the clamps on the pump. Check the drying line and make sure that it is clean. Put fresh stannous chloride solution in the stannous chloride bottle. Fill the rinse bath or rinse bottle with fresh 10% nitric acid. The bath should be filled no more than ¾ full. Place the autosampler line and the stannous chloride line in the rinse container.

11.1.3 Turn on the analyzer and allow it to warm up.

11.1.3.1 Open the Envoy software. Go to Method and click Instrument Control. On the Instrument Control page, click the startup icon. This will turn on the lamp, gas, and pump. You may also turn on/off the lamp, gas and pump individually on the Instrument Control Page.

11.1.4 Tighten the pump clamps until the flow is coming evenly through the lines. Do not overtighten.

11.1.5 Go to the Instrument control tab and pick the gas control test option. The input should be approximately 0.25 LPM. If the pressures are not correct, check with the area supervisor or manager before proceeding.

11.1.6 Start a batch to save your data.

11.1.6.1 Create a new chapter (Data File) by clicking Analysis. The batch should normally be named H5 followed by the month date and year, followed by the matrix designation for the batch, following by the run number. For example, the first water batch on instrument for 3/24/03 would be named H5032411w1. The realtime print option can also be turned on from this tab.

11.1.7 Set up autosampler racks containing the samples that are going to be run.

11.1.7.1 Create a new sequence by clicking sequence-new. Type the sequence name. After typing the samples in to sequence page make sure to click update and save. CCV and CCB checks can be entered in the macro column of the sequence page.

11.1.8 Set up the calibration.

11.1.8.1 For the Hydra AA II, go to the Method menu, enter or verify the standard concentration by clicking on the standard tab. Also select number of replicates to be run for each standard. Normally one replicate is run per standard. The check standard concentrations and acceptance ranges are also defined under this standard info tab. Make sure to always click apply when any changes are made in a tab.

11.2 Finish the preparation of the samples and standards as outlined below.

11.2.1 For samples that were digested in the water bath or the graphite digestion block, add 6 ml of hydoxylamine hydrochloride or hydroxylamine hydrosulfate to each sample and standard and mix well. Transfer the entire digestate to a calibrated glass tube. Rinse the digestion tube 3 times with approximately 10 ml aliquots of DI water and add them to the digestate in the calibrated glass tube. Then bring the sample to a final volume of 100 ml with DI water and mix well.

11.2.1.1 These reagents can be added with a bottle pipettor that is accurate to within 90 to 110%.

11.3 Measure out aliquots of the digested standards and samples into the autosampler cups. Work from the prep log and double check all transfers. Let all samples sit uncovered in the open autosampler vials for a minimum of one minute. Place the racks in the autosampler. Move the stannous chloride line into the stannous chloride bottle.

11.4 Start the calibration.

11.4.1 Click run sequence. The instrument will run the calibration and then pause. Click stop. Go to the Calibration page. Accept the calibration and then print the calibration. Click the Document icon, then choose HG5-PDF. Rename the file as MA*****_cal.

11.5 After the calibration has been accepted, start to run the samples.

11.5.1 For the Hydra AA II, go to the Sequence page. Right click on the first sample (i.e. ICV) and click start from here.

11.5.2 Review the data. Any samples that are over the range of the curve should be diluted with the dilution acid (see 8.1.2) and reanalyzed. It is recommended that any sample analyzed after a sample with a value over the curve be reanalyzed for confirmation. Make sure to bracket every 10 samples with CCV and CCB checks.

11.6 Both paper and electronic reports can be generated using the report option. Never delete any samples from the reports. Electronic reports should be transferred into the LIMS system where the final calculations are done.

11.6.1 Go to analysis-Click result-Click chapter. Then go to report and select report spec. The normal report spec is "ACCUTEST". Click OK. Click on chapter in order to select all samples. Then click report output and then csv.file. Save as MA*****.csv. To print, select printer output and then type the report title (i.e. MA*****) and enter OK.

11.7 The calculations are done in the LIMS as described below. . For soils, the calculation shown below is used. A final volume of 100 ml is used for calculation purposes. (The final volume is factored out since all standards and samples are brought up to the same final volume and standard concentrations are calculated based on 100 ml.)

$$\text{Final sample concentration in mg/kg} = \frac{\text{concentration in the digestate in ug/l x final volume}}{\text{Initial weight in g x (\%solids/100)}}$$

11.8 Review the data in the LIMS, adding comments and accepting results as appropriate.

11.9 Shut down the instruments.

11.9.1 To shut down the Hydra AA II, move the stannous chloride line from the stannous chloride bottle to the 10% HNO3 rinse bottle. Let the system rinse with 10% HNO3 for several minutes. Then switch the line to DI water bottle and let rinse for several more minutes. Let the pump and gas run until the lines are completely dry. Then go to instrument control menu and click off icon for Lamp, Gas and Pump.

12.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

12.1 Instrument Detection Limits (IDLs). The instrument detection limits are determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of 7 consecutive replicates of a standard solution at a concentration from 3 to 5 times the estimated detection limit. IDLs must be done quarterly (every 3 months) for each instrument.

12.2 Method Detection Limits (MDLs). MDLs should be established using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.143, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

12.3 Instrument Calibration. The instrument must be calibrated daily or at a minimum of once every 24 hours and each time the instrument is set up. Calibration standards must be digested using the same procedure as the samples. A minimum of a blank and 5 standards are required. The correlation coefficient of the curve must be a minimum of 0.995. No samples should be analyzed until all of the calibration criteria are met.

12.3.1 A linear calibration using the equation y = mx + b is applied where m is the slope and b is the intercept. The calibration is not forced through zero.

12.3.2 The correlation coefficient is calculated using the following equation:

$$Correl(X,Y) = \frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2}}$$

where x is the measured absorbance and y is the standard concentration.

12.3.3 If the calibration curve does not meet criteria, and is redigestion, then any samples digested along with that calibration curve must also be redigested.

12.4 Initial Calibration Verification Standard (ICV)). During each analysis, a standard from a different source than the calibration standard should be analyzed. Normally this is analyzed at the beginning of the run. For this method, the ICV should be within 10 percent of the true value. When the measurements exceed these control limits, the analysis shall be terminated, and the problem corrected before proceeding. All reported results must be bracketed by compliant QC. The exception is, if the ICV is biased high (110 to 150 % recovery) and no mercury is found in the samples, then the sample results may be reported for mercury.

12.5 Continuing Calibration Verification. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCV solution is not within 20 percent of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.)

12.6 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by the failing CCB.

12.7 CRA (Low) Check or LLQC (Lower Limit of Quantitation Check). For all runs, a low check at the level of the reporting limit must be analyzed at the beginning of the run before analyzing any samples, but not before the ICV. A criterion of 50 to 150% recovery is applied to this low check standard. If this criterion is not met, then all samples associated with this CRA check must be reanalyzed along with a compliant CRA check.

12.7.1 A number of clients have specific program requirements for frequency and recovery ranges on CRA checks. Check with the metals supervisor for additional information on these programs.

12.7.2 If the CRA is biased high and there is no mercury found in the samples, then the sample results may be reported for mercury. If the CRA is biased high and there is mercury found in the samples, then the samples with Hg at levels ranging from the CCV to the high standard may be reported. Samples with levels of mercury between the CRA and the CCV standard may be biased high and cannot be reported.

12.8 Method Blank. The laboratory must digest and analyze a method blank with each batch of 20 samples. A minimum of one method blank is required for every 20 samples. A sample batch is defined as a maximum of 20 field samples in a preparation batch over a time period of 24 hours. A matrix spike/matrix spike duplicate, matrix spikes and/or duplicate is required every 20 samples. The method blank must contain mercury at less that the reporting limit. If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

12.9 Lab Control Sample. The laboratory must digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control or spike blank is required for every 20 samples. Note: For soils, if a lab control is not available, a spike blank can be used. For a running batch, a new lab control sample is required for each different digestion day. The laboratory should assess laboratory performance of an aqueous lab control against recovery limits of 80 to 120%. In house lab control limits may also be generated to support these default limits. For solid lab controls, the elements should be within the range given by the lab control supplier. If the lab control is outside of the control limits for a given element, all samples must be redigested and reanalyzed for that element. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

12.10 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. The laboratory should assess the matrix spike recovery against control limits of 80 to 120. (In house control limits are generated annually for information purposes only.). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

((Spiked Sample Result - Sample Result)/Amount Spiked) x 100 = matrix spike recovery

12.11 Matrix Spike Duplicate or Matrix Duplicate. The laboratory must digest a matrix spike duplicate or a duplicate sample for a minimum of 1 in 20 samples. Matrix spike duplicates are normally used unless otherwise specified by client requirements. The relative percent difference (rpd) between the matrix spike duplicate and the matrix spike or between the duplicate and the original sample should be assessed. The rpds are calculated as shown below and should be assessed against a limit of 20% RPD. (In house control limits are generated annually for information purposes only.). If a matrix spike duplicate or a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control. Note: Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

$$\frac{(\text{Sample Result} - \text{Duplicate Result}) \times 100}{(\text{Sample Result} + \text{Duplicate Result}) \times 0.5} = \%\ \text{RPD}$$

or

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

13.0 DOCUMENTATION REQUIREMENTS

Refer to the laboratory Quality Assurance Manual for additional documentation requirements.

13.1 Sample Worksheets. Digestion data sheets for the Hg soil samples must show all digestion information including the sample ID's, sample weights, bottle numbers, type of heating used, start times, end times, and pressure or temperature, as appropriate for all digestions. All sample information should be clearly entered on these sheets. In addition, any unusual characteristics of the samples or the digestion procedure should be noted in the comments sections. Make sure also that all dilutions are clearly documented.

13.2 Make sure to record thermometer ID, correction factor, and corrected and uncorrected temperatures for all temperature measurements.

13.3 Standards and Reagents. All stocks and reagents must be recorded in the reagent log book. All standards should be recorded on the digestion log with the samples.

13.4 Any run comments should be written on the raw data for the analysis and on the run log in the LIMS.

13.5 Annual bottle calibration verifications must be documented in the Mercury Bottle calibration log.

14.0 DATA REVIEW AND REPORTING

14.1 All samples should be updated to QC batches in the LIMS system. The analyst is responsible for reviewing all data for compliance with the QC outlined in this SOP. They are responsible for making sure that the raw data is fully documented and it is loaded into the LIMS system. They are responsible for submitting samples for redigestion and reanalysis, when appropriate.

14.2 After the analyst review is completed, the supervisor or a designated reviewer shall review the run for technical compliance to the SOP. The reviewer is also responsible for making sure that the QC calculations are done correctly and that appropriate flags are added.

14.3 After the reviewer completes their review, the data is released for client access in the LIMS. The raw data and the run log are submitted to the area manager. The manager periodically does an additional review on data for technical completeness. Any hardcopy raw data is transferred to the report generation department for scanning and storage. Instrument data is transferred electronically.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes.

15.2.2 Hazardous aqueous wastes.

15.2.3 Chlorinated organic solvents.

15.2.4 Non-chlorinated organic solvents.

15.2.5 Hazardous solid wastes.

15.2.6 Non hazardous aqueous wastes.

16.0 ADDITIONAL REFERENCES

16.1 Leeman Hydra AA instrument manual.

16.2 Leeman Hydra AA II instrument manual.

Lab Manager _____

QA Manager _____

Effective Date 5/30/13

TEST NAME: METHOD 8260B, VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC/MS)

METHOD REFERENCE: SW846 8260B (Revision 2, December 1996)

Revised Sections: Table 10

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the analytical procedures, which are utilized by Accutest to acquire samples for analysis of volatile organic compounds by gas chromatographic/mass spectrometric (GC/MS) following purge and trap utilizing the internal standard technique. The compounds in Table 1 may be determined by this method. An option has been included for the analysis of 1,4-Dioxane by selected ion monitoring GC/MS (GC/SIM-SIM).

1.2 This analytical method is designed for nearly all types of samples, regardless of water content, including ground water, aqueous sludges, liquors, waste solvents, oily wastes, tars, filter cakes, sediments and soils.

1.3 The applicable concentration range of this method is compound, matrix, and instrument dependent. Volatile water-soluble compounds can be included in this analytical technique. However, for some low-molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides, quantitation limits are approximately ten times higher because of poor purging efficiency. Determination of some structural isomers (i.e. xylenes) may also be hampered by coelution.

2.0 SUMMARY OF METHOD

2.1 Volatile compounds are introduced into the gas chromatograph by purge-and-trap (Method 5030/5035). Method 5030 may be used directly on ground water samples. Method 5035 is used for low-concentration and medium-concentration soils, sediments, and wastes. Medium concentration samples are preserved and stored in methanol prior to purge-and-trap analysis.

2.2 An inert gas is bubbled through a 5 ml sample contained in a specifically designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic (GC) column.

2.3 The volatile compounds are separated by the temperature programmed GC column and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.4 The peaks detected are qualitated by comparison to characteristic ions and retention times specific to the known target list of compounds.

2.5 Once identified the compound is quantitated by comparing the response of major (quantitation) ion relative to an internal standard technique with an average response factor generated from a calibration curve.

2.5 Once identified the compound is quantitated by comparing the response of major (quantitation) ion relative to an internal standard technique with an average response factor generated from a calibration curve.

2.6 Additional unknown peaks with a response > 10 % of the closest internal standard may be processed through a library search with comparison to a database of approximately 75,000 spectra. An estimated concentration is quantitated by assuming a response factor of 1.

2.7 Water soluble volatile organic and other poor purging compounds maybe analyzed using this methodology, however this method is not the method of choice for these compounds and the laboratory's ability to achieve all calibration and quality control criteria for this method cannot be guaranteed. These compounds are noted as (pp) in Table 7.

2.8 The method includes an analytical option for the analysis of 1,4-Dioxane by GC/MS-SIM. The selected ions that are characteristic of the analytes of interest are analyzed using lower concentrations of calibration standards under the same MS conditions. SIM analysis is performed upon client request and is documented in the report.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve and may vary depending on matrix interferences, sample volume or weight and percent moisture. Detected concentrations below this concentration cannot be reported without qualification. See Table 10.

3.1.1 Compounds detected at concentrations between the reporting limit and MDL are quantitated and qualified as "J", estimated value. Program or project specifications may dictate that "J" qualified compounds are not to be reported.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. See individual types of Blanks: Method Blank, Instrument Blank, Storage Blank, Cleanup Blank and Sulfur Blank.

4-BROMOFLUOROBENZENE (BFB) - the compound chosen to establish mass spectral instrument performance for volatile (VOA) analyses.

CALIBRATION FACTOR (CF) - a measure of the gas chromatographic response of a target analyte to the mass injected. The calibration factor is analogous to the Relative Response Factor (RRF) used in the Volatile and Semivolatile fractions.

CONTINUING CALIBRATION - analytical standard run every 12 hours to verify the initial calibration of the system.

CONTINUOUS LIQUID-LIQUID EXTRACTION - used herein synonymously with the terms continuous extraction, continuous liquid extraction, and liquid extraction. This extraction technique involves boiling the extraction solvent in a flask and condensing the solvent above the aqueous sample. The condensed solvent drips through the sample, extracting the compounds of interest from the aqueous phase.

EXTRACTED ION CURRENT PROFILE (EICP) - a plot of ion abundance versus time (or scan number) for ion(s) of specified mass (Es).

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the mass spectrometer to the target compounds.

INTERNAL STANDARDS - compounds added to every standard, blank, matrix spike, matrix spike duplicate, sample (for volatiles), and sample extract (for semivolatiles) at a known concentration, prior to analysis. Internal standards are used as the basis for quantitation of the target compounds.

MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

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.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards and surrogate standards that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) - The minimum concentration of a substance 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. MDLs should be determined approximately once per year for frequently analyzed parameters.

PERCENT DIFFERENCE (%D) - As used in this SOP and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105^{o}C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105 ^{o}C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

PRIMARY QUANTITATION ION - a contract specified ion used to quantitate a target analyte.

REAGENT WATER - water in which an interferant is not observed at or above the minimum detection limit of the parameters of interest.

RECONSTRUCTED ION CHROMATOGRAM (RIC) - a mass spectral graphical representation of the separation achieved by a gas chromatograph: a plot of total ion current versus retention time.

RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOP and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the relative mass spectral response of an analyte compared to its internal standard. Relative Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RELATIVE RETENTION TIME (RRT) - the ratio of the retention time of a compound to that of a standard (such as an internal standard).

INSTRUMENT BLANK – a system evaluation sample containing lab reagent grade water with internal standards and surrogate standards added. An instrument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/Mass approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 INTERFERENCES

6.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

6.2 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of

the analysis by running laboratory reagent blanks. The use of non-TFE tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

6.3 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

6.4 Contamination by carry-over can occur whenever high level and low-level samples are sequentially analyzed.

6.4.1 Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of an instrument blank to check for cross contamination. Refer to Table 11 for compounds that may cause carryover for this method.

6.4.2 It may be necessary to wash the purging device with methanol, rinse it with organic-free water, and then dry the purging device in an oven at 105^0 C. Follow the instrument manual for instructions on cleaning. Document the occurrence in the maintenance log and notify the manager/supervisor.

6.4.2.1 Clean and bake purging tube.

6.4.2.2 Clean or replace purge needle.

6.4.2.3 Clean and bake sample filter or sparge filter.

6.4.2.4 Clean and bake sample loop.

6.4.2.5 Replace trap if necessary.

6.4.2.6 Replace water management module if necessary.

6.4.2.7 Rinse transfer line with methanol. Caution: disconnect the trap before rinsing.

6.4.3 In extreme situations, the entire purge-and trap device may require dismantling and cleaning. Follow the instrument's manual for instructions on disassembly. Document the occurrence in the maintenance log and notify the manager/supervisor. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples.

6.4.4 If the contamination has been transferred to gas chromatograph, any of the following approaches may be used to cleanup the instrument.

6.4.4.1 Baking out the column between analyses.

6.4.4.2 Change the injector liner to reduce the potential for cross-contamination.

6.4.4.3 Remove a portion of the analytical column in the case of extreme contamination.

6.4.5 The oven temperature program must include a post-analysis bake out period to ensure that semivolatile hydrocarbons are stripped from the chromatographic column.

6.4 Special precautions must be taken during the analysis to avoid contamination from methylene chloride and other common laboratory solvents.

6.5.1 The sample storage and analytical area should be isolated from all atmospheric sources of methylene chloride or other common solvents.

6.5.2 Laboratory clothing worn by the analyst should be clean and used in designated areas only. Clothing previously exposed to solvent vapors in the organics sample preparation laboratory can contribute to sample contamination.

7.0 SAMPLE HANDLING AND PRESERVATION AND HOLDING TIME

7.1 HANDLING and PRESERVATION

7.1.1 Water samples

7.1.1.1 Container - 40 ml glass screw-cap VOA vial with Teflon-faced silicone septum. The 40-ml glass VOA vials are pre-cleaned and certified.

7.1.1.2 Collect all samples in duplicate. Test all samples for residual chlorine using test paper for free and total chlorine. If samples contain residual chlorine, three milligrams of sodium thiosulfate should be added for each 40 ml of water sample.

7.1.1.3 Fill sample bottles to overflowing, but do not flush out the dechlorinating agent. Sample should be taken with care so as to prevent any air or bubbles entering vials creating headspace.

7.1.1.4 Adjust the pH of all samples to ≤ 2 at the time of collection, but after dechlorination, by carefully adding two drops of 1:1 HCl for each 40 ml of sample. Seal the sample bottles, Teflon face down, and mix for one minute. Or VOA vials containing the preservative(HCL) may be used.

Note: Do not mix the sodium thiosulfate with the HCl in the sample bottle prior to sampling.

7.1.1.5 The samples must be protected from light and refrigerated at 0 - ≤ 6 °C from the time of receipt until analysis.

7.1.2 Soil Samples

7.1.2.1 Refer to the SOP for SW846 Method 5035 for preservation requirement of non-aqueous solids. For Ohio VAP freezing is not allowed; samples must be preserved with sodium bisulfate.

7.2 HOLDING TIME

7.2.1 Water Samples.

7.2.1.1 All samples are to be analyzed within 14 days of sampling (HCl preserved for aqueous sample) unless otherwise specified by the contract. The sample preservation deficiency is noted in the analytical run logbook when the analyst checks the pH at the bench. If the pH is not <2, the analyst notifies the supervisor, who then notifies Client Service Dept. A comment is added to the result page and Non-Conformance Summary.

7.2.2 Soil Samples

7.2.2.1 Refer to the SOP for SW846 Method 5035 for holding time requirement of non-aqueous solids.

7.2.2.2 All samples are analyzed within 14 days of sampling unless otherwise specified.

8.0 APPARATUS AND MATERIALS

8.1 SYRINGE

8.1.1 10, 25, 50, 100, 500 and 5000 µl graduated syringes, manually held (Hamilton/equiv.).

8.1.2 5 ml and 50 ml glass gas tight syringes with Luerlok end, if appropriate for the purging device.

8.2 BALANCE

8.2.1 Analytical balance capable of weighing 0.0001 gram.

8.2.2 Top loading balance capable of weighing 0.1 gram.

8.3 PURGE AND TRAP DEVICES

8.3.1 The autosampler models are used for purging, trapping and desorbing the sample into GC column.

- O.I. Model 4560 sample concentrator with 4551 vial multi-sampler
- O.I. Model 4560 sample concentrator with 4552 Water/Soil multi-sampler

8.3.2 The sample purge vial must be designed to accept 5 ml samples with a water column at least 3 cm deep.

8.3.3 The auto-sampler is equipped with a heater capable of maintaining the purge chamber at 40 °C to improve purging efficiency. The heater is to be used for low level soil/sediment analysis, but not for water or medium level soil/sediment analysis.

8.3.4 The OI #10 trap is 42 cm with an inside diameter of 0.105 inches. The trap must be packed to contain the following absorbents (3-ring) and should be conditioned at 180 °C for 30 minutes by backflushing with a Helium gas flow at least 20 ml/min before initial use.

- Tenax (2,6-Diphenylene oxide polymer).
- Silica gel.
- Carbon Molecule Sieve (CMS).

8.3.5 The desorber should be capable of rapidly heating the trap to 190^0 C for desorption. Do not exceed $210\ ^0$C during bake-out mode. Alternatively, follow manufacturer's instructions.

8.3.6 The response of chloromethane and bromonethane can be tracked for thermal decomposition products formed. If levels over the calibration requirement, the trap must be replaced and the system re-calibrated after the manager/supervisor been notified.

8.4 GAS CHROMATOGRAPH/MASS SPECTROMETER SYSTEM

8.4.1 Gas Chromatograph.

8.4.1.1 An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

8.4.1.2 The injection port should be suitable for split or splitless with appropriate interface.

8.4.1.3 The narrow bore capillary column is directly coupled to the source for HP-6890 model.

8.4.1.4 The wide bore capillary column is interfaced through a jet separator to the source for HP-5890 model.

8.4.2 Column.

- 75 m x 0.53mm ID x 3 μm film thickness capillary column coated with DB-624 (J&W Scientific), or equivalent. Condition as per manufactures directions.

- 105 m x 0.53mm ID x 3 μm film thickness capillary column coated with HP-VOA, or equivalent. Condition as per manufactures directions.

- 60 m x 0.25mm ID x 1.4 μm film thickness capillary column coated with DB-624 (J&W Scientific), or equivalent. Condition as per manufactures directions.

- 60 m x 0.45mm ID x 1.7 μm film thickness capillary column coated with DB-VRX (J&W Scientific), or equivalent. Condition as per manufactures directions.

8.4.3 Mass Spectrometer.

8.4.3.1 HP5973 or HP5970 is capable of scanning from 35 to 300 amu every 2 seconds or less, utilizing a 70 volt (nominal) electron energy in the electron impact ionization mode.

8.4.3.2 The mass spectrometer must be capable of producing a mass spectrum which meets all the criteria in Table 3 when injecting or purging 50 ng of the GC/MS tuning standard - Bromofluorobenzene (BFB).

8.4.3.3 SIM Mode – Capable of selective ion grouping at specified retention times for increased compound sensitivity (Table 2a).

8.5 DATA SYSTEM

8.5.1 Data Acquisition and Instrument Control (HP Chemstation) **-** A computer system is interfaced to the mass spectrometer, which allows the continuous acquisition and storage on a machine-readable media (disc) of all mass spectra obtained throughout the duration of the chromatographic program.

8.5.2 Data Processing (HP Enviroquant) - The software accommodates searching of GC/MS data file for target analytes which display specific fragmentation patterns. The software also allows integrating the abundance of an EICP between specified time or scan number limits. The data system includes the recent version of the EPA/NBS or NIST98 mass spectral library for qualitative searches of non-target compounds present in the chromatogram. The data system flags all data files that have been edited manually by laboratory personnel.

8.5.3 Off line Magnetic Tape Storage Device (Lagato Networker) - The magnetic tape storage device copies data for long-term, off-line storage.

9.0 REAGENTS AND STANDARDS

9.1 Solvent

9.1.1 Methanol: purge-and-trap grade quality or equivalent. Store separately, away from the other solvents.

9.2 Reagent Water

9.2.1 Reagent water is defined as water in which an interferant is not observed at the method detection limit of the parameters of interest.

9.2.2 Reagent water is generated by either passing tap water through a bed of approximately one pound of activated carbon or by using the water purification system at Accutest that is a series of deionizers and carbon cartridges.

9.3 Stock Standard Solutions

9.3.1 Commercially prepared standards used.

9.3.1.1 EPA Method 524.2 Volatiles (78 components): Absolute (or equivalent) at 200 μg/ml or 2,000 μg/ml concentration.

9.3.1.2 Custom Volatiles Mix A: Restek (or equivalent) at 2,000 μg/ml concentration.

9.3.1.3 Custom Volatiles Mix B: Restek (or equivalent) at 2,000 - 100,000 μg/ml concentration.

9.3.1.4 VOC Gas Mixture: Ultra (or equivalent) contains 200 μg/ml or 2,000 μg/ml of the following compound**s** in methanol.

- Bromomethane
- Chloroethane
- Chloromethane
- Dichlorodifluoromethane
- Trichlorofluoromethane
- Vinyl Chloride

9.3.1.5 Multiple neat compounds.

9.3.1.6 Surrogate standard mixture: Ultra (or equivalent) at a concentration of 2,500 μg/ml each surrogate compound.

- 1,2-Dichloroethane-d_4
- Dibromofluoromethane
- Toluene-d_8
- 4-Bromofluorobenzene

9.3.1.7 Internal standard mixture: Ultra (or equivalent) at a concentration of 2,000 μg/ml for all the compounds except Tert Butyl Alcohol-d_9, which is from Absolute (or equivalent) at a concentration of 50,000 μg/ml. The following five internal standards are used that exhibit similar analytical behavior to the compounds of interest.

- 1,4-Dichlorobenzene-d_4
- 1,4-Difluorobenzene
- Chlorobenzene-d_5
- Pentafluorobenzene
- Tert Butyl Alcohol-d_9

9.3.1.8 1,4-Dioxane Solution for SIMS : Ultra (or equivalent) at 100 μg/ml in methanol .

9.3.2 Unopened stock standard (ampoules) must be stored according to manufacturer's documented holding time and storage temperature recommendations (usually placed on the ampoule).

9.3.3 After opened, stock standards, internal standards, and surrogate solutions must be replaced after 6 months (one month for purgeable gases standard) or sooner if manufacture expiration date come first or comparison with quality control check samples indicates degradation.

9.3.4 Store all stock standards in vials with minimal headspace and Teflon lid liners after open, protect from light, and refrigerate to –10°C or colder or as recommended by the standard manufacturer.

9.3.5 Return the standards to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

9.4 Internal Standard and Surrogate Solution

9.4.1 Five internal standard and surrogate spiking solutions are prepared in methanol per Table 8.A.

9.4.1.1 25 μg /ml internal standard and surrogate mixture.

9.4.1.2 250 μg /ml internal standard and surrogate mixture.

9.4.1.3 100 μg/ml surrogate mixture.

9.4.1.4 25 μg /ml internal standard mixture.

9.4.1.5 250 μg /ml internal standard mixture.

9.4.2 A calibration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed with each calibration solution to define a range similar to the target compounds.

9.4.3 Each 5 ml sample, QC sample, and blank undergoing analysis should be spiked with any one of the above spiking solutions (depending upon the type of standards addition modules used), resulting in a concentration of 50 μg/l of each compound.

9.4.4 Prepare fresh internal standard and surrogate spiking solutions every six months, or sooner, if manufacturer's expiration dates come first or if the solution has degraded or evaporated.

9.5 Secondary Dilution Standards

9.5.1 Using stock standard solutions, prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together.

9.5.1.1 100 μg /ml V8260 mixture: prepared from 2,000 μg /ml stock solution. (see Table 8-C)

9.5.1.2 100 μg /ml V8260 custom mixture: prepared from 2,000 μg /ml stock solution. (see Table 8-C)

9.5.1.3 100 μg /ml Gas mixture: prepared from 2,000 μg /ml stock solution. (see Table 8-C)

9.5.2 Replace after one month for non-gas mixtures (one week for gas mixtures) or sooner if manufacture expiration date come first or comparison with quality control check samples indicates degradation.

9.5.3 Store all secondary dilution standards in vials with no headspace and Teflon lid liners, protect from light, and refrigerate to – 10°C or colder or according to manufacturer's storage temperature recommendation.

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9.5.4 Return the standards to the freezer as soon as preparation is finished to prevent the evaporation of volatile compounds.

9.6 Aqueous Calibration Standard Solutions

9.6.1 Initial Calibration Standards

9.6.1.1 Prepare a minimum of five aqueous calibration standard solutions containing the surrogate compounds as Table 8-D.1 or 8-D.2.

9.6.1.2 To prepare a calibration standard, add a measured volume of secondary dilution standard solutions and the surrogate spiking solution to an aliquot of reagent water in the flask. Use a micro-syringe and rapidly inject the methanol standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Bring to volume. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask.

9.6.1.2.1 1,4-Dioxane for SIMS analysis is prepared from primary stock standard (100ppm).

9.6.2 Continuing Calibration Standard

9.6.2.1 A continuing calibration standard at a concentration of 50 μg/l is prepared as the scheme outlined in Table 8-E.

9.6.3 Aqueous standards are not stable and may be stored up to 24 hours if held in Teflon sealed screw-cap vials with zero headspace at 4°C (± 2°C). Protect the standards from light. If not so stored, they must be discarded after use, unless they are set up to be purged by an autosampler.

9.6.4 When using an autosampler, standards may be retained up to 12 hours if they are in purge tubes connected via the autosampler to the purge and trap device.

9.7 Second Source Calibration Check Standard (ICV)

9.7.1 Prepare the second source calibration check standards from separate sources of stock standards from the calibration curve following the procedures in Section 9.6. At a minimum, an ICV should be analyzed with every initial calibration.

9.7.2 For 1,4-Dioxane via SIMS: Prepare the second source calibration check standard using 2.5 µl of a 1000ppm (Absolute or equivalent) to 50 mL of reagent water which yields a 50 ppb standard.

9.8 4-Bromofluorobenzene (BFB) Standard

9.8.1 Two BFB solutions are prepared in methanol per Table 8-B.

9.8.1.1 25 μg /ml solution for direct injection.

9.8.1.2 250 μg /ml solution for purging.

9.8.2 The solution must be replaced after 6 months or sooner if mass spectrum indicates degradation or if manufacture expiration date comes first.

10.0 CALIBRATION

10.1 Daily Maintenance. Routine Daily maintenance must be performed before any tuning, calibration or sample analysis activities are initiated. These include checks of the following items:

Purge and Trap Device:

Clean & bake purge tube
Bake trap and transfer lines
Check or refill internal/surrogate spike solution on SIM/SAM vials
Clean/replace syringe (if necessary)
Change and refill rinse bottle
Empty and rinse waste bottle

GC Oven: (if necessary)

Change septum
Change liner
Clip column, indicated by carbon build-up

10.2 Initial Calibration

10.2.1 The calibration range covered for routine analysis under RCRA, and SIM, employs standards of 1(specified compounds only), (2)*, 5, 10, 20, 50, 100, 200,(300 or 400)* μg/l. (*instrument dependent). A minimum of five standards must be run sequentially. The low calibration standard defines the reporting limit. Lower concentration standards (1.0 or 2.0 μg/l) may be needed to meet the reporting limit requirements of state specific regulatory programs. Refer to Table 8-D-1 and 8-D-2 for calibration standard preparation.

10.2.2 A calibration range must be constructed for each surrogate compound. Accordingly, add appropriate amounts of each surrogate compound to the calibration solution to define a range similar to the target compounds.

10.2.2.1 For most samples and spikes both the internal standard and the surrogate are added automatically. When doing an initial calibration surrogates are added manually. In order to compensate for the difference between the automatic and manual surrogate additions a correction factor must be applied to the amount of surrogate added in Table 8-D. To determine the correction factor divide the surrogate concentration from an automatic injection by the surrogate concentration from a manual injection for each of the surrogates. Average the result for each of the surrogates to determine the correction factor. Finally multiply the correction factor by the appropriate amount of surrogate from Table 8-D and add this amount to the standard.

10.2.3 For water and medium-level soil calibration: Transfer and fill up (no air space) each standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray.

10.2.4 For low-level soil calibration: Transfer 5 ml of each standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray.

10.2.4.1 When calibrating for Method 5035 low-level samples, if the sodium bisulfate option was used, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of each standard into vial otherwise do not add sodium bisulfate. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds. Cap the vial with Teflon septum and place it into O.I sample tray.

10.2.5 The linear range covered by this calibration is the highest concentration standard.

10.2.6 Program the autosampler to add internal standard mixture to each standard. This results in a concentration of 50 μg/l for each internal standard.

10.2.6.1 For O.I. SIM spiker: Automatically adds 10 μl of 25 μg/ml internal standard solution **(**Section 9.4.1.4) to each standard.

10.2.6.2 For O.I. SAM spiker: Automatically adds 1 μl of 250 μg/ml internal standard solution (Section 9.4.1.5) to each standard.

10.2.7 Analyze the standard solutions using the conditions established in Section 11.0. Whenever the highest concentration standard is analyzed, it is usually followed by the analyses of two reagent water blanks. Further analysis may not proceed until the blank analysis is demonstrated to be free of interferences.

10.2.8 Each analyte is quantitatively determined by internal standard technique using the closest eluting internal standard and the corresponding area of the major ion. See Table 7.

10.2.9 The Response Factor (RF) is defined in Section 13.1. Calculate the mean RF for each target analyte using minimum of five RF values calculated from the initial calibration curve.

10.2.10 For the initial calibration to be valid, the following criteria must be met.

10.2.10.1 Five compounds (System Performance Check Compounds, SPCCs) are checked for a minimum average response factor. The minimum mean response factors are listed in Table 6. If the initial calibration criteria for SPCCs are not achieved, perform corrective action before completing the calibration

10.2.10.2 The % RSD for each individual Calibration Check Compound (CCC) must be less than 30 %. This check is used to identify gross instrument operating problems. If the initial calibration criteria for CCCs are not achieved, perform corrective action before completing the calibration.

10.2.10.3 The percent relative standard deviation (% RSD) (see Section 13.2) of all target analytes must be less than 15 %.

10.2.10.4 If the average response factor criteria cannot be achieved, and if the problem is associated with one or more of the standards, reanalyze the

standards and recalculate the RSD. The instrument logbook should have clear documentation as to what the suspected problem was.

10.2.10.4.1 A calibration standard is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed. Notify the team leader/manager. Document this occurrence in the instrument log.

10.2.10.5 Alternately, if the average response factor criteria cannot be achieved, the calibration range can be narrowed by dropping the low or high point of the curve.

10.2.10.5.1 The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end.

10.2.10.6 If the average response factor criteria still cannot be achieved, employ an alternative calibration linearity model. Specifically, linear regression using a least squares approach may be employed.

10.2.10.6.1 If Linear regression is employed select the linear regression calibration option of the mass spectrometer data system. Do not force the regression line through the origin and do not employ 0,0 as a sixth calibration standard.

10.2.10.6.2 The correlation coefficient (r value) must be $\geq$0.99 for each compound to be acceptable.

10.2.10.6.3 Perform corrective action and recalibrate if the calibration criteria cannot be achieved.

10.2.10.7 The initial calibration criteria for this method applies to all additional compounds of concern specified by the client.

10.2.10.8 The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units.

10.3 Initial Calibration Verification (ICV) - Second Source Calibration Check Standard

10.3.1 The calibration is verified with a calibration check standard at 50 µg/l from an external source (Section 9.7). It must be analyzed immediately following the initial calibration.

10.3.2 The percent difference (% D) (Section 13.3) for this standard must meet the criteria of 20% for all the target compounds.

10.3.2.1 If % D is greater than 20%, reanalyze the second source check. If the criteria cannot be met upon re-injection, re-prepare the second source solution using a fresh ampoule and repeat the process.

10.3.2.2 If the %D criteria cannot be achieved after re-preparation of the second source, prepare a third source and repeat the process. Make fresh calibration standards using one of the two standard sources that matches each other and repeat the initial calibration.

10.4 Continuing Calibration Verification Standard(CCV)

10.4.1 A continuing calibration verification standard at a concentration near mid-level of the initial calibration range (50 μg/l) must be acquired every 12 hrs or at the beginning of each analytical batch.

10.4.1.1 For water and medium level soil analysis: Transfer and fill up (no air space) the calibration verification standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray. Analyze as per Section 11.7.

10.4.1.1.1 Vary the concentration of the continuing calibration verification standard on alternate verifications (i.e. every other calibration verification) using an alternative concentration standard. The standard selected must be lower than the midpoint calibration standard.

10.4.1.2 For low-level soil analysis: Transfer 5 ml of the calibration verification standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray. Analyze as per Section 11.7.

10.4.1.2.1 When calibrating for Method 5035 low-level samples, if the sodium bisulfate option was used add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of the calibration verification standard into vial, otherwise do not use sodium bisulfate. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds. Analyze as per Section 11.7.

10.4.1.3 A continuing calibration standard is analyzed whenever the analyst suspects that the analytical system is out of calibration. If the calibration cannot be verified, corrective action is performed to bring the system into control. Analysis may not continue until the system is under control.

10.4.2 For the continuing calibration to be valid, all of the following specified criteria must be met.

10.4.2.1 The minimum RF for SPCC compound is shown on Table 6. Each SPCC compound in the calibration verification standard must meet its minimum response factor.

10.4.2.2 The percent difference (% D, see Section 13.3) for CCC must be less than 20%.

10.4.2.2.1 If the CCCs and SPCCs are not required analytes, such as the shortlist analysis for BTEX only, then all required project analytes must meet the 20 %D.

10.4.3 If the first continuing calibration verification(CCV) does not meet criteria, a second consecutive standard can be analyzed immediately. If the second CCV fails to meet criteria then corrective actions shall be performed. Such as: auto-tuning, routine system cleaning and routine system maintenance. Notify the team leader/manager.

10.4.3.1 If the second CCV trial fails, the lab must demonstrate acceptable performance after corrective action with two consecutive passing calibration verifications(CCVs) OR a new initial calibration. The Instrument Logbook and Maintenance Logbook must have clear documented notations as to what the problem was and what corrective action was implemented.

10.4.3.1.1 If the lab has not verified calibration, samples cannot be analyzed.

10.4.3.1.2 However, in the case where samples are analyzed on the system where the CCV does not meet the criteria the data must be flagged.

10.4.3.1.2.1 The data may be usable if the response for the verification exceed high(high bias) and the associated samples are non-detects.

10.4.3.1.2.2 If the criteria for the CCV is low (low bias), those sample results may be reported only if they exceed a maximum regulatory limit/decision level.

10.4.3.2 If the calibration verification is being performed using an auto sampler for night batch, two (2) vials of standard solution are placed in the device for analysis. The second standard must meet continuing calibration criteria and is used for calibration verification. The second check may be discarded only if there is a purge failure or incorrect spike concentration provided the first calibration standard meets the requirement. In this case, the first calibration standard is used as calibration verification following team leader/manager approval. Document this occurrence on instrument log.

