PHILIS

PHILIS Operations and Maintenance Support Contract

CONTRACT NUMBER: 68HERH21D0002

QUALITY ASSURANCE PROJECT PLAN

PHILIS MOBILE LABORATORIES
CASTLE ROCK, CO & EDISON, NJ

FOR

2024 Republican and Democratic National Conventions

July 10, 2024

Revision No. 1

Prepared for

U.S. Environmental Protection Agency
William Jefferson Clinton-North Building
1200 Pennsylvania Avenue, N.W.
Mail Code: 5104A
Washington, D.C. 20460

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ATTACHMENTS & APPENDICES

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Title and Approval Page

Site Name/Project Name:	Republican National Convention 2024, Portable High Throughput Integrated Laboratory Identification System (PHILIS) Mobile Laboratories
Site Location:	Republican Convention in Milwaukee, WI, Democratic Convention is Chicago, IL. Lab setup for both events in Willowbrook, IL.
Document Title:	Quality Assurance Project Plan (QAPP) Republican and Democratic National Conventions 2024
Lead Organization:	CSS
Preparer's Name and Organizational Affiliation	Tom Antony CSS Program Quality Assurance Manager
Preparer's Address, Telephone Number, and E-mail Address:	1230 Park Street, Castle Rock, CO 80109 859-391-5505 tantony@css-inc.com
Preparation Date:	June 17, 2024

Signatures:

Julia Capri	7/10/2024	Tom Antony	7/10/2024
Julia Capri, CSS Program Manager	Date	Tom Antony, CSS QA Manager	Date
	7/10/2024		7/10/2024
Tom Fowler, CSS Lead Chemist Castle Rock, CO	Date	Sang Chung, CSS Lead Chemist Edison, NJ	Date
lawrence kaelin	7/9/2024	Duane A Newell	7/10/2024
Larry Kaelin, EPA EPA Approval	Date	Duane Newell, EPA EPA Approval	Date
		william nichols	7/9/2024
Kevin Turner/ Jim Mitchell, EPA OSC EPA Approval	Date	Nick Nichols OEM QA Manager	Date

QAPP Worksheet #2.
QAPP Identifying Information

Site Name/Project Name:	2024 Republican National Convention
Site Location:	Milwaukee, WI
Site Number/Code:	**PHI2-001: Task 23**
Operable Unit:	APL01, APL02, SPA-01 Edison and PAL, SPA Castle Rock
Contractor Name:	CSS
Contract Number:	68HERH21D0002
Contract Title:	PHILIS
Work Assignment Number:	N/A

1. Identify guidance used to prepare QAPP:
   EPA Federal Policy for Quality Assurance Project Plans
2. Identify regulatory program:
   U.S. Environmental Protection Agency (EPA) Office of Emergency Management (OEM)
3. Identify approval entity:
   CSS
4. Indicate whether the QAPP is a generic or a project-specific QAPP. (circle one)
5. List dates of scoping sessions that were held:
   06/10/2024, 06/17/2024.
6. List dates and titles of QAPP documents written for previous site work, if applicable:

Title	**Approval Date**
Not Applicable	

7. List organizational partners (stakeholders) and connection with lead organization:
   US EPA Region 5
8. List data users:
   US EPA Region 5
9. If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusion below:

Identify where each required QAPP element is located in the QAPP (provide section, worksheet, table, or figure number) or other project planning documents (provide complete document title, date, section number, page numbers, and location of the information in the document). Circle QAPP elements and required information that are not applicable to the project. Provide an explanation in the QAPP.

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COC – Chain-of-Custody
PQO – Project Quality Objectives
QA – Quality Assurance
QAPP – Quality Assurance Project Plan
QC – Quality Control
SOP – Standard Operating Procedure

QAPP Worksheet #3.
Distribution List

QAPP Recipients	Title	Organization	Telephone Number	Fax Number	E-mail Address	DCN
Julia Capri	Program Manager	CSS	513-708-5982	NA	Jcapri@css-inc.com	NA
Tom Antony	Quality Assurance (QA) Manager	CSS	859-391-5505	NA	tantony@css-inc.com	NA
Tom Fowler	Project Manager Lead Chemist Castle Rock, CO	CSS	719-325-6473	NA	tfowler@css-inc.com	NA
Sang Chung	Lead Chemist Edison, NJ	CSS	219-477-8860	NA	schung@css-inc.com	NA
Ed Argenta	EPA Branch Chief	EPA	202-564-4528	NA	Argenta.edward@epa.gov	NA
Larry Kaelin	EPA COR	EPA	513-675-4751	NA	Kaelin.Lawrence@epa.gov	NA
Duane Newell	EPA ACOR	EPA	720-219-9394	NA	Newell.duane@epa.gov	NA
Kevin Turner	EPA Region 5 OSC	EPA	618-525-3665	NA	Turner.Kevin@epa.gov	NA
Christina Langlois-Miller	EPA	EPA	202-564-0062	NA	Langlois-Miller.Christina@EPA.gov	NA

QAPP Worksheet #4.
Project Personnel Sign-Off Sheet

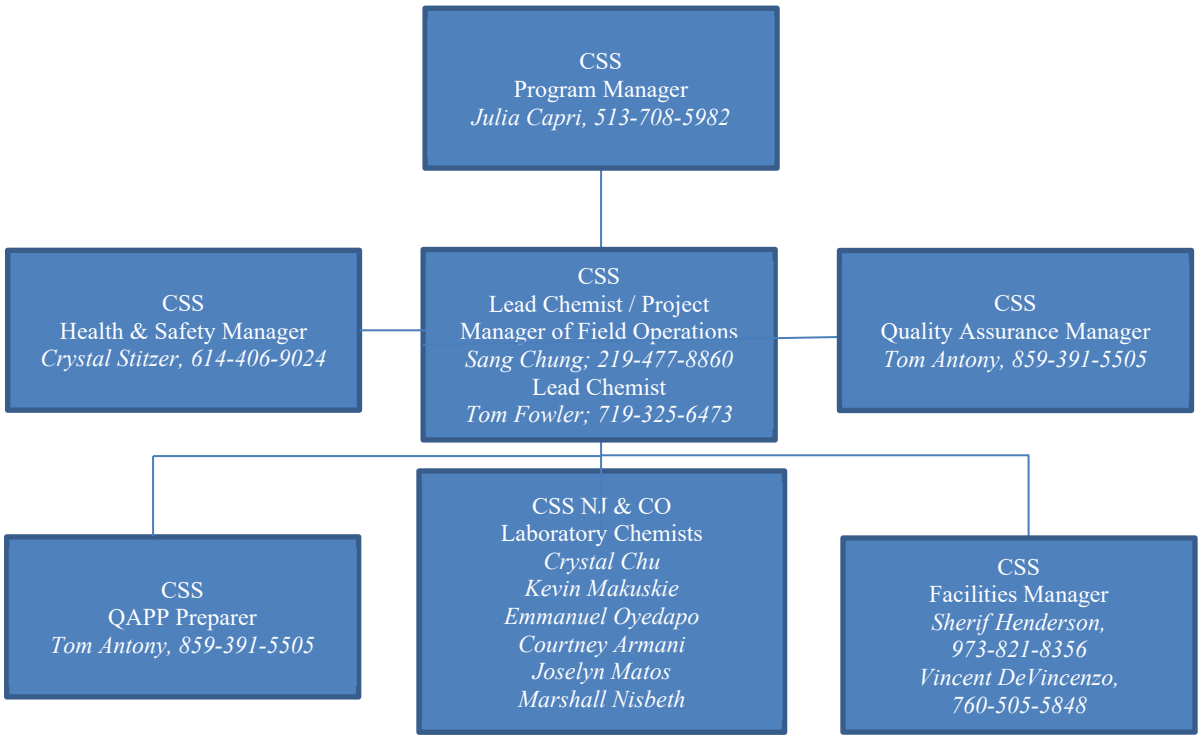
Organization: CSS

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Julia Capri	Program Manager	513-708-5982		7/9/2024
Tom Antony	QA Manager	859-391-5505		7/9/2024
Sang Chung	Lead Chemist	219-477-8860		7/9/2024
Tom Fowler	Lead Chemist	719-325-6473		7/9/2024

Notes:

QA – Quality Assurance
QAPP – Quality Assurance Project Plan

QAPP Worksheet #5.
Project Organizational Chart



QAPP Worksheet #6.
Communication Pathways

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Project scope changes	Program Manager	Julia Capri	513-708-5982	The Program Manager will inform the Project Manager and Lead Chemist regarding any project scope changes.
Management of required project tasks	Program Manager	Julia Capri	513-708-5982	The Project Manager will inform the appropriate CSS project staff of tasks to complete and the required completion date. The project staff will communicate with the Project Manager of task progress and resources/information required to complete tasks.
Delays or changes to field work	Lead Chemist Lead Chemist	Sang Chung Tom Fowler	219-477-8860 719-325-6473	The sampling team leader will inform the project manager of daily field progress. The site project manager will inform the Project Manager of field work progress by telephone, email, or direct communication in the field.
Daily field updates	N/A	N/A	N/A	The sampling team leader will inform the project manager of daily field progress. The site project manager will inform the Project Manager of field work progress by telephone, email, or direct communication in the field.
Reporting of Laboratory Data Quality Issues	Laboratory Chemists	Courtney Armani Marshall Nisbeth Crystal Chu	N/A	The laboratory chemists will inform the Project Manager of any issues related to data quality upon receipt of samples or during analyses.
Recommendations to stop work and initiation of corrective actions	QA Manager Project Manager Program Manager Lead Chemist	Tom Antony Sang Chung Julia Capri Tom Fowler	859-391-5505 219-477-8860 513-708-5982 719-325-6473	The QA Manager, PM, and OSC all have the authority to stop work and initiate corrective actions should there be a reason to do so. Whoever stops the work or initiates corrective actions will inform the Site Leader and PM immediately. The PM will ensure that the QA Manager and OSC are informed of the stop work and corrective actions.
Distribution of analytical data	Program Manager	Julia Capri	513-708-5982	The Project Manager/Lead Chemist will receive all deliverables from the laboratory and distribute them to the Program Manager, who will in-turn distribute the data to any other interested parties.
Approval of QAPP Amendments	QA Manager	Tom Antony	859-391-5505	Approval of all QAPP amendments will be by the QA Manager prior to the changes being implemented.