10.4.3.2.1 Both CCVs must be evaluated. If vial 1 fails and vial 2 passes this meets the criteria of 10.4.3 of consecutive and immediate passing CCV.

10.4.3.2.2 If CCV number 2 fails, the analysis cannot continue unless it was determined that there was an isolated mechanical failure.

10.4.4 If any of the internal standard areas change by a factor of two (- 50% to + 100%) or the retention time changes by more than 30 seconds from the midpoint standard of the last initial calibration, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

10.4.5.1 Reanalyze the continuing calibration standard. New initial calibration is required if reanalyzed standard continues to fail the internal standard requirements.

10.4.5.2 All samples analyzed while the system was out of control must be reanalyzed following corrective action.

10.5 Corrective Action Maintenance For Failed Tuning and Calibration Procedures

10.5.1 Inability to achieve criteria for instrument tuning or calibration may indicate the need for instrument maintenance. Maintenance may include routine system cleaning and replacement of worn expendables or the need for outside service if the scope of the repair exceeds the capability of the staff.

10.5.2 If maintenance is performed on an instrument, return to control must be demonstrated before analysis can continue. Return to control is demonstrated as follows:

10.5.2.1 Successful instrument tune using PFTBA.

10.5.2.2 Successful tune verification by the analysis of 4-bromofluorobenzene.

10.5.2.3 Successful initial calibration or continuing calibration.

11.0 PROCEDURE

11.1 Instrument conditions.

11.1.1 Recommended instrument conditions are listed in Table 2 and 2a (SIM only). Modifications of parameters specified with an asterisk are allowed as long as criteria of calibration are met. Any modification should be approved by team leader/manger.

11.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, use the same GC conditions for the analysis of all standards, blanks, samples, and QC samples.

11.2 Purge and Trap Device conditions.

11.2.1 See Table 2.

11.2.2 Daily Maintenance. Routine Daily maintenance must be performed before any tuning, calibration or sample analysis activities are initiated. These include checks of the following items:

<u>Purge and Trap Device:</u>

- Clean & bake purge tube.
- Bake trap and transfer lines.
- Check or refill internal/surrogate spike solution on SIM/SAM vials.
- Clean/replace syringe (if necessary).
- Change and refill rinse bottle.
- Empty and rinse waste bottle.

11.3 Step 1: Daily GC/MS performance check.

11.3.1 Every 12 hours, either

- Inject 2 μl (50 ng) of BFB solution directly on column or
- Purge 10 μg/l of 5ml (50ng) to GC column.

11.3.2 The GC/MS system must be checked to verify acceptable performance criteria are achieved (see Table 3).

11.3.3 This performance test must be passed before any samples, blanks or standards are analyzed. Evaluate the tune spectrum using three mass scans from the chromatographic peak and a subtraction of instrument background.

11.3.3.1 Select the scans at the peak apex and one to each side of the apex.

11.3.3.2 Calculate an average of the mass abundances from the three scans.

11.3.3.3 Background subtraction is required. Select a single scan in the chromatogram that is absent of any interfering compound peaks and no more than 20 scans prior to the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the tuning compound peak.

11.3.4 If all the criteria are not achieved, the analyst must retune the mass spectrometer with team leader/manager and repeat the test until all criteria are met.

11.3.4.5 Alternatively, an additional scan on each side of the peak apex may be selected and included in the averaging of the mass scans. This will provide a mass spectrum of five averaged scans centered on the peak apex. NOTE: The selection of additional mass scans for tuning may only be performed with supervisory approval on a case by case basis.

11.3.5 The injection time of the acceptable tune analysis is considered the start of the 12-hour clock.

11.3.6 Until performance check is acceptable, then calibration check (step 2) can be analyzed.

11.4 Step 2 : Daily calibration check

11.4.1 Initial calibration

11.4.1.1 Refer to Section 10.2.

11.4.1.2 An initial calibration must be established (or reestablished) on each instrument:

- Prior to any sample analyses;
- Whenever a new column is installed;
- Whenever instrument adjustments that affect sensitivity are made; and
- Whenever a continuing calibration standard fails to meet the specified acceptance criteria, on the second trial.

11.4.2 Initial Calibration Verification - Second Source Calibration Check Standard

11.4.2.1 This standard is only analyzed when initial calibration provided. Refer to Section 10.3.

11.4.3 Continuing Calibration verification standard

11.4.3.1 Refer to Section 10.4.

11.4.4 The method blank (step 3) cannot be analyzed until the continuing calibration verification meets the criteria.

11.5 Step 3 : Method blank

11.5.1 The acceptable method blank must be analyzed for every 12-hour time period or sooner.

11.5.1.1 Water and medium-level soil samples - Place a 40 ml vial, filled with DI water onto the autosampler.

11.5.1.2 Low-level soil samples without sodium bisulfate - Transfer 5 ml of DI water to a 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray.

11.5.1.2.1 Low-level soil samples with sodium bisulfate (Method 5035) - Add 1g of sodium bisulfate to a 40 ml vial before aliquot 5 ml of DI water into the vial and cap with Teflon septum, then place the vial onto the autosampler.

11.5.2 Program the autosampler to add internal standard and surrogate solution to the method blank for a concentration of 50 μg/l for each internal standard and surrogate.

11.5.2.1 For O.I. SIM spiker: Automatically adds 10 μl of 25 μg/ml internal standard and surrogate solution (Section 9.4.1.1) to the method blank.

11.5.2.2 For O.I. SAM spiker: Automatically adds 1 μl of 250 μg/ml internal standard and surrogate solution (Section 9.4.1.2) to the method blank.

11.5.3 No compound can be present above the laboratory's MDL. If common laboratory solvents (i.e. methylene chloride, acetone) are present in the sample between the MDL and RL, the analyst must determine if the contamination will negatively impact data quality. If the contamination impacts data quality, all affected samples must be re-analyzed.

11.5.4 Surrogates must meet recovery criteria specified in house limits.

11.5.5 If the method blank does not meet surrogate criteria or contains target analytes above the MDL, then

11.5.5.1 All samples analyzed following an out of control method blank must be reanalyzed.

11.5.5.2 Check for the potential of contamination interference from the following areas. Make sure all items are free contamination.

- the analytical system,
- dust and vapor in the air,
- glassware and
- Reagents.

11.5.5.3 Re-analyze the method blank following the system evaluation. In this situation, the instrument logbook should have clear documented notations as to what the problem was and what corrective action was implemented to enable the second blank to pass.

11.5.5.4 If re-analyzed method blank remains out of control, notify team leader or manager.

11.5.6 If two consecutive method blanks are analyzed during unattended operations, the second analysis must meet criteria for the subsequent sample analysis to be valid. Always report the second method blank. The second analysis can only be discarded because of a purge failure provided that the first blank meets the requirement. In this case, the first blank is reported following team leader/manager approval. Document this occurrence on the instrument log.

11.5.7 The blank spike (BS) (step 4) cannot be analyzed until the method blank meets criteria.

11.6 Step 4: Blank spike (BS)

11.6.1 An acceptable blank spike must be analyzed with every analytical batch. The maximum number of samples per analytical batch is twenty.

11.6.2 Spike 50 ml of reagent water with appropriate amount of the standards to prepare a blank spike containing 50 μg/L of each analyte. In situations where lower detection limits are required, a blank spike at 20 μg/L may be prepared. The stock solution for the BS must be from a different source than the initial calibration solution. Refer to Table 8-F for the preparations of the blank spikes.

11.6.2.1 Water and medium-level soil samples - Place a 40 ml vial, filled with DI water onto the autosampler.

11.6.2.2 Low-level soil samples without sodium bisulfate - Aliquot 5 ml of the blank spike into vial and cap with Teflon septum, then place the vial into O.I. sample tray.

11.6.2.2.1 Low-level soil samples with sodium bisulfate for Method 5035 - Add 1g of sodium bisulfate to labeled 40 ml vial before aliquot 5 ml of the blank spike into vial and cap with Teflon septum, then place the vial into O.I. sample tray.

11.6.3 Initiate auto addition of internal standard and surrogate into the syringe per 11.5.2.

11.6.4 Compare the percent recoveries (% R) (see Section 13.5) to the in house limits acceptance criteria. If a blank spike is out of control, all the associated samples must be reanalyzed. The exception is if the blank spike recovery is high and no hits reported in associated samples and QC batch. In that case, the sample results can be reported with footnote (remark) and no further action is required. Or if the blank spike recovery is low and the hits in the samples are above regulatory levels.

11.6.5 Do not analyze samples and MS/MSD (step 5) unless the BS meets acceptance criteria.

11.7 Step 5: Samples /MS/MSD analysis

11.7.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

11.7.2 Select the sample dilution factor to assure the highest concentration analyte is above the calibration range midpoint, but below the upper limit of the range depend on project requirements. See Table 9 for dilution guideline.

- Utilize FID screen data.
- Utilize acquired sample data.
- Utilize the history program.
- Sample characteristics (appearance, odor).

11.7.3 Water samples.

11.7.3.1 Using O.I.Model 4560 sample concentrator with 4551 or 4552 vial multisampler,

- Place the 40 ml vial in the tray, or
- Load 5ml sample into purge tube if sample volume limited.

11.7.4 Sediment/ soil sample

11.7.4.1 Low-level soil method

11.7.4.1.1 Collect the sample using the procedures detailed in the SOP for SW846 Method 5035 low - level soil samples.

11.7.4.1.2 Weigh out 5 g of each sample into a labeled vial. Add 5 ml of reagent water and cap the vial quickly. Transfer the 40ml vial to the autosampler tray. Stir and heat the sample at the time of analysis.

11.7.4.2 Medium-level soil method

11.7.4.2.1 Collect the sample using the procedures detailed in the SOP for SW846 Method 5035 medium - level soil samples.

11.7.4.2.2 Select a methanol aliquot of appropriate volume (see Table 9) determined via screening and transfer to 40 ml of reagent water.

11.7.5 Program the autosampler to inject the internal standard and surrogate solution into the robotic syringe used to withdraw sample from the 40 ml vial. This addition to 5 ml of sample is equivalent to a concentration of 50 μg/L of each internal standard and surrogate.

11.7.5.1 For O.I. SIM spiker: Automatically adds 10 μl of 25 μg/ml internal standard and surrogate solution (Section 9.4.1.1) to each sample.

11.7.5.2 For O.I. SAM spiker: Automatically adds 1 μl of 250 μg/ml internal standard and surrogate solution (Section 9.4.1.2) to each sample.

11.7.6 Purge the sample for 11 minutes with Helium.

11.7.6.1 Low-level soil sample must be performed at 40 °C while the sample is being agitated with the magnetic stirring bar or other mechanical means.

11.7.6.2 To improve the purging efficiency of water-soluble compounds, aqueous samples may also be purged at 40 °C as long as all calibration standards, samples and QC samples are purged at the same temperature and acceptable method performance is demonstrated.

11.7.7 One sample is randomly selected from each analytical batch of similar matrix types and spiked in duplicate to determine whether the sample matrix contributes bias to the analytical results. A matrix spike and matrix spike duplicate are performed by spiking the sample for a concentration of 50 µg/l or 50 µg/kg based on 5 g dry weight. In situations where lower detection limits are required, a blank spike at lower concentration may be prepared.

11.7.8 Desorb the sample for 4 minutes by rapidly heating the trap to 190 °C while backflushing with Helium. Desorb time may require performance optimum between 2.0 and 4.0 minutes as dictated by trap manufacturers specifications or instrument characteristics.

11.7.9 Program the purge and trap system to automatically rinse purge tube at least twice with heated organic-free water (reagent water) between analyses to avoid carryover of target compounds. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with methanol solution between analyses, rinse it with distilled water.

11.7.10 Bake the trap at least 10 minutes at 210 °C to remove any residual purgeable compounds.

11.7.11 If the initial analysis of the sample or a dilution of the sample has a response for any ion of interest that exceeds the working range of the GC/MS system, the sample must be reanalyzed at a higher dilution.

11.7.11.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

11.8 Sample dilutions

11.8.1 Using Screening Data to Determine Dilution Factors

11.8.1.1 Dilution for High Concentration Analytes Exceeding The Calibration Range

11.8.1.1.1 The highest concentration target compound detected in the screen data is compared to the highest concentration calibration standard used for determinative volatile organics analysis.

11.8.1.1.1.1 Divide the calibration concentration of the highest concentration calibration standard by the screen concentration.

11.8.1.1.1.2 If the result is >1, sample dilution is considered.

11.8.1.1.2 The result from step 11.8.1.1.1 determines the dilution factor. The dilution factor is targeted to assure that the highest concentration diluted analyte is at the mid-range concentration of the calibration curve for the determinative analysis.

11.8.1.1.3 In all cases a conservative approach to dilution is applied to minimize the increase of detection and reporting limits

11.8.1.2 Dilution for High Concentration Matrix Interferences

11.8.1.2.1 The peak height of the background is compared to the peak height of the later eluting calibration standards from the screening analysis.

11.8.1.2.1.1 A rough estimate of background concentration is calculated by dividing the background peak height by the peak height of the selected screening standard and multiplying by its concentration.

11.8.1.2.2 If the result is >1, sample dilution is considered.

11.8.1.2.3 The result from step 11.8.1.2.1 determines the dilution factor. The dilution factor is targeted to avoid Carry-over contamination between samples and facilitate qualitative and quantitative analysis of target compounds present in the sample.

11.8.1.2.4 In all cases a conservative approach to dilution is applied to minimize the increase of detection and reporting limits

11.8.2 If the concentration of any target compound in any sample exceeds the initial calibration range, a new aliquot of that sample must be diluted and re-analyzed. Until the diluted sample is in a sealed sample vial, all steps in the dilution procedure must be performed without delay.

11.8.3 Water Samples.

11.8.3.1 Prepare all dilutions of water samples in volumetric flasks (10 ml to 100 ml). Intermediate dilutions may be necessary for extremely large dilutions.

11.8.3.2 Calculate the approximate volume of reagent water, which will be added to the volumetric flask, and add slightly less than this quantity to the flask. Refer to Table 9 for dilution guideline.

11.8.3.3 Inject the proper sample aliquot from a syringe into the volumetric flask. Dilute the flask to the volume mark with reagent water. Cap the flask and invert the flask three times.

11.8.3.4 Fill a 40 ml sample vial and seal with a Teflon baked silicon septa, load the diluted sample into the autosampler and analyze according to Section 11.7.

11.8.3 Low-level Soil Samples.

11.8.3.1 The screening data are used to determine which is the appropriate sample preparation procedure for the particular sample, the low-level soil method or the medium-level soil method.

11.8.3.2 If any target compound exceeds the initial calibration range from the analysis of 5 g sample, a smaller sample size must be analyzed. However, the smallest sample size permitted is 0.5 g. If smaller than 0.5 g sample size is needed to prevent any target compounds from exceeding the initial calibration range, the medium level method must be used.

11.9 Data interpretation

11.9.1 Qualitative identification.

11.9.1.1 The targeted compounds shall be identified by analyst with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound.

11.9.1.2 The characteristic ions for target compounds that can be determined are listed in Table 7. Table 4 and Table 5 list the characteristic ions for internal standards and surrogate compounds respectively.

11.9.1.3 The criteria required for a positive identification are listed below.

11.9.1.3.1 The sample component must elute at the same relative retention time (RRT) as the daily standard. Criteria are the RRT of sample component must be within ± 0.06 RRT units of the standard component.

11.9.1.3.2 The relative intensities of these ions must agree within ± 30 % between the daily 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 %.)

11.9.1.3.2.1 Compounds can have secondary ions outside criteria from co-eluting compounds and/or matrix effect that can contribute to ion abundances. The interference on ion ratios can't always be subtracted out by software programs resulting in qualified compound identification.

11.9.1.3.2.2 Quantitation reports display compounds that have secondary ions outside the ratio criteria with a "#" flag.

11.9.1.3.2.3 Any quant reports with compounds that are deemed to be reportable despite the "#" flag, will be initialed in the "#" column by the analyst. Further review to the reporting of qualified compounds will be done by a supervisor or team leader and initialed on the quantitation.

11.9.1.3.3 Structural isomers that produce very similar mass specrtra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25 % of sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

11.9.2 Quantitative analysis

11.9.2.1 Once a target compound has been identified, its concentration (Section 13.4) will be based on the integrated area of the quantitation ion, normally the base peak (Table 7). The compound is quantitated by internal standard technique with an average response factor generated from the initial calibration curve.

11.9.2.2 If the sample produces interference for the primary ion, use a secondary ion to quantitate (see Table 7). This is characterized by an excessive background signal of the same ion, which distorts the peak shape beyond a definitive integration. Also interference could severely inhibit the response of the internal standard ion. This secondary ion must also be used to generate new calibration response factors.

11.10 Library search for tentatively identified compounds.

11.10.1 If a library search is requested, the analyst should perform a forward library search of NBS or NIST98 mass spectral library to tentatively identify 15 non-reported compounds.

11.10.2 Guidelines for making tentative identification are listed below.

11.10.2.1 These compounds should have a response greater than 10 % of the nearest internal standard. The response is obtained from the integration for peak area of the Total Ion Chromatogram (TIC).

11.10.2.2 The search is to include a spectral printout of the 3 best library matches for a particular substance. The results are to be interpreted by analyst.

11.10.2.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

11.10.2.4 Relative intensities of major ions in the reference spectrum (ions > 10 % of the most abundant ion) should be present in the sample spectrum.

11.10.2.5 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 must between 30 and 70%).

11.10.2.6 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

11.10.2.7 Ions present in the reference spectrum but not in the sample spectrum should be verified by performing further manual background subtraction to eliminate the interference created by coeluting peaks and/or matrix interference.

11.10.2.8 Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 and is to be tabulated on the library search summary data sheet.

11.10.2.9 The resulting concentration should be reported indicating: (1) that the value is estimate, and (2) which internal standard was used to determine concentration. Quantitation is performed on the nearest internal standard.

11.11 An instrument blank is a system evaluation sample containing lab reagent grade water with internal standards and surrogates. An instrument blank is used to remove and or evaluate residual carryover from high level standards, spike samples and field samples. Since target compound lists have expanded to overlap some volatile and semi-volatile compounds, instrument blanks are necessary to remove carryover contamination.

11.11.1 The compounds that may exhibit carryover for this method are listed in Table 11.

11.11.2 If instrument blanks following a standard or spike sample exhibits carrry-over effect, then any samples that show the same carryover profile, after a comparable concentration must be considered suspect and rerun for confirmation. For example, if an instrument blank has 1ppb detected after a 200ppb standard, then any sample following a sample containing 200ppb or above of the same compound must be confirmed for possible carryover.

11.11.3 If an Instrument Blank(s) was run following suspect high concentration samples and it exhibits the same carryover profile after a comparable concentration must be considered suspect and rerun for confirmation.

11.11.4 In some cases, several instrument blanks may have to be run to eliminate contamination from over loaded samples.

11.11.5 The analytical system is considered free of carryover, when no target analytes can be detected above the MDL.

11.12 Selected Ion Monitoring (SIM) Option Selected Ion Monitoring (SIM) Option

11.12.1 Instrument Set-Up: Modify the method for SIM analysis and define ion groups with retention times, ions and dwell times to include base peak ion for the target compounds of interest, surrogates, and internal standards (Table 2a.) Select a mass dwell time of 50 milliseconds for all compounds.

11.12.2 Calibration: Calibrate the mass spectrometer in the selected ion monitoring mode using 6 calibration standards of 5, 10, 20, 50, 100, 200 ug/l. Spike each standard with the SIM specific internal standard solution at 4ug/ml. Calculate individual response factors and response factor RSDs.

11.12.3 Initial Calibration Verification. Verify the initial calibration after its completion using a 50 ug/l calibration standard purchased or prepared from a second standards reference materials source. The initial calibration verification must meet the criteria of Section 10.2.

11.12.4 Continuing Calibration Verification. Verify the initial calibration every 12 hours using a 50 ug/l calibration. The continuing calibration verification must meet the criteria of Section 10.4.

11.12.5 Surrogate Standard Calculation.. Report surrogate spike accuracy for the surrogates spiked for the full scan GC/MS analysis.

12.0 QUALITY CONTROL

12.1 QC Requirements Summary

BFB	Beginning of the analytical shift and every 12 hours
ICV - Second Source Calibration Check Standard	Following initial calibration
Calibration Verification Standard	Every 12 hours
Method Blank	Every 12 hours
Blank Spike	One per analytical batch*
Matrix Spike	One per analytical batch*
Matrix Spike Duplicate	One per analytical batch*
Surrogate	Every sample and standard
Internal Standard	Every sample and standard

*The maximum number of samples per analytical batch is twenty.

12.2 Daily GC/MS Performance Check - BFB

12.2.1 Refer to Section 11.3.

12.3 Second Source Calibration Check Standard

12.3.1 Refer to Section 10.3.

12.3.2 Calibration Verification Standard

12.3.3 Refer to Section 10.4.

12.5 Method Blank

12.5.1 Refer to Section 11.5.

12.6 Blank Spike

12.6.1 Refer to Section 11.6.

12.7 Matrix Spike (MS)/Matrix Spike Duplicate (MSD)

12.7.1 One sample is selected at random from each analytical batch of similar matrix types and spiked in duplicate to check precision and accuracy.

12.7.2 Assess the matrix spike recoveries (Section 13.5) and relative percent difference (RPD) (Section 13.6) against the control limits..

12.7.3 If the matrix spike recoveries do not meet the criteria, check the blank spike recovery to verify that the method is in control. If the blank spike did not meet criteria, the method is out of control for the parameter in question and should be reanalyzed or qualified with an estimate of potential bias. Otherwise, matrix interference is assumed and the data is reportable. No further corrective action is required.

12.8 Surrogates

12.8.1 All standards, blanks, samples, and matrix spikes contain surrogate compounds, which are used to monitor method performance. If the recovery of any surrogate compound does not meet the control limits, the result must be flagged and:

12.8.1.1 The calculation must be checked.

12.8.1.2 The sample must be reanalyzed if the recovery of any one surrogate is out of control limit.

12.8.2 If the sample exhibits matrix interference, defined as excessive signal levels from target or non-target interfering peaks. In this case, reanalysis may not be required following team leader/manager approval.

12.8.3 If surrogate recoveries are acceptable upon reanalysis, the data from the reanalysis is reported. If the reanalysis date did not meet the hold time, then both sets of data must be submitted with the reanalysis reported.

12.8.4 If surrogates are still outside control limits upon reanalysis, then both sets of data should be submitted with the first analysis reported.

12.9 Internal Standard

12.9.1 Retention time for all internal standards must be within $\pm$ 30 seconds of the corresponding internal standard in the latest continuing calibration or 50 μg/l standard of initial calibration.

12.9.2 The area (Extracted Ion Current Profile) of the internal standard in all analyses must be within 50 to 200 % of the corresponding area in the latest calibration standard (12 hr. time period).

12.9.3 If area of internal standard does not meet control limits, the calculations must be checked. If a problem is not discovered, the sample must be reanalyzed.

12.9.4 If areas are acceptable upon reanalysis, the reanalysis data is reported.

12.9.5 If areas are unacceptable upon reanalysis, then both sets of data are submitted with the original analysis reported.

13.0 CALCULATION

13.1 Response Factor (RF)

$$RF = \frac{As \times Cis}{Ais \times Cs}$$

where:
As = Area of the characteristic ion for the compound being measured.
Ais = Area of the characteristic ion for the specific internal standard.
Cs = Concentration of the compound being measured (ug/l).
Cis = Concentration of the specific internal standard (ug/l).

13.2 Percent Relative Standard Deviation (% RSD)

$$\%RSD = \frac{SD}{RFav} \times 100$$

where:
SD = Standard Deviation
RFav = Average response factor from initial calibration.

13.3 Percent Difference (%D)

$$\%D = \frac{(RFav - RFcv)}{RFav} \times 100$$

where:
RFcv = Response factor from Calibration Verification standard.
RFav = Average response factor from initial calibration.

13.4 Concentration (Conc.)

For water:

$$\text{Conc. } (\mu g/l) = \frac{Ac \times Cis \times Vp}{Ais \times RF \times Vi}$$

For soil/sediment low level (on a dry weight basis):

$$\text{Conc. } (\mu g/kg) = \frac{Ac \times Cis \times Vp}{Ais \times RF \times Ws \times M}$$

For soil/ sediment medium level (on a dry weight basis)

$$\text{Conc. } (\mu g/kg) = \frac{Ac \times Cis \times Vp \times Vt}{Ais \times RF \times Vme \times Ws \times M}$$

Where:
Ac = Area of characteristic ion for compound being measured.
Ais = Area of characteristic ion for internal standard.
Cis = Concentration of internal standard
RF = Response factor of compound being measured(from initial calibration)
Vi = Initial volume of water purged (ml)
Vp = 5 ml (Total Purge Volume)
Vme = Volume of Methanol aliquot
Vt = Ml Solvent + ((100-% solid)/100 x Ws)
Ws = Weight of sample extracted (g).
M = (100 - % moisture in sample) / 100 or % solids / 100

13.5 Percent Recovery (% R)

$$\%\ R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

13.6 Relative Percent Difference (RPD)

$$RPD = \frac{|\ MSC - MSDC\ |}{(1/2)\ (MSC+MSDC)} \times 100$$

Where:
MSC = Matrix Spike Concentration
MSDC = Matrix Spike Duplicate Concentration

13.7 Linear regression by the internal standard technique.

$$C_s = \left(\frac{\frac{A_s}{A_{is}} - b}{A} \right) \times C_{is}$$

Where:
Cs = concentration of target analyte
As = Area of target analyte
Cis = concentration of the internal standard
b = Intercept
a = slope of the line

$$a = \frac{N \Sigma xy - \Sigma x \Sigma y}{N \Sigma x^2 - (\Sigma x)^2}$$

$$b = \frac{\Sigma y - a \Sigma x}{N}$$

N = number of points
x = amount of analyte
y = response of instrument

13.8 Correlation Coefficient

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where r = correlation coefficient
x = amount of analyte
y = response of instrument

$\bar{x}$ = average of x values

$\bar{y}$ = average of y values

14.0 DOCUMENTATION

14.1 The Analytical Logbook records the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

14.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in the Comments section.

14.2 Standards Preparation Logbook must be completed for all standard preparations. All information must be completed; the page must be signed and dated by the appropriate person.

14.2.1 The Accutest lot number must be cross-referenced on the standard vial.

14.3 Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument has a separate log.

14.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

14.5 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information should also be verified during this review.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes

15.2.2 Hazardous aqueous wastes

15.2.3 Chlorinated organic solvents

15.2.4 Non-chlorinated organic solvents

15.2.5 Hazardous solid wastes

15.2.6 Non-hazardous solid wastes

Table 1. TARGET COMPOUNDS		
Acetone	1,4-Dichlorobenzene	Methylene Bromide
Acetonitrile	Dichlorodifluoromethane	Methylene Chloride
Acrolein	1,1-Dichloroethane	1-Methylnaphthalene (1)
Acrylonitrile	1,2-Dichloroethane	2-Methylnaphthalene (1)
Allyl Chloride	1,1-Dichloroethene	Naphthalene
Benzene	cis-1,2-Dichloroethene	2-Nitropropane (1)
Benzyl chloride	trans-1,2-Dichloroethene	Pentachloroethane
Bromobenzene	1,2-Dichloropropane	Propionitrile
Bromochloromethane	1,3-Dichloropropane	Propyl Acetate (1)
Bromodichloromethane	2,2-Dichloropropane	n-Propylbenzene
Bromoform	1,1-Dichloropropene	Styrene
Bromomethane	cis-1,3-Dichloropropene	Tert Butyl Alcohol
2-Butanone (MEK)	trans-1,3-Dichloropropene	tert-Amyl Methyl Ether
Butyl Acetate (1)	1,4-Dioxane	tert-Butyl Ethyl Ether
n-Butyl Alcohol (1)	Epichlorohydrin (1)	1,1,1,2-Tetrachloroethane
n-Butylbenzene	Ethyl Acetate	1,1,2,2-Tetrachloroethane
sec-Butylbenzene	Ethyl Ether	Tetrachloroethene
tert-Butylbenzene	Ethyl Methacrylate	Tetrahydrofuran
Carbon Disulfide	Ethylbenzene	Toluene
Carbon Tetrachloride	p-Ethyltoluene (1)	trans-1,4-Dichloro-2-Butene
Chlorobenzene	Freon 113	1,2,3-Trichlorobenzene
Chlorodifluoromethane (1)	Heptane (1)	1,2,4-Trichlorobenzene
Chloroethane	Hexachlorobutadine	1,1,1-Trichloroethane
2-Chloroethyl Vinyl Ether	Hexachloroethane	1,1,2-Trichloroethane
Chloroform	Hexane (1)	Trichloroethene
Chloromethane	2-Hexanone	Trichlorofluoromethane
Chloroprene (2-chloro-1,3-butadiene)	Iodomethane (Methy iodide)	1,2,3-Trichloropropane
o-Chlorotoluene	IsoAmyl Alcohol (1)	1,2,4-Trimethlylbenzene
p-Chlorotoluene	Isobutyl Alcohol	1,3,5-Trimethylbenzene
Cyclohexane (1)	Isopropyl Acetate (1)	2,2,4 Trimethylpentane
Cyclohexanone	Isopropylbenzene	Vinyl Acetate
di-Isobutylene (1)	p-Isopropyltoluene	Vinyl Chloride
di-Isopropyl Ether	Methacrylonitrile	Vinyltoluene (1)
1,2-Dibromo-3-Chloropropane	Methyl Acetate (1)	m,p-Xylene
Dibromochloromethane	3 Methyl-1-Butanol (1)	o-Xylene
1,2-Dibromoethane	Methyl Tert Butyl Ether	Ethanol
Dibromomethane (1)	Methylcyclohexane	Methyl Acrylate
1,2-Dichlorobenzene	Methyl Methacrylate	1-chloro-1,1-difluoroethane
1,3-Dichlorobenzene	4-Methyl-2-pentanone (MIBK)	1,1,1-trifluoroethane
1,1-dichloro-1-fluroethane	2,2-Dichloropropane	

(1) NELAC Accreditation is not offered for this compound. Results may not be useable for regulatory purposes in States where this accreditation option is not offered.

Table 2. RECOMMENDED OPERATING CONDITION	
Gas Chromatograph/ Mass Spectrometer	
Carrier Gas (linear velocity)	Helium at *30 cm/sec
Mass range	35 – 300 amu
Electron Energy	70 volts (nominal)
Scan time	not to exceed 2 sec. per scan
Injection port temperature	200 - 225 °C
Source temperature	200 - 250 °C
Transfer line temperature	220 - 280 °C
Analyzer temperature	220 - 250 °C
Gas Chromatograph temperature program*	
Initial temperature	*40 °C
Time 1	*3 minutes
Column temperature rate	*8 degrees/min.
Final temperature	*220 °C.- 240 °C
Total run time	*25 – 50 mins
Purge and Trap Device	
Purge time	9 min. (at 40 °C for low-level soil) SIM – 6 min @ 50 °C
Desorb**	4 min. at 190 °C
Bake	>10 min. at 210 °C
Transfer line	100 - 130 °C
Valve temperature	approx. transfer line temperature

* Parameter modification allowed for performance optimization provided operational and QC criteria is achieved.(must be approved by team leader/manager)

** Desorb time may require performance optimum between 2.0 and 4.0 minutes as dictated by trap manufacturers specifications or instrument characteristics

Table 2a – SIM Group Parameters		
Group No.	**Retention Time (minutes)**	**Ions**
1	0 – 10.8	58, 65, 66, 88
2	10.8 – 16.0	95, 174, 176, 98, 100, 70

Table 3. BFB KEY IONS AND ION ABUNDANCE CRITERIA	
Mass	**Ion Abundance Criteria**
50	15-40% of mass 95
75	30-60% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5-9% of mass 174
176	>95% and <101% of mass 174
177	5-9% of mass 176

Table 4. INTERNAL STANDARD QUANTITION IONS	
Internal Standard	**Primary/Secondary Ions**
1,4-Difluorobenzene	114 / 63,88
Chlorobenzene-d5	117 / 82, 119
Pentafluorobenzene	168
1,4-Dichlorobenzene-d4	152 / 115, 150
Tert Butyl Alcohol-d9	65/66
Internal Standard (SIM)	
Tert Butyl Alcohol-d9	65/66

Table 5. SURROGATE QUANTITION IONS	
Surrogate Compound	**Primary/Secondary Ions**
1,2 Dichloroethane – d_4	102
Dibromofluoromethane	113
Toluene-d8	98
4-Bromofluorobenzene	95 / 174, 176

Table 6. CRITERIA FOR CCC AND SPCC		
Initial Calibration	Maximum % RSD for CCC is 30 %	
Continuing Calibration	Maximum % D for CCC is 20 %	
Calibration check compounds (CCC)	**Volatile Compound**	
	Vinyl chloride 1,1-Dichloroethene Chloroform 1,2-Dichloropropane Toluene Ethylbenzene	
System Performance Check Compounds (SPCC)	**Compound Name**	**Minimum RF**
	Chloromethane	0.1
	1,1-Dichloroethane	0.1
	Bromoform	0.1
	1,1,2,2-Tetrachloroethane	0.3
	Chlorobenzene	0.3

Table 7. Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)	Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
Tert Butyl Alcohol-d9			Dibromomethane	93	95, 174
Tert Butyl alcohol	59	57	Di-isobutylene	57	
Ethanol	45	46	Epichlorohydrin (pp)	57	57, 49, 62, 51
Pentafluorobenzene			Ethyl methacrylate	69	69, 41, 99, 86, 114
1,1,1-Trichloroethane	97	99, 61	Heptane	57	
1,1-Dichlorethane	63	65, 83	Hexane	56	
1,1-Dichloroethene	96	61, 63	Isopropyl acetate	43	
2,2-Dichloropropane	77	97	Methyl cyclohexane	83	
2-Butanone (pp)	72	43, 72	Methyl methacrylate	69	69, 41, 100, 39
Acetone (pp)	58	43	n-Butanol (pp)	56	41
Acetonitrile (pp)	41	41, 40, 39	Propyl Acetate	43	
Acrolein (pp)	56	55,58	tert Amyl Methyl Ether	73	
Acrylonitrile (pp)	53	52, 51	Toluene	92	91
Allyl Chloride	41		Toluene-d_8	98	
Bromochloromethane	128	49, 130	trans-1,3-Dichloropropene	75	77, 39
Bromomethane	94	96	Trichloroethene	95	97, 130, 132
Carbon disulfide	76	78			
Chlorodifluouromethane	51	86	**Chlorobenzene-d5**	117	82,119
Chloroethane	64	66	1,1,1,2-Tetrachloroethane	131	133, 119
Chloroform	83	85	1,2-Dibromoethane	107	109, 188
Chloromethane	50	52	1,3-Dichloropropane	76	78
Chloroprene	53	53, 88, 90, 51	Bromoform	173	175, 254
cis-1,2-Dichloroethene	96	61, 98	Butyl Acetate	56	
Cyclohexane	84		Chlorobenzene	112	77, 114
Dibromofluoromethane	113		Dibromochloromethane	129	127
Dichlorodifluoromethane	85	87	Ethylbenzene	91	106
Dichloroethane-d_4	102	65	m-Xylene	106	91
Diethyl ether	74	45, 59	o-Xylene	106	91
Diisopropyl ether	45	102	p-Xylene	106	91
Ethyl acetate (pp)	88	43, 45, 61	Styrene	104	78
Ethyl tert Butyl Ether	59		Tetrachloroethene	164	129,131,166
Freon 113	151				
Iodomethane	142	127, 141	**1,4 Dichlorobenzene-d4**	152	115,150
Isobutyl alcohol (pp)	43	43, 41, 42, 74	1,1,2,2-Tetrachloroethane	83	131, 85
Methacrylonitrile (pp)	41	41, 67, 39, 52, 66	1,2,3-Trichlorobenzene	180	182, 145
Methyl Acetate	43	74	1,2,3-Trichloropropane	75	77
Methylene chloride	84	86, 49	1,2,4-Trichlorobenzene	180	182, 145
Methyl-t-butyl ether	73	57	1,2,4-Trimethylbenzene	105	120
Propionitrile (ethyl cyanide)(pp)	54	54, 52, 55, 40	1,2-Dibromo-3-chloropropane(pp)	75	155, 157
Tetrahydrofuran	42		1,2-Dichlorobenzene	146	111,148
trans-1,2-Dichloroethene	96	61, 98	1,3,5-Trimethylbenzene	105	120
Trichlorofluoromethane	151	101, 153	1,3-Dichlorobenzene	146	111, 148
Vinyl acetate	43	86	1,4-Dichlorobenzene	146	111, 148
Vinyl chloride	62	64	2-Chlorotoluene	91	126
Methyl Acrylate	55	85	4-Bromofluorobenzene	95	174, 176
2,2,4 Trimethylpentane	57				
1-chloro-1, 1-difluoroethane	65	45,85			
1,1,1-trifluoroethane	69	69,45			
1,1-dichloro-1-fluroethane	81	45,61			
2,2-Dichloropropane	77	97,79			
1,4 Difluorobenzene	114	63, 88	4-Chlorotoluene	91	126
1,1,2-Trichloroethane	83	97, 85	Benzyl chloride	91	91, 126, 65, 128
1,1-Dichloropropene	75	110, 77	Bromobenzene	156	77, 158

Table 7. Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)	Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
1,2 Dichloroethane	62	98	Cyclohexanone	55	
1,2 Dichloropropane	63	112	Hexachlorobutadiene	225	223, 227
1,4-Dioxane (pp)	88	88, 58, 43, 57	Hexachloroethane (pp)	201	166, 199, 203
2-Chloroethyl-vinylether (pp)	63	65, 106	Isopropylbenzene	105	120
2 – Hexanone	43	58,57,100	Naphthalene	128	-
2-Hexanone (pp)	43	58, 57, 100	n-Butylbenzene	91	92, 134
2-Nitropropane	46	-	n-Propylbenzene	91	120
3 Methyl –1 butanol	55		Pentachloroethane (pp)	167	167,130,132,165,169
4-Methyl-2-pentanone (pp)	100	43, 58, 85	p-isopropyltoluene	119	134,91
Benzene	78	-	sec-Butylbenzene	105	134
Bromodichloromethane	83	85, 127	tert-Buytlbenzene	119	91, 134
Carbon tetrachloride	117	119	trans-1,4-Dichloro-2-butene (pp)	53	88, 75
cis-1,3-Dichloropropene	75	77, 39			
Methylcyclohexane	83		**(pp) = Poor Purging Efficiency**		

Table 7-1 SIM - Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
Tert Butyl Alcohol-d9		
1,4-Dioxane	88	58
Toluene –d8	98	100
4-BFB	95	174, 176

Table 8. STANDARDS PREPARATION

A) Internal standard and Surrogate mixtures:

	a) 25/250 μg/ml	b) 250/2,500 μg/ml
Internal Standard Mixture (2,000 μg/ml)	1.25 ml	1 .25 ml
Tert Butyl Alcohol-d_9 (50,000 μg/ml)	0.5 ml	0.5 ml
Surrogate Mixture (2,500 μg/ml)	1 ml	1 ml
Methanol	97.25 ml	7.25 ml
Total	100 ml	10 ml

- 25/250 μg /ml internal standard and surrogate mixture: The mixture is prepared by measuring 1.25ml of 2,000 μg /ml Internal Standard Mixture (Ultra or equivalent), 0.5 ml of 50,000 μg/ml TBA-d_9 (Absolute or equivalent), 1 ml of 2,500 μg /ml Method 8260A Surrogate Standard Mixture (Ultra or equivalent) and bringing to 100 ml with methanol.

- 250/2,500 μg /ml internal standard and surrogate mixture: The mixture is prepared by measuring 1.25 ml of 2,000 μg /ml Internal Standard Mixture (Ultra or equivalent), 0.5 ml of 50,000 μg/ml TBA-d_9 (Absolute or equivalent), 1 ml of 2,500 μg /ml Method 8260A Surrogate Standard Mixture (Ultra or equivalent) and bringing to 10 ml with methanol.