QAPP Worksheet #7.
Personnel Responsibilities and Qualifications Table

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Julia Capri	Program Manager	CSS	The Program Manager is responsible for ensuring the quality of work performed under the PHILIS contract. The Program Manager interfaces directly with the U.S. EPA Contracting Officer and Project Officer and has overall responsibility and direction for task assignments.	M.S. Chemistry 40+ years of experience
Sang Chung	Project Manager Lead Chemist	CSS	The project manager is responsible for managing all aspects of the project, CSS project personnel, and subcontractors. The project manager interfaces directly with the above Project Manager and QA Manager regarding all project tasks.	B.S. Biology 25 years of experience
Tom Fowler	Project Manager Lead Chemist	CSS	The project manager is responsible for managing all aspects of the project, CSS project personnel, and subcontractors. The project manager interfaces directly with the above Project Manager and QA Manager regarding all project tasks.	B.S. Chemistry 35+ years of experience
Tom Antony	QA Manager	CSS	The QA Manager reviews the project QAPP and has overall responsibility for project QA. The QA Manager will also perform a compliance check of all data received from the laboratory.	M.S. Environmental Science 8+ years of experience
Crystal Stitzer	Health and Safety (H&S) Officer	CSS	The H&S officer approves the Health and Safety Plan (HASP) and provides guidance to field personnel on H&S issues.	MS Environment Science 14 years of experience
Crystal Chu Kevin Makuskie Emmanuel Oyedapo Courtney Armani Joselyn Matos Marshall Nisbeth	Chemists	CSS	The Chemist is the main interface with the project manager regarding project deliverables and QA/QC aspects of the analyses. The Lead Chemist also coordinates sample delivery and ensures that all analyses are performed with results delivered on time.	Degreed with various years of experience
N/A	Sampling Team Leader	N/A	The sampling team leader manages the field team and all work performed in the field. The sampling team leader interfaces directly with the project manager regarding field tasks and any issues that arise while in the field.	N/A
Tom Antony	QAPP Preparer	CSS	The QAPP preparer is responsible for preparing the site-specific QAPP and is in close communication with the Project managers regarding all aspects of project-specific requirements.	M.S. Environmental Science 8+ years of experience

QAPP Worksheet #8.
Special Personnel Training Requirements Table

Project Function	Specialized Training – Title or Description of Course	Training Provider	Training Date	Personnel/Groups Receiving Training	Location of Training Records/Certificates[1]
Sample preparation Activities	40-Hour OSHA HAZWOPER Training and Recurrently Annual 8-hour refreshers	CSS	Various	Chemists	SharePoint with internet access
Laboratory Analyses	40-Hour OSHA HAZWOPER Training and Recurrently Annual 8-hour refreshers	CSS	Various	Chemists	SharePoint with internet access

Notes:
HAZWOPER – Hazardous Waste Operations and Emergency Response
OSHA – Occupational Safety and Health Administration

QAPP Worksheet #9.
Project Scoping Session Participants Sheet

Project Name: REPUBLICAN NATIONAL CONVENTION **Projected Date(s) of Project:** July 15 through 18, 2024 **Project Managers:** Julia Capri, CSS	**Site Name:** REPUBLICAN NATIONAL CONVENTION **Site Location**: Milwaukee, WISCONSIN

Date of Session: 6/10/2024
Scoping Session Purpose: Discuss Scope of Work for Project

Name	Title	Affiliation	Phone #	E-mail Address	Project Role
Julia Capri	Program Manager	CSS	513-708-5982	jcapri@css-inc.com	Program Manager
Tom Antony	QA Manager	CSS	859-391-5505	tantony@css-inc.com	QA Manager
Krystal Stotts	EPA Branch Chief (acting)	EPA	202-564-4528	Argenta.edward@epa.gov	CMAD Deployable Branch Chief
Larry Kaelin	EPA COR	EPA CMAD	513-675-4751	Kaelin.Lawrence@epa.gov	Onsite EPA Rep
Duane Newell	EPA ACOR	EPA CMAD	720-219-2213	Newell.Duane@epa.gov	Onsite EPA Rep
Christina Langlois-Miller	EPA Chemist	EPA	202-564-0062	Langlois-Miller.Christina@EPA.gov	EPA Rep
Tom Fowler	Lead Chemist	CSS	719-325-6473	tfowler@css-inc.com	Lead Chemist
Sang Chung	Project Manager Lead Chemist	CSS	219-477-8860	schung@css-inc.com	Project Manager Lead Chemist

Comments/Decisions: The purpose of the project is to analyze soil, water, air, and wipe samples for Chemical Warfare Agents, opioids, and other organic environmental contaminates that may be present to determine problems or problem areas. Other types of analytes may be requested based on the situation.

Consensus Decisions: Not Applicable.

QAPP Worksheet #10.
Problem Definition

The problem to be addressed by the project PHILIS Laboratories, Edison, NJ and Castle Rock, CO will perform analyses for CWAs, opioids, and other organic environmental contaminants in soil, water, air, and wipe samples to determine if the analytes are present above Hazardous Assessment Levels.

The environmental questions being asked: Does the site need remediation for these analytes.

The possible classes of contaminants and the affected matrices: Chemical Warfare Agents (CWAs), opioids and other organic environmental contaminants. Other types of analytes may be requested based on the situation.

The rationale for inclusion of chemical and non-chemical analyses: N/A

Project decision conditions ("If..., then..." statements): N/A

If any issues arise from analyses during the project, then corrective actions will be implemented.

QAPP Worksheet #11.
Project Quality Objectives/Systematic Planning Process Statements

Who will use the data? CSS will evaluate analytical results to verify compliance with method, SOP, and QAPP requirements. The results will be provided to the EPA.

What will the data be used for? Extent of Contamination, effectiveness of remedial approach and clean confirmation analysis.

What type(s) of data are needed? (target analytes, analytical groups, on-site analytical or off-site laboratory techniques, sampling techniques): Analyze soil, water, wipe, and air samples for CWAs, Opioids, and organic environmental contaminates by UPLCMSMS or GCMS LVI Quad, meeting QC requirements.

How "good" does the data need to be in order to support the environmental decision? Data must meet analytical method and or QAPP requirements for data acceptance.

How much data are needed? (number of samples for each analytical group, matrix, and concentration): Sample density will be determined by the site manager based on the contamination.

Where, when, and how should the data be collected/generated? PHILIS personnel will prepare and analyze samples per CSS SOPs: L-P-107, L-P-101, L-P-114, L-P-203, L-A-101, L-A-201, L-A-310, L-A-601, L-A-502, L-A-704 and L-A-603. Data will be provided in a spreadsheet to meet client requirements and followed up with a full data package supporting the results.

Who will collect and generate the data? CSS chemists will generate and process data and the Lead Chemist and assigned representatives will review results following standard CSS procedures and submitting data to the EPA or assigned representatives for distribution.

How will the data be reported? An EDD spreadsheet with results and a 4.0 report will be sent to the QA Manager for review prior to reporting the EDD spreadsheet as a FINAL result.

How will the data be archived? The report(s) and associated data will be archived per CSS standard procedures. Instrument and other data supporting these reports is also archived at multiple locations per requirements.

QAPP Worksheet #12.
Measurement Performance Criteria Table

Matrix	Soil, Water, Wipes, & Air
Analytical Group	CWA
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[1]	Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
NA	CWAs by GCMS/L-A-502 CWAs by	Overall Precision	30%	Laboratory or Client Duplicates	A
		Laboratory Precision	30% difference of replicate samples	Laboratory Duplicates	A
		Overall Accuracy/Bias	50% to 150%	Laboratory Control Samples	A
		Accuracy/Bias Contamination	Any detection of target analytes in the blank above MDL.	Method Blanks	A
		Representativeness	NA	NA	A
		Sensitivity	Quantitation limits predetermined	Calibration Curve Low Point	A
		Completeness	Minimum 90%	Project manager assesses completeness of samples collected; lead chemist or QA Manager assesses completeness of analytical requirements per the QAPP	A

Notes:
[1]Reference number from QAPP Worksheet #23 (see Section 3.2).

% - Percent
≤ – Less than or equal to
N/A—Not Applicable
RPD – Relative Percent Difference
SOP – Standard Operating Procedure

Matrix	Soil & Water
Analytical Group	Volatile and Semivolatile organic compounds
Concentration Level	Low level

Sampling Procedure	Analytical Method/SOP[1]	Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
NA	Volatiles SOP L-A-101	Laboratory Precision	30% RPD	Laboratory or Sample Duplicates	A
	Volatiles SOP L-A-101	Laboratory Accuracy	Various Recoveries based on analyte and 50% to 150% Recovery for compounds added for this project until statistical acceptance criteria can be determined.	Laboratory Blank Spikes	A
	Volatiles SOP L-A-101	Laboratory Contamination	Any detection of target analytes in the blank above the reporting limit.	Laboratory Method Blanks	A
	Semivolatiles SOP L-A-201	Laboratory Precision	30% RPD	Laboratory Duplicates	A
	Semivolatiles SOP L-A-201	Laboratory Accuracy	Various Recoveries based on analyte. 50% to 150% Recovery for compounds added for this project until statistical criteria can be determined.	Laboratory Blank Spikes	A
	Semivolatiles SOP L-A-201	Laboratory Contamination	Any detection of target analytes in the blank above the reporting limit.	Laboratory Method Blanks	A
	% Moisture SOP L-A-100	Laboratory Accuracy	30% RPD	Laboratory Duplicates	A

Matrix	Wipes, Soils, Waters
Analytical Group	Opioids
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
NA	L-A-310	Overall Precision	30%	Laboratory or Client Duplicates	A
		Laboratory Precision	30% difference of replicate samples	Laboratory Duplicates	A
		Overall Accuracy/Bias	50% to 150%	Laboratory Control Samples	A
		Accuracy/Bias Contamination	Any detection of target analytes in the blank above Reporting Limit.	Method Blanks	A
N/A	L-A-704	Overall Precision	+/-50%	Laboratory or Client Duplicates	A
		Laboratory Precision	+/-50%	Laboratory Duplicates	A
		Overall Accuracy/Bias	50% to 150% with RPD ≤20	Laboratory Control Samples	A
		Accuracy/Bias Contamination	Any detection of target analytes in the blank above Reporting Limit.	Method Blanks	A

QAPP Worksheet #13.
Secondary Data Criteria and Limitations Table

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
Not Applicable	NA	NA		

QAPP Worksheet #14.
Summary of Project Tasks

Sampling Tasks:
Sampling will be performed by a different contractor team from Region 5. PHILIS will not participate in sampling.