- 100 μg/ml surrogate mixture: The solution is prepared at 100 μg/ml by measuring 0.4 ml of 2,500 μg/ml Method 8260A Surrogate Standard Mixture (Ultra or equivalent) and bringing to 10 ml with methanol.

- 25/250 μg /ml internal standard mixture: The solution is prepared by measuring 1.25 ml of 2,000 μg /ml Internal Standard Mixture (Ultra or equivalent), 0.5 ml of 50,000 μg/ml TBA-d_9 (Absolute or equivalent), and bringing to 100 ml with methanol.

- 250/2,500 μg /ml internal standard mixture: The solution is prepared by measuring 1.25 ml of 2,000 μg /ml Internal Standard Mixture (Ultra or equivalent), 0.5 ml of 50,000 μg/ml TBA-d_9 (Absolute or equivalent), and bringing to 10 ml with methanol.

B) Bromofluorobenzene (BFB):

	a) 25 μg/ml	b)) 250 μg/ml
BFB (25,000 μg/ml)	0.1 ml	0.1 ml
Methanol	99.9 ml	9.9 ml
Total	100 ml	10 ml

- 25 μg /ml solution for direct injection: The BFB is prepared at 25 μg /ml by measuring 0.1 ml of 25,000 μg /ml (Absolute Stock or equivalent) and diluting to 100 ml with methanol.

- 250 μg /ml solution for purging: The BFB is prepared at 250 μg /ml by measuring 0.1 ml of 25,000 μg /ml (Absolute Stock or equivalent) and diluting to 10 ml with methanol.

Table 8. STANDARD PREPARATION (Continued)

C) Secondary dilution standards:

2nd Dilution Standards	Stock Solution	Concentration (μg/ml)	Volume Added (μl)	Final Volume in Methanol (ml)	Final Concentration (μg/ml)
V8260 Mixture	EPA Method 524.2 Volatiles	2,000	2,500	50	100
	Acrolein	Neat (90%)	66.2		1,000
	Acrylonitrile*	Neat	25		500+
	Propionitrile**	Neat	58.9		1,000++
	Di-iso Butylene	Neat	7.1		100
	Cyclohexane	Neat	6.5		100
	Cyclohexanone	Neat	52.9		1,000
V8260 Custom Mixture	Custom Volatiles Mix A	2,000	2,500	50	100
	Custom Volatiles Mix B	2,000 -100,000	2,500		100 - 5,000
	Epichlorohydrin	Neat	21.4		500
	Iso-Amyl alcohol	Neat	125		2,000
	2-Chloroethyl vinyl ether	Neat	20.1		500
	Ethyl tert-butyl ether	Neat	6.8		100
	Tert-Amyl methyl ether	Neat	6.56		100
	Benzyl chloride	Neat	4.6		100
Gas Mixture	VOC Gas Mixture	2,000	1,000	20	100

- 100 μg /ml V8260 mixture: The mixture is prepared at 100 μg /ml by measuring 2 ml of 2,000 μg /ml EPA Method 524.2 Volatiles stock standard, appropriate amount of some neat compounds, and bringing to 50 ml with methanol.
  * Acrylonitrile = 400 μg /ml (Neat) + 100 μg /ml (EPA Method 524.2 Volatiles)
  ** Propionitrile = 900 μg /ml (Neat) + 100 μg /ml (EPA Method 524.2 Volatiles)

- 100 μg /ml V8260 custom mixture: The mixture is prepared at 100 - 5,000 μg /ml by measuring 2.5ml of 2,000 μg /ml Custom Volatiles Mix A, 2.5 ml of 2,000 - 100,000 μg/ml Custom Volatiles Mix B, appropriate amount of some neat compounds, and bringing to 50 ml with methanol.

- 100 μg /ml gas mixture ***: The mixture is prepared at 100 μg /ml by measuring 1 ml of 2,000 μg /ml stock standard and bring to 20 ml with methanol.
  ******* Gas mixture should be prepared weekly.

Table 8. STANDARD PREPARATION (Continued)

D).1 Initial Calibration Standards: using DI water bring to 50 ml final volume: all mixtures used should be **secondary dilution** standards at **100 ppm**.

Standard and Surrogate Concentration	V8260 Mix (100 ppm)	V8260 Custom Mix (100 ppm)	Gas compound Mix (100 ppm)	Surrogate Mix (100ppm)
1 ppb	0.5 µl	0.5 µl	0.5 µl	0.5 µl#
2 ppb *	1.0 µl	1.0 µl	1.0 µl	1.0 µl#
5 ppb	2.5 µl	2.5 µl	2.5 µl	2.5 µl#
10 ppb *	5 µl	5 µl	5 µl	5 µl#
20 ppb	10 µl	10 µl	10 µl	10 µl#
50 ppb	25 µl	25 µl	25 µl	25 µl#
100 ppb	50 µl	50 µl	50 µl	50 µl#
200 ppb	100 µl	100 µl	100 µl	100 µl#
300 ppb *	150 µl	150 µl	150 µl	150 µl#
400 ppb *	200 µl	200 µl	200 µl	200 µl#

* depending upon the instrument.
\# See Section 10.2.2.1 for correction factor.

- When calibrating for Method 5035 low-level soil samples, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of each standard into vial. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds.

D).2 Initial Calibration Standards for 1,4-Dioxane using SIMS

Standard and Surrogate Concentration (ppb)	1,4-Dioxane Solution (100ppm)	Surrogate Mix (100ppm)	DI Water – Final Volume (ml)
2	2 µl	1 µl	100
5	5 µl	2 µl	100
25	25 µl	5 µl	100
50	25 µl	2.5 µl	50
100	50 µl	5 µl	50
200	100 µl	10 µl	50
400	200 µl	20 µl	50

Table 8. STANDARD PREPARATION (Continued)

E) Continuing Calibration Standard: using DI water bring to 50 ml final volume: All mixtures used are secondary dilution standards at 100 ppm.

Concentration	V8260 Mix (100 ppm)	V8260 Custom Mix (100 ppm)	Gas compound Mix (100 ppm)
50 ppb	25 µl	25 µl	25 µl

- When calibrating for Method 5035 low-level soil samples, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of the continuing calibration standard into vial. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds.

F) Blank Spike (BS): using DI water bring to 50 ml final volume: All mixtures used are 100 ppm secondary dilution standards.

Concentration	V8260 Mix (100 ppm)	V8260 Custom Mix (100 ppm)	Gas compound Mix (100 ppm)
50 ppb	25 ul	25 ul	25 ul

For lower detection level required (test code: V8260LL)

Concentration	V8260 Mix (100 ppm)	V8260 Custom Mix (100 ppm)	Gas compound Mix (100 ppm)
20 ppb	10 ul	10 ul	10 ul

- When calibrating for Method 5035 low-level soil samples, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of the blank spike into vial. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds.

Table 9. GUIDELINE FOR DILUTION PREPARATION

Water Sample

Dilution	Sample amount taken	Final volume A (volumetric)	Take from final volume A	Final volume B (volumetric)
1:2	25 ml	50 ml		
1:5	10 ml	50 ml		
1:10	5 ml	50 ml		
1:20	2.5 ml	50 ml		
1: 25	2 ml	50 ml		
1:50	1 ml	50 ml		
1:100	0.5 ml	50 ml		
1:200	250 µl	50 ml		
1:250	200 µl	50 ml		
1:500	100 µl	50 ml		
1:1000	50 µl	50 ml		
1:2000	25 µl	50 ml		
1:2500	20 µl	50 ml		
1:5000	10 µl	50 ml		
1:10000	0.5 ml	50 ml	0.5 ml	50 ml
1:20000	0.5 ml	50 ml	250 µl	50 ml
1:25000	0.5 ml	50 ml	200 µl	50 ml
1:50000	0.5 ml	50 ml	100 µl	50 ml
1:100000	0.5 ml	50 ml	50 µl	50 ml

Soil-Low level (Non-Encore sample)

Dilution	Sample amount taken	Final volume
1:2	2.5 gram	5 ml
1:5	1 gram	5 ml
1:10	0.5 gram	5 ml

Soil-medium level

Additional Dilution	Sample in Methanol amount taken	Final volume (volumetric)
1:1	1 ml	50 ml
1:2	0.5 ml	50 ml
1:5	200 µl	50 ml
1:10	100 µl	50 ml
1:20	50 µl	50 ml
1: 25	40 µl	50 ml
1:50	20 µl	50 ml
1:100	10 µl	50 ml
1:200	5 µl	50 ml
1:250	4 µl	50 ml
1:500	2 µl	50 ml

Table 10. REPORTING LIMITS

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Chlorodifluoromethane	5	5	Chloroform	5	5
Dichlorodifluoromethane	5	5	Freon 113	5	5
Chloromethane	5	5	Methacrylonitrile	10	10
Vinyl chloride	5	5	Butyl Acetate	5	5
Bromomethane	5	5	1,1,1-Trichloroethane	5	5
Chloroethane	5	5	Heptane	5	5
Trichlorofluoromethane	5	5	n-Propyl acetate	5	5
Ethyl ether	5	5	2-Nitropropane	10	10
Acrolein	50	50	Tetrahydrofuran	10	10
1,1-Dichloroethene	2	2	2-Chloroethyl Vinyl Ether	20	20
Tertiary butyl alcohol	50	50	n-Butyl alcohol	250	250
Acetone	5	5	Cyclohexane	5	5
Methyl acetate	5	5	Carbon Tetrachloride	1	1
Allyl chloride	5	5	1,1-Dichloropropene	5	5
Acetonitrile	100	100	Isopropyl Acetate	5	5
Iodomethane	25	25	Benzene	1	1
Iso-butyl alcohol	50	50	1,2-Dichloroethane	2	2
Carbon disulfide	5	5	Trichloroethene	1	1
Methylene chloride	2	2	Methyl methacrylate	10	10
Methyl tert butyl ether	1	1	1,2 Dichloropropane	1	1
Trans-1,2-Dichloroethene	5	5	Di-isobutylene	5	5
Di-isopropyl ether	5	5	Dibromomethane	5	5
2-Butanone	5	5	1,4 Dioxane	125	125
1,1-Dichloroethane	2	2	Bromodichloromethane	1	1
Hexane	5	5	cis-1,3-Dichloropropene	1	1
Chloroprene	5	5	4-Methyl-2-pentanone	5	5
Acrylonitrile	5	5	Toluene	1	1
Vinyl acetate	10	10	trans-1,3-Dichloropropene	1	1
Ethyl acetate	5	5	Ethyl methacrylate	10	10
2,2-Dichloropropane	5	5	1,1,2-Trichloroethane	3	3
Cis-1,2-Dichloroethene	5	5	2-Hexanone	5	5
Bromochloromethane	5	5	Cyclohexanone	5	5

Table 10. REPORTING LIMITS (Continued)

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Tetrachloroethene	1	1	4-Chlorotoluene	5	5
1,3-Dichloropropane	5	5	1,3,5-Trimethylbenzene	5	5
Dibromchloromethane	5	5	tert-Butylbenzene	5	5
1,2-Dibromoethane	2	2	1,2,4 Trimethylbenzene	5	5
Chlorobenzene	2	2	sec-Butylbenzene	5	5
1,1,1,2-Tetrachloroethane	5	5	1,3-Dichlorobenzene	5	5
Ethylbenzene	1	1	p-Isopropyltoluene	5	5
M,p-Xylene	1	1	1,4-Dichlorobenzene	5	5
o-Xylene	1	1	1,2-Dichlorobenzene	5	5
Styrene	5	5	n-Butylbenzene	5	5
Bromoform	4	4	1,2-Dibromo-3-choropropane	10	10
Isopropylbenzene	2	2	1,2,4-Trichlorobenzene	5	5
Bromobenzene	5	5	Hexachlorobutadiene	5	5
1,1,2,2-Tetrachloroethane	2	2	Naphthalene	5	5
Trans-1,4-Dichloro-2-butene	5	5	1,2,3-Trichlorobenzene	5	5
1,2,3-Trichloropropane	5	5	Epichlorohydrin	100	100
n-Proplybenzene	5	5	3-Methyl-1-butanol	5	5
2-Chlorotoluene	5	5	Hexachloroethane	5	5
Ethanol	50	--	Methyl Acrylate	5	--
Benzyl Chloride	1	--	Methylcyclohexane	5	5
2,2,4 Trimethylpentane	5	5	1,1,1 trifluoroethane	5	10
1-chloro-1,1-difluoroethane	5	10	1,1-dichloro-1-fluoroethane	5	10

Table 11. COMPOUNDS THAT MAY EXHIBIT CARRYOVER

Compound
1,2,4-Trichlorobenzene
Hexachlorobutadiene
Naphthalene
1,2,3-Trichlorobenzene

Lab Manager

QA Manager

Effective Date: 6/11/13

TEST NAME: METHOD 8270D, SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

REFERENCE: SW846 8270D (Revision 4, February 2007)

Revised Sections: ***10.3.2.4.1, 10.3.2.4.2***

SCOPE AND APPLICATION

1.1 The following method describes the analytical procedure that is utilized by Accutest to analyze semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and water samples. Options are incorporated for the analysis of sixteen (16) polyaromatic hydrocarbons (PAH) and other compounds listed in table 8A by selected ion monitoring GC/MS (GC/MS-SIM).

1.2 Table 1 lists the neutral, acidic, and basic organic compounds that can be determined by this method. The applicable concentration range of this method is compound and instrument dependent. Some compounds may require special treatment due to the limitations caused by sample preparation and/or chromatographic problems.

2.0 SUMMARY OF METHOD

2.1 This method is performed in accordance with the following extraction methodologies in SW846: 3510, 3520, 3545, 3550 and 3580.

2.2 The resultant methylene chloride extract is injected into a tuned and calibrated GC/MS system equipped with a fused silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 The peaks detected are qualitated by comparison to characteristic ions and retention times specific to the known target list of compounds.

2.4 Once identified, the compound is quantitated by internal standard techniques with an average response factor generated from the calibration curve.

2.5 Additional unknown peaks with a response greater than 10 % of the closest internal standard may be processed through a library search with comparison to a NIST98 database. An estimated concentration is quantitated by assuming a response factor of 1.

2.6 This method includes analytical options for PAHs and other selected compounds by GC/MS-SIM. The extract is fortified with an additional SIM specific internal standard mix and analyzed using selected ions that are characteristic of the compounds of interest following the analysis of lower concentration calibration standards analyzed under the same MS scan conditions. Qualitative and quantitative identification is conducted using the procedures employed for full scan analysis.

3.0 REPORTING LIMIT & METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at either method detection limit or the lowest concentration standard in the calibration curve, depending on the requirements of different regulatory programs. Detected concentrations below this concentration cannot be reported without qualification. See table 9.

3.1.1 Compounds detected at concentrations between the reporting limit and MDL are quantitated and qualified as "J", estimated value. Program or project specifications may dictate that "J" qualified compounds are not to be reported.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BATCH - a group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

BLANK - an analytical sample designed to assess specific sources of laboratory contamination.

CONTINUING CALIBRATION - a mid-range calibration check standard run every 12 hours to verify the initial calibration of the system.

EXTRACTED ION CURRENT PROFILE (EICP) - a plot of ion abundance versus time (or scan number) for ion(s) of specified mass (Es).

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations which cover the working range of the instrument; used to define the linearity and dynamic range of the response of the mass spectrometer to the target compounds.

INTERNAL STANDARDS - compounds added to every standard, blank, matrix spike, matrix spike duplicate, and sample extract at a known concentration, prior to analysis. Internal standards are used as the basis for quantitation of the target compounds and must be analytes that are not sample components.

MATRIX - the predominant material of which the sample to be analyzed is composed.

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.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards and surrogate standards, is carried throughout the entire preparatory and analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) - The minimum concentration of a substance 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. MDLs must be determined approximately once per year for frequently analyzed parameters.

PERCENT DIFFERENCE (%D) - As used to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PRIMARY QUANTITATION ION - a contract specified ion used to quantitate a target analyte.

REAGENT WATER - water in which no interferant is observed at or above the minimum detection limit of the parameters of interest.

RECONSTRUCTED ION CHROMATOGRAM (RIC) - a mass spectral graphical representation of the separation achieved by a gas chromatograph; a plot of total ion current versus retention time.

RELATIVE PERCENT DIFFERENCE (RPD) - As used to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the relative mass spectral response of an analyte compared to its internal standard. Relative Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RELATIVE RETENTION TIME (RRT) - the ratio of the retention time of a compound to that of a standard (such as an internal standard).

RESOLUTION - also termed separation or percent resolution, the separation between peaks on a chromatogram, calculated by dividing the depth of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by 100.

INITIAL CALIBRATUION VERIFICATION (SECOND SOURCE CALIBRATION STANDARD) - a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run whenever an initial calibration is performed.

SURROGATES - pure analytes added to every blank, sample, matrix spike, matrix spike duplicate, and standard in known amounts before extraction or other processing; used to evaluate analytical efficiency by measuring recovery. Surrogates are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental media.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets is made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, N-nitrosodimethylamine, and 4,4'-DDT. Prepare primary standards of these toxic compounds in a hood. A NIOSH/Mass approved toxic gas respirator must be worn when the analyst handles high concentrations of these toxic compounds.

6.0 INTERFERENCES

6.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

6.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other stages of sample processing. Refer to "The Preparation of Glassware for Extraction of organic contaminants" SOP for practices utilized in the extraction department.

6.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

6.4 To reduce carryover when high-concentration samples are sequentially analyzed, the syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of solvent to check for cross contamination.

7.0 SAMPLE COLLECTION, PRESERVATION, & HOLDING TIMES

7.1 Water samples may be collected in 1-liter glass bottles with Teflon insert in caps. Soil samples may be collected in 250-ml wide-mouth amber glass bottles.

7.1.1 Samples must be taken with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus avoiding possible phthalate contamination.

7.2 Test all aqueous samples for residual chlorine using test paper for free and total chlorine. If the sample tests positive for residual chlorine, add 80 mg of sodium thiosulfate to each liter of sample.

7.3 The samples must be protected from light and refrigerated at $\leq 6°$ C from the time of receipt until extraction and analysis.

7.4 Store the sample extracts at -10 °C in amber vials (protected from light), in sealed vials equipped with unpierced PTFE-lined septa.

7.5 HOLDING TIME

7.5.1 Aqueous samples must be extracted within 7 days of sampling.

7.5.2 Soil, sediments and concentrated waste samples must be extracted within 14 days of sampling.

7.5.3 Extracts must be analyzed within 40 days following extraction.

8.0 APPARATUS & MATERIALS

8.1 GAS CHROMATOGRAPH/MASS SPECTROMETER SYSTEM

8.1.1 Gas Chromatograph. HP-5890, HP-6890, or Agilent 6890-N which includes an analytical system that is complete with a temperature programmable gas chromatograph and all required accessories including syringes, capillary chromatographic columns, and gases.

8.1.1.1 The injection port is designed for split or splitless injection with capillary columns.

8.1.1.2 The capillary column is directly coupled to the source.

8.1.2 Column.

8.1.2.1 30 m x 0.25 mm fused silica (0.25 μm film thickness) DB-5MS or equivalent capillary column. Condition the column as per manufacture's directions.

8.1.3 Mass Spectrometer (HP-5972, HP-5973 or Agilent 5975).

8.1.3.1 Full Scan Mode -Capable of scanning from 35-500 amu every 1 second or less utilizing 70 volt (nominal) electron energy in the electron impact ionization mode.

8.1.3.2 SIM Mode- Capable of selective ion grouping at specified retention times for increased compound sensitivity (table 2a).

8.1.3.3 Capable of producing a mass spectrum which meets all the EPA performance criteria in Table 3 when injecting 50 ng of Decafluorotriphenyl phosphine (DFTPP).

8.2 DATA SYSTEM

8.2.1 Acquisition and Instrument Control: HP Chemstation. A computer system is interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media (disc) of all mass spectra obtained throughout the duration of the chromatographic program.

8.2.2 Data Processing: HP Enviroquant. The software accommodates searching of GC/MS data files for analytes which display specific fragmentation patterns. The software also allows integrating the abundance of an EICP between specified time or scan number limits. The

data system includes the NIST98 spectra library for qualitative searches of non-target compounds present in the chromatogram. It flags all data files that have been edited manually by laboratory personnel.

8.2.3 Offline Magnetic Tape Storage Device (Lagato Networker) - the magnetic tape storage device copies data for long term, offline storage.

8.3 SYRINGE

8.3.1 10 μl graduated, auto sampler (Hamilton or equiv.).

8.3.2 Micro liter syringes, various sizes

9.0 REAGENTS AND STANDARDS

9.1 Solvents - Ultra pure, chromatography grade methylene chloride and acetone.

9.2 Stock Standard Solutions.

9.2.1 Certified, commercially prepared standards, from two separate sources are used.

9.2.1.1 Base Neutrals.

- Base/Neutrals Mix #1 (Absolute: Semivolatile Organics Standard Mix # 1).
- Base/Neutrals Mix #2 (Absolute: Semivolatile Organics Standard Mix # 2).
- PAH Mix (Absolute: Semivolatile Organics Standard Mix # 7).
- PAH Mixture #2 (Ultra).
- PAH Selected Ion Monitoring Mixture
- Benzidines Mix (Absolute: Semivolatile Organics Standard Mix # 6).
- Toxic Substances #2 (Absolute: Semivolatile Organics Standard Mix # 5).
- Pyridines Mixture (Ultra).
- Additonal requested compound(s) mix (Absolute).
- Base Neutral Mixture (2nd Source).

Acids.

- Phenols Mix (Absolute: Semivolatile Organics Standard Mix # 8).
- Toxic Substances #1(Absolute: Semivolatile Organics Standard Mix # 4).
- Acid Mixture (2nd Source).Internal Standard Mixtures.

9.2.2 Internal Standard Mixtures

9.2.2.1 Ultra (or equivalent) at a concentration of 4,000 μg/ml for each of the following compounds.

Full Scan

- 1,4-Dichlorobenzene-d4
- Naphthalene-d8

- Acenaphthene-d10
- Phenanthrene-d10
- Chrysene-d12
- Perylene-d12

SIM

- 1,2-Dichlorobenzene-d4
- 1-Methylnaphthalene-d10
- Fluorene-d10
- Fluoranthene-d10
- Benzo(a)pyrene-d12

9.2.2.2 The internal standards must permit most of the components of interest in a chromatogram to have retention times of 0.8 - 1.20 relative to one of the internal standards.

9.2.2.3 Each 1 ml sample extract, and standard undergoing analysis must be spiked with 10 μl of the internal standard mixtures, resulting in a concentration of 40 μg/ml of each internal standard for full scan analysis and 4 ug/ml for SIM analysis.

9.2.3 Surrogate Standard Mixture.

9.2.3.1 B/N Surrogate Standard Mix: RESTEK (or equivalent) at a concentration of 5,000 μg/ml each surrogate compound.

- Nitrobenzene-d5.
- 2-Fluorobiphenyl.
- p-Terphenyl-d14.

9.2.3.2 Acid Surrogate Standard Mix: RESTEK (or equivalent) at a concentration of 7,500 μg/ml each surrogate compound.

- Phenol-d5.
- 2-Fluorophenol.
- 2,4,6-Tribromophenol.

9.2.4 DFTPP Tune Stock.

9.2.4.1 Protocol (or equivalent) at a concentration of 2,500 μg/ml for the following compounds.

- Decafluorotriphenylphosphine.
- 4,4'-DDT.
- Benzidine.
- Pentachlorophenol.

9.2.5 Store at -10 ^{o}C or less when not in use or according to the manufacturer's documented holding time and storage temperature recommendations. Stock standard solutions must be replaced after 1 year or sooner if manufacture's expiration date comes first or comparison with quality control check samples indicates degradation.

9.3 Surrogate Spiking Solutions.

9.3.1 Two surrogate spiking solutions, base/neutral surrogate solution and acid surrogate solution, at a concentration of 100 μg/ml are prepared in Extraction. Spike each sample, and blank with 0.5 ml of each solution, prior to extraction, for a final concentration of 50 μg/l of each surrogate compound in the extract.

9.3.2 A calibration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed with each calibration solution to define a range similar to the target compounds.

9.3.3 Store at -10 °C or less or according to the manufacturer's documented storage temperature recommendations. Prepare fresh surrogate spiking solutions every year, or sooner, if the manufacturer's expiration dates come first or if the solution has degraded or evaporated.

9.4 Intermediate Calibration Standard Solution.

9.4.1 The calibration stock solution is prepared by adding an appropriate amount of each stock and surrogate compounds into a 10 ml volumetric flask. Dilute the solution to the volume with methylene chloride and mix thoroughly. Refer to Table 7A for details.

9.5 Calibration Standards.

9.5.1 Initial Calibration Standards.

9.5.1.1 Calibration standards containing the surrogate compounds must be made by quantitative dilutions of the above intermediate solution. The calibration standards are prepared at a minimum of five concentrations to cover the range of 1 - 100 μg/ml for full scan and 0.02 – 5ug/ml for SIM, depending upon project specific requirements. Suggested levels and preparations are shown in Table 7A and 7B.

9.5.2 Continuing Calibration Verification.

9.5.2.1 The concentration of the mid range standard used for continuing calibration verification is alternated between 25 and 50 μg/ml for full scan and 2.5 and 1.0 for SIM.

9.5.3 Store the calibration standards in a refrigerator at $\leq$ 6 °C and prepare every 6 months or before the manufacturer's expiration date, whichever is sooner. Standards must be replaced immediately if the analysis of check standards indicates degradation.

9.6 Initial Calibration verification (ICV) -Second source calibration check standard.

9.6.1 The ICV standard is prepared per Table 7E, using the intermediate solutions prepared in Extraction.

9.6.2 The ICV is analyzed after each initial calibration.

9.7 Daily GC/MS Performance Checks.

9.7.1 The solution is prepared at 50 μg/ml by making a 1:50 dilution of DFTPP stock solution (Section 9.2.4) in methylene chloride.

9.8 Matrix Spike Solutions.

9.8.1 The matrix spike solutions for both Base/Neutral and Acid are prepared in Acetone at a concentration of 100 μg/ml for each compound. Prepare the matrix spike, matrix spike duplicate and blank spike by spiking the selected sample and the blank with 0.5 ml of these solutions for a final concentration of 50 μg/l of each compound.

9.9 All organic new standard solutions are analyzed prior to use to verify the accuracy of the prepared concentration.

9.9.1 The prepared standard solution is analyzed using the determinative (instrumental) technique for the method.

9.9.2 The solution is analyzed following the completion of instrument calibration or a calibration check.

9.9.3 The concentration of the standard solution is determined using the software routines used in determining the acceptability of calibration verification.

9.9.4 The data is evaluated and the percent difference determined. The standard solution is approved for use if all designated compounds are present in the solution and the percent difference is less than the established criteria (±20%).

10.0 CALIBRATION

10.1 Initial Calibration.

10.1.1 The calibration range covered for routine analysis under RCRA employs standards of 1, 2, 5, 10, 25, 50, 80, 100 μg/ml for full scan and 0.02, 0.05, 0.10, 0.20, 1.0, 2.5, 5.0 ug/ml for SIM. A minimum of five standards must be run sequentially. The reporting limit is established by the concentration of the lowest standard analyzed during the initial calibration. Lower concentration standard may be needed to meet the reporting limit requirements of state specific regulatory program. The linear range covered by this calibration is the highest concentration standard.

10.1.2 A calibration range must be constructed for each surrogate compound. Accordingly, add appropriate amounts of surrogate spiking solutions to the calibration solution to define a range similar to the target compounds.

10.1.3 Aliquot 1 ml of each calibration standard into a 2 ml crimp top vial.

10.1.4 Prior to analysis, add 10 μl of the applicable (Full scan and/or SIM) internal standard solution (Section 9.2.2) to each standard. This results in a concentration of 40 μg/ml (Full scan) and 4ug/ml (SIM) for each internal standard.

10.1.5 Analyze the standard solutions using the conditions established in Section 11.0. Each analyte is quantitatively determined by internal standard technique using the closest eluting internal standard and the corresponding area of the major ion. See Table 6.

10.1.6 The Response Factor (RF) is defined in Section 13.1. Calculate the mean RF for each target analyte, using minimum of five RF values calculated from the initial calibration curve.

10.1.7 For the initial calibration to be valid, the following criteria must be met.

10.1.7.1 The percent relative standard deviation (% RSD) (see Section 13.2) of all target analytes must be less than or equal to 20%.

10.1.7.2 If the %RSD of any individual compound is $\geq$20%, employ an alternative calibration linearity model. Specifically, linear regression using a least squares approach may be employed.

10.1.7.2.1 If a linear regression is employed, select the linear regression calibration option of the mass spectrometer data system. Do not force the regression line through the origin and do not employ 0,0 as a sixth calibration standard.

10.1.7.2.2 The correlation coefficient (r value) must be $\geq$0.99 for each compound to be acceptable.

10.1.7.2.2.1 When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point must be performed by re-fitting the response from the low concentration calibration standard back into the curve.

10.1.7.2.2.2 The recalculated concentration of the low calibration point must be within $\pm$ 30% of the standard's true concentration.

10.1.7.2.3 If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient for the linear calibration option, then the chromatographic system is considered too reactive for the analysis to begin. Perform corrective action and recalibrate if the calibration criteria cannot be achieved.

10.1.7.3 It is recommended that the minimum response factor for the most common target analytes in the following table must be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected.

Minimum Response Factor Table

Semivolatile Compounds	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800

Bis (2-chloroethyl) ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxyl)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800
2-Nitroaniline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrobenzene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700

Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

10.1.7.3.1 Due to the large number of compounds, some compounds will fail to meet the minimum response factor criteria. They may be used as qualified data or estimated values for screening purposes. Non-detects may be reported if adequate sensitivity has been demonstrated at the applicable lower quantitation limit.

10.1.7.4 The initial calibration criteria for this method applies to all additional compounds of concern specified by the client.

10.1.7.5 The relative retention times of each target analyte in each calibration standard must agree within 0.06 relative retention time units.

10.1.7.6 Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is more than 50% of the average of the two peak heights. Otherwise structural isomers are identified as isomeric pairs. The resolution must be verified on the mid - point concentration of the initial calibration (e.g., benzo(b)flouranthene and benzo(k)fluoranthene). Print the check and keep it on file.

10.2 Initial Calibration Verification (ICV) - Source Calibration Check Standard.

10.2.1 The calibration is verified with a calibration check standard at 50 μg/ml (Full scan) or 1ug/ml (SIM) from an external source (Section 9.6). It must be analyzed immediately following the initial calibration.

10.2.2 The percent difference (% D) (Section 13.3) for this standard must meet the criteria of 30% for all the target compounds.

10.2.2.1 If % D is greater than 30%, reanalyze the second source check. If the criteria cannot be met upon re-injection, re-prepare the second source solution using a fresh ampoule and repeat the process.

10.2.2.2 If the %D criteria cannot be achieved after re-preparation of the second source, prepare a third source and repeat the process. Make fresh calibration standards using one of the two standard sources that match each other.

10.3 Continuing Calibration Verification Standard - CCV

10.3.1 A calibration verification standard at close mid-level concentration of the initial calibration range at alternating 25 and 50ug/ml for full scan and 2.5ug/ml and 1ug/ml for SIM must be acquired every 12 hrs.

10.3.1.1 The calibration verification standard selected must be near concentration of the midpoint calibration standard or near the action level for the project specified.

10.3.2 For the continuing calibration to be valid, all of the following specified criteria must be met.

10.3.2.1 Each of the most common target analytes in the calibration verification standard must meet the minimum response factors as noted in the Minimum Response Factor Table in section 10.1.7.3.

10.3.2.2 All target compounds of interest must be evaluated using a 20% D criteria. If the percent difference or percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid.

10.3.2.3 Due to the large numbers of compounds that may be analyzed by this method, it is expected that some compounds will fail to meet the 20% D criterion. If the criterion is not met (i.e., greater than 20% difference or drift) for more than 20% of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples.

10.3.2.4 In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to the compound at the applicable quantitation limits. For situation when the failed compound is present, the concentrations must be reported as estimated.

10.3.2.4.1 Compounds with response factors that exceed the 20% D in the CCV compared to the initial calibration with high bias may only be reported when the target analyte is non-detect.

10.3.2.4.2 Compounds that do not meet the 20% D in the CCV compared to the initial calibration due to low response factors can only be reported if the low sensitivity of the instrument is still achieved. This sensitivity must be verified by running a low level standard check at 2-4 times the MDL. If a positive result for the compound is found then adequate sensitivity has been demonstrated and the run can proceed. Non-detect results for samples may be reported, positive results are re-analyzed. This low level sensitivity check does not apply to the PAH compounds.

10.3.2.5 The resolution check for structural isomers must be verified for each CCV standard Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise structural isomers are identified as isomeric pairs. Print the check and keep it on file.

10.3.3 If the first continuing calibration verification does not meet criteria, a second standard may be injected after notifying the team leader/manager and checking the system for defects.

10.3.3.1 A continuing calibration check is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed or refer to section 10.3.2.4. In situations where the first check fails to meet the criteria, the instrument logbook must have clear documented notations as to what the problem was and what corrective action was implemented to enable the second check to pass.

10.3.4 If the verification criteria cannot be achieved, a new initial calibration must be performed or refer to section 10.3.2.4.

10.3.5 If any of the internal standard areas change by a factor of two (- 50% to + 100%) or the retention time changes by more than 30 seconds from the midpoint standard of the last initial calibration, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

10.3.5.1 Reanalyze the continuing calibration standard. New initial calibration is required if reanalyzed standard continues to fail the internal standard requirements.

10.3.5.2 All samples analyzed while the system was out of control must be reanalyzed following corrective action.

11.0 PROCEDURE

11.1 Instrument Conditions.

11.1.1 Recommended instrument conditions are listed in Table 2 and 2a (SIM only). Modifications of parameters specified with an asterisk are allowed as long as criteria of calibration are met. Any modification must be approved by team leader/manger. DFTPP, Standards, QC and samples must all be run under the exact same operating conditions, including EM voltage.

11.2 Daily GC/MS Performance Checks.

11.2.1 Mass Spectrometer Tuning. Every 12-hour, inject 1 μl of 50 ng/μl DFTPP solution directly on to the column.

11.2.2 The GC/MS system must be checked to verify that acceptable performance criteria are achieved (see Table 3).

11.2.3 This performance test must be passed before any sample extracts, blanks or standards are analyzed. Evaluate the tune spectrum using three mass scans from the chromatographic peak and a subtraction of instrument background.

11.2.3.1 Select the scans at the peak apex and one to each side of the apex.

11.2.3.2 Calculate an average of the mass abundances from the three scans.

11.2.3.3 Background subtraction is required. Select a single scan in the chromatogram that is absent of any interfering compound peak and acquired within no more than 20 scans to the elution of DFTPP. The background subtraction must be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the tuning compound peak.

11.2.4 If all the criteria are not achieved, the analyst must retune the mass spectrometer with team leader/manager and repeat the test until all criteria are met.

11.2.4.1 Alternatively, an additional scan on each side of the peak apex may be selected and included in the averaging of the mass scans. This will provide a mass spectrum of five averaged scans centered on the peak apex. NOTE: The selection of additional mass scans for tuning may only be performed with supervisory approval on a case by case basis.

11.2.5 The injection time of the acceptable tune analysis is considered the start of the 12-hour clock.

11.2.6 In order to assess GC column performance and injection port inertness, the DFTPP tune standard also contains appropriate amount of 4,4'-DDT, benzidine and pentachlorophenol.

11.2.7 All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

11.2.6.1 Injection Port Inertness Check.

11.2.6.1.1 The injection port inertness of the GC portion of the GC/MS is evaluated by the percent breakdown of 4,4'-DDT. DDT is easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated by high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a GC/MS tune standard containing 4,4'-DDT every 12 hour, regardless of whether DDT is a target analyte. The degradation of DDT to DDE and DDD must not exceed 20%, in order to proceed with calibration procedures. Refer to Section 13.7 for calculation. Print the check and keep it on file.

11.2.6.2 Column Performance Check.

11.2.6.2.1 The condition of the GC column is evaluated by the tailing of benzidine and pentachlorophenol every 12 hour. Benzidine and pentachlorophenol must be present at their normal responses, with no visible peak tailing, as demonstrated by the peak tailing factors. The tailing factor criteria for benzidine (base-neutral fraction) must be ≤ 2 and for pentachlorophenol (acid fraction) must be ≤ 2. Print the check daily and keep on file:

11.2.6.3 If degradation is excessive and/or poor chromatography is observed, the injector port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column.

11.3 Initial Calibration

11.3.1 Refer to Section 10.1.

11.4 Initial calibration Verification (ICV) - Second Source Calibration Check

11.4.1 This standard must at least be analyzed when initial calibration provided. Refer to Section 10.2.

11.5 Continuing Calibration Checks

11.5.1 Refer to Section 10.3.

11.6 Sample Analysis.

11.6.1 Allow the sample extract to warm to room temperature. Spike 10 μl of the appropriate internal standard mix (4,000 μg/ml for full scan and 400ug/ml for SIM) into 1 ml sample extract, just prior to analysis. This is equivalent to a concentration of 40 μg/ml (full scan) and 4ug/ml (SIM) of each internal standard.

11.6.2 Inject 1 μl aliquot of the sample extract into the GC/MS system. A splitless injection technology is used.

11.6.3 If the response for any ion of interest exceeds the working range of the GC/MS system, dilute a stored extract if available and reanalyze.

11.6.4 When the extracts are not being used for the analyses, store them at -10°C, protected from light, in sealed vials equipped with unpierced PTFE-lined septa.

11.7 Sample Dilution

11.7.1 Establish dilution of sample in order to fall within calibration range or to minimize the matrix interference.

- Utilize screen data (specific project only).
- Utilize acquired sample data.
- Utilize the history program or approval from client/project.
- Sample characteristics (appearance, odor).

11.7.2 If no lower dilution has been reported, the dilution factor chosen must keep the response of the largest peak for a target analyte in the upper half of the initial calibration range of the instrument.

11.7.3 Preparing Dilutions.

11.7.3.1 Prepare sample dilutions quantitatively. Dilute the sample extract with methylene chloride using logical volume to volume ratios, i.e., 1:5, 1:10, 1:50, etc. Large dilutions may require serial dilutions or the use of a Class A 10 ml volumetric flask.

11.7.3.2 Syringe dilutions. – Calibrated syringes are used to prepare dilutions. Add the appropriate amount of methylene chloride to a clean autosampler vial. Add the proper amount of sample using a calibrated syringe of the appropriate volume for the dilution. Add sufficient internal standard to maintain a concentration of 40ug/ml. Cap the vial and gently shake to disperse the sample through the solvent.

11.7.3.3 Volumetric Flask Dilutions – Large dilutions may require the use of a 10 ml Class A Volumetric flask.

11.8 Establishing Search Criteria for target compounds. Search criteria for each compound listed in the method must be entered into the method quantitation/identification file in the Enviroquant software package. This activity must be performed before attempting qualitative and quantitative analysis on any acquired data file. The search criteria are based on compound retention time and the characteristic ions from the reference mass spectrum. Characteristic ions are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. The number of secondary ions displayed for each compound search varies between compounds.

11.8.1 Select the primary ion for the target compound from the characteristic ions in Table 6. If multiple characteristic ions are listed, the first ion is the major (primary) ion. Enter this ion as the search ion. Enter the relative abundance of this ion (100% for base peak ions) and set the relative abundance window at $\pm$ 30%.

11.8.1.2 Alternate primary ions may be selected when interferences exist from ion abundance contribution from close eluting compounds.

11.8.2 Enter the remaining ions as secondary ions. Secondary ions are not be used to locate peaks within the search window, but are be used to support the qualitative identification of selected peaks. The number of secondary ions displayed for each compound search varies between compounds depending on the number of ions in the spectra >30% relative abundance.

11.8.3 Set the relative abundance windows for the secondary ions at $\pm$ 30%.

11.8.4 Establish the relative retention window for each compound. Because it is a relative retention window the same width window applies to all compounds on the quantitation list. The window must be established at a minimum of 0.06 relative retention time units.

11.9 Data Interpretation.

11.9.1 Executing Qualitative Searches. The target compounds shall be identified by analyst with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound.

11.9.1.1 The search procedure will identify peaks within the search window using the primary ion only. Secondary ions and the relative retention are used to determine "the best match". If the best match contains secondary ions outside the relative abundance window, they will be flagged with a # sign.

11.9.2 Qualitative Identification. The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. Compounds are identified when the following criteria are met.

11.9.2.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other.

11.9.2.2 The sample component must elute at the same relative retention time (RRT) as the daily standard. Criterion is the RRT of sample component must be within ± 0.06 RRT units of the standard.

11.9.2.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%).

11.9.2.3.1 If a chromatographic peak exhibits a spectrum containing an ion with relative abundance outside the relative abundance window is selected for reporting, the analyst must annotate the spectra that the compound qualified based on his/her best judgement. This circumstance will most often occur from coeluting compounds with similar ions or background matrix interferences.

11.9.3 Quantitative Analysis.

11.9.3.1 Once a target compound has been identified, its concentration (Section 13.4) will be based on the integrated area of the quantitation ion, normally the base peak (Table 6). The compound is quantitated by internal standard technique with an average response factor generated from the initial calibration curve.

11.9.3.2 If the sample produces interference for the primary ion, use a secondary ion to quantitate. This may be characterized by an excessive background signal of the same ion, which distorts the peak shape beyond a definitive integration. Also interference could severely inhibit the response of the internal standard ion. The secondary ion must be used to generate a new response factor.

11.10 Library Search for Tentatively Identified Compounds.

11.10.1 If a library search is requested, the analyst must perform a forward library search of the NIST98 mass spectral library to tentatively identify 10 to 15 non-reported compounds (15 for base, 10 for acid, 25 for base/acid fraction).

11.10.2 Guidelines for making tentative identification are listed below.

11.10.2.1 These compounds must have a response greater than 10% of the nearest internal standard. The response is obtained from the integration for peak area of the Total Ion Chromatogram (TIC).

11.10.2.2 The search is to include a spectral printout of the 3 best library matches for a particular substance. The results are to be interpreted by analyst.

11.10.2.3 Molecular ions present in the reference spectrum must be present in the sample spectrum.

11.10.2.4 Relative intensities of major ions in the reference spectrum (ions > 10 % of the most abundant ion) must be present in the sample spectrum.

11.10.2.5 The relative intensities of the major ions must agree within ± 20 %. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must between 30 and 70%).

11.10.2.6 Ions present in the sample spectrum but not in the reference spectrum must be reviewed for possible background contamination or presence of coeluting compounds.

11.10.2.7 Ions present in the reference spectrum but not in the sample spectrum must be verified by performing further manual background subtraction to eliminate the interference created by coeluting peaks and/or matrix interference.

11.10.3 Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 and is to be tabulated on the library search summary data sheet.

11.10.4 The resulting concentration must be reported indicating: (1) that the value is estimate, and (2) which internal standard was used to determine concentration. Quantitation is performed on the nearest internal standard.

11.10.5 Peaks that are suspected to be aldol-condensation reaction products (i.e., 4-methyl-4-hydroxy-2-pentanone and 4-methyl-3-pentene-2-one) shall be searched and reported but not counted towards the total TIC count.

11.10.6 Any peak naming as “System artifact” (from the column bleedings) or “Internal Standard” (added by lab for other test, like SIM analysis) shall be searched and reported but not counted towards the total TIC count.

11.11 Selected Ion Monitoring (SIM) Option

NOTE: The use of SIM is not allowed by the SCDHEC for samples from South Carolina.

11.11.1 Instrument Set-Up: Modify the method for SIM analysis and define ion groups with retention times, ions and dwell times to include base peak ion for the target compounds of interest, surrogates, and internal standards (Table 2a, Table 8a) Select a mass dwell time of 50 milliseconds for all compounds.

11.11.2 Calibration: Calibrate the mass spectrometer in the selected ion monitoring mode using 7 calibration standards of 0.02, 0.05, 0.10, 0.20, 1.0, 2.5, 5.0 ug/ml. Spike each standard with the SIM specific internal standard solution at 4ug/ml. Calculate individual response factors and response factor RSDs using the procedures and criteria described in Section 10.1.6, 10.1.7.3 and 10.1.7.4.

11.11.3 Initial Calibration Verification. Verify the initial calibration after its completion using a 1.0 ug/ml calibration standard purchased or prepared from a second standards reference materials source. The initial calibration verification must meet the criteria of Section 10.2.2.

11.11.4 Continuing Calibration Verification. Verify the initial calibration every 12 hours using a 1.0 or 2.5 ug/ml calibration. The continuing calibration verification must meet the criteria of Section 10.3.

11.11.5 Sample Extract Analysis: Each extract has been previously spike with the SIM internal standard at 4 ug/ml. Analyze the sample extracts for the compounds of interest using the SIM scan parameters employed for the calibration standards.

11.11.6 Surrogate Standard Calculation.. Report surrogate spike accuracy for the surrogates spiked for the full scan GC/MS analysis at 50 ug/ml.

12.0 QUALITY CONTROL

12.1 QC Requirements Summary.

Daily GC/MS Performance Checks	Beginning of the analytical shift and every 12 hours
Initial Calibration	Whenever needed.
Second Source Calibration Check	Following initial calibration
Continuing Calibration Verification	Every 12 hours.
Method Blank	One per extraction batch*.
Blank Spike	One per extraction batch*.
Matrix Spike	One per extraction batch*.
Matrix Spike Duplicate	One per extraction batch*.
Surrogate	Every sample extract and standard.
Internal Standard	Every sample extract and standard.

*The maximum number of samples per batch is twenty or per project specification.

12.2 Daily GC/MS Performance Checks.

12.2.1 Refer to Section 11.2.

12.3 Initial Calibration.

12.3.1 Refer to Section 10.1.

12.4 Initial Calibration Verification (ICV) - Source Calibration Check.

12.4.1 Refer to Section 10.2.

12.5 Continuing Calibration Verification.

12.5.1 Refer to section 10.3.

12.6 Method blank.

12.6.1 The method blank is either reagent water or anhydrous sodium sulfate (depending on the sample matrix) which must be extracted with each set of 20 or less samples. For a running batch, a new method blank is required for each different extraction day. The method blank is then extracted and carried through all stages of the sample preparation and measurement.

12.6.2 If the method blank contains a target analyte above its MDL , the entire batch must be re-extracted and re-analyzed.

12.6.3 Surrogate compounds are added to the method blank prior to extraction. If the surrogate accuracy in the method blank does not meet in house criteria , it must be reanalyzed. If the reanalysis confirms the original data, the entire batch must be re-extracted.

12.7 Blank Spike

12.7.1 A blank spike must be extracted with each set of 20 or less samples. For a running batch, a new blank spike is required for each different extraction day. The blank spike consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same volume. It is spiked with the same analytes at the same concentrations as the matrix spike/matrix spike duplicate.

12.7.2 The blank spike recoveries must be assessed using laboratory in house limits.

12.7.3 If a blank spike is out of control, the following corrective actions must be taken and all the associated samples must be re-extracted and reanalyzed. The exception is if the blank spike recovery is high and no hits reported in associated samples and QC batch. In that case, the sample results can be reported with footnote (remark) and no further action is required.

12.7.3.1 Check to be sure that there are no errors in the calculations, or spike solutions. If errors are found, recalculate the data accordingly.

12.7.3.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample batch.

12.7.3.3 If no problem is found, re-extract and reanalyze the sample batch.

12.8 Matrix Spike(MS) / Matrix Spike Duplicate(MSD)

12.8.1 One sample is randomly selected from each extraction batch and spiked in duplicate to assess the performance of the method as applied to a particular matrix and to provide

information on the homogeneity of the matrix. Both the MS and MSD are carried through the complete sample preparation, and determinative procedures.

12.8.2 Matrix spikes are prepared by spiking an actual sample at a concentration of 50 μg/l for both base/neutral and acids.

12.8.3 Assess the matrix spike recoveries (% R) (Section 13.5) and relative percent difference (RPD) (Section 13.6) against the in house control limits.

12.8.4 If the matrix spike accuracy of any individual compound is out of control, the accuracy for the compound in the blank spike must be within control. In such case, matrix interference is assumed and the data is reported with footnote (e.g., spike recovery indicates possible matrix interference). No further corrective action is required.

12.9 Surrogates

12.9.1 All standards, blanks, sample extracts, and matrix spikes contain surrogate compounds which are used to monitor the performance of the extraction and analytical system.

12.9.2 The recoveries (Section 13.5) of the surrogates must be evaluated to determine whether or not they fall within surrogate control limits developed by the laboratory annually.

12.9.3 If the recovery of any surrogate compound does not meet the control limits, the calculation must be checked for possible error. The surrogate solution must be checked for degradation. Contamination and instrument performance must also be reviewed.

12.9.3.1 Reanalyze the extract if no calculation errors are detected. If the surrogate recoveries for the reanalyzed extract are in control, report the data from the reanalysis only.

12.9.3.2 If the data from the reanalysis is also out of control, re-extract and reanalyze the sample.

12.9.3.3 If, upon reanalysis, the surrogate recoveries are acceptable, report the reanalysis data. If the holding time has expired prior to the reanalysis, report both the original and reanalysis results and note the holding time problem.

12.9.3.4 If the recovery is again not within limits, the problem is considered to be matrix interference. Submit both data sets with the original analysis being reported.

12.9.4 If the sample exhibits matrix interference, defined as excessive signal where target or non-target responses are greater than the response of the internal standards. In this case, reanalysis may not be required following team leader/manager approval; the surrogates will be qualified as outside the limits due to matrix interference. Alternatively, sample may be reanalyzed on dilution, if the reanalysis is again not within the limit, the sample must be reported with a footnote indicating that there were possible matrix interference.

12.10 Internal Standards.

12.10.1 Retention time for all internal standards must be within ± 30 seconds of the corresponding internal standard in the latest continuing calibration or 50 μg/ml standard of initial calibration.

12.10.2 The area (Extracted Ion Current Profile) of the internal standard in all analyses must be within 50 to 200 % of the corresponding area of the latest calibration standard (12 hr. time period).

12.10.3 If the area of internal standard does not meet control limits, the calculations must be checked. If a problem is not discovered, the sample must be reanalyzed.

12.10.4 If the areas are acceptable upon reanalysis, the reanalysis data is reported.

12.10.5 If the areas are unacceptable upon reanalysis, then both sets of data are submitted with the original analysis reported.

12.11 Refer to Project Specific Bench Notes(MS8270) for additional program or client specific QC requirements

13.0 CALCULATION

13.1 Response Factor (RF).

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_s = Concentration of the compound being measured (μg/ml).
C_{is} = Concentration of the specific internal standard (μg/ml).

13.2 Percent Relative Standard Deviation (%RSD).

$$\%RSD = \frac{SD}{RF_{av}} \times 100$$

where:

SD = Standard Deviation.
RF_{av} = Average response factor from initial calibration.

13.3 Percent Difference (%D).

$$\%\ D = \frac{|\ RF_{av} - RF_{cv}\ |}{RF_{av}} \times 100$$

where: RF_{cv} = Response factor from Calibration Verification Standard.

13.4 Concentration (Conc.).

13.4.1 <u>for water:</u>

$$\text{Conc. } (\mu g/l) = \frac{A_s \times C_{is} \times V_f \times D \times 1000}{A_{is} \times RF_{av} \times V_i}$$

13.4.2 <u>for soil/sediment</u> (on a dry weight basis):

$$\text{Conc. } (\mu g/kg) = \frac{A_s \times C_{is} \times V_f \times D \times 1000}{A_{is} \times RF_{av} \times W_s \times S}$$

where:

V_f = Final Volume of total extract (ml).
D = Secondary dilution factor.
V_i = Initial volume of water extracted (ml).
W_s = Weight of sample extracted (g).
S = (100 - % moisture in sample) / 100.

13.5 Percent Recovery (%R).

$$\%\ R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

13.6 Relative Percent Difference (RPD).

$$RPD = \frac{|MSC - MSDC|}{(1/2)(MSC+MSDC)} \times 100$$

where:

MSC = Matrix Spike Concentration.
MSDC = Matrix Spike Duplicate Concentration.

13.7 Percent Breakdown.

$$\%\ \text{Breakdown for DDT} = \frac{\text{Total DDT degradation peak area}}{\text{Total DDT peak area}} \times 100$$

where:

Total DDT degradation peak area = DDE + DDD
Total DDT peak area = DDT + DDE + DDD.

13.8 Linear regression by the internal standard technique.

$$C_s = \left(\frac{\frac{A_s}{A_{is}} - b}{a} \right) \times C_{is}$$

Where:
Cs = concentration of target analyte
As = Area of target analyte
Cis = concentration of the internal standard
b = Intercept
a = slope of the line

$$a = \frac{N \Sigma xy - \Sigma x \Sigma y}{N \Sigma x^2 - (\Sigma x)^2}$$

$$b = \frac{\Sigma y - a \Sigma x}{N}$$

N = number of points
x = amount of analyte
y = response of instrument

13.9 Correlation Coefficient

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where r = correlation coefficient
x = amount of analyte
y = response of instrument

$\bar{x}$ = average of x values

$\bar{y}$ = average of y values

14.0 DOCUMENTATION

14.1 The Analytical Logbook is a record of the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

14.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in this log.

14.1.2 Overwriting of data files is never allowed.

14.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed, the page must be signed and dated by the respective person.

14.2.1 The Accutest Lot Number must be cross-referenced on the standard vial.

14.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument has a separate log.

14.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

14.5 Unused blocks of any form must be X'ed and Z'ed by the analyst before submitting the data for review.

14.6 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information must also be verified during this review.

15.0 DATA REVIEW AND REPORTING

15.1 Initial and continuing calibration check. Verify that all calibration and continuing calibration criteria have been achieved. If the criteria had not been achieved, corrective action must be performed to bring the system in control before analyzing any samples.

15.1.1 If samples had been analyzed under non-compliant calibration criteria, all sample extracts must be re-analyzed once the system is brought into control.

15.2 Quality Control Data Review. Review all QC data. If QC criteria were not achieved, perform corrective action before proceeding with analysis.

15.2.1 In some situation, corrective action may demand that the entire sample batch be re-extracted and re-analyzed before processing data.

15.3 Chromatogram Review. The chromatogram of each sample is evaluated for target analytes.

15.3.1 Each sample may require the reporting of different target analytes. Review the login to assure that the correct target compounds are identified.

15.3.2 Manual integration of chromatographic peaks must be identified by the analysts. Upon review, the supervisor will initial and date the changes made to the report.

15.4 Transfer to LIMS. Following the initial screen review, transfer the processed data to the LIMS.

15.4.1 Compare the printed values to the original values to verify transfer accuracy.

15.4.2 If transfer errors occurred, the errors must be corrected before the data is re-submitted.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non hazardous aqueous wastes.
16.2.2 Hazardous aqueous wastes
16.2.3 Chlorinated organic solvents
16.2.4 Non-chlorinated organic solvents
16.2.5 Hazardous solid wastes
16.2.6 Non-hazardous solid wastes

Table 1 – Target Compounds by SW846 8270C			
Benzenethiol (1)	4-Bromophenyl phenyl ether	Di-n-octyl phthalate	5-Nitro-o-toluidine (1)
Benzoic Acid	Butyl benzyl phthalate	Diethyl phthalate	Naphthalene
2-Chlorophenol	Benzyl Alcohol	Dimethyl phthalate	Nitrobenzene
4-Chloro-3-methyl phenol	1,1'-Biphenyl (1)	2,3-Dichloroaniline (1)	n-Nitrosodimethylamine
2,4-Dichlorophenol	Butyl Stearate (1)	Decane	4-Nitroquinoline 1-Oxide (1)
2,4-Dimethylphenol	2-Chloronaphthalene	Octadecane (1)	N-Nitroso-di-n-propylamine
2,4-Dinitrophenol	4-Chloroaniline	bis(2-Ethylhexyl)phthalate	N-Nitrosodi-n-butylamine
2,6-Dichlorophenol	Carbazole	Ethyl methanesulfonate	N-Nitrosodiethylamine
4,6-Dinitro-2-methylphenol	Caprolactam (1)	Famphur	N-Nitrosodiphenylamine
Dinoseb	Chlorobenzilate	Fluoranthene	N-Nitrosomethylethylamine
2-Methylphenol	Chrysene	Fluorene	N-Nitrosomorpholine
3&4-Methylphenol	Cumene (1)	Hexachlorobenzene	N-Nitrosopiperidine
2-Nitrophenol	bis(2-Chloroethoxy)methane	Hexachlorobutadiene	N-Nitrosopyrrolidine
4-Nitrophenol	bis(2-Chloroethyl)ether	Hexachlorocyclopentadiene	O,O,O-Triethyl phosphorothioat
Pentachlorophenol	bis(2-Chloroisopropyl)ether	Hexachloroethane	2-Picoline
Phenol	4-Chlorophenyl phenyl ether	Hexachlorophene	Parathion
2,3,4,6-Tetrachlorophenol	1,2-Dichlorobenzene	Hexachloropropene	Pentachloroethane (1)
2,4,5-Trichlorophenol	1,2-Diphenylhydrazine	Indene (1)	Pentachlorobenzene
2,4,6-Trichlorophenol	1,3-Dichlorobenzene	Indeno(1,2,3-cd)pyrene	Pentachloronitrobenzene
2-Acetylaminofluorene	1,4-Dichlorobenzene	Isodrin	Phenacetin
4-Aminobiphenyl	2,4-Dinitrotoluene	Isophorone	Phenanthrene
Acenaphthene	2,6-Dinitrotoluene	Isosafrole	Phorate
Acenaphthylene	3,3'-Dichlorobenzidine	Kepone	Pronamide
Acetophenone	3,3'-Dimethylbenzidine	1-Methylnaphthalene	Pyrene
Aniline	1,4-Dioxane (1)	2-Methylnaphthalene	Pyridine
Anthracene	7,12-Dimethylbenz(a)anthracene	3-Methylcholanthrene	p-Phenylenediamine
Aramite	Dimethylnaphthalenes (total) (1)	4,4'-Methylenebis(2-chloroaniline)	Quinoline (1)
Atrazine (1)	Diallate	Methapyrilene	Safrole
alpha-Terpineol	Dibenz(a,h)acridine	Methyl methanesulfonate	1,2,4,5-Tetrachlorobenzene
A,A-Dimethylphenethylamine	Dibenzo(a,h)anthracene	Methyl parathion (1)	1,2,4-Trichlorobenzene
Benzidine	Dibenzofuran	6-Methyl Chrysene (1)	1,2,3-Trichlorobenzene (1)
Benzaldehyde (1)	Dimethoate	1,4-Naphthoquinone	1,3,5-Trichlorobenzene (1)

Benzo(a)anthracene	Diphenylamine	1-Naphthylamine	Thionazin (1)
Benzo(a)pyrene	Disulfoton	2-Naphthylamine	o-Toluidine
Benzo(b)fluoranthene	m-Dinitrobenzene	2-Nitroaniline	sym-Trinitrobenzene (1)
Benzo(g,h,i)perylene	p-(Dimethylamine) azobenzene (1)	3-Nitroaniline	Tetraethyl dithiopyrophosphate (1)
Benzo(k)fluoranthene	Di-n-butyl phthalate	4-Nitroaniline	

(1) NELAC Accreditation is not offered for this compound.

Table 2 – RECOMMENDED OPERATING CONDITIONS: Gas Chromatograph/ Mass Spectrometer	
Injection Type	Splitless
Carrier Gas (linear velocity)	Helium at 30 cm/sec*
Mass range	35-500 AMU
Electron Energy	70 volts (nominal)
Scan time	not to exceed 1 sec. per scan
Injection port temperature	200-300 °C
Source temperature	220-270 °C
Transfer line temperature	250-300 °C
Analyzer temperature	220-250 °C
Gas Chromatograph Temperature Program*	
Initial temperature	40-50 °C*
Time 1	2-4 minutes*
Column temperature rate	8-25 degrees/min*
Final temperature	290-320 °C according to column type*
Total run time	*20-40 minutes*

***** Parameter modification allowed for performance optimization as long as QC criteria are achieved.

Table 2a – SIM Group Parameters		
Group No.	**Retention Time (minutes)**	**Ions**
1	0 – 7.8	150, 64, 93, 82, 152, 99, 63, 128, 112, 42, 95
2	7.8 – 11	150, 128, 225, 142, 172, 152, 129, 223, 141, 171, 122, 127, 227, 115, 170
3	11 – 13.8	172, 152, 166, 182, 334, 266, 176, 153, 165, 330, 284, 264, 174, 154, 77, 332, 286, 268
4	13.8 – 18	266, 179, 202, 122, 268, 212, 203, 284, 178, 213, 244, 286
5	18 – 22	244, 229, 167, 122, 226, 202, 228, 149, 203
6	22 – 34.7	264, 149, 253, 278, 263, 150, 250, 139, 265, 252, 276, 138

Table 3 - 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 4 – INTERNAL STANDARDS	
Internal Standard (Full Scan)	**Prim/Sec. ions**
1,4-Dichlorobenzene-d4	152 / 150, 115
Naphthalene-d8	136 / 68
Acenaphthene-d10	164 / 162, 160
Phenanthrene-d10	188 / 94, 80
Chrysene-d12	240 / 120, 236
Perylene-d12	264 / 260, 265
Internal Standard (SIM)	**Prim/Sec. ions**
1,2-Dichlorobenzene-d4	152/ 150
1-Methylnaphthalene-d10	150/ 152, 122
Fluorene-d10	174/ 176
Fluoranthene-d10	212/ 213
Benzo(a)pyrene- d12	264/ 263, 265

Table 6 – Full Scan Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation			
1,4-Dichlorobenzene-d4	**Ions**	**Acenaphthene-d10**	**Ions**
Aniline	(93/66,65)	Acenaphthene	(154/153,152)
Benzaldehyde	(105)	Acenaphthylene	(152/151,153)
Benzenethiol	(110)	1-Chloronaphthalene	(162/127,164)
Benzyl alcohol	(108/79,77)	2-Chloronaphthalene	(162/127,164)
Bis(2-chloroethyl)ether	(93/63,95)	4-Chlorophenylphenyl ether	(204/206,141)
Bis (2-chloroisopropyl)ether	121	Dibenzofuran	(168/139)
2-Chlorophenol	(128/64,130)	Diethyl phthalate	(149/177,150)
Cumene	(105,120)	Dimethyl phthalate	(163/149,164)
Decane	(43)	m-Dinitrobenzene	(168)
1,3-Dichlorobenzene	(146/148,111)	2,4-Dinitrophenol	(184/63,154)
1,4-Dichlorobenzene	(146/148,111)	2,4-Dinitrotoluene	(165/63,89)
1,2-Dichlorobenzene	(146/148,111)	2,6-Dinitrotoluene	(165/63,89)
1,4 Dioxane	(88)	Fluorene	(166/165,167)
Ethyl methanesulfonate	(79/109,97)	Hexachlorocyclopentadiene	(295/237,142)
2-Fluorophenol (SURR.)	(112)	1,4 – Naphthoquinone	(158)
Hexachloroethane	(117/201,199)	1- Naphthylamine	(143/115,116)
Indene	(116)	2- Naphthylamine	(143/115,116)
Methyl methanesulfonate	(80/79,64)	2-Nitroaniline	(65/92,138)
2-Methylphenol	(108/107,79)	3-Nitroaniline	(138/108,92)
4-Methylphenol	(108/107,79)	4-Nitroaniline	(138/108,92)
N-Nitrosodiethylamine	(102)	4-Nitrophenol	(139/109,65)
N-Nitrosodimethylamine	(74/42)	5 Nitro-o-toluidine	(152)
N-Nitroso-di-n-propylamine	(70/101,130)	Pentachlorobenzene	(250/252,248)
N-Nitrosomethyethylamine	(42)	Pentachloronitrobenzene	(237/235,272)
N-Nitrosomorpholine	(56)	Phenacetin	(108/109,179)
N-Nitrosoptrrolidine	(41)	Phorate	(75)
O-Toluidine	(106)	Pronamide	(173/175,145)
Petachloroethane	(167)	1,2,4,5-Tetrachlorobenzene	(216/214,218)
Phenol	(94)	2,3,4,6-Tetrachlorphenol	(232/230,131)
Phenol-d5 (SURR.)	(99)	Tetraethyldithiopyrophosphate	(322)
2-Picoline	(93/66,92)	Thioazin	(143)
Pyridine	(79)	2,4,6-Trichlorophenol	(196/198,200)
		2,4,5-Trichlorophenol	(196/198,200)

Table 6 (cont'd) – Full Scan Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation			
Naphthalene-d8	**Ions**	**Phenanthrene-d10**	**Ions**
A,A-Dimethylphenethylamine	(58)	4-Aminobiphenyl	(169/168,170)
Acetophenone	(105/77,51)	Anthracene	(178/176,179)
Benzoic acid	(184/92,185)	Atrazine	(58)
Bis(2-chloroethoxy)methane	(93/95,123)	4-Bromophenyl phenyl ether	(248/250,141)
Caprolactam	(55)	Carbazole	(167)
4-Chloroaniline	(127)	Diallate	(86)
4-Chloro-methylphenol	(107/144)	Dimethoate	(87)
2,3 Dichloroaniline	(161)	Di-n-Butyl phthalate	(149/150)
2,4-Dichlorophenol	(162/164,98)	4,6-Dinitro-2-methylphenol	(198/51,105)
2,6-Dichlorophenol	(162/164,98)	Dinoseb	(211)
Dimethylnaphthalene	(156)	Diphenylamine	(169/168,167)
2,4-Dimethylphenol	(122/107)	1,2-Diphenylhydrazine	(77/105)
a,a-Dimethyl-phenethylamine	(58/91,42)	Disulfoton	(88)
Hexachlorobutadiene	(225/223,227)	Fluoranthene	(202/101,203)
Hexachloroprene	(213)	2-Fluorobiphenyl (SURR)	(172)
Isophorone	(82/95,138)	Hexachlorobenzene	(284/142,249)
Isosafrole	(127)	Isodrin	(193)
1-Methylnaphthalene	(142)	Methapyriline	(58)
2-Methylnaphthalene	(142/141)	Methyl Parathion	(125)
Naphthalene	(128/129,127)	N-Nitrosodiphenylamine	(169/168,167)
Nitrobenzene	(77/123,65)	4-Nitroquinoline 1-oxide	(190)
Nitrobenzene-d5 (SURR.)	(82)	Octadecane	(57)
N-Nitroso-di-n-butylamine	(84/57/41)	Parathion	(109)
2-Nitrophenol	(139/109,65)	Pentachlorophenol	(266/264,268)
Quinoline	(129)	Phenanthrene	(178/179,176)
N-Nitrosopiperidine	(42/114,55)	Pronamide	(173)
p-Phenylenediamine	(108)	sym- Trinitrobenzene	(213)
O,O,O-Triethylphosphorthioat	(198)	2,4,6 Tribromophenol (SURR)	(330)
Safrole	(162)		
alpha –Terpineol	(128)	**Perylene-d12**	**Ions**
1,2,3-Trichlorobenzene	(180/182,145)	Benzo(b)fluoranthene	(252/125)
1,2,4-Trichlorobenzene	(180/182,145)	Benzo(k)fluoranthene	(252/125)
1,3,5-Trichlorobenzene	(180/182,145)	Benzo(g.h.i)perylene	(276/138,277)
		Benzo(a)pyrene	(252/253,125)
Chrysene-d12	**Ions**	Dibenz(a,j)acridine	(279/280)
2 –Acetylaminofluorene	(181)	Dibenz(a,h)anthracene	(278/139,279)
Aramite	(194)	7,12-Dimethylbenz(a)anthracene	(256/241,257)
Benzidine	(184)	Di-n-Octyl Phthalate	(149)
Benzo(a)anthracene	(228/229/226)	Hexachlorophene	(196)
Bis(2-ethylhexyl)phthalate	(149/167,279)	Indeno(1,2,3-d)pyrene	(276)
Butylbenzyl phthalate	(149/91)	3-Methylchloanthrene	(268/253)
Chlorobenzilate	(251)		
Chrysene	(228/226,229)		
3,3'-Dichlorobenzidine	(252/254,126)		
p-Dimethylaminoazobenzene	(120/225,77)		
3,3 Dimethylbenzidine	(212)		
Famphur	(218)		
Kepone	(272)		
Methyl Chrysene	(242)		
Pyrene	(202/200,203)		

Terphenyl-d14 (SURR.)	(244)		
Table 6a – SIM Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation			
1,4-Dichlorobenzene-d4	**Ions**	**Fluoranthene-d10**	**Ions**
2-Fluorophenol (Surr)	(112)	Fluoranthene	202, 101, 203
Phenol-d5 (Surr)	(99)	Pyrene	202, 203
Bis-(2-chloro-ethyl)ether	93, 63, 95	Terphenyl-d14 (Surr)	(244)
Nitrobenzene-d5 (Surr)	(82)	Benzo(a)anthracene	228, 229, 226
		Chrysene	228, 226, 229
1-Methylnaphthalene-d10	**Ions**	Bis(2-ethylhexylphthalate	149, 167, 279
Naphthalene	128, 129, 127		
Hexachlorobutadiene	225, 223, 227	**Benzo(a) pyrene-d12**	**Ions**
2-Methyl Naphthalene	142, 141, 115	Di-n-octyl phthalate	149, 150, 43
2-Fluorobiphenyl (Surr)	(172)	Benzo(b)fluoranthene	252, 253
		Benzo(k)fluoranthene	252, 125
Fluorene-d10	**Ions**	Benzo(a)pyrene	252, 253, 125
Acenaphthylene	152, 151, 153	Indeno(1,2,3-cd)pyrene	276, 277, 138
Acenaphthene	153, 152, 154	Dibenzo(a,h)anthracene	278, 139, 279
Fluorene	166, 165, 167	Benzo(g,h,i)perylene	276, 138, 277
1,2-Diphenylhydrazine	77, 105, 182		
2,4,6-Tribromophenol (Surr)	(330)		
Hexachlorobenzene	284, 286		
Pentachlorophenol	266, 264		
Phenanthrene	178, 179, 176		
Anthracene	178, 176, 179		

Table 7. STANDARD PREPARATION

Table 7A – Intermediate Calibration Standard Solution				
Stock Solution	**Stock Conc., µg/ml**	**Volume Added, µl**	**Final Vol. in $MeCl_2$, ml**	**Final Conc. µg/ml**
Semivolatile Standard Mix # 1	2,000	500	10	100
Semivolatile Standard Mix # 2	2,000	500	10	100
Semivolatile Standard Mix # 4	2,000	500	10	100
Semivolatile Standard Mix # 5	2,000	500	10	100
Semivolatile Standard Mix # 6	2,000	500	10	100
Semivolatile Standard Mix # 7	2,000	500	10	100
PAH Mixture #2	2,000	500	10	100
Semivolatile Standard Mix # 8	2,000	500	10	100
Additional Requested Compound(s) Mix	2,000	500	10	100
Pyridines Mixture	2,000	500	10	100
1,2,3-Trichlorobenzene	1,000	1,000	10	100
1,3,5-Trichlorobenzene	1,000	1,000	10	100
Butyl Stearate	10,000	200	10	200
Pentachlorophenol	1,000	1,000	10	100
B/N Surrogate Standard Mix	5,000	200	10	100
Acid Surrogate Standard Mix	7,500	134	10	100.5

Table 7B – Intermediate Calibration Standard Solution -SIM				
Stock Solution	**Stock Conc., µg/ml**	**Volume Added, µl**	**Final Vol. in $MeCl_2$, ml**	**Final Conc. µg/ml**
Semivolatile Standard Mix # 1	2,000	50	10	10
Semivolatile Standard Mix # 2	2,000	50	10	10
Toxic #2	2,000	50	10	10
PAH Mixture #2	2,000	50	10	10
Semivolatile Standard Mix # 8 (Acids)	2,000	250	10	50
1-Methynaphthalene	1,000	100	10	10
B/N Surrogate Standard Mix	5,000	100	10	50
Acid Surrogate Standard Mix (Full Scan)	7500	67	10	50

Table 7C – Initial Calibration Standards Prep Scheme

Standard Solution	**Intermediate Conc., µg/ml**	**Intermediate added, µl Full Scan**	**Final Volume in $MeCl_2$, ml**	**Final Conc., µg/ml – Full Scan**
STD 1	100	1,000	1	100
STD 2	100	800	1	80
STD 3	100	500	1	50
STD 4	100	250	1	25
STD 5	100/10 (SIM)	100	1	10
STD 6	100	50	1	5
STD 7	100	20	1	2
STD8	100	10	1	1

Table 7D Initial Preparation Standards Prep Scheme - SIM				
Standard Solution	**Intermediate Conc., µg/ml**	**Intermediate added, µl SIM**	**Final Volume in $MeCl_2$, ml**	**Final Conc., µg/ml – SIM Scan**
STD 1	10/50	500	1	5 BN / 25 Acids
STD 2	10/50	250	1	2.5 BN / 12.5 Ac
STD 3	10/50	100	1	1 BN / 5 Acids
STD 4	1	200	1	0.2 BN / 1 Acids
STD 5	1	100	1	0.1 BN / 0.5 Acids
STD7	0.1	500	1	0.05 BN / 0.25 AC
STD 6	0.1	200	1	0.02 BN / 0.1 AC

Table 7E– ICV -Second Source Calibration Check Standard				
Intermediate	**Intermediate Conc., µg/ml**	**Volume Used, µl (Full/SIM)**	**Final Volume in Acetone, ml**	**Final Conc., µg/ml (Full/SIM)**
Base Neutrals Mixture	100	500/ 50	1	50/ 5
Acid Mixture	100	500/ 50	1	50/ 5

Table 8a –Selected Ion Monitoring: Masses and Dwell Times		
Compound	**Mass Ion (m/z)**	**Dwell Time (ms)**
Acenaphthene	153, 152, 154	50
Acenaphthylene	152, 151, 153	50
Anthracene	178, 176, 179	50
Benzo(a)anthracene	228, 229, 226	50
Benzo(a)pyrene	252, 253, 125	50
Benzo(b)fluoranthene	252, 253	50
Benzo(g,h,i)perylene	276, 138, 277	50
Benzo(k)fluoranthene	252, 125	50
Chrysene	228, 226, 229	50
Dibenzo(a,h)anthracene	278, 139, 279	50
Fluoranthene	202, 101, 203	50
Fluorene	166, 165, 167	50
Indeno(1,2,3-cd)pyrene	276, 277, 138	50
Naphthalene	128, 129, 127	50
Phenanthrene	178, 179, 176	50
Pyrene	202, 203	50
2-Methyl Naphthalene	142, 141, 115	50
Bis-(2-chloro-ethyl)ether	93, 63, 95	50
Pentachlorophenol	266, 264	50
Hexachlorobutadiene	225, 223, 227	50
1,2-Diphenylhydrazine	77, 105, 182	50
Bis(2-ethylhexylphthalate	149, 167, 279	50
Di-n-octyl phthalate	149, 150, 43	50
Hexachlorobenzene	284, 286	50
2-Fluorophenol	112, 64, 63	50
Phenol-d5	99, 42	50
Nitrobenzene-d5	82, 128	50
2-Fluorobiphenyl	172, 171, 170	50
2,4,6-Tribromophenol	330, 332, 334	50
Terphenyl-d14	244, 122	50

Table 9. REPORTING LIMITS

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Benzoic Acid	20	667	Chlorobenzilate	5	167
2-Chlorophenol	5	167	Chrysene	1	33
4-Chloro-3-methylphenol	5	167	bis(2-Chloroethoxy)methane	2	67
2,4-Dichlorophenol	5	167	bis(2-Chloroethyl)ether	2	67
2,4-Dimethlyphenol	5	167	Bis(2-Chloroisopropyl)ether	2	67
2,4-Dinitrophenol	20	667	4-Chlorophenyl phenyl ether	2	67
4,6-Dinitro-o-cresol	20	667	1,2-Dichlorobenzene	2	67
Dinoseb	5	167	1,3-Dichlorobenzene	2	67
2-Methylphenol	2	67	1,4-Dichlorobenzene	2	67
4-Methylphenol	2	67	2,4-Dinitrotoluene	2	67
2-Nitrophenol	5	167	2,6-Dinitrotoluene	2	67
4-Nitrophenol	10	333	3,3'-Dichlorobenzidine	5	167
Pentachlorophenol	10	333	3,3'-Dimethylbenzidine	5	167
Phenol	2	67	7,12-Dimethylbenz(a)anthracene	5	167
2,3,4,6-Tetrachlorophenol	5	167	Diallate	5	167
2,4,5-Trichlorophenol	5	167	Dibenzo(a,h)anthracene	1	33
2,4,6-Trichlorophenol	5	167	Dibenzofuran	2	67
2-Acetylaminofluorene	5	167	Dimethoate	5	167
4-Aminobiphenyl	5	167	Diphenylamine	5	167
Acenaphthene	1	33	Disulfuton	5	167
Acenaphthylene	1	33	m-Dinitrobenzene	5	167
Acetophenone	5	167	p-(Dimethylamine)azobenzene	5	167
Aniline	2	67	Di-n-butyl phthalate	2	67
Anthracene	1	33	Di-n-octyl phthalate	2	67
Aramite	5	167	Diethyl phthalate	2	67
A,A-Dimethylphenethylamine	5	167	Dimethyl phthalate	2	67
Benzo(a)anthracene	1	33	bis(2-Ethylhexyl)phthalate	2	67
Benzo(a)pyrene	1	33	Ethyl methansulfonate	5	167
Benzo(b)fluoranthene	1	33	Famphur	30	1000
Benzo(g,h,i)perylene	1	33	Fluoranthene	1	33
Benzo (k)fluoranthene	1	33	Fluorene	1	33
4-Bromophenyl phenyl ether	2	67	Hexachlorobenzene	2	67
Butyl benzyl phthalate	2	67	Hexachlorobutadiene	1	33
Benzyl Alcohol	2	67	Hexachlorocyclopentadiene	20	667
2-Chloronaphthalene	2	67	Hexachloroethane	5	167
4-Chloroaniline	5	167	Hexachlorophene	50	1700
Carbazole	1	67	Hexachloropropene	5	167

Table 9 (Cont'd)

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Indeno(1,2,3-cd)pyrene	1	33	N-Nitrosomethylethylamine	5	167
Isodrin	5	167	N-Nitrosomorpholine	5	167
Isophorone	2	67	N-Nitrosopiperidine	5	167
Isosafrole	5	167	N-Nitrosopyrrolidine	5	167
Kepone	30	1000	O,O,O Triethylphosphorothioat	5	167
2-Methylnaphthalene	2	667	2-Picoline	5	167
3-Methylcholanthene	5	167	Parathion	5	167
Methapyrilene	5	167	Pentachlorobenzene	5	167
Methyl Methanesulfonate	5	167	Pentachloroethane	5	167
Methyl Parathion	5	167	Pentachloronitrobenzene	5	167
1,4 Naphthoquinone	5	167	Phenacetin	5	167
1-Naphthylamine	5	167	Phenanthrene	1	33
2-Naphthylamine	5	167	Phorate	5	167
2-Nitroaniline	5	167	Pronamide	5	167
3-Nitroaniline	5	167	Pyrene	1	33
4-Nitroaniline	5	167	Pyridine	2	67
5-Nitro-o-toluidine	5	167	p-Phenylenediamine	5	167
Naphthalene	1	33	Safrole	5	167
Nitrobenzene	2	67	1,2,4,5 Tetrachlorobenzene	5	167
n-Nitrosodimethylamine	2	67	1,2,4-Trichlorobenzene	2	67
4-Nitroquinoline-1-Oxide	10	333	Thionazin	5	167
N-Nitroso-di-n-propylamine	2	67	o-Toluidine	5	167
N-Nitrosodi-n-butylamine	5	167	sym-Trinitrobenzene	5	167
N-Nitrosodiethylamine	5	167	Tetraethyl dithiopyrophosphate	5	167
N-Nitrosodiphenylamine	5	167			

Table 10. Selected Ion Monitoring Reporting Limits

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Pentachlorophenol	0.3	17	Fluoranthene	0.1	3.3
Acenaphthene	0.1	3.3	Fluorene	0.1	3.3
Acenaphthylene	0.1	3.3	Hexachlorobenzene	0.02	3.3
Anthracene	0.1	3.3	Hexachlorobutadiene	0.1	3.3
Benzo(a)anthracene	0.1	3.3	Indeno(1,2,3-cd)pyrene	0.1	3.3
Benzo(a)pyrene	0.1	3.3	2-Methylnaphthalene	0.1	3.3
Benzo(b)fluoranthene	0.1	3.3	Naphthalene	0.1	3.3
Benzo(g,h,i)perylene	0.1	3.3	Phenanthrene	0.1	3.3
Benzo (k)fluoranthene	0.1	3.3	Pyrene	0.1	3.3
Chrysene	0.1	3.3	bis(2-Chloroethyl)ether	0.2	6.6
Dibenzo(a,h)anthracene	0.1	3.3	Bis (2-ethylhexyl) phthalate	0.2	6.6
1,2-Diphenylhydrazine	0.2	6.6	Di-n-octyl phthalate	0.2	6.6

New Jersey Department of Environmental Protection
Site Remediation Program

EXTRACTABLE PETROLEUM HYDROCARBONS METHODOLOGY (Version 3.0)

New Jersey Department of Environmental Protection
Office of Data Quality
Analytical Method

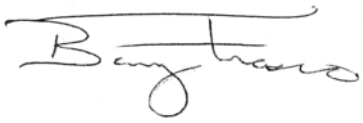
Title:
Analysis of Extractable Petroleum Hydrocarbon Compounds (EPH) in Aqueous and Soil/Sediment/Sludge Matrices

Document #:
NJDEP EPH 10/08

Date: August 2010 Revision: 3

Prepared by: Greg Toffoli

Cleared for Issue by: Barry Frasco



Location: Master Set @ DEP/SRP/ODQ

1.0 SCOPE OF APPLICATION

1.1 Scope

This method utilizes a gas chromatograph (GC) fitted with a flame ionization detector (FID) to determine the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons in water and soil/sediment matrices. A mass spectrometer (MS) may be used in lieu of a flame detector. However, the GC/MS must be operated in the scanning mode using the scan rate, scanning range and tuning criteria specified in USEPA Method SW-846 8270C or USEPA Method SW-846 8270D. Selected ion monitoring is not permitted. If GC/MS is used, then it should be used for both fractions.