Analysis Tasks:
1. Prepare and analyze soil, water, wipe, and air samples for CWAs, opioids, and organic environmental contaminants to meet the needs of the convention.

Quality Control Tasks:
1. Establish an acceptable calibration curve with a minimum of 5 points meeting criteria for all analytes.
2. Each preparation batch must contain a method blank, laboratory control sample, no more than 20 samples, and one MS/MSD. All QC samples must meet recovery criteria or be addressed in the case narrative.
3. Analyze a passing tune when calibrating the system or a CCV prior to analyzing samples or QC, then analyze a method blank, blank spike, then analyze samples and MS/MSD.

Secondary Data:
NA

Data Management Tasks:
1. Prepare a spreadsheet containing the results obtained per client specifications and a level 4 data package where required.
2. Prepare a full data package of the results obtained that would include all raw data where required. Submit reports and maintain data per CSS, project, or contract requirements.
3. Maintain reports and raw data per CSS and client requirements.

Documentation and Records:
All analysis data will be managed and stored on PHILIS system drives for report production and archiving for future use.

Assessment/Audit Tasks:
There will be an initial data review by the analyst and then a second review by a supervisor or peer. PHILIS Quality Assurance Manager will perform a final data review to confirm QC criteria were performed and they are within acceptance criteria. The Program Manager will perform a review for completeness.

Data Review Tasks:
There will be an initial data review by the analyst and then a second review by a supervisor or peer. PHILIS Quality Assurance Manager will perform a final data review to confirm QC criteria were performed and they are within acceptance criteria.

QAPP Worksheet #15.
Reference Limits and Evaluation Table A

Matrix	Soil, Wipes
Analytical Group[1]	CWA
Concentration Level	Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit µg/g, µg/mL	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Sarin (GB)	107-44-8	TBD	TBD	SOP L-A-502 SOP L-A-603 SIM	0.10 µg/Kg 0.005 µg/Wipe	0.255 µg/Kg 0.00303 µg/Wipe	0.50 µg/Kg 0.01 µg/Wipe
Soman, Total	96-64-0	TBD	TBD	SOP L-A-502 SOP L-A-603 SIM	0.20 µg/Kg 0.0050 µg/Wipe	0.267 µg/Kg 0.0057 µg/Wipe	0.50 µg/Kg 0.010 µg/Wipe
Mustard (HD)	505-60-2	TBD	TBD	SOP L-A-502 SOP L-A-603 SIM	0.10 µg/Kg 0.0010 µg/Wipe	0.197 µg/Kg 0.00121µg/Wipe	0.50 µg/Kg 0.005 µg/Wipe
Cyclosarin (GF)	329-99-7	TBD	TBD	SOP L-A-502 SOP L-A-603 SIM	0.10 µg/Kg 0.0020 µg/Wipe	0.274 µg/Kg 0.00443 µg/Wipe	0.60 µg/Kg 0.010 µg/Wipe
VX	50782-69-9	TBD	TBD	SOP L-A-502 SOP L-A-603 SIM	0.010 µg/Wipe	0.0389 µg/Wipe	0.070 µg/Wipe

Notes:
[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.
Analysis performed for wipes and soils on GCMS LVI

Reference Limits and Evaluation Table B

PHILIS current instruments and associated detection limit capability is provided in Attachment 1.

Matrix	Water
Analytical Group[1]	8260
Concentration Level	Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit µg/L, µg/Kg, µg/Wipe	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs ug/L	Method QLs ug/L	MDLs ug/L	QLs ug/L
Dichlorodifluoromethane	75-71-8	TBD	TBD	0.3	5.0	0.73	2.0
Chloromethane	74-87-3	TBD	TBD	0.6	5.0	0.66	2.0
Vinyl Chloride	75-01-4	TBD	TBD	0.7	5.0	0.71	2.0
Bromomethane	74-83-9	TBD	TBD	1.1	5.0	0.60	2.0
Chloroethane	75-00-3	TBD	TBD	0.8	5.0	0.59	2.0
Trichlorofluoromethane	75-69-4	TBD	TBD	0.5	5.0	0.78	2.0
Acetone	67-64-1	TBD	TBD	8.4	25.0	18.98	25.0
1,1-Dichloroethene	75-35-4	TBD	TBD	1.4	5.0	6.5	13.0
t-Butyl alcohol	75-65-0	TBD	TBD	10.1	25	0.7	10
Methylene chloride	75-09-2	TBD	TBD	0.6	10.0	0.65	5.0
Methyl tert-butyl ether	1634-04-4	TBD	TBD	0.3	5.0	0.59	2.0
trans-1,2-Dichloroethene	156-60-5	TBD	TBD	1.4	5.0	0.64	2.0
Diisopropyl ether	108-20-3	TBD	TBD	0.3	5.0	0.51	2.0
2-Butanone	78-93-3	TBD	TBD	4.7	25.0	0.55	10
Ethyl tert-butyl ether	637-92-3	TBD	TBD	0.2	5.0	1.1	2.0
1,1-Dichloroethane	75-34-3	TBD	TBD	0.5	5.0	0.48	2.0
cis-1,2-Dichloroethene	156-59-2	TBD	TBD	0.6	5.0	0.6	2.0
2,2-Dichloropropane	594-20-7	TBD	TBD	2.0	10.0	0.81	2.0
Bromochloromethane	74-97-5	TBD	TBD	0.7	5.0	0.50	2.0
Chloroform	67-66-3	TBD	TBD	0.6	5.0	0.55	2.0
1,1,1-Trichloroethane	71-55-6	TBD	TBD	1.7	5.0	0.5	2.0
1,1-Dichloropropene	563-58-6	TBD	TBD	0.5	5.0	0.4	2.0
Carbon tetrachloride	56-23-5	TBD	TBD	1.0	5.0	0.5	2.0
tert-Amyl methyl ether	994-05-8	TBD	TBD	0.3	5.0	0.58	2.0
1,2-Dichloroethane	107-06-2	TBD	TBD	0.5	5.0	0.55	2.0