1.1.1 This method can be used for the quantitative analysis of environmental samples (water, soil, sediment, and sludge) for residues from commercial petroleum products such as crude oil, diesel fuel, waste oil, fuel oil Nos. 2-6, lubricating oil, processed oil and bunker fuel.

1.1.2 This method shall not be used for the quantitative analysis of gasoline, mineral spirits, petroleum naphtha and other petroleum products which contain a significant percentage of hydrocarbons lighter than C9 in water and soil/sediment/sludge matrices at contaminated sites.

1.2 Applicable Programs

Underground Storage Tanks (UST), New Jersey Spill Fund, Comprehensive Environmental Response Compensation and Liability Act (CERCLA), Industrial Site Recovery Act (ISRA), Sludge Residuals, and Resource Conservation and Recovery Act (RCRA).

1.3 Method Advantages

1.3.1 This method replaces the Total Petroleum Hydrocarbons (TPH) method based on Freon 113 extraction and analysis by infrared spectroscopy (i.e., Method 418.1).

1.3.2 The FID response produces extractable petroleum hydrocarbon (EPH) chromatograms that can be used to calculate concentrations of specified carbon ranges for both aliphatic and aromatic fractions.

1.3.3 This method provides results for specific carbon number ranges in both aliphatic and aromatic fractions of EPH thereby providing a more accurate assessment of potential health risk at environmental sites.

1.3.4 This method provides an option where extracts from samples may be analyzed without having to be fractionated.

1.4 Method Limitations

1.4.1 Lower boiling hydrocarbons may co-elute with extraction solvents.

1.4.2 The EPH measured by this method is quantitatively restricted to the semi-volatile components as partial loss of volatiles (including those compounds lighter than C9) occurs during the extraction and/or concentration process.

1.4.3 The gas chromatographic conditions are not designed for samples containing EPH with carbon numbers greater than C44.

1.5 Applicable Matrices

1.5.1 Surface water, ground water, and wastewater.

1.5.2 Soil, sediments or high solids sludge (>50%).

2.0 SUMMARY OF METHOD

2.1 This quantitative EPH method is adopted from the "Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)," Massachusetts Department of Environmental Protection (1); the "Method for the Determination of Extractable Petroleum Hydrocarbons (EPH) Fractions," Washington State Department of Ecology (2); the "Leaking Underground Fuel Tanks Field Manual" of the California State Water Resources Control Board (3); "Test Methods for Evaluating Solid Waste" USEPA Method 8015B (4);

"Method for the Determination of Total Petroleum Range Organics," Florida Department of Environmental Protection (5); and "Quantitation of Semi-Volatile Petroleum Products in Water, Soil, Sediment and Sludge," New Jersey Department of Environmental Protection OQA-QAM-025-02/08 (6).

2.2 This method is adapted with modifications from ASTM Method D3328-82 and the US Coast Guard Oil Spill Identification Procedure for Total Petroleum (7, 8).

2.3 Petroleum residues are extracted from sample matrices with methylene chloride, dried over sodium sulfate, solvent exchanged to hexane and concentrated in a Kuderna-Danish apparatus. However, if a non-aqueous sample is known to be contaminated with #2 fuel/diesel or the concentration of a non-#2 fuel/diesel petroleum product in a non-aqueous sample has been determined by this method to be below the number generated by the EPH calculator when it is assumed that 100% of the contamination is in the carbon range with the most conservative toxicity factor (as of June 1, 2010, the number is 1700 mg/Kg, subject to change), then solvent exchange and fractionation are not required. Additionally, aqueous samples are not required to undergo solvent exchange and fractionation. Quantitation for non-fractionated samples is performed using the total area of all peaks present and dividing the chromatography into the eight carbon ranges is not required. For all other instances, the extracts are separated into aliphatic and aromatic fractions using silica gel columns, either commercially available or lab prepared. Each of the aliphatic and aromatic fractions are re-concentrated and subsequently analyzed separately by capillary column GC/FID. Each of the resultant chromatograms of the aliphatic and aromatic fractions are used to quantitate four distinct carbon number ranges. Each carbon number range is defined using equivalent carbon (EC) numbers. The EC number is related to a compound's boiling point and retention time on a gas chromatography column normalized to the actual carbon numbers of n-alkanes. For example, the EC of acenaphthylene is 15.06 because its boiling point and GC retention time are halfway between those of n-tetradecane (a straight 14-carbon chain compound) and n-hexadecane (a straight 16-carbon chain compound). The EC numbers are used because they are more closely related to environmental mobility. The four EC number ranges for the aliphatic fractions are: EC9 to EC12, EC12 to EC16, EC16 to EC21 and EC21 to EC40. Similarly, the resultant chromatograms of the aromatic fractions are used to quantitate four distinct carbon number ranges. The four carbon number ranges for the aromatic fractions are: EC10 to EC12, EC12 to EC16, EC16 to EC21 and EC21 to EC36.

Surrogate compounds are added to all samples before extraction and their recoveries are monitored. Percent recoveries for the surrogates can be expected to be in the 50 - 90 % range. If fractionation is required, then fractionating surrogates are added to the hexane extract just prior to fractionation to monitor the efficiency of the fractionation process. Percent recoveries for the fractionating surrogates should be between 40% – 140 %.

2.3.1 The EPH concentration is determined by integration of the FID chromatogram (see section 11.2). Average calibration factors or response factors using the aliphatic standard mixture are used to calculate the concentration of each carbon range. Average calibration factors or response factors using the aromatic standard mixture are used to calculate the concentration of each carbon range. Concentrations of each carbon range from both fractions are summed for a total EPH concentration.

2.3.2 For extracts not undergoing fractionation, the concentration is determined by integration of the FID chromatogram (see section 11.3). Average calibration factors or response factors using the standard mixture are used to calculate the concentrations.

2.3.3 The sensitivity of the method may be dependent on the level of interference rather than on instrumental limitations. The quantitation limit for each carbon range in soil is approximately 10 mg/kg and in water 100 ug/L.

2.3.4 Approximate Dynamic Range

2.3.4.1 EPH, both Fractionated and Non-fractionated Samples

Soil 80 -16000 mg/kg
Aqueous 0.8 - 160 mg/L

2.3.4.2 Individual Carbon Ranges

Soil 10 - 2000 mg/kg
Aqueous 0.10 - 20 mg/L

2.4 Compounds

2.4.1 Aliphatic Hydrocarbon Standard

Aliphatic Hydrocarbon (EC #)
n-Nonane (C9)
n-Decane (C10)
n-Dodecane (C12)
n-Tetradecane (C14)
n-Hexadecane (C16)
n-Octadecane (C18)
n-Eicosane (C20)
n-Heneicosane (C21)
n-Docosane (C22)
n-Tetracosane (C24)
n-Hexacosane (C26)
n-Octacosane (C28)
n-Triacontane (C30)
n-Dotriacontane (C32)
n-Tetratriacontane (C34)
n-Hexatriacontane (C36)
n-Octatriacontane (C38)
n-Tetracontane (C40)

2.4.2 Aromatic Hydrocarbon Standard

Aromatic Hydrocarbon (EC #)
Acenaphthene (C15.5)
Acenaphthylene (C15.06)
Anthracene (C19.43)
Benzo[a]anthracene (C26.37)
Benzo[a]pyrene (C31.34)
Benzo[b]fluoranthene (C30.14)
Benzo[g,h,i]perylene (C34.01)
Benzo[k]fluoranthene (C30.14)
Chrysene (C27.41)
Dibenz[a,h]anthracene (C30.36)
Fluoranthene (C21.85)
Fluorene (C16.55)
Indeno[1,2,3-cd]pyrene (C35.01)
2-Methylnaphthalene (C12.89)

Naphthalene (C11.7)
Phenanthrene (C19.36)
Pyrene (C20.8)
1,2,3-Trimethylbenzene (C10.1)

2.5 #2 Diesel Fuel Standard

The standard used for the LCS for #2 Fuel/Diesel analyses is #2 Diesel Fuel (available from Restek (item 31233), Supelco and NSI Solutions)

3.0 INTERFERENCES

3.1 Method interferences are reduced by washing all glassware and then rinsing with tap water, distilled water, methanol, and methylene chloride.

3.2 High purity reagents such as Burdick and Jackson GC^2 methylene chloride, Baker capillary grade methylene chloride or equivalent must be used to minimize interference problems.

3.3 Before processing any sample, the analyst shall demonstrate daily, through the analysis of a method blank, that the entire system is interference-free.

3.4 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interference will vary considerably from source to source (e.g., fatty acids, biogenic materials, oxidized biodegradation products), depending upon the nature and diversity of the site being sampled. The silica gel cleanup procedure, USEPA SW-846 Method 3630B, can be used to overcome many of these interferences but unique samples may require additional cleanup approaches such as SW-846 Methods 3610B, 3620B and 3660B to achieve the necessary analytical sensitivity.

3.5 Naturally occurring alkanes may be detected by this method and may interfere with product identification. Naturally occurring plant waxes include predominantly odd carbon number alkanes from n-C25 through n-C35, and exhibit a dominant odd/even chain length distribution.

4.0 SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been defined precisely. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for use by the analyst (9, 10).

5.0 APPARATUS AND EQUIPMENT

5.1 Sampling Containers

5.1.1 Prior to use, wash bottles and cap liners with aqueous detergent solutions and rinse with tap water, distilled water, and methylene chloride. Allow the bottles and containers to air dry at room temperature, place in a 105^{o}C (minimum temperature) oven for one hour, then remove and allow them to cool in an area known to be free of organic analytes.

5.1.2 Screw cap bottle - 40 mL PTFE-faced silicone cap liners.

5.1.3 Narrow mouth bottles - 1 liter, amber, PTFE faced silicone cap liners.

5.1.4 Wide-mouth glass jar-four ounce, amber, PTFE faced silicone cap liners.

5.2 Glassware

5.2.1 Serum bottles - 100 mL, 10 mL, 2 mL crimp-top, PTFE-faced silicone cap liners.

5.2.2 Pasteur pipettes.

5.2.3 Screw-cap Erlenmeyer flasks - 250 mL, with PTFE faced silicone cap liners.

5.2.4 Volumetric flasks - 10 mL, 25 mL, 100 mL.

5.2.5 Kuderna-Danish apparatus (KD), 500 mL flask.

5.2.6 Separatory funnels - 2 L Pyrex, Teflon stopcock.

5.2.7 Soxhlet Extractor with 500 mL flask.

5.2.8 1 cm I.D. by 10 to 20 cm long glass column with glass or Teflon stopcock.

5.3 Apparatus

5.3.1 Analytical balance capable of accurately weighing 0.0001 g.

5.3.2 A gas chromatograph with split/splitless injector, equipped with a capillary column, capable of temperature programming. The analytical column chosen must adequately resolve the n-C9 to n-C40 aliphatic standard compounds and the aromatic standard compounds listed in 6.8.1 and 6.8.2 below. The recommended column is:

5.3.2.1 Column - 30m long x 0.32mm I.D., 0.25um film thickness, 95% dimethyl-5% diphenyl polysiloxane (Restek RTX-5 or equivalent).

Recommended Conditions:
Oven Temperature: 60^{o}C; hold for 1 minute; 8^{o}/minute to 290^{o}C, hold for 7 minutes
Injection size: 1 - 4 uL
Gas Flow Rates: Carrier Gas - Helium @ 2 -3 mL/minute;
Oxidizer - Air @ 400 mL/minute;
Fuel - Hydrogen @ 35 mL/minute;
Make up - Air @ 30 mL/minute.

Injection Port Temperature: 285°C
Column Inlet Pressure 15 p.s.i.
Detector Temperature: FID @ 315°C
Linear Velocity: 50 cm/sec

5.3.2.2 Detector - Flame Ionization Detector is required.

5.3.3 An autosampler is recommended.

5.3.4 Boiling chips (Teflon® preferred) - Solvent extracted approximately 10/40 mesh.

5.3.5 Water bath - Top, with concentric ring cover, capable of temperature control. The bath should be used in a hood.

5.3.6 Gas-tight syringe - One milliliter (mL) with chromatographic needles.

5.3.7 Microsyringes - l0uL, 100uL, 200uL.

5.3.8 Magnetic stirrer and 2-inch Teflon coated stirring bars.

5.3.9 Nitrogen concentration system composed of a precleaned pasteur pipette, with a small plug of glass wool (previously washed with solvent and dried) loaded at the tip end, and filled with approximately 1-2 cm of precleaned alumina. The top of the pipette is attached to a hydrocarbon free nitrogen gas source using precleaned Teflon tubing. This concentration step should be performed at room temperature or lower to retain light end compounds.

6.0 REAGENTS

6.1 Purity of Reagents - Reagents are to be of the highest quality appropriate and shall conform to all pertinent specifications of the American Chemical Society.

6.2 Reagent water - Reagent water is defined as a water in which an interference is not observed at the MDL of each parameter of interest (ASTM Specification D1193, Type ii).

6.3 Methylene chloride, methanol, carbon disulfide and hexane - pesticide grade, Burdick and Jackson GC[2], Baker Capillary Grade or equivalent.

6.4 Sodium sulfate - (ACS) granular, anhydrous. Purify by heating at 400°C for four hours in a shallow tray, cool in a desiccator and store in a sealed glass bottle.

6.5 Silica gel desiccant (for fractionation) - 100/200 mesh (Davison Chemical Grade 923 or equivalent). Before use, activate for at least 16 hours at 130°C in a shallow glass tray that is loosely covered in foil. Cool and store as in section 6.4. Commercially available Solid Phase Extraction (SPE) cartridges (20 ml tube volume/5 g bed weight) may be used (Restek - Massachusetts TPH Specialty SPE Cartridge or equivalent). (Please note: Silica gel is hygroscopic. Unused cartridges must be stored in properly maintained desiccators prior to use to prevent absorption of moisture from air.)

6.6 Ottawa and/or masonry sand, free from extractable petroleum products, may be used in lieu of sodium sulfate where applicable (such as for sections 9.2.1 and 9.2.2.2)

6.7 Hydrochloric acid, 1:1 - Mix equal volumes of (ACS grade) concentrated HCl and distilled water.

6.8 Standard Solutions

6.8.1 Aliphatic Hydrocarbon Stock Standard - Prepare a hexane solution containing at a minimum the aliphatic compounds listed in Section 2.4.1, naphthalene, 2-methylnaphthalene and the surrogates (1-chlorooctadecane and ortho-terphenyl) each at a concentration of 1 mg/ml. (Naphthalene and 2-methylnaphthalene are added to the aliphatic standard as their presence in the laboratory control sample and/or laboratory control sample duplicate is used to determine if fractionation for a batch is acceptable. Ortho-terphenyl is added to allow for surrogate recovery calculations from those extracts not undergoing fractionation.) For those extracts undergoing fractionation, the area from the surrogate ortho-terphenyl is not used in aliphatic calculations. Aliphatic mixtures are available from Supelco, Restek (Cat. # 31266), NSI Solutions and Ultrex. (Note: Due to the commercial availability of standards, it may be necessary to combine two commercially available standard mixtures which may result in the addition of compounds such as n-Nonane (C9) and n-Nonadecane (C19) to the aliphatic hydrocarbon standard.)

6.8.2 Aromatic Hydrocarbon Stock Standard - Prepare a methylene chloride solution containing the aromatic compounds listed in Section 2.4.2, the surrogate compound (ortho-terphenyl) and the fractionating surrogate compounds (2-Bromonaphthalene and 2-Fluorobiphenyl) each at a concentration of 1 mg/ml. (Aromatic mixtures are available from Supelco, Restek (Cat. # 31469), NSI Solutions and Ultrex.)

6.8.3 Surrogate - The surrogate ortho-terphenyl (OTP) is prepared by weighing 0.0100 g of pure material in a 10 mL volumetric flask. Dissolve the material to volume in methylene chloride. The surrogate 1-chlorooctadecane (COD) is prepared by carefully weighing 0.0100 g of pure material in a 10 mL volumetric flask. Dissolve the material to volume with hexane. (Surrogate solutions are available from Restek Inc. [11].)

6.8.4 Surrogate Spiking Solution - Prepare a surrogate spiking solution containing OTP and COD at a concentration of 100 ng/uL each in acetone. Each sample, blank, and matrix spike is fortified with 1.0 ml of the surrogate spiking solution. Alternative concentrations are permissible and, in instances when spiking highly contaminated samples, the use of higher concentrations is advisable.

6.8.5 Laboratory Control Sample (LCS) (Blank Spike) Solution - The LCS solution is the same as the matrix spiking solution described in 6.8.6 below. 1 mL is used to fortify either reagent water or clean sand (or sodium sulfate).

6.8.6 Matrix spiking solution (MSS) - Prepare the MSS containing all the compounds in sections 2.4.1 and 2.4.2 in pentane each at a concentration of 100 ng/uL. The source of the standards shall be different than those from which the calibration standards are made. A 1 mL aliquot is added to the sample designated as the matrix spike. Alternative concentrations are permissible and, in instances when spiking highly contaminated samples, the use of higher concentrations is advisable. (Matrix spiking solutions are available from Restek.)

6.8.7 Fractionating Surrogates: The fractionating surrogates (2-Bromonaphthalene and 2-Fluorobiphenyl) are prepared by weighing 0.0100 g of pure material in a 10-ml volumetric flask and dissolving the material in Methylene Chloride. (Surrogates are available from Restek Inc.)

6.8.8 Fractionating Surrogate Spiking Solution - Prepare the solution containing 2-Bromonaphthalene and 2-Fluorobiphenyl at concentrations of 100 ng/ul each in hexane. An aliquot of 1 ml of the fractionating surrogate spiking solution is added to the 1 ml EPH sample extract prepared in accordance with sections 10.1 and 10.2 just prior to fraction separation with silica gel. Alternative concentrations are permissible and, in instances when spiking highly contaminated samples, the use of higher concentrations is advisable.

6.8.9 Fractionating Check Solution - This solution is used to monitor the fractionation efficiency of the silica gel cartridge/column and establish the optimum hexane volume required to efficiently elute the aliphatic fraction without significant aromatic breakthrough.

Prepare the solution containing 200 ng/uL of all the compounds listed in the aliphatic hydrocarbon standard and 200 ng/uL of all the compounds listed in the aromatic hydrocarbon standard cited in sections 6.8.1 and 6.8.2 respectively, in hexane.

6.8.10 #2 Fuel/Diesel Laboratory Control Sample (LCS) (Blank Spike) Solution – Prepare a #2 Diesel fuel (purchased from an analytical standards provider such as Supelco, cat. # 31233) in methylene chloride at a recommended concentration of 250 ng/uL) 1 mL is used to fortify either reagent water or clean sand (or sodium sulfate).

6.8.11 #2 Diesel Fuel Standard (Optional). Prepare in methylene chloride a standard of # 2 Diesel fuel at a recommended concentration of 250 ng/uL and OTP and COD at concentrations of 100 ng/uL. This standard may be used to determine the recoveries of the #2 Fuel/Diesel LCS and LCSDs in lieu of using the Aliphatic Hydrocarbon Standard.

7.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

7.1 Aqueous Matrix

7.1.1 Collect a representative water sample in a 1 L narrow mouth bottle. A delay between sampling and analysis of greater than four hours requires sample preservation by the addition of 5 ml HCl (see section 6.7). Confirmation of a pH < 2 must be obtained in the field.

7.1.2 Sample must be chilled to 4±2^{o}C at the time of collection and stored at 4±2^{o}C until received at the laboratory.

7.1.3 The laboratory must determine the pH of all water samples as soon as possible after sample receipt and prior to extraction. Any sample found to contain a pH > 2 must be noted in a laboratory notebook and the pH must be adjusted as soon as possible. Samples are to be stored at 4±2^{o}C until extraction.

7.1.4 Samples must be extracted within fourteen days from the time of collection. Extracts must be analyzed within 40 days of extraction.

7.2 Solid Matrix

7.2.1 Collect a representative soil-sediment sample in a four-ounce, wide-mouth jar with a minimum of air space.

7.2.2 Samples must be chilled at 4±2^{o}C at the time of collection and stored at 4±2^{o}C until analyzed.

7.2.3 Samples must be extracted within fourteen days from the time of collection. Extracts must be analyzed within 40 days of extraction.

8.0 CALIBRATION

8.1 Initial Calibration for samples undergoing fractionation

8.1.1 Retention time windows

8.1.1.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of the Aromatic Hydrocarbon and Aliphatic Hydrocarbon standard mixtures. Serial injections over less than a 72 hr period result in retention time windows that are too restrictive.

8.1.1.2 Calculate the mean and the standard deviation of the three retention times (use any function of retention time including absolute retention time or relative retention time) for each individual compound in the aromatic standard, each individual compound in the aliphatic standard and all surrogates.

8.1.1.3 Plus or minus three times the standard deviation of the mean retention times for each compound in the aromatic and aliphatic standards will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. The default value for the retention time shall be a minimum of ± 0.1 minutes, if the standard deviation is zero or close to zero.

8.1.1.4 Establish the midpoint of the retention time window for each surrogate by using the absolute retention for each surrogate from the mid-concentration standard of the initial calibration. The absolute retention time window equals the midpoint + 3 SD, where the standard deviation is determined as described in section 8.1.1.2.

8.1.1.5 The laboratory must calculate retention time windows for each aromatic standard compound, each aliphatic standard compound and each surrogate on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

8.1.2 FID External Standard Calibration for Quantitation of EPH. - Calibrate the GC-FID with an initial five-point calibration. The recommended standard concentrations of each individual component are 20 ng/uL, 100 ng/ul, 250 ng/uL, 500 ng/uL and 1000 ng/uL. Separate calibrations are to be conducted for each fraction (see sections 6.8.1 and 6.8.2). The highest concentration

point should be twice the expected sample concentration and within the linear range of the instrument. To maintain the standards in solution, a 10% carbon disulfide / 90% methylene chloride solvent may be required. Standards with concentrations greater than 20 mg/L may need to be equilibrated to room temperature prior to analysis. Prepare the calibration standards to contain the surrogates at the same concentrations as the individual components. The surrogate OTP and the fractionating surrogates are included in the Aromatic Hydrocarbon Standard. The surrogates COD and OTP are included in the Aliphatic Hydrocarbon Standard.

A calibration factor (CF) must be established for each individual component. Also, a separate calibration factor (CF) must be established for each carbon range of interest. Calculate CFs for the C9-C12, C12-C16, C16-C-21 and C21-C40 Aliphatic Hydrocarbon carbon ranges from the appropriate aliphatic analysis chromatogram. Calculate CFs for C10-C12, C12-C16, C16-C-21 and C21-C36 Aromatic Hydrocarbon carbon ranges from the appropriate aromatic analysis chromatogram.

For the aliphatic fraction, use the following compounds as carbon range markers:

Range	Compound	EC
C9-C12	n-Nonane	9.0
	n-Dodecane	12.0
C12-C16	n-Dodecane + 0.1 min	
	n-Hexadecane	16.0
C16-C21	n-Hexadecane + 0.1 min	
	n-Heneicosane	21.0
C21-C40	n-Heneicosane + 0.1min	
	n-Tetracontane	40.0

For the aromatic fraction, use the following compounds as carbon range markers:

Range	Compound	EC
C10-C12	1,2,3-Trimethylbenzene	10.1
	Naphthalene	11.7
C12-C16	Naphthalene + 0.1 min	
	Acenaphthene	15.5
C16-C21	Acenaphthene + 0.1 min	
	Pyrene	20.8
C21-C36	Pyrene + 0.1min	
	Benzo(g,h,i)perylene + 1.0 minute	34.01

(Please note: The "+ 0.1 minutes" noted above in both the aromatic and aliphatic fractions are maximums. The laboratory should use less than the "compound + 0.1 minute" as the carbon range marker if peak shape and chromatographic resolution are favorable.)

The Calibration Factor (CF) is defined as the ratio of the peak area to the concentration injected.

For individual compounds, the calibration factors are determined by the following equation.

$$CF = \frac{Area\ of\ Peak}{Concentration\ Injected\ (ng/uL)}$$

For the carbon ranges, tabulate the summation of the peak areas of all the compounds in each carbon range against the total concentration injected for that carbon range. The Calibration Factor (CF), defined as the ratio of the summed peak area to the concentration injected, is calculated for each carbon range using the following equation:

$$Carbon\ Range\ CF = \frac{Summed\ Area\ of\ Peaks\ in\ the Range}{Total\ Concentration\ Injected\ (ng/uL)}$$

Note that the areas for the surrogates must be subtracted out from the area summation of the range in which they elute. Also, any areas associated with naphthalene and 2-methylnaphthalene in the aliphatic fraction must be subtracted out from the appropriate carbon range.

The percent relative standard deviation (%RSD) of the calibration factors for each compound and surrogate must be ≤ 25% over the working calibration range.

$$\%\ RSD = \frac{Standard\ Deviation\ of\ 5\ CFs}{Mean\ of\ 5\ CFs}$$

The percent relative standard deviation (%RSD) of the calibration factors for each carbon range for the compounds and surrogates must be ≤ 25% over the working calibration range.

$$\%\ RSD = \frac{Standard\ Deviation\ of\ 5\ Range\ CFs}{Mean\ of\ 5\ Range\ CFs}$$

If any %RSD is >25%, the source of the problem should be identified and the problem resolved.

8.2 Daily Calibration for samples undergoing fractionation

8.2.1 At a minimum, the working calibration factors must be verified on each working day, after every 20 samples or every 24 hours (whichever is more frequent) and at the end of the analytical sequence by the injection of the mid-level calibration standards (both aliphatic and aromatic). Calculate the percent differences (D %) between the continuing calibration factors and the average calibration factors from the initial calibrations for each compound, for each carbon range for each fraction and for the surrogates. If the %D of any carbon range is >25% (>30% for any single compound in a range) then a new calibration curve has to be generated for that range. Any sample associated with a non-compliant calibration shall be reanalyzed.

$$\%D = \frac{CF_{AVG} - CF_{cc}}{CF_{AVG}}$$

Where:

CF_{AVG} = Average Calibration Factor calculated from initial calibration
CF_{CC} = Calibration Factor calculated from continuing calibration standard

8.2.2 The retention times of surrogates in the calibration verification standard analyzed at the beginning of the analytical shift must fall within the absolute retention time windows calculated in Sec. 8.1.1.2. The purpose of this check is to ensure that retention times do not continually drift further from those used to establish the widths of the retention time windows. If the retention time of any surrogate at the beginning of the analytical shift does not fall within the ± 3 SD window (minimum ±0.10 min.), then a new initial calibration is necessary.

In addition, the retention times of all surrogates in the subsequent calibration verification standards analyzed during the analytical shift must fall within the absolute retention time windows established in Sec. 8.1.1.4.

8.2.3 Surrogate Standards (SS) - The SS responses and retention times in the calibration check standard must be evaluated during or immediately after data acquisition. If the retention time(s) for the SS is outside the determined RT window, the chromatographic system must be inspected for malfunctions and corrections must be made. If the area(s) for the SS changes by ±50% from the last daily calibration standard check, the GC must be inspected for malfunctions and corrections must be made.

8.3 Initial Calibration for samples <u>not</u> requiring fractionation

8.3.1 Retention time windows
The same retention time window criteria described in 8.1.1 are used to satisfy the requirements of this section. It is only necessary to address the aliphatic components of the section.

8.3.2 FID External Standard Calibration for Quantitation of pre-fractionated extract analyses

The same calibration standards analyzed pursuant to Section 8.1.2 above are used to determine concentrations found in the extracts that have not undergone fractionation. Only the aliphatic fraction is used for the calibration standards for extracts that have not undergone fractionation. However, the aliphatic calibration standards are to include both surrogates OTP and COD. Additionally, for extracts from samples known to be contaminated with #2 Fuel/Diesel, the gas chromatographic analyses may be stopped after C28 elutes, providing no peaks in the sample analysis elute after the peak represented by C28.

As noted above in 8.1.2, a calibration factor (CF) must be established for each individual component. The calibration factors established in section 8.1.2 above are used. Additionally, a separate calibration factor (CF) must be established for the total range from those compounds listed in section 2.4.1 including the first and last eluting compounds in the series (i.e., C-9 through and including C-40). For extracts from samples known to be contaminated

with #2 Fuel/Diesel, the total range calibration factor is determined using the areas from the C9 through and including the C28 peaks.

The Calibration Factor (CF) is defined as the ratio of the peak area to the concentration injected.

For individual compounds, the calibration factors are determined by the following equation.

$$CF = \frac{Area\ of\ Peak}{Concentration\ Injected\ (ng/uL)}$$

For the total range, tabulate the summation of the peak areas of all the compounds against the total concentration injected. The Calibration Factor (CF), defined as the ratio of the summed peak area to the concentration injected, is calculated for the total range using the following equation:

$$Total\ Range\ CF = \frac{Summed\ Area\ of\ Peaks\ in\ the\ Range}{Total\ Concentration\ Injected\ (ng/uL)}$$

Note that the areas for the surrogates must be subtracted out from the area summation of the range.

The percent relative standard deviation (%RSD) of the calibration factors for each compound and surrogate must be ≤ 25% over the working calibration range.

$$\%\ RSD = \frac{Standard\ Deviation\ of\ 5\ CFs}{Mean\ of\ 5\ CFs}$$

The percent relative standard deviation (%RSD) of the calibration factors for the total range for the compounds must be ≤ 25% over the working calibration range.

$$\%\ RSD = \frac{Standard\ Deviation\ of\ 5\ Total\ Range\ CFs}{Mean\ of\ 5\ Total\ Range\ CFs}$$

If any %RSD is >25%, the source of the problem should be identified and the problem resolved.

8.4 Daily Calibration for samples <u>not</u> requiring fractionation

8.4.1 The same calibration standards analyzed pursuant to Section 8.2.1 above *are* used to determine the concentrations found in the extracts that have not undergone fractionation. At a minimum, the working calibration factors must be verified on each working day, after every 20 samples or every 24 hours (whichever is more frequent) and at the end of the analytical sequence by the injection of the mid-level calibration standards. It is only necessary to calculate the percent differences (%D) between the continuing calibration factors and the average calibration factors from the initial calibrations for each compound, for the total range for aliphatic compounds and for the surrogates. If the %D of the total range is >25% (>30% for any single compound) then a new calibration

curve has to be generated. Any sample associated with a non-compliant calibration shall be reanalyzed.

$$\%D = \frac{CF_{AVG} - CF_{cc}}{CF_{AVG}}$$

Where:

CF_{AVG} = Average Calibration Factor calculated from initial calibration
CF_{CC} = Calibration Factor calculated from continuing calibration standard

8.4.2 The retention times of surrogates in the calibration verification standard analyzed at the beginning of the analytical shift must fall within the absolute retention time windows calculated in Sec. 8.3.1. The purpose of this check is to ensure that retention times do not continually drift further from those used to establish the widths of the retention time windows. If the retention time of any surrogate at the beginning of the analytical shift does not fall within the ± 3 SD window (minimum ±0.10 min.), then a new initial calibration is necessary.

In addition, the retention times of all surrogates in the subsequent calibration verification standards analyzed during the analytical shift must fall within the absolute retention time windows established in Sec. 8.3.1.4.

8.4.3 Surrogate Standards (SS) - The SS responses and retention times in the calibration check standard must be evaluated during or immediately after data acquisition. If the retention time(s) for the SS is outside the determined RT window, the chromatographic system must be inspected for malfunctions and corrections must be made. If the area(s) for the SS changes by ±50% from the last daily calibration standard check, the GC must be inspected for malfunctions and corrections must be made.

8.5 #2 Diesel Fuel Standard (optional) – This standard may be used for calculations associated with the #2 Fuel/Diesel LCS calculations only. Linearity of the gas chromatography system is demonstrated through the analyses of the individual standards noted in previous sections. As such, it is not required to generate an additional calibration curve for the #2 diesel fuel standard. The calibration factor used to calculate the LCS data is determined by the following equation

$$\#2\ Diesel\ Fuel\ CF = \frac{Summed\ Area\ of\ Peaks\ in\ the\ Range}{Total\ Concentration\ Injected\ (ng/uL)}$$

8.6 Mass Discrimination Check

8.6.1 Mass discrimination can take place in the injection port of the gas chromatograph. The higher boiling point molecules may not enter the column with the same efficiency as the lower boiling point molecules with a resulting bias toward the lower boiling molecules. This phenomenon must be checked and if present corrected prior to calibrating and analyzing samples.

8.6.2 Mass discrimination is minimized by placing a small plug of silanized glass wool one centimeter from the base of the glass injection liner. The end of the capillary column is placed just below the glass wool. The capillary column should be placed flush with the surface of the gold seal. A full range alkane standard should be run to test the degree of mass discrimination before

performing any actual sample analyses. For non-#2 Fuel/Diesel analyses, the response ratio of C30/C20 shall be ≥ 0.8. . For #2 Fuel/Diesel analyses, if the chromatography range ends at C28, then the response ratio of C28/C20 shall be ≥ 0.8. If the response ratio is less than 0.8, the column should be repositioned until the mass discrimination is minimized.

9.0 QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality control program which conforms to New Jersey Regulation N.J.A.C. 7:18-4.7 (12). The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of QC samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with laboratory established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst must make an initial, one-time demonstration of the ability to generate acceptable accuracy and precision with this method (see section 9.2).

9.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted to improve the separations by changing the GC conditions or column. Each time such a modification is made to the method, the analyst is required to repeat and document the procedure in section 9.2.

9.1.3 Each day before calibration and after the calibration, the analyst shall analyze a reagent blank (instrument blank) to demonstrate that interferences from the analytical system are under control. Peaks should not be detected above the quantitation limit within the retention time window of any carbon range of interest. If so, re-extraction of all associated samples may be warranted.

9.1.4 With each sample batch, the analyst must analyze a method blank to demonstrate that interferences from sample extraction are under control. Target compounds' concentrations in the blank should be no more than 5X MDL. If blank levels for any component are above 5X MDL and the sample concentrations present in the samples are greater than 10X then the samples may be quantified and qualified. If the blank concentration is greater than 5X MDL and the sample concentrations present in the samples are less than 10X the blank level, the affected samples should be re-extracted and re-analyzed. If a sample cannot be re-extracted or re-analyzed, the data must be qualified as such.

9.1.5 Contamination by carryover may occur when high concentration samples are analyzed. When highly contaminated sample extracts are analyzed, it is recommended that a solvent blank be analyzed immediately following to check for cross contamination. If contamination is present, the system must be cleaned before continuing sample analysis. If a sample immediately analyzed after the highly contaminated sample is free from contamination then it is safe to make the assumption that carryover or cross contamination is not an issue. However, if the sample(s) analyzed after the highly contaminated sample exhibits the same compounds and/or same chromatographic fingerprint and no system cleaning was implemented, then carryover or cross-contamination may be suspected and all affected samples may be required to be reanalyzed.

9.1.6 The laboratory must, on an ongoing basis, demonstrate through the analyses of a Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD) that the operation of the measurement system is in control. This procedure is described in sections 9.3 and 9.4. The frequency of the LCS/LCSD pair is one in every 20 samples of similar matrix.

9.1.7 The laboratory must spike all samples with the surrogates to monitor recovery. This procedure is described in section 9.5.

9.1.8 For all samples undergoing fractionation, the laboratory must spike all extracts with fractionating surrogate compounds prior to the extract being separated into aliphatic and aromatic fractions. The fractionating procedure is described in section 10.3.

9.1.9 The laboratory must spike a minimum of five percent or one per batch, which ever is more frequent of all samples in each matrix, with the MSS (see section 6.8.6) to monitor and evaluate laboratory data quality. This procedure is described in section 9.7.

9.1.10 An auto sampler vial septum should be penetrated and extracted with methylene chloride to evaluate the potential alkane distribution that could occur in re-analyzed extracts. Vial septa should be changed after each analysis.

9.2 To initially establish the ability to generate acceptable precision and accuracy, the laboratory must perform the following operations.

9.2.1 Samples undergoing fractionation

Multiple extraction and analysis of the LCSs containing aliphatic and aromatic compounds described in section 6.8.6 is required. The LCS concentrates must be prepared by the laboratory using stock standards prepared from a second source (i.e., other than the source used for calibration). All the LCSs must be prepared, extracted, fractionated and analyzed exactly as a typical environmental sample submitted for analysis.

9.2.1.1 For Soil and Sediments, prepare seven 10 g aliquots of clean sand (or sodium sulfate) spiked with 1.0 mL of MSS from section 6.8.6 and 1.0 mL of the Surrogate Spiking Solution from section 6.8.4. Follow all extraction, fractionation and analytical procedures described in this method.

9.2.1.2 Calculate the mean recovery (C_{mean}) for each of the aliphatic and aromatic compounds using the seven results. The average percent recovery for each compound must be between ±40% of the true value.

9.2.1.3 Calculate the percent relative standard deviation (%RSD) of the seven replicate analyses using the following calculation:

$$\%RSD = \frac{S_{n-1}}{C_{mean}}$$

Where

S_{n-1} = standard deviation (n-1) of the replicates

C_{mean} = mean of the concentration of a compound from the replicates

The %RSD for each compound must be less than or equal to 25%. A higher %RSD is allowed for n-Nonane but the value must be documented.

9.2.1.4 The FID retention times of the surrogates must match those in the calibration standard as described in section 8.1.1.

9.2.2 #2 Fuel/Diesel

Multiple extraction and analysis of the LCSs containing the solution described in section 6.8.10 is required. LCSs must be prepared, extracted and analyzed exactly as a typical environmental sample submitted for analysis.

9.2.2.1 Aqueous

Prepare seven 1 L aliquots of the well-mixed reagent water spiked with 1.0 mL of LCS solutions from section 6.8.10. Follow all extraction and analytical procedures described in this method.

9.2.2.2 Soil and Sediment

Prepare seven 10 g aliquots of clean sand (or sodium sulfate) spiked with 1.0 mL of LCS solution from section 6.8.10. Follow all extraction and analytical procedures described in this method.

9.2.2.3 For each matrix, calculate the mean recovery (C_{mean}) for #2 diesel fuel using the seven results. The average percent recovery for each compound must be between ±40% of the true value.

9.2.2.4 For each matrix calculate the percent relative standard deviation (%RSD) of the seven replicate analyses using the following calculation:

$$\%RSD = \frac{S_{n-1}}{C_{mean}}$$

Where

S_{n-1} = standard deviation (n-1) of the replicates

C_{mean} = mean of the concentration of a compound from the replicates

The %RSD for each compound must be less than or equal to 25%.
.

9.2.2.5 For each matrix, the FID retention times of the surrogates must match those in the calibration standard as described in section 8.1.1.

9.2.3 Aqueous samples other than #2 Fuel/Diesel

Prepare seven 1 L aliquots of the well-mixed reagent water spiked with 1.0 mL of MSS from section 6.8.6 and 1.0 mL of the Surrogate Spiking Solution from

section 6.8.4. Follow all extraction and analytical procedures described in this method.

9.3 For each analytical batch (up to 20 samples of a similar matrix) the laboratory must analyze a LCS.

9.3.1 Samples undergoing fractionation

For each analytical batch (up to 20 samples of a similar matrix) the laboratory must analyze a LCS. The LCS shall be prepared by fortifying a clean sand (or sodium sulfate) blank with 1.0 mL of the matrix spiking solution (section 6.8.6). The recoveries of each of the compounds in the LCS must be between 40% - 140%. Lower recoveries are permissible for n-Nonane but the recoveries must be greater than 25% and must be noted in the case narrative. In addition to the individual recoveries, the recoveries of each of the carbon ranges should be determined and reported. The FID retention times of the surrogates must match the previous calibration as described in section 8.1.1.

9.3.2 #2 Fuel/Diesel Samples

For each analytical batch (up to 20 samples of a similar matrix) the laboratory must analyze a LCS. The LCS shall be prepared by fortifying a reagent water or clean sand (or sodium sulfate) blank with 1.0 mL of the LCS solution (section 6.8.10). The recovery of the #2 diesel fuel used for the LCS must be between 40% - 140%. The FID retention times of the surrogates must match the previous calibration as described in section 8.1.1.

9.3.3 Aqueous samples other than #2 Fuel/Diesel

For each analytical batch (up to 20 samples of a similar matrix) the laboratory must analyze a LCS. The LCS shall be prepared by fortifying a reagent water blank with 1.0 mL of the matrix spiking solution (section 6.8.6). The recoveries of each of the compounds in the LCS must be between 40% - 140%. Lower recoveries are permissible for n-Nonane but the recoveries must be greater than 25% and must be noted in the case narrative. The FID retention times of the surrogates must match the previous calibration as described in section 8.1.1.

9.4 For the same analytical batch described in section 9.3 above, (up to 20 samples of a similar matrix) the laboratory must analyze a LCSD. The LCSD is separately prepared, processed and analyzed in the same manner as the LCS.

9.4.1 Samples undergoing fractionation

The recoveries of each of the compounds in the LCSD must be between 40% - 140%. Lower recoveries are permissible for n-Nonane but the recoveries must be greater than 25% and must be noted in the case narrative. In addition to the individual recoveries, the recoveries of each of the carbon ranges should be determined and reported. The Analytical batch precision is determined from the Relative Percent Difference (RPD) of the concentrations (not the recoveries) of the LCS/LCSD pair. The RPDs for the aliphatic and aromatic carbon range concentrations (the sum of the individual compounds'

concentrations within a carbon range) must be ≤25%. The FID retention times of the surrogates must match the previous calibration as described in section 8.3.1.

9.4.2 #2 Fuel/Diesel Samples

The recovery of #2 Diesel Fuel used for the LCSD must be between 40% - 140%. The Analytical batch precision is determined from the Relative Percent Difference (RPD) of the concentrations (not the recoveries) of the LCS/LCSD pair. The RPDs for the #2 diesel fuel must be ≤25%. The FID retention times of the surrogates must match the previous calibration as described in section 8.3.1.

9.4.3 Aqueous samples other than #2 Fuel/Diesel

The recoveries of each of the compounds in the LCSD must be between 40% - 140%. Lower recoveries are permissible for n-Nonane but the recoveries must be greater than 25% and must be noted in the case narrative. The Analytical batch precision is determined from the Relative Percent Difference (RPD) of the concentrations (not the recoveries) of the LCS/LCSD pair. The RPDs for the concentrations must be ≤25%. The FID retention times of the surrogates must match the previous calibration as described in section 8.3.1.

9.5 As a quality control check, the laboratory must spike all samples with the surrogates in section 6.8.3 and calculate the percent recovery (%R) of the Surrogate based on the FID response.

$$\%R = \frac{A_x}{A_s} * 100$$

A_x = Area response of SS in check sample
A_s = Average area response of SS in standard

9.5.1 For the surrogate standards, the laboratory must develop separate accuracy statements of laboratory performance for each matrix and for both fractionated and non-fractionated extract analyses. An accuracy statement for the method is defined as Percent Recovery ± Standard Deviation (R ± s). The accuracy statement should be developed by the analysis of four aliquots as described in section 9.2, followed by the calculation of R and s. Alternatively, the analyst may use four data points gathered through the requirement for continuing quality control in section 9.3. The accuracy statements should be updated regularly. The recovery must be within 40% - 140%.

9.5.2 Calculate upper and lower control limits for %R for the surrogate standard in each matrix.

Upper Control Limit (UCL) = R + 3s
Lower Control Limit (LCL) = R - 3s

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

9.5.3 The following corrective actions can be taken when the percent recovery of OTP and/or COD are outside of the recovery ranges:

9.5.3.1 Check calculations to assure there are no errors.

9.5.3.2 Check instrument performance. Check the sample preparation procedure for loses due to temperature control and surrogate solutions for degradation contamination, etc.

9.5.3.3 Reanalyze the extract if the steps above fail to reveal a problem. If reanalysis yields surrogate recoveries within the stated limits, the reanalysis data should be used.

9.5.3.4 For samples undergoing fractionation, if COD recovery is below the acceptance range and is observed in the aromatic fraction and/or OTP recovery is below the acceptance range and is observed in the aliphatic fraction, then re-fractionate the extract with the remaining 1 mL aliquot of extract and analyze the new extracts.

9.5.3.5 If the surrogate could not be measured because the sample was diluted prior to analysis, then qualify the surrogate recovery. Qualify the out of range surrogate on the data table. No additional corrective action is required.

9.5.3.6 If the steps above fail to reveal a problem, then it may be necessary to re-extract and re-analyze the sample.

9.6 For all samples requiring fractionation, each field and QC sample must be evaluated for potential breakthrough on a sample-specific basis by evaluating the %recovery of the fractionation surrogates and on a batch-specific basis by quantifying the concentrations of naphthalene and 2-methylnaphthalene in both the aliphatic and aromatic fractions of the LCS and LCSD. (Because naphthalene and substituted naphthalenes are weakly polar, the compounds readily mobilize into the aliphatic extract if excessive amounts of hexane are used to elute the silica gel column. As a result, the aliphatic fraction is monitored for the presence of naphthalene and 2-methylnaphthalene in the LCS and LCSD on a batch basis.) If either the concentration of naphthalene or 2-methylnaphthalene in the aliphatic fraction exceeds 5% of the total concentration for naphthalene or 2-methylnaphthalene in the LCS or LCS duplicate, then fractionation must be repeated on all stored affected sample extracts. (Note the total concentration for naphthalene or 2-methylnaphthalene in the LCS/LCS duplicate pair includes the summation of the concentration detected in the aliphatic and aromatic fractions.)

Example of Naphthalene % Breakthrough Calculation

Naphthalene in aromatic fraction	=	50
Naphthalene in aliphatic fraction	=	1.5
Total Naphthalene concentration	=	51.5
% Naphthalene Breakthrough	=	$1.5 \div 51.5 \times 100$ = 2.9%

(Note: This calculation also may be applied to determine the breakthrough of 2-methylnaphthalene.)

Additionally, if the fractionation surrogate recovery for either compound is outside 40%-140% for any sample extract then fractionation must be repeated on the affected sample.

9.7 Matrix Spike Analysis - The laboratory must, on an ongoing basis, spike and analyze at least 5% of the samples for each matrix for fractionated sample extract analyses being monitored and at least 5% of the samples for each matrix for non-fractionated sample

extract analyses being monitored to assess accuracy with the MS. It may be necessary, at the request of the Department, to perform a matrix spike for each matrix from each site even though the frequency may be greater than 5%.

9.7.1 Samples requiring fractionation

The spike is the matrix spiking standard (MSS) defined in section 6.8.6. (If a Matrix Spike Duplicate is requested, then the Relative Percent Difference (RPD) should be ≤50.)

9.7.1.1 Report the recoveries for each of the carbon ranges for each fraction.

9.7.1.2 The laboratory should establish their own acceptance criteria for % recovery (R) as in section 9.5. However, recoveries of 40-140% should be achieved for each compound.

9.7.2 Samples <u>not</u> requiring fractionation

The spike is the matrix spiking standard (MSS) defined in section 6.8.6. (If a Matrix Spike Duplicate is requested, then the Relative Percent Difference (RPD) should be ≤50.)

9.7.2.1 Report the recoveries for each compound. For a matrix spike sample associated with a batch of all #2 Fuel/Diesel sample extracts, it is only required to report recoveries of the compounds that elute up to and including C-28. If #2 Fuel/Diesel sample extracts are analyzed in a batch that contains other non-fractionated extracts, then all recoveries for all compounds in the matrix spike are to be reported.

9.7.2.2 The laboratory should establish their own acceptance criteria for % recovery (R) as in section 9.5. However, recoveries of 40-140% should be achieved for each compound.

9.8 Sample Duplicate – For both fractionated and non-fractionated extract sample analyses, the laboratory must, on an ongoing basis, analyze 5% of the samples for each matrix in duplicate. Both results are to be reported. (No specific criteria concerning the relative percent difference (RPD) exist at this time. However, results should not differ by more than 50 %.) The laboratory should establish their own acceptance criteria for RPD based on control charts. A matrix spike duplicate may be used if no positive EPH samples are in the batch.

9.9 Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.10 The laboratory shall determine the method detection limits (MDLs) for the fuels of interest using the methods of 40 CFR 136 Appendix B (13). The MDLs must be confirmed by analyzing a low level standard (2-3 X MDL).

9.11 Vendor-prepared Quality Control Samples may be requested to be both purchased and analyzed by the laboratory on a case specific basis. The results are to be within the acceptance limits provided by the vendor for that sample. If acceptable results cannot be obtained then corrective measures should be taken within the laboratory prior to any analysis of environmental samples.

10.0 PROCEDURES

In this method, the extraction procedures for aqueous and soil/sediment samples that have been detailed are manual separatory funnel liquid-liquid extraction (SW-846 Method 3510C) and Soxhlet Extraction (SW-846 Method 3540C), respectively. However, the following alternative extraction procedures and/or concentration procedures listed are acceptable provided the laboratory can demonstrate acceptable performance as described by this method: Aqueous samples may be extracted by Continuous Liquid-Liquid Extraction (SW-846 Method 3520C) or micro-extraction techniques similar to SW-846 Method 3511.. Soil/Sediment samples may be extracted by Automated Soxhlet Extraction (SW-846 Method 3541), Pressurized Fluid Extraction (SW-846 Method 3545A) or Microwave extraction (SW-846 Method 3546). The use of automated fractionation instrumentation is allowed. The use of TurboVap® and Dionex® equipment as an alternative to the method's evaporative technique is allowed.

The NJDEP will consider the use of ultrasonic extraction on a case by case basis providing the laboratory can demonstrate acceptable performance as described by this method AND the following is observed. Any laboratory wishing to use ultrasonic extraction shall have to perform side-by-side extractions, comparing sonication with an approved technique (such as soxhlet extraction) on both fortifications AND "real" samples whose identification of the petroleum product contamination has been established. For the "real" samples, at a minimum, a laboratory shall have to analyze samples contaminated with #2 fuel and samples contaminated with a heavier petroleum product (such as #4 fuel or #6 fuel). A minimum of four replicates per petroleum product type are required. Sonicaton is allowed in the Wisconsin diesel range organics method (Method for the Determination of Diesel Range Organics, Wisconsin Department of Natural Resources, PUBL-SW-141, 1992) provided samples are sonicated for 20 minutes, the solvent removed, new solvent added and sonication repeated for 20 minutes. NJDEP recommends laboratories follow that procedure. Acceptance criteria must be in line with those followed in routine gas chromatography methods.

10.1 Exceptions to Fractionation:

This procedure also allows for samples to be analyzed without fractionation. All non-aqueous samples known to be contaminated with #2 Fuel/Diesel are not required to be fractionated. Additionally, all other non-aqueous samples may first be analyzed without undergoing fractionation. If the concentration in the extract that is obtained by following the procedure noted in section 10.3.1 through and including section 10.3.2.3 below is less than 1700 mg/kg dry weight (subject to change), then no fractionation is required on the extract. Finally, aqueous samples are not fractionated.

10.2 Dissolved Product (Aqueous Samples): Separatory Funnel Extraction

10.2.1 Aqueous samples are extracted using separatory funnel techniques. The separatory funnel extraction scheme described below assumes a sample volume of 1 L. When a sample volume of 2 L is to be extracted, use 250, 100 and 100-mL volumes of methylene chloride for the serial extraction.

10.2.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2 L separatory funnel. Measure/adjust pH to 2 with 6N HCL. Add 100 ug of surrogates (1 ml of the surrogate spiking solution, section 6.8.3) into the separatory funnel and mix well.

10.2.3 Add 60 mL of methylene chloride to the sample bottle, seal and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with

periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 5 minutes.

If the analyst must employ mechanical techniques to the complete phase separation, the optimum technique depends upon the sample. The techniques may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250 mL Erlenmeyer flask with a glass stopper.

10.2.4 Add a second 60 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract. It is recommended to screen the extract (see section 10.4) before concentrating.

10.2.5 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask.

10.2.6 Pour the combined extract through a solvent rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.2.7 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Prewet each Snyder column by adding about 1 mL of methylene chloride to the top. Position the K-D apparatus in a hot water bath (60^{o}C to 65^{o}C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of the distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid has been reduced to 1 mL or less, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

10.2.8 Transfer the contents into a labeled graduated concentrator tube. Concentrate the extract to a final volume of 1 mL under a gentle stream of nitrogen. Proceed to the Section 10.5.

10.2.9 Determine the original sample volume by refilling the sample bottle to the mark with water and transferring the liquid to a 1000 mL graduated cylinder. Record sample volume to the nearest five mL.

10.3 Sample preparation, soils and sediments: Soxhlet Extraction

10.3.1 Homogenize the soil sample with a solvent-rinsed stainless steel spatula. Weigh about five grams ±.01g of the sample into a tared aluminum pan. Dry at 105 degrees Celsius for 12 hours and calculate the percent solids content (see section 11.4).

10.3.2 The Soxhlet Extraction method USEPA SW-846 Method 3540 is recommended and may be used for all sample types.

10.3.2.1 Blend 10-30g of the solid sample with 10-30g of anhydrous sodium sulfate and place in an extraction thimble. (The sample weight

used should be such that, after correction for % moisture, the dry weight of the sample is equivalent to 10 grams. Samples with expected concentrations greater than 2500 mg/Kg may be extracted using a smaller sample size.) The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet Extractor is an acceptable alternative for the thimble. Add 100 ug of the surrogate standard spiking solution onto the sample.

10.3.2.2 Place 300 mL of the extraction solvent into a 500-mL round-bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract sample for 16-24 hours at 4-6 cycles/hr.

10.3.2.3 Allow the extract to cool after the extraction is complete. Extracts may be screened before continuing (see section 10.5). Dry and concentrate the extract as in section 10.2.5 through 10.2.7. At this point, the extract may be analyzed without undergoing solvent exchange and fractionation. (Please note all extracts from samples known to be contaminated with #2 Fuel/Diesel do not require solvent exchange and fractionation.) If this is the case then proceed to Section 10.2.8. If extracts need to be fractionated, then proceed to section 10.3.2.4 below. (Note: Samples extracted for #2 Fuel/Diesel: stop at Section 10.2.7 then continue at Section 10.5.)

10.3.2.4 Exchange the methylene chloride with hexane by adding 50 ml of hexane to the top of the Snyder column. Concentrate the extract to less than 10 mL as described in 10.2.7, raising the temperature of the water bath, if necessary, to maintain proper distillation.

10.3.2.5 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of hexane. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus (see section 5.3.9). Adjust the final volume to 1.0 mL with the solvent under a gentle stream of nitrogen. (Note: Caution must be exercised during blowdown to prevent the loss of the lower boiling EPC constituents. The fraction extract volume should never be reduced below 1 mL.)

10.3.2.6 Add 1 mL of the concentrated fractionation surrogate spiking solution to the 1mL hexane extract. The resultant 2 mL extract is ready to be cleaned and fractionated using either commercially available or self-packed silica gel SPE cartridges. If cleanup will not be performed immediately, transfer the extract to a Teflon lined screw cap vial and refrigerate.

10.4 Extract fractionation

10.4.1 The silica gel cleanup and fractionation step is a critical and sensitive procedure. Small changes in the volumes of eluting solvents, fractionation equipment including the preparation of the silica gel columns and fractionation technique can impact the proportion of the hydrocarbons separated into their respective aliphatic and aromatic fractions. Care and attention is required to ensure acceptable results.

Each sample fractionation requires 1 mL of sample extract. As the final volume of the extract prior to fractionation is 2 mL, an additional fractionation is available should it be required. For example, if the original fractionation yields unacceptable breakthrough of naphthalene and/or unacceptable recoveries for the fractionation surrogate standards, the remaining 1 mL extract may have to undergo fractionation.

A commercially available 5g/20mL SPE cartridge may be used. Alternatively, columns packed with activated silica gel by the laboratory may be used. The use of activated silica gel is described in USEPA SW-846 Method 3630C.

Silica gel columns/cartridges must never be overloaded. Overloading may result in the premature breakthrough of the aromatic fraction. It is recommended that for a 1mL extract fractionated on a 5g cartridge, the extract should contain no more than 5 mg total EPH. (This equates to 25000 ug/mL in the extract or 2500 mg/Kg in the sample.)

10.4.2 Demonstrate Fractionation Capability

Every new lot of silica gel/SPE cartridges must be evaluated with the Fractionating Check Solution to establish the optimum volume of hexane to efficiently elute aliphatic hydrocarbons while not allowing significant aromatic hydrocarbon breakthrough. The amount of hexane used is critical and is to be optimized prior to the analysis of any samples. Excessive hexane can cause the elution of lighter aromatics into the aliphatic fraction. Insufficient hexane could result in low recoveries of the aliphatics. The volume of hexane used should not exceed 20 mL. A fractionation check solution (FCS) is prepared in hexane containing all the compounds listed in section 6.8.9 at a nominal concentration of 200 ng/uL each component. To demonstrate proper fractionating capability, at least four 1mL replicates of the FCSs must be fractionated using the procedures detailed in 10.3.3 below and analyzed. The mean measured concentration (C_{xmean}) of the individual fractionation compounds is determined using the following equation:

$$\%\,Mean\,Recovery = \frac{C_{x\,mean} - True\,Concentration}{True\,Concentration} * 100$$

Where $C_{x\,mean} = \frac{C_1 + C_2 + C_3 + ... + C_n}{n}$

For each analyte included in the FCS, the % mean recovery must be between 40% and 140%. Lower recoveries are permissible for n-Nonane. However, if recovery is <25% then the problem must be found and the fractionation check repeated.

10.4.3 Fractionate the extract into separate aromatic and aliphatic components.

10.4.3.1 Prepare the column by placing about 1 cm of glass wool (moderately packed) at the bottom of the column. Make sure the stopcock turns smoothly.

10.4.3.2 Fill the column with a slurry of 5 g activated silica gel in about 10 ml methylene chloride. Tap the side of the column to assure

uniform packing. Top the column with approximately 1 to 2 cm sodium sulfate.

10.4.3.3 Rinse the column/SPE cartridge with 30 ml methylene chloride if there are concerns of contaminants in the silica gel. Let the solvent flow through the column until the head of the solvent is just above the top of the column packing. Discard the eluted methylene chloride.

10.4.3.4 Rinse the column with 30 mL of hexane (60 mL if pre-rinsed with methylene chloride). Let the hexane flow through the column until the head of the column is just above the frit. Close the stopcock to stop flow. Discard the hexane.

10.4.3.5 Load 1 mL of the combined sample extract/fractionation surrogate solution (from section 10.1.10 or section 10.2.2.4) onto the column. Open the stopcock and start collecting the elutant immediately in a 25 mL flask labeled "aliphatics."

10.4.3.6 Just prior to the exposure of the column frit to air, elute the column with an additional 19 mL of hexane so a total of 20 mL of hexane has passed through the column. (It is essential that "plug flow" of the extract be achieved through the silica gel column/cartridge.) Hexane should be added in 1 to 2 mL increments with additions occurring when the level of solvent drops to a point just prior to exposing the column frit to air. The use of a stopcock is required. Ensure that the silica gel is uniformly packed in the column. The technician must be aware of any channeling, streaking or changes in the silica gel matrix during fractionation. If any occurs, it is probable that procedure shall have to be repeated with another 1 mL aliquot.

10.4.3.7 Following the recovery of the aliphatic fraction, elute the column with 20 mL methylene chloride. Collect the elutant in a 25 mL volumetric flask. Label this fraction aromatics.

10.4.3.8 Transfer the contents of the aliphatic and aromatic volumetric flasks into separate, labeled graduated concentrator tubes. Concentrate each of the extracts to a final volume of 1 mL under a gentle stream of nitrogen. Analyze each of the extracts separately.

10.4.3.9 Analyze the extracts separately.

10.4.3.10 The recoveries of the fractionation surrogates must be within 40% - 40%. If the fractionation surrogate recovery is outside 40% - 140% then fractionation must be repeated on the affected sample.

10.5 Preliminary Analysis of Extracts (Screening)

To minimize the frequency of sample reanalysis because the extract concentrations exceed the quantitation limits, screening of the extract prior to fractionation is recommended.

10.5.1 Adjust the chromatograph for maximum sensitivity.

10.5.2 Inject 1 uL of the sample extract using an auto sampler.

10.5.3 A complete profile of the extract should be obtained without saturating the detectors. The largest peak should be within the linearity of the instrument for that compound. If the response is too high, the extract should be diluted accordingly.

10.6 Chromatographic Analysis

10.6.1 One milliliter of extract ready for analysis should be transferred to a one mL GC auto sampler vial.

10.6.2 Inject 1 to 4 uL of extract using an autosampler device or the solvent plug method.

10.6.3 Instrument Performance

10.6.3.1 All of the peaks contained in the standard chromatograms must be sharp and symmetrical. Peak tailing must be corrected.

10.6.3.2 Check the precision between consecutive QC check samples. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks.

10.6.3.3 Monitor the retention time for each analyte using data generated from calibration standards. If individual retention times vary by more than ±3 standard deviations (see section 7.1.1) over a twelve hour period, then the source of retention data variance must be corrected before acceptable data can be generated.

10.6.3.4 The instrument sensitivity must be maximized. Injection of 2ul of a 1ng/ul hydrocarbon standard should yield a detector signal-to-noise ratio of at least 5:1 for the individual alkanes.

10.7 Analysis Sequence

10.7.1 This method uses a 24 hour clock or a 20 sample analytical batch, whichever time is shorter. The time sequence begins with the analysis of the first initial calibration standard or continuing calibration standard and ends with a closing calibration standard. The calibration curve must be verified every 24 hours or 20 samples, whichever is more frequent.

10.7.2 Sequence (for each fraction)

1. Instrument Blank.
2. Analytical Batch Opening Initial Calibration or mid range Continuing Calibration (required).
3. #2 Diesel Fuel Standard – optional (if samples are analyzed for #2 Fuel/Diesel)
4. Method Blanks (required).
5. Extraction Batch LCS* (required at 5% frequency of an extract type).
6. Extraction Batch LCS Duplicate* (required).
7. Samples (up to 20).
8. Matrix Spike (required).
9. Matrix Spike Duplicate (if requested).

10. Closing mid-range Continuing Calibration Standard after 20 samples (at a minimum of once every 24 hours) and at the end of an analytical batch (required). This standard may be used as the Analytical Batch Opening Continuing Calibration for the next analytical batch if batches are processed continuously.

* LCS and LCSDs are analyzed at a frequency of 1 pair per 20 sample extracts of a particular type and matrix. Due to the potential number of LCS pairs, it is suggested that sample batches be organized such that fractionated and non-fractionated sample extracts are separated and analyzed in different batches.

11.0 CALCULATIONS

11.1 Concentration of Petroleum Products

11.1.1 To calculate the concentrations in non-fractionated extracts (including #2 Fuel/Diesel extracts) and for fractionated extracts, the concentration of carbon ranges in the sample, the area response attributed to the petroleum must first be determined. This area includes all of the resolved peaks and the unresolved "envelope." This total area must be adjusted to remove area response of the solvent, surrogates and the GC column bleed.

11.1.2 Establishing the baseline

11.1.2.1 Column bleed is defined as the reproducible baseline shift that occurs during temperature programming of the GC column oven. The instrument baseline must be established by the direct injection of a system solvent blank. The injection of an air blank or activation of a temperature programmed chromatographic run without the injection of any material would be used to verify that the system noise is not attributable to solvent contamination. The instrument must be run at the actual operating conditions used to analyze all standards and samples. A system solvent blank injection should be analyzed at the beginning of the day and at a minimum after every 24 hours to determine the baseline response. The baseline is then set at a stable reproducible point just before the solvent peak. This baseline should be extended horizontally to the end of the run. When quantifying on peak areas, collective peak area integration for the fractional ranges must be from baseline (i.e., must include the unresolved complex mixture "hump" areas). However, the unresolved "hump" areas are not to be included in the integration of individual compounds such as surrogates.

11.1.2.2 The baseline for the sample should be set in the same manner. The area in the sample will contain the area attributed to petroleum and that attributable to the baseline. Aliphatic and aromatic hydrocarbon carbon range data for the area between C9 and C40 may be corrected by the automatic or manual subtraction of the baseline area from the system solvent blank. Correction in this manner is not recommended or preferred but permissible in cases where reasonable steps have been taken to minimize or eliminate excessive baseline bias associated with analytical system noise.

11.1.2.3 If baseline correction is used, then the baseline must be re-established for every analytical batch by the analysis of a system solvent blank.

11.1.2.4 As the concentration of any carbon range in the sample approaches the quantitation limit, the baseline correction becomes more critical.

11.2 External standard calibration for fractionated extracts

The concentration of each carbon range for each fraction in the sample is to be determined by calculating the amount of analyte injected, from the peak response, using the calibration factor. The area of the surrogates must be subtracted from their corresponding carbon range summed area. Additionally, any areas associated with naphthalene and/or 2-methylnaphthalene in an aliphatic carbon range are to be subtracted from the appropriate aliphatic carbon range summed area prior to calculating the calibration factors. The concentration of a specific carbon range is calculated as follows:

11.2.1 Nonaqueous - Soils/Sediments/Sludge

$$C(ug/g) = \frac{(A)(D)(V_e)}{CF(S)}$$

Where:

C = Concentration of each compound or hydrocarbon carbon range, ug/g (dry weight basis)

A = Area response of each compound or carbon range to be measured.

D = Dilution Factor

V_e = Final volume of the extract, uL

CF = Calibration Factor of each compound or carbon range for each fraction (see section 8.1.2).

Where:

$$CF = \frac{Summed\ area\ or\ peaks\ or\ Summed\ area\ of\ peaks\ in\ carbon\ range}{Total\ concentration\ injected\ (ng/uL)}$$

S = Dry sample weight, mg

11.2.2 Total EPH Concentration = Total of the 4 Aromatic carbon ranges and 4 Aliphatic carbon ranges.

11.3 External Calibration for non-fractionated extracts (including #2 Fuel/Diesel extracts and aqueous samples) - The concentration in the sample is to be determined by calculating the amount of analyte injected, from the peak response, using the calibration factor. The area of the surrogates must be subtracted from the summed area. The concentration is calculated as follows:

11.3.1 Aqueous samples

$$C(ug/L) = \frac{(A)(D)(V_e)}{CF(V_s)}$$

Where:

C = Concentration of each compound, ug/L

A = Area response of each compound to be measured.

D = Dilution Factor

V_s = Volume of sample extracted, mL

V_e = Final volume of the extract, uL

CF = Calibration Factor of each compound (see section 8.3.2)

Where:

$$CF = \frac{Peak\ Area\ or\ Summed\ area\ of\ peaks\ in\ carbon\ range}{Total\ concentration\ injected\ (ng/uL)}$$

11.3.2 Nonaqueous - Soils/Sediments/Sludge

$$C(ug/g) = \frac{(A)(D)(V_e)}{CF(S)}$$

Where:

C = Concentration of each compound, ug/g (dry weight basis)

A = Area response of each compound to be measured.

D = Dilution Factor

Ve = Final volume of the extract, uL

CF = Calibration Factor of each compound (see section 8.3.2).

Where:

$$CF = \frac{Summed\ area\ or\ peaks\ or\ Summed\ area\ of\ peaks\ in\ carbon\ range}{Total\ concentration\ injected\ (ng/uL)}$$

S = Dry sample weight, mg

11.4 Percent Recovery of Surrogate Standard(s)

Percent recovery based on External Calibration

$$\%\ SS\ Recovery = \frac{C_{of}}{C_{ot}} * 100$$

Where:

C_{of} = Concentration of surrogate found
C_{ot} = Concentration of surrogate added

11.5 Percent Solids (P)

$$P = \frac{D_s}{T_s} * 100$$

Where:

D_s = Weight dry Sample, g
T_s = Weight wet Sample, g

11.6 Dry Weight (S)

$$S = \frac{Wet\ Weight\ x\ P}{100}$$

Where:

P = Percent solids

12.0 REPORTING REQUIREMENTS AND DELIVERABLES

The following information must be provided to the Department upon request. The Laboratory must keep this information on file and available for inspection by the Department as per N.J.A.C. 7:18 (12).

12.1 Chain of Custody Documents.

For every sample submitted to the laboratory, both field (external) and laboratory (internal) chain of custody documents MUST be provided at the end of the final data report. The chain of custody must show the signatures of the sample custodian, extraction supervisors and any other personnel who handled the sample. It must clearly track the movement of the sample through the laboratory by showing the relinquishing and acceptance of the sample by each person. Tracking may be accomplished electronically if laboratory personnel have user specific password-protected access to their respective LIM systems that track sample movement through the laboratory.

12.2 Methodology Review

The laboratory shall provide a brief narrative outlining the essential points of each method actually employed in the analysis of the samples submitted to the laboratory.

12.3 Non-Conformance Summary Report

The laboratory shall describe in narrative and/or tabular form any item which does not conform to the requirements of this method. This shall include but is not limited to a discussion of missed holding times, failed Quality Assurance/Quality Control criteria, sample matrix effects on the analysis, sample dilutions, re-analyses, corrective actions

taken and deviations from the analytical method specified on the analytical request form or the preparative methods permitted.

12.4 Sample Data Package - must contain the following information. The information should be provided in the following sequence.

12.4.1 Quantitative Sample Results Summary (uncorrected for blank), Blank Results and Method Detection Limits. For samples that have undergone fractionation, results for each of the concentrations calculated for the eight (8) carbon ranges plus a total EPH concentration must be provided; none of these results are to be rounded. For samples that have not undergone fractionation, results for the total concentrations are to be reported; none of these results are to be rounded.

12.4.2 Quantitation Reports. All field samples, QC samples, standards and blanks must have the following information provided:

12.4.2.1 date collected.
12.4.2.2 date received.
12.4.2.3 date extracted.
12.4.2.4 date analyzed.
12.4.2.5 time analyzed.
12.4.2.6 dilution factor.
12.4.2.7 % Moisture (or % solids).
12.4.2.8 Concentrations of individual peaks and/or carbon ranges.

12.4.3 Sample Chromatograms

The chromatograms must be clearly labeled with the following information:

12.4.3.1 Sample identification number.
12.4.3.2 Volume injected.
12.4.3.3 Date and time of injection.
12.4.3.4 GC Column identification.
12.4.3.5 GC instrument identification - exact instrument employed.
12.4.3.6 Carbon ranges identified, either directly above the peak or on a printout of retention times, if the retention times are printed on chromatograms.
12.4.3.7 Surrogates labeled.
12.4.3.8 Fractionation Surrogates labeled.
12.4.3.9 Analyst signature.

12.4.4 Quality Control Summary - must contain the following items:

12.4.4.1 Surrogate Recoveries (for all field samples and QC samples) including fractionation and extraction surrogates.
12.4.4.2 QC Check Sample Results (if analyzed).
12.4.4.3 LCS Results.
12.4.4.4 LCSD Results.
12.4.4.5 Method Blank Summary.
12.4.4.6 Matrix Spike Summary.
12.4.4.7 Matrix Spike Duplicate Summary (if requested).
12.4.4.8 Duplicate Sample Results Summary.
12.4.4.9 Percentage of total naphthalene and 2-methylnaphthalene concentrations detected in the aliphatic fractions of the LCS/LCSD (where applicable).

12.4.4.10 Fractionation Check Solution results (where applicable).

12.4.5 Standard Data Packages - must contain the following items:

12.4.5.1 Initial Calibration Data Summary.
12.4.5.2 Continuing Calibration Data Summary.
12.4.5.3 Chromatograms of Standards.
12.4.5.4 Quantitation Reports.
12.4.5.5 Summary of retention times of each identified marker compound used to define the beginning and end of each carbon range for each fraction.

12.4.6 Raw QC Data Package - additionally must contain the following items:

12.4.6.1 Blank Chromatograms.
12.4.6.2 QC Check Sample Chromatograms (if analyzed).
12.4.6.3 LCS/LCSD Chromatograms.
12.4.6.4 Quantitation Reports

12.4.7 Raw Sample Data package - must contain the following items:

12.4.7.1 Sample chromatograms.
12.4.7.2 Quantitation reports containing at a minimum the retention times and associated areas of <u>all</u> individual chromatographic peaks from the analysis.

REFERENCES

1. Method for the Determination of Extractable Petroleum Hydrocarbons (EPH), Massachusetts Department of Environmental Protection; Division of Environmental Analysis, Office of Research and Standards, Bureau of Waste Cleanup, May 2004, Revision 1.1.

2. Method for the Determination of Extractable Petroleum Hydrocarbons (EPH) Fractions, Washington State Department of Ecology, June 1997.

3. Leaking Underground Fuel Tank, Task Force "Leaking Underground Fuel Tanks Field Manual," Appendix C, State Water Resources Control Board, Sacramento, CA 1988.

4. U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste -- Physical Chemical Methods, Office of Solid Waste, Washington, DC, Publication SW846, 3rd ed. update III 1996.

5. Florida Department of Environmental Protection, "Method for Determination of Petroleum Range Organics," Method #FL-PRO, rev.1a, March 14, 1997.

6. Miller, M., "Quantitation of Semi-Volatile Petroleum Products in Water, Soil, Sediment, and Sludge," NJDEP OQA-QAM-025-02/08.

7. ASTM, "Comparison of Waterborne Petroleum Oils by Gas Chromatography," Method D3328-90, Annual Book of ASTM Standards, Volume 11.01, Philadelphia, PA, 1990.

8. Staff, Oil Spill Identification System, Report No. GCD-52-77, U.S. Coast Guard R & D Center, page D1, National Technical Information Center, Springfield, VA 1977.

9. "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).

10. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

11. "Chromatography Products," RESTEK; Bellefonte, PA, 2006.

12. New Jersey Department of Environmental Protection, "Regulations Governing Laboratory Certification and Standards of Performance," N.J.A.C. 7:18.

13. U.S. Environmental Protection Agency, Federal Register, 40CFR136, Appendix B, Volume 49, No. 209, July 1, 1990.

LIST OF MAJOR METHOD CHANGES IN THIS REVISION

Numerous sections have been modified and/or added to allow for the extraction and analysis of samples without having to perform fractionation (Sections 1.3.4; 2.3; 2.3.2; 2.5; 6.8.1; 6.8.10; 6.8.11; 8.3; 8.4; 8.5; 8.6.2; 9.2.2; 9.2.3; 9.3.2; 9.3.3; 9.4.2; 9.4.3; 9.7; 9.8 ; 10.2; 10.3; 10.7.2; 11.1.1; 11.3; and 12.4). Specifically, known #2 fuel/diesel samples and all aqueous samples do not undergo fractionation. Additionally, the method allows for non-#2 fuel/diesel samples to first undergo analysis without fractionation and depending on the result, the sample extraction may be allowed without further fractionation. As a result of these changes, sections have been added to allow for the new method approach.

Section numbers have been updated in some instances for accuracy and consistency.

Section 1.1: A mass spectrometer has been added as a detector option.

Section 2.5: A #2 Diesel fuel standard has been added for quantitation of a #2 Fuel/Diesel LCS.

Section 6.8.1: Ortho-terphenyl is added to the aliphatic standard solution to allow for surrogate recovery calculations from those extracts not undergoing fractionation.

Section 6.8.6: Methanol and acetone has been removed as it is difficult to get all the compounds in solution using either of the solvents. Pentane has been added to the section.

Section 6.8.10: A #2 Fuel/Diesel LCS Solution has been added.

Sections 8.2 : “for samples undergoing fractionation” has been added.

Sections 8.3, 8.4 and 8.5: Calibration requirements for samples not requiring fractionation have been added.

Section 8.12: Surrogates are at the same concentrations as the individual components.

Section 9.1.8: “For all samples undergoing fractionation” has been added.

Section 9.5: “P” was changed to “R” in all equations.

Section 9.6: “For all samples requiring fractionation” was added.

Section 10: Alternate extraction and/or concentration procedures have been added to the method.