Benzene	71-43-2	TBD	TBD	0.4	1.0	0.44	2.0
Trichloroethene	79-01-6	TBD	TBD	0.6	5.0	0.5	2.0
1,2-Dichloropropane	78-87-5	TBD	TBD	0.5	5.0	0.46	2.0
Dibromomethane	74-95-3	TBD	TBD	0.6	5.0	0.5	2.0
Bromodichloromethane	75-27-4	TBD	TBD	0.5	5.0	0.50	10.0
4-Methyl-2-Pentanone	108-10-1	TBD	TBD	7.0	25.0	1.2	2
cis-1,3-Dichloropropene	10061-01-5	TBD	TBD	1.0	5.0	0.70	2.0
Toluene	108-88-3	TBD	TBD	0.5	5.0	0.49	2.0
trans-1,3-Dichloropropene	10061-02-6	TBD	TBD	0.8	5.0	0.84	10.0
1,1,2-Trichloroethane	79-00-5	TBD	TBD	0.6	5.0	0.59	2.0
2-Hexanone	591-78-6	TBD	TBD	7.1	25.0	2.13	2
1,3-Dichloropropane	142-28-9	TBD	TBD	0.6	5.0	0.72	2.0
Tetrachloroethene	127-18-4	TBD	TBD	0.3	5.0	0.47	2.0
Dibromochloromethane	124-48-1	TBD	TBD	0.3	10.0	0.5	2.0
1,2-Dibromoethane	106-93-4	TBD	TBD	0.8	5.0	0.82	2.0
Chlorobenzene	108-90-7	TBD	TBD	0.6	5.0	0.42	2.0
1,1,1,2-Tetrachloroethane	630-20-6	TBD	TBD	0.5	5.0	0.57	4.0
Ethyl benzene	100-41-4	TBD	TBD	0.3	5.0	0.36	2.0
m,p-Xylenes	108-38-3	TBD	TBD	0.4	10.0	0.7	6.0
o-Xylene	95-47-6	TBD	TBD	0.5	5.0	0.51	2.0
Xylenes, Total	NA	TBD	TBD			1.2	10.0
Styrene	100-42-5	TBD	TBD	0.4	0.5	0.47	2.0
Bromoform	75-25-2	TBD	TBD	0.4	5.0	0.54	2.0
Isopropylbenzene	98-82-8	TBD	TBD	0.3	5.0	0.41	2.0
1,1,2,2-Tetrachloroethane	96-18-4	TBD	TBD	1.0	5.0	0.71	2.0
1,2,3-Trichloropropane	96-18-4	TBD	TBD	0.9	5.0	0.68	2.0
Bromobenzene	108-86-1	TBD	TBD	0.5	5.0	0.56	2.0
n-Propylbenzene	103-65-1	TBD	TBD	0.4	5.0	0.42	2.0
2-Chlorotoluene	106-43-4	TBD	TBD	0.3	5.0	0.40	2.0
1,3,5-Trimethylbenzene	108-67-8	TBD	TBD	0.3	5.0	0.42	2.0
4-Chlorotoluene	106-43-4	TBD	TBD	0.4	5.0	0.57	2.0
tert-Butylbenzene	98-06-6	TBD	TBD	0.3	5.0	0.50	2.0
1,2,4-Trimethylbenzene	95-63-6	TBD	TBD	0.4	5.0	0.46	2.0
sec-Butylbenzene	135-98-8	TBD	TBD	0.3	5.0	0.38	2.0

p-Isopropyltoluene	99-87-6	TBD	TBD	0.4	5.0	0.44	2.0
1,3-Dichlorobenzene	541-73-1	TBD	TBD	0.5	5.0	0.38	2.0
1,4-Dichlorobenzene	106-46-7	TBD	TBD	0.5	5.0	0.41	2.0
n-Butylbenzene	104-51-8	TBD	TBD	0.4	5.0	0.45	5.0
1,2-Dichlorobenzene	95-50-1	TBD	TBD	0.7	5.0	0.48	2.0
1,2-Dibromo-3-chloropropane	96-12-8	TBD	TBD	0.6	5.0	0.51	5.0
1,2,4-Trichlorobenzene	120-82-1	TBD	TBD	1.0	5.0	0.72	2.0
Hexachlorobutadiene	87-68-3	TBD	TBD	0.8	5.0	0.45	2.0
Naphthalene	91-20-3	TBD	TBD	1.1	5.0	0.67	2.0
1,2,3-Trichlorobenzene	87-61-6	TBD	TBD	1.0	5.0	0.65	2.0