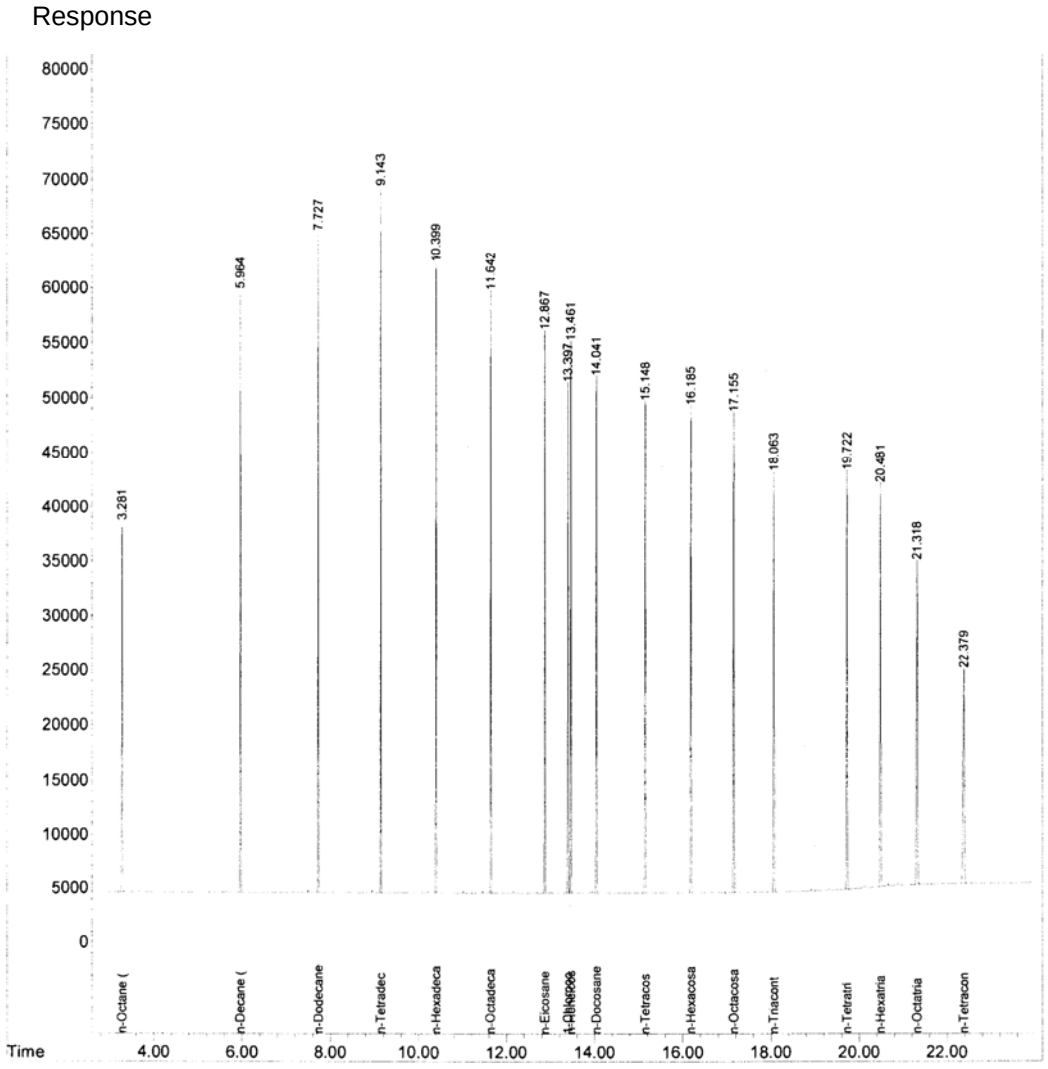
Section 10.1: Exceptions to fractionation are listed.

Sections 10.2.8 and 10.3.2.3: These sections are included to bypass the fractionation procedure.

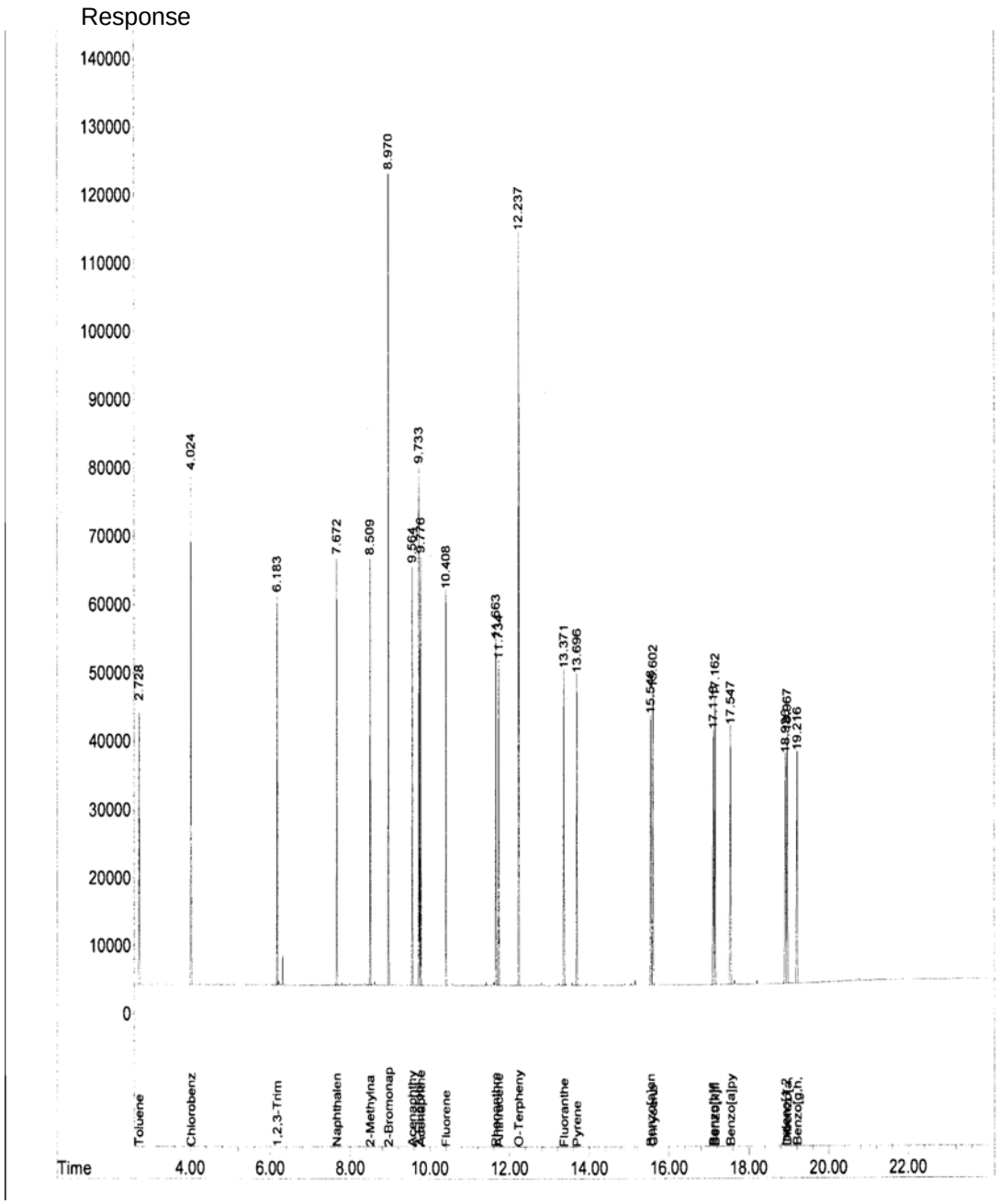
Section 12.4.1: The rounding of sample results has been addressed.

EXAMPLE CHROMATOGRAMS

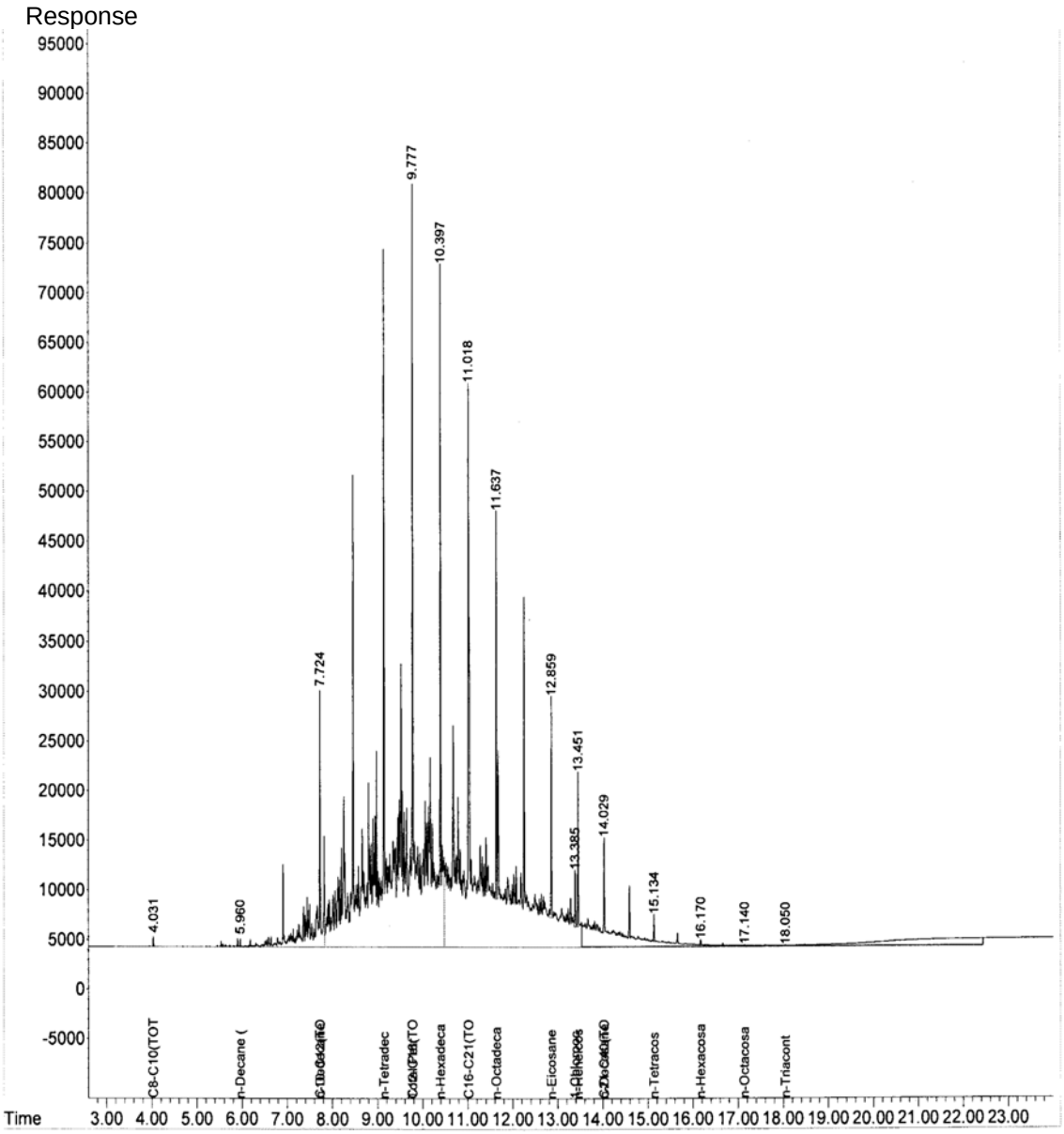
Aliphatic Standard (Each component at 100 mg/Kg)



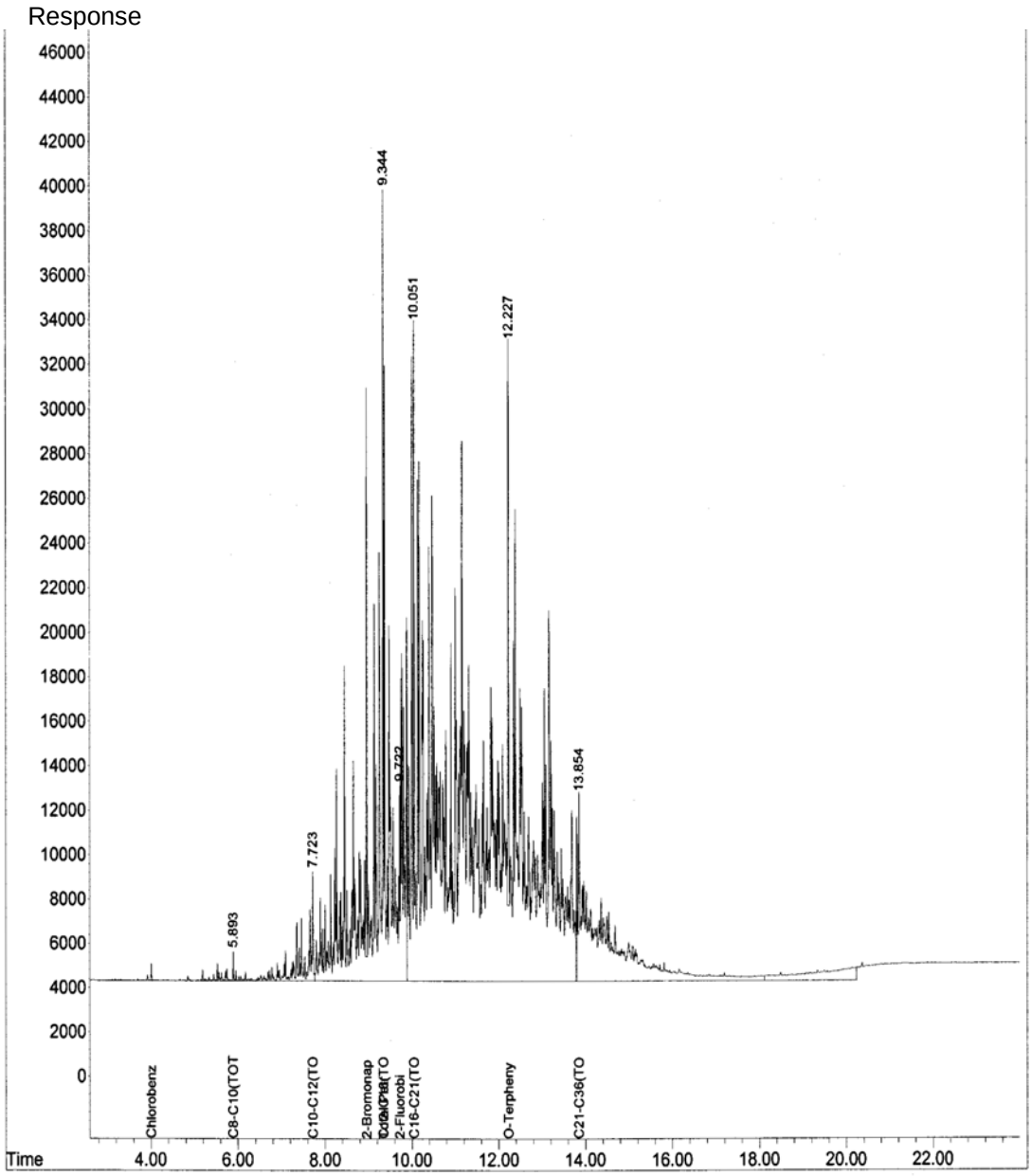
Aromatic Standard (Each component @ 100 mg/Kg)



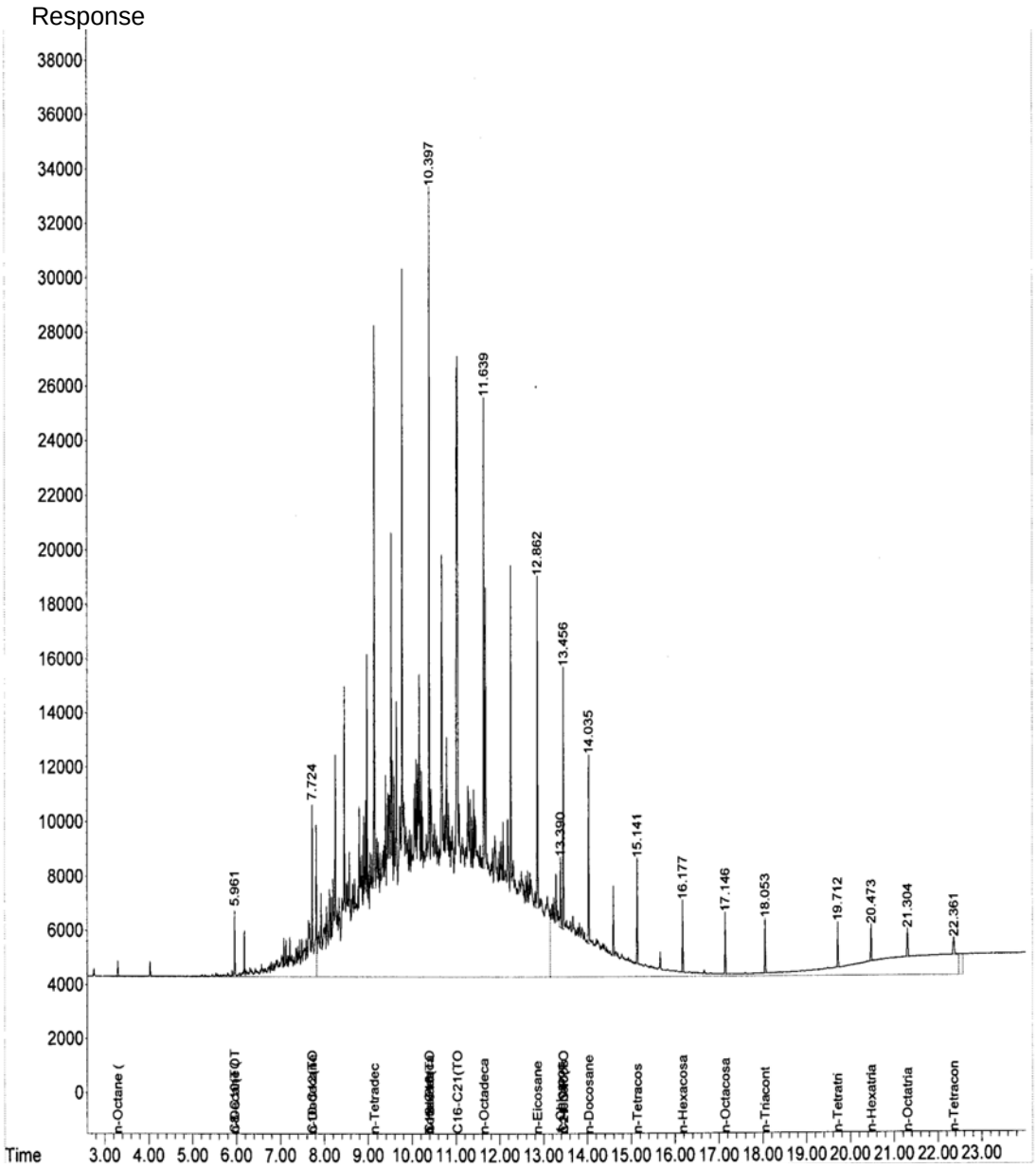
Soil Sample
Aliphatic Fraction
Total EPH Concentration @ 5800 mg/Kg



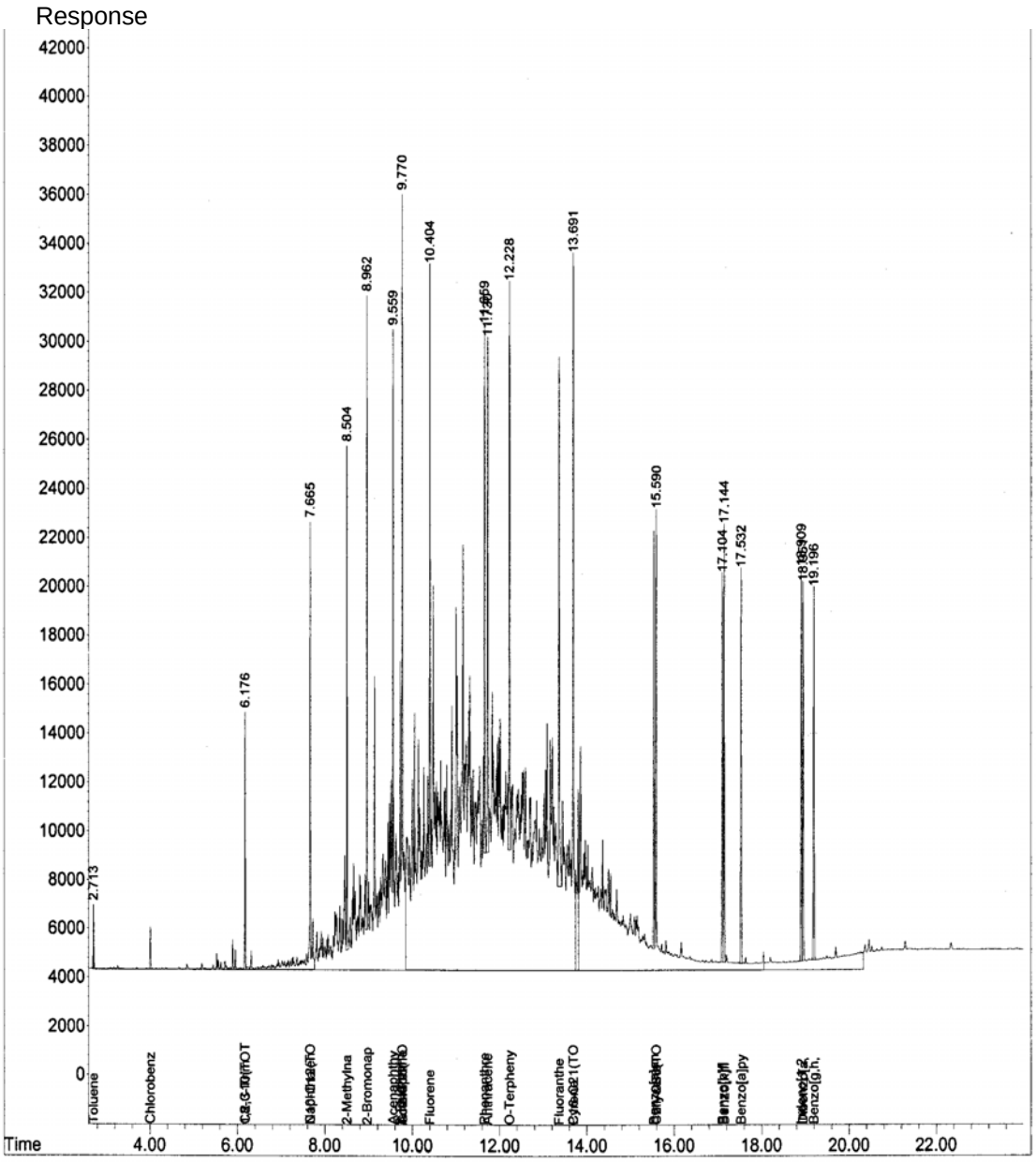
Soil Sample
Aromatic Fraction
Total EPH Concentration @ 5800 mg/Kg



Matrix Spike
Soil Sample
Aliphatic Fraction



Matrix Spike
Soil Sample
Aromatic Fraction



APPENDIX B

RESUMES

CAROL S. GRAFF, PG, LSRP, PROJECT MANAGER

EDUCATION

Bachelor of Science in Geology
Juniata College, Huntingdon, Pennsylvania

EXPERIENCE

Ms. Graff has over 35 years of hydrogeological and environmental science experience in public service and as a consultant. She was a section chief for the New Jersey Department of Environmental Protection's Bureau of Water Allocation as a supervising geologist in the NJDEP Bureau of Geology and Topography before becoming a consultant. She was the President of the Northeast section of the American Institute of Professional Geologists and New Jersey Groundwater Association. She is currently the Treasurer of the New Jersey Groundwater Association.

REGULATORY COMPLIANCE

Ms Graff spent over 20 years with the New Jersey Department of Environmental Protection, in her positions she was involved at both the technical and managerial levels with the management and implementation of programs related to water management and the contamination of private and industrial wells during the beginning of the environmental movement.

In the private sector, Ms Graff was involved in regulatory audits of industrial clients. This work enabled companies to come into conformance with the many environmental initiatives of the federal and state governments.

PROPERTY ASSESSMENTS

Ms. Graff has participated in the investigation and inspection of properties ranging from low environmental concerns through major Superfund sites. These projects have involved the simple walkthrough with verbal recommendations for improvements to full RCRA audits.

Ms. Graff has conducted property reviews equivalent to Phase I Environmental Site Assessments in ten states, evaluating the operations and site conditions of forges, metal finishing operations, hat manufacturers, pharmaceutical manufacturers, junk and salvage yards, garden apartment complexes and numerous other operations.

Ms. Graff has participated in the successful completion of ISRA/ECRA projects for a wide variety of clients - a non-exhaustive sampling includes: tool and die works, chemical plants, pharmaceutical facilities, metal workers, tanning facilities and woodworking shops, printers, plating operations and tank fabricators.

Other ISRA/ECRA services provided include preparation of applications for Innocent Party Grants, Expedited Review, Letters of Nonapplicability, Certificates of Limited Conveyance, De

Minimis exemptions, Negative Declaration approvals, and negotiations with the NJDEP on ACO conditions and financial assurance levels.

HAZARDOUS MATERIALS

Ms. Graff is fully versed in the requirements of the USEPA, USDOT, NJDEP and PADEP governing the treatment, storage and disposal of hazardous materials. She has inspected regulated sites and maintained daily logs as well as arranging transport/disposal and completing manifests and related documents.

DUE DILIGENCE REVIEWS

Ms. Graff has served attorneys, banks, realtors and private concerns by reviewing historical and ongoing projects for both technical accuracy and administrative completeness. These activities have ensured that there are no lingering environmental questions that could adversely affect buyers, sellers and future operators. In a number of cases, these reviews have led to litigation support in the form of discovery preparation, depositions and court appearances as an expert witness.

LITIGATION SUPPORT

Ms. Graff has assisted in the preparation of interrogatories and the deposition of opposing witnesses. Her work includes writing expert reports for pending litigation and supporting those reports as an expert witness at deposition and in court. This support has been provided to plaintiffs and defendants at the state and federal court levels.

CONTRACT RESPONSIBILITIES

- Coordinate and schedule all soil and ground water sampling investigation activities and provide overall supervision.
- Prepare bid specifications, cost estimates and letter agreements.
- Provide training to junior staff in all technical and administrative areas.
- Provides environmental consulting on soil and ground water investigations.
- Ensures compliance with regulations and safety guidelines.
- Reviews contract drawings and specifications.
- Prepare contracts and specifications for water supply development projects and provide overall supervision.

REGISTRATION AND PROFESSIONAL CERTIFICATION

NJDEP Licensed Site Remediation Professional No. 573809,
OSHA HAZWOPER Training (29 CFR 1910.120),
Certified Professional Geologist, No. 6429
Professional geologist licensed in the States of Florida, Kentucky and Pennsylvania

SERGIO CARDOSO, PROGRAM MANAGER

222 Thies Road, Sewell, NJ 08080

EDUCATION

Philadelphia College of Art, 1988
Associate of Architectural Design, Design Institute, 1986

PROFESSIONAL DATA AND CERTIFICATIONS

OSHA 40 Hour Hazardous Waste Operations Certification - 29 CFR 1910.120 (e)
Asbestos Project Inspector Certification - New Jersey
Lead Hazard and Abatement Certification - EPA/HUD, Maryland
Licensed XRF Spectrum Analyzer Operator

PROFESSIONAL SUMMARY

Mr. Cardoso has more than 20 years experience in the environmental consulting arena. His expertise is in the management, design and preparation of construction documents as well as the management of environmental remediation projects. Mr. Cardoso has managed a wide variety of environmental projects including environmental remediations, environmental site investigations, building surveys for the presence of environmental contaminants and sub-surface evaluation for soil contaminants. In addition, Mr. Cardoso has provided contractor oversight services for a variety of clients including, The City of Philadelphia and The Chester County Housing Authority. Through his work on construction and remediation projects he has gained valuable insight on the management of waste streams with local and out of state disposal facilities. Mr. Cardoso's diverse project experience affords him the ability to interface effectively on a wide range of projects including Architectural, Mechanical and Civil Engineering disciplines.

REMEDIATION PROJECTS

- **Former RCA Nipper Building, Camden, New Jersey** - Mr. Cardoso served as the project manager for the environmental remediation of this former industrial facility. The project included No. 2 and No. 6 heating oil underground storage tank removals, soil excavation and disposal, and groundwater remediation. The contaminants discovered in the soil included very high levels of Polychlorinated biphenyls (PCB's) and Trichloroethene (TCE). As a result of the high concentrations of contaminants this project offered unique challenges relative to treating and disposing of the hazardous soil and groundwater. Hydrogen Release Compound (HRC) was introduced to the soil/groundwater interface as a remedial alternative to the remaining on-site TCE contaminated groundwater. In addition, this project presented logistical challenges due to the on-going building renovation and the high profile nature of the project. The project was completed within the stringent deadline and the final cost was below forecasted budget.

- **Curtiss Wright Facility, Fairfield, New Jersey** - Mr. Cardoso served as project manager for a soil remediation project at this former aircraft parts manufacturing facility. As a result of the former function of this facility the subsurface soils were impacted with Polychlorinated biphenyls (PCB's) and Trichloroethene (TCE) as well as other solvent related compounds and metals. The impacted area of concern was located inside the building. As such, constant respiratory protection, ventilation and monitoring controls were utilized. This project presented unique challenges mostly because of work area constraints. Various pieces of heavy equipment were utilized to remove the floor, excavate the soil and stockpile the materials outside the building. Upon completion of the excavation the contaminated soil, which had been segregated according to its hazardous or non-hazardous classification, was disposed off-site at state approved facilities accordingly, and the site was restored.

- **Domestic Violence Center of Chester County, West Chester, Pennsylvania** - Mr. Cardoso served as the project manager and project designer for the environmental remediation and building renovation of this facility. The purpose of this project was to completely remove and dispose of all asbestos containing materials and remediate all lead-based painted materials. In addition the project included the complete renovation of the facility interior as well as exterior. Mr. Cardoso prepared plans and specifications for this project which included asbestos and lead-based paint abatement, roof replacement, window and door replacement, drywall enclosures, heating system upgrade along with many other building system component renovation and replacement. Mr. Cardoso was responsible for enforcing contractors schedule, approving all replacement material submittals and maintaining the project within budget.

- **Private Residence, Florence, New Jersey** - Mr. Cardoso served as the project manager for the removal of seven underground storage tanks. Upon removal of the tanks impacted soils were discovered. As such, impacted soils were excavated and disposed off site at a state approved recycling facility. Subsequent to the excavation and confirmatory sample collection the excavation was backfilled with certified clean fill. The site was restored in accordance with local and county requirements. Restoration services included the installation of a new concrete driveway and walkway, new topsoil and seed. Although there was no evidence of an impact to groundwater, the site was relatively close a public water supply well and water testing was required to be performed. Monitoring wells were installed and testing was performed in accordance with New Jersey Department of Environmental Protection requirements.

PHASE I AND PHASE II ENVIRONMENTAL SITE INVESTIGATIONS

- **Redevelopment Authority of the City of Philadelphia, Philadelphia, Pennsylvania** - Mr. Cardoso has served as the project manager for numerous environmental and demolition projects performed throughout the City of Philadelphia. Projects typically consist of entire city blocks, which are deemed to be demolished. A typical project will involve performing a Phase I environmental assessment including a comprehensive asbestos containing building material (ACBM) investigation. Once the assessment is completed, a remedial work plan is prepared for each individual building and distributed to contractors for bid solicitation. Mr. Cardoso remains as the city's representative throughout the abatement and demolition process in order to maintain quality assurance, resolve unforeseen issues and approve contractor's payment.

- **CCHA 57 Phase I Sites** – Mr. Cardoso was the Project Manager, responsible for the implementation of fifty-seven Phase I Environmental Site Assessments for the Chester County Housing Authority. The sites consisted of both occupied and unoccupied lands of varying size. The ESA included evaluation for both ASTM recognized environmental conditions and potential asbestos containing materials when structures were encountered. The Phase I ESA was competed on time and on budget.

- **Remington & Vernick Engineers, Haddonfield, New Jersey** - Mr. Cardoso continues to serve as the Project Manager for various environmental site investigations undertaken throughout the State of New Jersey. Conducted in conformance with NJDEP requirements, past projects have included evaluations pertaining to the disposition of underground and aboveground storage tanks, asbestos-containing materials and lead-based paint. Typically these projects require the utilization of heavy construction equipment for test pit excavation, and usually require demolition, replacement of overburden and disposal of waste materials. Mr. Cardoso's responsibility included site safety, crew supervision, excavation, overburden replacement, development of sampling protocols and report preparation.

- **Housing Authority of Chester County, West Chester, Pennsylvania** - Mr. Cardoso served as the project manager for a Phase I environmental assessment of two county owned facilities. As a result of the Phase I environmental assessment one of the facilities required a Phase II environmental assessment and the removal of an underground storage tank. During the course of removing the underground storage tank contaminated soil was encountered. The contaminated soil was removed until clean uncontaminated soil was encountered. The contaminated soils waste stream was managed and disposed of under local and state regulations. This was a full service environmental project, from the Phase I environmental assessment to all necessary environmental remediation, in order to give the client an environmentally clean property for future development.

ASBESTOS AND LEAD BASED PAINT AND HAZARDOUS MATERIALS

- **Con Edison of New York, Inc., White Plains, New York** - Mr. Cardoso was the Project Manager for a multi-facility asbestos-containing material and lead-based paint investigation conducted for Con Edison at their White Plains Sub-Station and affiliated Service Centers in New York State. The constraints of this project were especially challenging in that the Sub-Station had to remain on-line during the investigation. Mr. Cardoso developed the sampling plan for the project in accordance with applicable State and Federal regulations. Subsequent to the survey, Mr. Cardoso prepared the reports and management plans for all four facilities utilizing a custom CAD software system. The project was conducted within the client's specified time frame and under budget.

- **Smithsonian National Museum of Natural History, Washington, DC -** Mr. Cardoso was the Project Manager for a comprehensive inspection for the presence of asbestos containing building materials (ACBM) in the Smithsonian National Museum of Natural History. Anticipating a major renovation of the HVAC and mechanical systems of the facility, Mr. Cardoso lead a team of licensed building inspectors through a comprehensive evaluation of the building with the intent of ascertaining the location and condition of suspect ACBM and evaluating the potential impact of same on the proposed multi-million dollar renovation. Subsequent to the assessment, Mr. Cardoso correlated all survey information with the laboratory data for use in the preparation of a comprehensive abatement design plan. Asbestos abatement plans and specifications were prepared in the Smithsonian National Museum of Natural History's required format.

- **Sunshine Biscuits, Inc., Nationwide** - Mr. Cardoso was responsible for the preparation of reports and plans associated with asbestos-containing material investigations for various facilities throughout the country. Reports and drawings were created utilizing a custom CAD software system. Project included the conversion and transfer of existing CAD drawing files to fit a format required by the client. All of the reports were exported into the Microsoft Access format for client manipulation. All of the reports and plans are revised periodically.

JORGE GOMEZ, PG, LSRP, PROGRAM MANAGER

WORK EXPERIENCE

2005 – Present	Program Manager, USA Environmental Management, Inc
2002 – 2005	Project Manager, TRC Raviv Associates, Inc.
1999 – 2002	Project Manager, Prestige Environmental, Inc
1998 – 1999	Project Manager, GA Environmental Services, Inc.
1993 – 1998	Senior Hydrogeologist, Vince Uhl Associates, Inc.
1988 – 1993	Staff Hydrogeologist, Geraghty & Miller, Inc.

EDUCATION

B.S., Geology, York College, The City University of New York.

EXPERIENCE

Mr. Gomez has over 20 years of experience encompassing:

- Remedial investigations at State and Federal Superfund sites
- NJDEP PA/SI/RI Remedial Oversight & Case Closure Reporting
- UST Closures and UST/AST installations
- Design of ground-water monitoring and recovery systems
- Delineation and remediation of soils and ground water
- Site assessments at commercial and industrial facilities
- Preparation of expert reports
- Ground-water exploration programs in unconsolidated and bedrock aquifers
- Interpretation and analysis of aquifer pumping test data
- Preparation of hydrogeologic study reports
- Implementation of well restoration programs

Mr. Gomez has managed numerous soil and ground water investigations projects at chemical plants, oil refineries, manufacturing facilities, and gas service stations in the Eastern United States and Puerto Rico. His responsibilities include preparation of cost estimates, coordination of field activities, meeting with clients, attorneys and regulatory agencies, subcontractor hiring and scheduling, implementation of monitoring programs and data management, preparation of preliminary assessment reports, preparation of remedial investigation reports (RIR) and remedial action workplans (RAW), preparation of underground storage tank (UST) closure reports, evaluation of technical documents, and preparation of expert reports. Mr. Gomez has also managed numerous ground water supply development projects in the northeastern United States, the Caribbean and Africa. Job responsibilities included: preparation of specifications, performance of aquifer pumping test, supervision of installation of large capacity wells, pumping test analysis using several models, preparation of hydrogeologic reports for water allocation permits, and rehabilitation of water supply wells.

ENVIRONMENTAL SITE ASSESSMENTS

Mr. Gomez has prepared numerous Phase I Environmental Site Assessments for residential, commercial, and industrial facilities. Job responsibilities include the following:

- Site inspections.
- Review of property records, aerial photographs, Sanborn Fire Maps, and environmental records.
- Preparation of Phase I reports.
- Clients included the City of Trenton, the City of Philadelphia, and many other private clients and/or lending agencies.

TANK CLOSURE AND UST/AST INSTALLATION

Managed large-scale underground storage tank (UST) projects in the State of New Jersey and the private sector. Tasks associated with these projects included the following:

- Preparation of bid specifications.
- Construction management.
- Preparation of air permits.
- Subcontractor procurement, contractor coordination and scheduling.
- Oversight of UST removals.
- Design and installation of USTs and above ground storage tanks (AST).
- Soil characterization, soil remediation, and post-excavation sampling activities.
- Preparation of UST closure reports.
- Clients include the State of New Jersey, the City of Trenton, several insurance companies, and private clients.

SOIL AND GROUND WATER INVESTIGATIONS

Mr. Gomez has managed numerous soil and ground water investigations projects at chemical plants, oil refineries, manufacturing facilities, and gas service stations in the Eastern United States and Puerto Rico. Tasks associated with these projects included the following:

- Preparation of cost estimates for small and large scale projects.
- Coordination of field activities, meeting with clients, attorneys and regulatory agencies, subcontractor hiring and scheduling.

- Implementation of monitoring programs and data management.
- Preparation of preliminary assessments, remedial investigation reports (RIR) and remedial action workplans (RAW).
- Evaluation of technical documents and preparation of expert reports.
- Preparation of Deed Notices and Classification Exception Areas (CEA) reports.
- Soil and ground water sampling and ground water flow analysis.
- Design of monitoring and recovery systems and investigation/remediation of hydrocarbon spills.

GROUND WATER SUPPLY DEVELOPMENT

Managed numerous ground water supply development projects in the northeastern United States, the Caribbean and Africa. Job responsibilities included:

- Preparation of specifications and design of large capacity supply wells.
- Review of hydrogeologic data and preparation of hydrogeologic test proposals.
- Ground water exploration in glacial deposits and bedrock formation.
- Supervision of surface geophysics, installation of test wells, and borehole logging.
- Supervision of installation of large capacity wells in glacial deposits and bedrock formations using several drilling methods.
- Performance of step-drawdown and long-term aquifer pumping test, and data analysis using several models.
- Preparation of a water allocation permit and hydrogeologic reports.
- Rehabilitation of water supply wells.

CONTRACT RESPONSIBILITIES

- Coordinate and schedule all soil and ground water sampling investigation activities and provide overall supervision.
- Prepare bid specifications, cost estimates and letter agreements.
- Provide training to junior staff in all technical and administrative areas.
- Provides environmental consulting on soil and ground water investigations.
- Ensures compliance with regulations and safety guidelines.
- Reviews contract drawings and specifications.
- Prepare contracts and specifications for water supply development projects and provide overall supervision.

REGISTRATION AND PROFESSIONAL CERTIFICATION

Certified Professional Geologist, American Institute of Professional Geologists License CPG-09509.
Professional Geologist - Commonwealth of Pennsylvania, License No. PG-003185-G.
Professional Geologist – State of Delaware, License No. S4-0001167.
New Jersey Department of Environmental Protection (NJDEP) Licensed Site Remediation Professional (LSRP) License No. 519188.
New Jersey Department of Environmental Protection (NJDEP) Subsurface Investigation, Underground Storage Tank (UST) License No. 0010902.
40-Hour Health and Safety Training Program, Geraghty & Miller, Inc., Conshohocken, Pennsylvania**,** 1988.
Annual 8-Hour Refresher Course, Occupational Health and Safety Training Program, 29 CFR 1910. 120, OSHA.
Regulatory Training in Underground Storage Tanks, Rutgers State University, Cook College, New Brunswick, New Jersey.
8-hour OSHA Supervisor Health and Safety Training, Geraghty & Miller, Inc, Conshohocken, Pennsylvania, 1991.
Fundamentals in GIS, Rutgers State University, Cook College, New Brunswick, New Jersey, 2001.
Site Remediation Basics, Rutgers State University, Cook College, New Brunswick, New Jersey, 2003.
Basic GIS Concepts, University College, Denver, Colorado. Spring 2004.
DOT/HM-126F HAZMAT Training 49CFR 172, subpart H, 2005.
Waste Management Employee Training Program 40 CFR 265.16, 2005.
EPA/AHERA/New Jersey Asbestos Contractor/Supervisor, August 2005.
EPA/AHERA/Pennsylvania Asbestos Building Inspector, November 2005.

JOHN T. DUGGAN, JR., REGIONAL MANAGER

WORK EXPERIENCE

1988 – 1994	Environmental Technician, Gaudet Associates, Inc.
1994 – 1998	Project Manager, GA Environmental Services, Inc.
1998 – 2000	Program Manager, GA Environmental Services, Inc.
2000 - Present	Regional Manager, USA Environmental Management, Inc.

EDUCATION

Bucks County Community College – Business Administration

EXPERIENCE

Mr. Duggan's experience as Regional Manager for USA's New Jersey operations has encompassed a wide range of environmental assessments/remedial operations from school districts to urban Brownfield's redevelopment issues, historic residential properties and high-rise office structures. His experience also includes Federal remedial design-build operations for such clients as the Department of Defense, the General Service Administration and the Department of the Interior. In addition, he has assisted State Agencies, Local Government Offices and Educational facilities with environmental issues such as bird guano, indoor air quality, mold and fungi studies, and asbestos/lead assessment, soil and groundwater contamination /remediation and property transfer historical studies.

Mr. Duggan manages USA's Federal Contracts throughout the Mid-Atlantic Region. He is the lead environmental professional for our Navy IDIQ Industrial Hygiene/3rd Party abatement monitoring contract that provided abatement oversight including Abatement Work Plan and Submittal Review, Abatement Action Designs, and Abatement Monitoring for the Navy at the Naval Station Newport in Rhode Island (3 Projects), Naval Submarine Base in New London Connecticut (5 Projects), and Naval Operations Support Centers and the Merchant Marine Academy in Long Island/Rochester/Buffalo, New York (7 Projects). He is also the lead environmental professional for a Navy IDIQ A/E Whole Center Repair Mid-Atlantic contract that has included Naval Operations Support Centers, New Construction and Facility Retrofits in Roanoke Virginia, Charlotte and Greensboro South Carolina, Erie Pennsylvania, Lakehurst New Jersey, Naval Underwater Warfare Center and the Naval Warfare College in Newport, Rhode Island.

CERTIFICATIONS & REGISTRATIONS:

- OSHA HAZWOPER Training
- NJ DEP UST Closure, Subsurface Evaluation

- UST Inspection– PA
- Certificate of Competence Highland Tank & Manufacturing Co. Xerxes Fiberglass Tanks
  Ameron Fiberglass Containment Piping
- Certified Operator – X-Ray Fluorescence
- Radioactive Materials Training
- EPA AHERA Project Designer
- EPA AHERA Management Planner
- EPA AHERA Building Inspector
- Asbestos Safety Technician – New Jersey
- Radon Measurement Technician – New Jersey
- Asbestos Project Inspector – Philadelphia
- USDOT HM-126F Hazmat Training

AFFILIATIONS:

- Bucks County Community College Foundation, Member
- Newtown Borough Environmental Advisory Council, Chairman
- The City of Trenton, Department of Housing and Economic Development, Small Business Week Committee Member and Kickoff Event Chairman
- The Society of American Military Engineers, Philadelphia Post Member
- Newtown Borough Ward 2 Committee Man

Locally in Central New Jersey, Mr. Duggan has been the Environmental Principal-in-charge for USA's recent work at various State Owned Facilities. These facilities include the following: Marie Katzenbach School for the Deaf Dormitory Renovations; Jersey City Schools NJEDA upgrades, Trenton Psychiatric Hospital Life Safety and Water Distribution Project; Greystone Psychiatric Hospitals recent Life Safety/facility Upgrade Project; Totowa Developmental Centers recent boiler replacement project; NJ Executive State House Security Renovations; NJDMV Facility Assessment Study; the NJ State Police Regional Training Center Feasibility Study and five NJSCC School Renovation projects.

PROJECT EXPERIENCE:

NEW JERSEY STATE POLICE REGIONAL TRAINING CENTER AND HEADQUARTERS COMPLEX – ENVIRONMENTAL PRINCIPAL–IN-CHARGE

As Environmental Manager for the assessment of the State Police facilities in West Trenton and Sea Girt New Jersey, Mr. Duggan managed the assessment of the existing buildings, soil, groundwater, plant & wild life for potential environmental impacts associated with the land acquisition and eventual construction of a new state-of-the-are facility. The building assessments included asbestos, lead based paint, mold & mildew, fuel storage, radioactive materials, hydraulic lifts and the like. The land surveys included comprehensive Environmental Site Assessment studies of the entire property in West

Trenton, which discovered hazardous dumping, out of compliance fuel storage systems and limited wetlands impacts. In addition, the study of the Sea Girt site revealed former septic dumping, hazardous materials storage, flood plane issues, and sensitive wild life and plant life habitats.

MARRIOTT TRENTON, HOTEL AND CONFERENCE CENTER –ENVIRONMENTAL COMPLIANCE MANAGER

As Environmental Compliance Manager for the assessment, remediation and environmental barrier design for the new hotel and conference center, Mr. Duggan managed the assessment of the existing improved parking lot for historical and regional environmental impacts associated with the land acquisition and eventual construction of a new facility. The land surveys included comprehensive Environmental Site Assessment studies of the entire property in downtown Trenton, NJ, which revealed historical hazardous dumping from such former operations as power generating canal operations and a former print shop, which left an adverse environmental impact on the subject site. Mr. Duggan managed and completed the Remedial Action Work Plan and Environmental Barrier design for submission and acceptance by NJDEP. In addition, he managed the implementation of the plan, which included contaminated soils and groundwater and sensitive environmental receptors. The oversight and remedial actions were approved ahead of schedule by NJDEP, and the Facility is operational today.

GREYSTONE PARK PSYCHIATRIC HOSPITAL – ENVIRONMENTAL PRINCIPAL-IN-CHARGE

As part of the recent renovation and life safety upgrades at the referenced facility, Mr. Duggan was the environmental Principal-In-Charge for the environmental impacts associated with a 10 existing buildings, one of which boosted the largest contiguous building foundation in the world before the construction of the Pentagon. The project involved the inspection, assessment, remedial design and eventual remediation of PCB transformer, asbestos, lead based paint and radioactive materials.

NJSCC – ENVIRONMENTAL MANAGER

Assisted the five school districts with the management of Asbestos, Lead and Hazardous Materials. Our list of services for this client includes testing, assessment, remedial design and oversight monitoring in over 15 buildings owned or managed by the NJSCC. As with any large agency, public relations play a prominent role in the performance of your duties. Our Project Managers have developed a keen sense of the reality surrounding the handling of teachers, parents and other ancillary staff to the point where we are frequently given immediate access to these parties when critical situations arise. The level of trust developed with this client based upon our years of unparallel service is unsurpassed.

DEPARTMENT OF THE NAVY – ENVIRONMENTAL MANAGER

Mr. Duggan has been managing the Industrial Hygiene abatement and monitoring program for the US Department of the Navy for the last five years. This contract covers the inspection, abatement design and abatement monitoring for Asbestos, Lead Paint, Mold, PCB's and Radon. For this client we have been providing all labor, material and equipment necessary to conduct third party monitoring for removal of asbestos containing materials, PCB containing ballasts, Under this contract we are asked to provide trained and certified personnel, laboratory analysis and perform quality assurance (QA) monitoring. This contract covers work from Virginia to Maine and we have completed work to date in Rochester New York, Buffalo New York. Long Island New York, Portland Maine, Kings Point New York, Albany New York, Groton Connecticut, and Central New Jersey.

NEW JERSEY STATE TERM CONTRACT MANAGER– ENVIRONMENTAL PRINCIPAL–IN-CHARGE

As Environmental Manager for the annual term contract for the NJ Department of Transportation, the NJ Department of Human Services and the NJ Department of Property Management and Construction and the NJ Department of Transportation Mr. Duggan managed the assessment of the State Owned buildings, for environmental Hazards. Hazards assessed and abated include as asbestos mold, bacteria, lead, fuel contamination, radon, The building assessments included asbestos, lead based paint, mold & mildew, fuel storage, radioactive materials, hydraulic lifts and the like. The land surveys included comprehensive Environmental Site Assessment studies of the entire property in West Trenton, which discovered hazardous dumping, out of compliance fuel storage systems and limited wetlands impacts. In addition, the study of the Sea Girt site revealed former septic dumping, hazardous materials storage, flood plane issues, and sensitive wild life and plant life habitats.

REGIONAL RESPONSIBILITIES

- Manage, evaluate and implement necessary policies and procedures to monitor contract performances to ensure that USA standards of excellence are maintained and customer requirements are met on time and within budget.
- Primary point of contact with Contracting Officers and State Regulators
- Perform financial management functions to include forecasting, budgeting, and cash flow analyses.
- Manage new business development activities.
- Ensure subcontractors/specialty consultants qualifications and references meet project and USA criteria.
- Train and instruct employees in corporate and OSHA safety procedures
- Conduct project site visits ensuring contract specifications are complied with and quality control plan is implemented properly
- Coordinates project supervisors, subcontractors and provide overall supervision and direction

- Coordinates site preparation, including material acquisition delivery, construction of containment and decontamination facilities
- Provides environmental consulting on asbestos, IAQ, site remediation/site investigation and lead issues to ensure compliance with EPA -OSHA
- Ensures compliance with regulations and safety guidelines including monitoring all projects to ensure safety guidelines are being implements
- Attends site visits, pre-bid, project and post-bid meetings
- Estimates projects costs and develop pricing in conjunction with the Program Manager
- Reviews contract drawings and specifications
- Federal Projects Manager - Mid-Atlantic Region

JULIAN T. HEAL, PROJECT MANAGER

EDUCATION

Bachelor of Science in Ecology
Juniata College, Huntingdon, PA - 1996

EXPERIENCE

Mr. Heal has approximately 14 years of experience in the environmental consulting arena, with extensive experience providing management and oversight of environmental remediation projects, conducting hazardous materials surveys, Phase I and Phase II Environmental Site Assessments, soil and groundwater sampling, remediation system operation and maintenance, and fisheries and aquatic sciences.

Environmental Remediation

- Managed numerous underground storage tank removal and soil remediation projects at industrial, commercial, and residential properties in Pennsylvania, New Jersey and New York.
- Prepared project submittals, such as Site Specific Work Plans, Material Handling Plans, Site Security Plans and Site Specific Health and Safety Plans.
- Prepared and submitted project status reports and daily activity reports.
- Site supervisor and health and safety officer for a large soil remediation project at a former industrial site in Philadelphia, Pennsylvania.
- Provided contractor supervision and safety compliance for a lead based paint abatement project in West Chester, Pennsylvania.
- Air monitoring of a large-scale demolition project for dust emissions in Coatesville, Pennsylvania.
- Operated and maintained a free product recovery and groundwater remediation system at a retail gasoline station in Philadelphia, Pennsylvania.

Phase I Environmental Assessments

- Performed numerous Phase I Environmental Site Assessments of commercial, residential, and industrial properties located in Pennsylvania, New Jersey, New York, Massachusetts, Texas, Louisiana and Illinois.
- Assessment responsibilities include site inspection, conducting asbestos surveys, hazardous materials surveys, background database searches, file reviews, historical reference research, chain-of-title searches, report preparation and submission.

Phase II Investigations

- Conducted Phase II Subsurface Investigations including soil boring investigations, test pits, sampling of temporary groundwater wells, and monthly, quarterly, and annual monitoring of groundwater permanent monitoring wells in Pennsylvania and New Jersey.

Fisheries and Aquatic Science

- Provided field support for Clean Water Act 316(a) variance for thermal discharge of an electric power generating facility in western Pennsylvania.
- Conducted field research and laboratory analysis in support of a yellow perch recruitment research project at the Lake Michigan Fisheries Research Station, Michigan City, Indiana.
- Performed field research for a migratory finfish survey in the New York harbor.

CERTIFICATIONS:

OSHA Hazardous Waste Site Worker
NJDEP UST Closure License #584167

APPENDIX C

COMPOUND LIST REPORTS

Compound List Report

Product: AB8270TCL20 TCL Semivolatiles
Matrix: SO Solid

Mar 21, 2014 12:06 pm

Method List:	AB8270 SO	**Method Ref:** SW846 8270D	LJ43648
Report List:	ABTCL20 ALL	ABN TCL List (SOM0 2.0)	LJ43295
RL/MDL Factor:	33.3		

					Control Limits (%) Rev: 7/13			
Compound	**CAS No.**	**RL**	**MDL**	**Units**	**MS/MSD**	**RPD**	**BS**	**DUP**
2-Chlorophenol	95-57-8	67	33	ug/kg	16-104	44	37-110	10
4-Chloro-3-methyl phenol	59-50-7	170	33	ug/kg	25-118	41	44-125	10
2,4-Dichlorophenol	120-83-2	170	54	ug/kg	20-111	42	41-120	10
2,4-Dimethylphenol	105-67-9	170	56	ug/kg	21-124	40	43-137	10
2,4-Dinitrophenol	51-28-5	670	41	ug/kg	10-110	54	21-147	10
4,6-Dinitro-o-cresol	534-52-1	670	41	ug/kg	10-111	55	37-136	10
2-Methylphenol	95-48-7	67	38	ug/kg	19-105	42	40-110	10
3&4-Methylphenol		67	42	ug/kg	17-108	43	39-111	10
2-Nitrophenol	88-75-5	170	35	ug/kg	11-103	44	36-117	10
4-Nitrophenol	100-02-7	330	56	ug/kg	10-141	48	26-143	10
Pentachlorophenol	87-86-5	330	57	ug/kg	10-114	47	21-123	10
Phenol	108-95-2	67	35	ug/kg	16-105	42	36-112	20
2,3,4,6-Tetrachlorophenol	58-90-2	170	34	ug/kg	20-116	42	40-121	10
2,4,5-Trichlorophenol	95-95-4	170	39	ug/kg	24-116	42	48-120	10
2,4,6-Trichlorophenol	88-06-2	170	31	ug/kg	21-117	40	48-119	10
Acenaphthene	83-32-9	33	9.7	ug/kg	25-106	38	46-110	10
Acenaphthylene	208-96-8	33	11	ug/kg	21-110	39	43-103	10
Acetophenone	98-86-2	170	5.9	ug/kg	13-117	43	35-120	10
Anthracene	120-12-7	33	12	ug/kg	27-123	40	56-118	36
Atrazine	1912-24-9	67	6.6	ug/kg	31-147	39	57-151	10
Benzo(a)anthracene	56-55-3	33	11	ug/kg	22-127	44	56-117	44
Benzo(a)pyrene	50-32-8	33	10	ug/kg	22-132	42	56-124	23
Benzo(b)fluoranthene	205-99-2	33	11	ug/kg	17-141	45	53-127	16
Benzo(g,h,i)perylene	191-24-2	33	12	ug/kg	23-129	42	52-126	61
Benzo(k)fluoranthene	207-08-9	33	13	ug/kg	20-124	44	51-122	7
4-Bromophenyl phenyl ether	101-55-3	67	12	ug/kg	30-116	38	51-121	10
Butyl benzyl phthalate	85-68-7	67	19	ug/kg	26-134	40	52-133	10
1,1'-Biphenyl	92-52-4	67	3.9	ug/kg	22-114	41	42-122	10
Benzaldehyde	100-52-7	170	7.7	ug/kg	10-115	42	30-119	10
2-Chloronaphthalene	91-58-7	67	10	ug/kg	24-101	40	42-110	10
4-Chloroaniline	106-47-8	170	11	ug/kg	15-110	44	32-102	10
Carbazole	86-74-8	67	15	ug/kg	27-123	38	53-119	10
Caprolactam	105-60-2	67	10	ug/kg	10-141	42	35-144	10
Chrysene	218-01-9	33	11	ug/kg	21-131	42	54-121	38
bis(2-Chloroethoxy)methane	111-91-1	67	13	ug/kg	21-108	40	40-118	10
bis(2-Chloroethyl)ether	111-44-4	67	10	ug/kg	13-104	44	33-110	10
bis(2-Chloroisopropyl)ether	108-60-1	67	9.9	ug/kg	13-110	42	30-108	10
4-Chlorophenyl phenyl ether	7005-72-3	67	10	ug/kg	27-111	38	48-116	10
2,4-Dinitrotoluene	121-14-2	33	15	ug/kg	20-124	40	51-126	10
2,6-Dinitrotoluene	606-20-2	33	13	ug/kg	24-122	38	52-126	10
3,3'-Dichlorobenzidine	91-94-1	67	8.5	ug/kg	10-121	45	49-115	10
1,4-Dioxane	123-91-1	33	22	ug/kg	10-110	48	10-110	10
Dibenzo(a,h)anthracene	53-70-3	33	11	ug/kg	26-129	42	53-126	13
Dibenzofuran	132-64-9	67	9.9	ug/kg	21-114	39	45-114	10

Compound List Report

Product: AB8270TCL20 TCL Semivolatiles
Matrix: SO Solid

Mar 21, 2014 12:06 pm

Method List:	AB8270 SO	**Method Ref:**	SW846 8270D	LJ43648
Report List:	ABTCL20 ALL	ABN TCL List (SOM0 2.0)		LJ43295
RL/MDL Factor:	33.3			

					Control Limits (%) Rev: 7/13			
Compound	**CAS No.**	**RL**	**MDL**	**Units**	**MS/MSD**	**RPD**	**BS**	**DUP**
Di-n-butyl phthalate	84-74-2	67	7.4	ug/kg	29-127	39	56-125	10
Di-n-octyl phthalate	117-84-0	67	16	ug/kg	25-140	43	49-145	10
Diethyl phthalate	84-66-2	67	11	ug/kg	32-115	37	52-118	10
Dimethyl phthalate	131-11-3	67	12	ug/kg	29-115	37	54-114	10
bis(2-Ethylhexyl)phthalate	117-81-7	67	29	ug/kg	26-140	43	52-138	10
Fluoranthene	206-44-0	33	15	ug/kg	16-134	44	55-119	38
Fluorene	86-73-7	33	11	ug/kg	24-116	39	51-114	10
Hexachlorobenzene	118-74-1	67	11	ug/kg	24-118	41	47-122	10
Hexachlorobutadiene	87-68-3	33	9.3	ug/kg	15-110	42	28-117	10
Hexachlorocyclopentadiene	77-47-4	330	34	ug/kg	10-110	52	22-126	10
Hexachloroethane	67-72-1	170	9.3	ug/kg	11-110	46	28-103	10
Indeno(1,2,3-cd)pyrene	193-39-5	33	12	ug/kg	23-132	43	53-128	54
Isophorone	78-59-1	67	9.0	ug/kg	22-105	41	37-117	10
2-Methylnaphthalene	91-57-6	67	19	ug/kg	16-108	40	34-114	10
2-Nitroaniline	88-74-4	170	15	ug/kg	23-130	39	46-135	10
3-Nitroaniline	99-09-2	170	13	ug/kg	19-116	40	44-114	10
4-Nitroaniline	100-01-6	170	13	ug/kg	18-124	42	44-128	10
Naphthalene	91-20-3	33	9.1	ug/kg	13-103	41	37-104	10
Nitrobenzene	98-95-3	67	9.6	ug/kg	14-109	41	34-117	10
N-Nitroso-di-n-propylamine	621-64-7	67	8.1	ug/kg	11-113	41	35-115	10
N-Nitrosodiphenylamine	86-30-6	170	20	ug/kg	26-119	38	51-114	10
Phenanthrene	85-01-8	33	15	ug/kg	19-126	42	55-113	91
Pyrene	129-00-0	33	13	ug/kg	17-136	45	54-120	67
1,2,4,5-Tetrachlorobenzene	95-94-3	170	10	ug/kg	22-110	41	38-112	10

2-Fluorophenol	367-12-4	Surrogate Limits:	13-110
Phenol-d5	4165-62-2	Surrogate Limits:	15-110
2-Chlorophenol-D4		Surrogate Limits:	70-130
2,4,6-Tribromophenol	118-79-6	Surrogate Limits:	20-123
1,2-Dichlorobenzene-d4	2199-69-1	Surrogate Limits:	70-130
Nitrobenzene-d5	4165-60-0	Surrogate Limits:	10-110
2-Fluorobiphenyl	321-60-8	Surrogate Limits:	17-110
o-Terphenyl	84-15-1	Surrogate Limits:	13-131
2-Bromonaphthalene	580-13-2	Surrogate Limits:	20-112
Terphenyl-d14	1718-51-0	Surrogate Limits:	30-124

68 compounds and 10 surrogates reported in list ABTCL20

Compound List Report

Product: P8082PCB11 PCBs w 1262 & 1268
Matrix: SO Solid

Jan 20, 2014 04:56 pm

Method List:	P8082 SO	**Method Ref:**	SW846 8082A	LJ35975
Report List:	PCB11 ALL		PCB List	LJ31661
RL/MDL Factor:	0.67			

Compound	CAS No.	RL	MDL	Units
Aroclor 1016	12674-11-2	34	8.7	ug/kg
Aroclor 1221	11104-28-2	34	20	ug/kg
Aroclor 1232	11141-16-5	34	17	ug/kg
Aroclor 1242	53469-21-9	34	11	ug/kg
Aroclor 1248	12672-29-6	34	10	ug/kg
Aroclor 1254	11097-69-1	34	16	ug/kg
Aroclor 1260	11096-82-5	34	11	ug/kg
Aroclor 1268	11100-14-4	34	9.8	ug/kg
Aroclor 1262	37324-23-5	34	11	ug/kg

9 compounds reported in list PCB11

Accutest NJ Normal Reporting Limits for Soil and Non-potable Water Matrices for 2013

(Soil values will be adjusted up for percent solids.)

TEST	Method 200.7/6010 waters - normal RL in ug/l - ICP	Method 200.7/6010 waters - pooled MDL for SS ICP's in ug/l	Method 6010 soils - normal RL in mg/kg - ICP	Method 6010 soils - pooled MDL for SS ICP's in mg/kg				
Al	200.0	10.92	50.0	1.474				
Sb	6.0	1.84	2.0	0.236				
As	3.0	1.48	2.0	0.228				
Ba	200.0	0.36	20.0	0.054				
Be	1.0	0.17	0.2	0.015				
Cd	3.0	0.24	0.5	0.071				
Ca	5000.0	55.21	500.0	8.374				
Cr	10.0	0.92	1.0	0.074				
Co	50.0	0.54	5.0	0.042				
Cu	10.0	1.02	2.5	0.083				
Fe	100.0	13.32	50.0	2.872				
Pb	3.0	2.42	2.0	0.213				
Mg	5000.0	22.82	500.0	9.265				
Mn	15.0	0.15	1.5	0.054				
Ni	10.0	1.55	4.0	0.079				
K	10000.0	41.11	1000.0	6.107				
Se	10.0	2.43	2.0	0.259				
Ag	10.0	1.45	0.5	0.101				
Na	10000.0	57.88	1000.0	2.005				
Tl	2.0	1.32	1.0	0.293				
V	50.0	0.72	5.0	0.073				
Zn	20.0	4.36	2.0	0.234				
B	100.0	2.04	10.0	0.144				
Bi	20.0	0.98	2.0	0.143				
Mo	20.0	2.03	2.0	0.142				
Li	20.0	2.36	2.0	0.141				
Pd	50.0	1.45	5.0	0.264				
SICP	50.0	5.86	5.0	0.338				
Si	200.0	28.93	NA	3.656				
Sr	10.0	0.59	1.0	0.024				
Sn	10.0	3.71	5.0	0.765				
Ti	10.0	1.21	1.0	0.093				
W	50.0	6.46	5.0	1.745				
Zr	10.0	1.20	2.0	0.057				
	EPA 245.1/SW846 7470A waters- normal RL in ug/l	EPA 245.1/SW846 7470A waters- normal MDL in ug/l	SW846 7471A soils- normal RL in mg/kg	SW846 7471A soils - normal MDL in mg/kg	SW846 7470A leachates- normal RL in mg/l	SW846 7470A leachates- normal MDL in mg/l		
Hg -CV	0.200	0.089	0.034	0.0043	0.000200	0.000089		

Compound List Report

Product: V8260TCL20+ TCL Volatile Organics + TICS
Matrix: AQ Aqueous

Jan 20, 2014 04:55 pm

Method List:	VAIX8260 AQ	**Method Ref:**	SW846 8260B	LJ43243
Report List:	VTCL20 ALL		VOA TCL List	LJ43234
RL/MDL Factor:	1			

Compound	CAS No.	RL	MDL	Units
Acetone	67-64-1	10	3.3	ug/l
Benzene	71-43-2	1.0	0.28	ug/l
Bromochloromethane	74-97-5	5.0	0.42	ug/l
Bromodichloromethane	75-27-4	1.0	0.21	ug/l
Bromoform	75-25-2	4.0	0.30	ug/l
Bromomethane	74-83-9	2.0	0.56	ug/l
2-Butanone (MEK)	78-93-3	10	3.2	ug/l
Carbon disulfide	75-15-0	2.0	0.18	ug/l
Carbon tetrachloride	56-23-5	1.0	0.23	ug/l
Chlorobenzene	108-90-7	1.0	0.35	ug/l
Chloroethane	75-00-3	1.0	0.39	ug/l
Chloroform	67-66-3	1.0	0.25	ug/l
Chloromethane	74-87-3	1.0	0.36	ug/l
Cyclohexane	110-82-7	5.0	0.18	ug/l
1,2-Dibromo-3-chloropropane	96-12-8	10	1.3	ug/l
Dibromochloromethane	124-48-1	1.0	0.19	ug/l
1,2-Dibromoethane	106-93-4	2.0	0.16	ug/l
1,2-Dichlorobenzene	95-50-1	1.0	0.20	ug/l
1,3-Dichlorobenzene	541-73-1	1.0	0.31	ug/l
1,4-Dichlorobenzene	106-46-7	1.0	0.30	ug/l
Dichlorodifluoromethane	75-71-8	5.0	0.63	ug/l
1,1-Dichloroethane	75-34-3	1.0	0.26	ug/l
1,2-Dichloroethane	107-06-2	1.0	0.22	ug/l
1,1-Dichloroethene	75-35-4	1.0	0.34	ug/l
cis-1,2-Dichloroethene	156-59-2	1.0	0.24	ug/l
trans-1,2-Dichloroethene	156-60-5	1.0	0.38	ug/l
1,2-Dichloropropane	78-87-5	1.0	0.28	ug/l
cis-1,3-Dichloropropene	10061-01-5	1.0	0.15	ug/l
trans-1,3-Dichloropropene	10061-02-6	1.0	0.21	ug/l
Ethylbenzene	100-41-4	1.0	0.21	ug/l
Freon 113	76-13-1	5.0	0.77	ug/l
2-Hexanone	591-78-6	5.0	1.7	ug/l
Isopropylbenzene	98-82-8	2.0	0.22	ug/l
Methyl Acetate	79-20-9	5.0	1.5	ug/l
Methylcyclohexane	108-87-2	5.0	0.15	ug/l
Methyl Tert Butyl Ether	1634-04-4	1.0	0.29	ug/l
4-Methyl-2-pentanone(MIBK)	108-10-1	5.0	1.5	ug/l
Methylene chloride	75-09-2	2.0	0.86	ug/l
Styrene	100-42-5	5.0	0.30	ug/l
1,1,2,2-Tetrachloroethane	79-34-5	1.0	0.20	ug/l
Tetrachloroethene	127-18-4	1.0	0.25	ug/l
Toluene	108-88-3	1.0	0.44	ug/l
1,2,3-Trichlorobenzene	87-61-6	5.0	0.24	ug/l
1,2,4-Trichlorobenzene	120-82-1	5.0	0.22	ug/l

Compound List Report

Product: V8260TCL20+ TCL Volatile Organics + TICS
Matrix: AQ Aqueous

Jan 20, 2014 04:55 pm

Method List:	VAIX8260 AQ	**Method Ref:**	SW846 8260B	LJ43243
Report List:	VTCL20 ALL		VOA TCL List	LJ43234
RL/MDL Factor:	1			

Compound	CAS No.	RL	MDL	Units
1,1,1-Trichloroethane	71-55-6	1.0	0.25	ug/l
1,1,2-Trichloroethane	79-00-5	1.0	0.21	ug/l
Trichloroethene	79-01-6	1.0	0.50	ug/l
Trichlorofluoromethane	75-69-4	5.0	0.33	ug/l
Vinyl chloride	75-01-4	1.0	0.41	ug/l
m,p-Xylene		1.0	0.40	ug/l
o-Xylene	95-47-6	1.0	0.19	ug/l
Xylene (total)	1330-20-7	1.0	0.19	ug/l

52 compounds reported in list VTCL20

Compound List Report

Product: V8011NJ EDB + 1,2-Dibromo-3-chloropropane
Matrix: AQ Aqueous

Feb 20, 2014 10:58 am

Method List:	V8011 AQ	**Method Ref:**	SW846-8011	LJ18782
Report List:	V8011NJ ALL	VOA List		LJ32000
RL/MDL Factor:	1			

Compound	CAS No.	RL	MDL	Units
1,2-Dibromo-3-chloropropane	96-12-8	0.020	0.014	ug/l
1,2-Dibromoethane	106-93-4	0.020	0.011	ug/l

2 compounds reported in list V8011NJ

Compound List Report

Product: AB8270TCL20+ TCL Semivolatiles, w/TICs
Matrix: AQ Aqueous

Jan 20, 2014 04:55 pm

Method List:	AB8270 AQ	**Method Ref:** SW846 8270D	LJ43649
Report List:	ABTCL20 ALL	ABN TCL List (SOM0 2.0)	LJ43295
RL/MDL Factor:	1		

Compound	CAS No.	RL	MDL	Units
2-Chlorophenol	95-57-8	5.0	0.97	ug/l
4-Chloro-3-methyl phenol	59-50-7	5.0	1.8	ug/l
2,4-Dichlorophenol	120-83-2	2.0	1.2	ug/l
2,4-Dimethylphenol	105-67-9	5.0	1.5	ug/l
2,4-Dinitrophenol	51-28-5	20	17	ug/l
4,6-Dinitro-o-cresol	534-52-1	20	0.99	ug/l
2-Methylphenol	95-48-7	2.0	1.0	ug/l
3&4-Methylphenol		2.0	0.93	ug/l
2-Nitrophenol	88-75-5	5.0	1.5	ug/l
4-Nitrophenol	100-02-7	10	5.2	ug/l
Pentachlorophenol	87-86-5	10	1.4	ug/l
Phenol	108-95-2	2.0	1.3	ug/l
2,3,4,6-Tetrachlorophenol	58-90-2	5.0	0.94	ug/l
2,4,5-Trichlorophenol	95-95-4	5.0	1.6	ug/l
2,4,6-Trichlorophenol	88-06-2	5.0	1.3	ug/l
Acenaphthene	83-32-9	1.0	0.26	ug/l
Acenaphthylene	208-96-8	1.0	0.23	ug/l
Acetophenone	98-86-2	2.0	0.29	ug/l
Anthracene	120-12-7	1.0	0.29	ug/l
Atrazine	1912-24-9	2.0	0.49	ug/l
Benzaldehyde	100-52-7	5.0	3.3	ug/l
Benzo(a)anthracene	56-55-3	1.0	0.23	ug/l
Benzo(a)pyrene	50-32-8	1.0	0.23	ug/l
Benzo(b)fluoranthene	205-99-2	1.0	0.46	ug/l
Benzo(g,h,i)perylene	191-24-2	1.0	0.32	ug/l
Benzo(k)fluoranthene	207-08-9	1.0	0.51	ug/l
4-Bromophenyl phenyl ether	101-55-3	2.0	0.36	ug/l
Butyl benzyl phthalate	85-68-7	2.0	0.29	ug/l
1,1'-Biphenyl	92-52-4	1.0	0.30	ug/l
2-Chloronaphthalene	91-58-7	2.0	0.30	ug/l
4-Chloroaniline	106-47-8	5.0	0.53	ug/l
Carbazole	86-74-8	1.0	0.36	ug/l
Caprolactam	105-60-2	2.0	0.69	ug/l
Chrysene	218-01-9	1.0	0.29	ug/l
bis(2-Chloroethoxy)methane	111-91-1	2.0	0.31	ug/l
bis(2-Chloroethyl)ether	111-44-4	2.0	0.31	ug/l
bis(2-Chloroisopropyl)ether	108-60-1	2.0	0.45	ug/l
4-Chlorophenyl phenyl ether	7005-72-3	2.0	0.31	ug/l
2,4-Dinitrotoluene	121-14-2	1.0	0.43	ug/l
2,6-Dinitrotoluene	606-20-2	1.0	0.46	ug/l
3,3'-Dichlorobenzidine	91-94-1	2.0	0.36	ug/l
1,4-Dioxane	123-91-1	1.0	0.27	ug/l
Dibenzo(a,h)anthracene	53-70-3	1.0	0.38	ug/l
Dibenzofuran	132-64-9	5.0	0.27	ug/l

Compound List Report

Product: AB8270TCL20+ TCL Semivolatiles, w/TICs
Matrix: AQ Aqueous

Jan 20, 2014 04:55 pm

Method List:	AB8270 AQ	**Method Ref:** SW846 8270D	LJ43649
Report List:	ABTCL20 ALL	ABN TCL List (SOM0 2.0)	LJ43295
RL/MDL Factor:	1		

Compound	CAS No.	RL	MDL	Units
Di-n-butyl phthalate	84-74-2	2.0	0.56	ug/l
Di-n-octyl phthalate	117-84-0	2.0	0.31	ug/l
Diethyl phthalate	84-66-2	2.0	0.33	ug/l
Dimethyl phthalate	131-11-3	2.0	0.28	ug/l
bis(2-Ethylhexyl)phthalate	117-81-7	2.0	0.59	ug/l
Fluoranthene	206-44-0	1.0	0.32	ug/l
Fluorene	86-73-7	1.0	0.28	ug/l
Hexachlorobenzene	118-74-1	1.0	0.34	ug/l
Hexachlorobutadiene	87-68-3	1.0	0.51	ug/l
Hexachlorocyclopentadiene	77-47-4	10	7.1	ug/l
Hexachloroethane	67-72-1	2.0	0.55	ug/l
Indeno(1,2,3-cd)pyrene	193-39-5	1.0	0.37	ug/l
Isophorone	78-59-1	2.0	0.27	ug/l
2-Methylnaphthalene	91-57-6	1.0	0.38	ug/l
2-Nitroaniline	88-74-4	5.0	1.1	ug/l
3-Nitroaniline	99-09-2	5.0	1.3	ug/l
4-Nitroaniline	100-01-6	5.0	1.7	ug/l
Naphthalene	91-20-3	1.0	0.26	ug/l
Nitrobenzene	98-95-3	2.0	0.42	ug/l
N-Nitroso-di-n-propylamine	621-64-7	2.0	0.30	ug/l
N-Nitrosodiphenylamine	86-30-6	5.0	0.31	ug/l
Phenanthrene	85-01-8	1.0	0.29	ug/l
Pyrene	129-00-0	1.0	0.27	ug/l
1,2,4,5-Tetrachlorobenzene	95-94-3	2.0	0.31	ug/l

68 compounds reported in list ABTCL20

Compound List Report

Product: AB8270SIMNJ Semivolatiles by SIM, NJ
Matrix: AQ Aqueous

Feb 20, 2014 10:58 am

Method List:	AB8270SIM AQ	**Method Ref:**	SW846 8270D BY SIM	LJ43655
Report List:	ABNJSIM ALL			LJ20436
RL/MDL Factor:	1			

Compound	CAS No.	RL	MDL	Units
Pentachlorophenol	87-86-5	0.30	0.10	ug/l
Acenaphthene	83-32-9	0.10	0.020	ug/l
Acenaphthylene	208-96-8	0.10	0.024	ug/l
Anthracene	120-12-7	0.10	0.020	ug/l
Benzo(a)anthracene	56-55-3	0.10	0.012	ug/l
Benzo(a)pyrene	50-32-8	0.10	0.012	ug/l
Benzo(b)fluoranthene	205-99-2	0.10	0.010	ug/l
Benzo(g,h,i)perylene	191-24-2	0.10	0.016	ug/l
Benzo(k)fluoranthene	207-08-9	0.10	0.015	ug/l
Chrysene	218-01-9	0.10	0.012	ug/l
Dibenzo(a,h)anthracene	53-70-3	0.10	0.017	ug/l
Fluoranthene	206-44-0	0.10	0.013	ug/l
Fluorene	86-73-7	0.10	0.017	ug/l
Hexachlorobenzene	118-74-1	0.020	0.017	ug/l
Indeno(1,2,3-cd)pyrene	193-39-5	0.10	0.014	ug/l
Naphthalene	91-20-3	0.10	0.036	ug/l
Phenanthrene	85-01-8	0.10	0.021	ug/l
Pyrene	129-00-0	0.10	0.015	ug/l

18 compounds reported in list ABNJSIM

Compound List Report

Product: P8081PESTTCL TCL Pesticides
Matrix: AQ Aqueous

Jan 20, 2014 04:57 pm

Method List:	P8081 AQ	**Method Ref:** SW846 8081B	LJ43002
Report List:	PTCL ALL	Pesticide TCL List	LJ1046
RL/MDL Factor:	0.01		

Compound	CAS No.	RL	MDL	Units
Aldrin	309-00-2	0.010	0.0079	ug/l
alpha-BHC	319-84-6	0.010	0.0023	ug/l
beta-BHC	319-85-7	0.010	0.0023	ug/l
delta-BHC	319-86-8	0.010	0.0019	ug/l
gamma-BHC (Lindane)	58-89-9	0.010	0.0017	ug/l
alpha-Chlordane	5103-71-9	0.010	0.0029	ug/l
gamma-Chlordane	5103-74-2	0.010	0.0021	ug/l
Dieldrin	60-57-1	0.010	0.0016	ug/l
4,4'-DDD	72-54-8	0.010	0.0025	ug/l
4,4'-DDE	72-55-9	0.010	0.0017	ug/l
4,4'-DDT	50-29-3	0.010	0.0032	ug/l
Endrin	72-20-8	0.010	0.0020	ug/l
Endosulfan sulfate	1031-07-8	0.010	0.0019	ug/l
Endrin aldehyde	7421-93-4	0.010	0.0037	ug/l
Endrin ketone	53494-70-5	0.010	0.0047	ug/l
Endosulfan-I	959-98-8	0.010	0.0028	ug/l
Endosulfan-II	33213-65-9	0.010	0.0020	ug/l
Heptachlor	76-44-8	0.010	0.0022	ug/l
Heptachlor epoxide	1024-57-3	0.010	0.0026	ug/l
Methoxychlor	72-43-5	0.020	0.0041	ug/l
Toxaphene	8001-35-2	0.25	0.15	ug/l

21 compounds reported in list PTCL

Compound List Report

Product: P8082PCB11 PCBs w 1262 & 1268
Matrix: AQ Aqueous

Jan 20, 2014 04:57 pm

Method List:	P8082 AQ	**Method Ref:**	SW846 8082A	LJ35825
Report List:	PCB11 ALL		PCB List	LJ31661
RL/MDL Factor:	0.01			

Compound	CAS No.	RL	MDL	Units
Aroclor 1016	12674-11-2	0.50	0.13	ug/l
Aroclor 1221	11104-28-2	0.50	0.27	ug/l
Aroclor 1232	11141-16-5	0.50	0.39	ug/l
Aroclor 1242	53469-21-9	0.50	0.086	ug/l
Aroclor 1248	12672-29-6	0.50	0.15	ug/l
Aroclor 1254	11097-69-1	0.50	0.14	ug/l
Aroclor 1260	11096-82-5	0.50	0.21	ug/l
Aroclor 1268	11100-14-4	0.50	0.13	ug/l
Aroclor 1262	37324-23-5	0.50	0.060	ug/l

9 compounds reported in list PCB11