Reference Limits and Evaluation Table C

Matrix	Soil
Analytical Group[1]	8270
Concentration Level	Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit µg/L, µg/Kg, µg/Wipe	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs ug/Kg	Method QLs	MDLs Ug/Kg	QLs
1,2,4-Trichlorobenzene	120-82-1	TBD	TBD	18.8	200	18.8	200
1,2-Dichlorobenzene	95-50-1	TBD	TBD	21.0	200	21.0	200
1,3-Dichlorobenzene	541-73-1	TBD	TBD	22.3	100	22.3	100
1,4-Dichlorobenzene	106-46-7	TBD	TBD	22.4	100	22.4	100
1-Methylnaphthalene	90-12-0	TBD	TBD	12.4	100	12.4	100
2,4,5-Trichlorophenol	95-95-4	TBD	TBD	10.6	100	10.6	100
2,4,6-Trichlorophenol	88-06-2	TBD	TBD	10.0	200	10.0	200
2,4-Dichlorophenol	120-83-2	TBD	TBD	13.5	200	13.5	200
2,4-Dimethylphenol	105-67-9	TBD	TBD	20.1	200	20.1	200
2,4-Dinitrophenol	51-28-5	TBD	TBD	49.4	200	49.4	200
2,4-Dinitrotoluene	121-14-2	TBD	TBD	9.6	200	9.6	200
2,6-Dinitrotoluene	606-20-2	TBD	TBD	11.3	200	11.3	200
2-Chloronaphthalene	91-58-7	TBD	TBD	10.8	200	10.8	200
2-Chlorophenol	95-57-8	TBD	TBD	19.2	200	19.2	200
2-Methyl-4,6-dinitrophenol	534-52-1	TBD	TBD	9.7	100	9.7	100
2-Methylnaphthalene	91-57-6	TBD	TBD	13.1	100	13.1	100
2-Methylphenol	95-48-7	TBD	TBD	14.6	200	14.6	200
2-Nitroaniline	88-74-4	TBD	TBD	10.2	200	10.2	200
2-Nitrophenol	88-75-5	TBD	TBD	16.8	100	16.8	100
3/4-Methylphenol	106-44-5	TBD	TBD	10.4	200	10.4	200
3-Nitroaniline	99-09-2	TBD	TBD	16.6	100	16.6	100
4-Bromophenyl phenyl ether	101-55-3	TBD	TBD	8.9	200	8.9	200
4-Chloro-3-methylphenol	59-50-7	TBD	TBD	10.6	100	10.6	100
4-Chloroaniline	106-47-8	TBD	TBD	6.0	100	6.0	100
4-Chlorophenyl phenyl ether	7005-72-3	TBD	TBD	9.6	100	9.6	100

4-Nitroaniline	100-01-6	TBD	TBD	10.7	100	10.7	100
4-Nitrophenol	100-02-7	TBD	TBD	47.0	200	47.0	200
Acenaphthene	83-32-9	TBD	TBD	9.3	200	9.3	200
Acenaphthylene	208-96-8	TBD	TBD	10.1	100	10.1	100
Aniline	62-53-3	TBD	TBD	12.5	100	12.5	100
Anthracene	120-12-7	TBD	TBD	8.2	200	8.2	200
Benzo(a)anthracene	56-55-3	TBD	TBD	9.2	100	9.2	100
Benzo(a)pyrene	50-32-8	TBD	TBD	8.0	100	8.0	100
Benzo(b)fluoranthene	205-99-2	TBD	TBD	8.0	200	8.0	200
Benzo(g,h,i)perylene	191-24-2	TBD	TBD	9.9	83.3	9.9	83.3
Benzo(k)fluoranthene	207-08-9	TBD	TBD	8.3	200	8.3	200
Benzyl alcohol	100-51-6	TBD	TBD	13.8	300	13.8	300
Bis(2-chloroethoxy) methane	111-91-1	TBD	TBD	13.6	100	13.6	100
Bis(2-chloroethyl) ether	111-44-4	TBD	TBD	19.3	200	19.3	200
Bis(2-chloroisopropyl) ether	108-60-1	TBD	TBD	19.8	100	19.8	100
Bis(2-ethylhexyl) phthalate	117-81-7	TBD	TBD	24.7	200	24.7	200
Butyl benzyl phthalate	85-68-7	TBD	TBD	11.0	200	11.0	200
Carbazole	86-74-8	TBD	TBD	8.8	200	8.8	200
Chrysene	218-01-9	TBD	TBD	9.1	200	9.1	200
Dibenz(a,h)anthracene	53-70-3	TBD	TBD	9.9	100	9.9	100
Dibenzofuran	132-64-9	TBD	TBD	11.0	100	11.0	100
Diethyl phthalate	84-66-2	TBD	TBD	18.7	100	18.7	100
Dimethyl phthalate	131-11-3	TBD	TBD	9.3	200	9.3	200
Di-n-butyl phthalate	84-74-2	TBD	TBD	9.2	200	9.2	200
Di-n-octyl phthalate	117-84-0	TBD	TBD	9.3	200	9.3	200
Fluoranthene	206-44-0	TBD	TBD	8.3	200	8.3	200
Fluorene	86-73-7	TBD	TBD	9.1	200	9.1	200
Hexachlorobenzene	118-74-1	TBD	TBD	9.9	100	9.9	100
Hexachlorobutadiene	87-68-3	TBD	TBD	22.1	100	22.1	100
Hexachlorocyclopentadiene	77-47-4	TBD	TBD	15.1	200	15.1	200
Hexachloroethane	67-72-1	TBD	TBD	21.6	200	21.6	200
Indeno(1,2,3-cd)pyrene	193-39-5	TBD	TBD	9.2	200	9.2	200
Isophorone	78-59-1	TBD	TBD	10.4	200	10.4	200
Naphthalene	91-20-3	TBD	TBD	17.6	100	17.6	100

Nitrobenzene	98-95-3	TBD	TBD	18.1	100	18.1	100
N-Nitrosodi-n-propylamine	621-64-7	TBD	TBD	52.8	200	52.8	200
Pentachlorophenol	87-86-5	TBD	TBD	45.0	100	45.0	100
Phenanthrene	85-01-8	TBD	TBD	9.0	100	9.0	100
Phenol	108-95-2	TBD	TBD	15.2	100	15.2	100
Pyrene	129-00-0	TBD	TBD	9.7	100	9.7	100

Reference Limits and Evaluation Table D

Matrix	Water
Analytical Group[1]	8270
Concentration Level	Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit µg/L, µg/Kg, µg/Wipe	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs ug/L	Method QLs	MDLs ug/L	QLs
1,2,4-Trichlorobenzene	120-82-1	TBD	TBD	0.70	5	0.70	5
1,2-Dichlorobenzene	95-50-1	TBD	TBD	1.04	5	1.04	5
1,3-Dichlorobenzene	541-73-1	TBD	TBD	1.31	5	1.31	5
1,4-Dichlorobenzene	106-46-7	TBD	TBD	0.97	5	0.97	5
1-Methylnaphthalene	90-12-0	TBD	TBD	0.79	5	0.79	5
2,4,5-Trichlorophenol	95-95-4	TBD	TBD	1.20	5	1.20	5
2,4,6-Trichlorophenol	88-06-2	TBD	TBD	0.92	5	0.92	5
2,4-Dichlorophenol	120-83-2	TBD	TBD	0.98	5	0.98	5
2,4-Dimethylphenol	105-67-9	TBD	TBD	0.86	10	0.86	10
2,4-Dinitrophenol	51-28-5	TBD	TBD	3.68	20	3.68	20
2,4-Dinitrotoluene	121-14-2	TBD	TBD	0.98	10	0.98	10
2,6-Dinitrotoluene	606-20-2	TBD	TBD	1.66	10	1.66	10
2-Chloronaphthalene	91-58-7	TBD	TBD	0.94	2.5	0.94	2.5
2-Chlorophenol	95-57-8	TBD	TBD	0.53	5	0.53	5
2-Methyl-4,6-dinitrophenol	534-52-1	TBD	TBD	1.44	10	1.44	10
2-Methylnaphthalene	91-57-6	TBD	TBD	0.73	5	0.73	5
2-Methylphenol	95-48-7	TBD	TBD	0.83	5	0.83	5
2-Nitroaniline	88-74-4	TBD	TBD	1.40	10	1.40	10
2-Nitrophenol	88-75-5	TBD	TBD	1.14	10	1.14	10
3/4-Methylphenol	106-44-5	TBD	TBD	0.62	5	0.62	5
3-Nitroaniline	99-09-2	TBD	TBD	0.44	5	0.44	5
4-Bromophenyl phenyl ether	101-55-3	TBD	TBD	0.97	5	0.97	5
4-Chloro-3-methylphenol	59-50-7	TBD	TBD	1.22	10	1.22	10
4-Chloroaniline	106-47-8	TBD	TBD	0.45	2.5	0.45	2.5
4-Chlorophenyl phenyl ether	7005-72-3	TBD	TBD	0.88	5	0.88	5
4-Nitroaniline	100-01-6	TBD	TBD	0.85	10	0.85	10
4-Nitrophenol	100-02-7	TBD	TBD	0.77	5	0.77	5
Acenaphthene	83-32-9	TBD	TBD	1.01	5	1.01	5

Acenaphthylene	208-96-8	TBD	TBD	0.86	5	0.86	5
Aniline	62-53-3	TBD	TBD	0.50	2.5	0.50	2.5
Anthracene	120-12-7	TBD	TBD	0.73	5	0.73	5
Benzo(a)anthracene	56-55-3	TBD	TBD	1.25	10	1.25	10
Benzo(a)pyrene	50-32-8	TBD	TBD	1.68	10	1.68	10
Benzo(b)fluoranthene	205-99-2	TBD	TBD	1.63	10	1.63	10
Benzo(g,h,i)perylene	191-24-2	TBD	TBD	2.37	10	2.37	10
Benzo(k)fluoranthene	207-08-9	TBD	TBD	1.90	5	1.90	5
Benzyl alcohol	100-51-6	TBD	TBD	0.91	5	0.91	5
Bis(2-chloroethoxy) methane	111-91-1	TBD	TBD	0.54	5	0.54	5
Bis(2-chloroethyl) ether	111-44-4	TBD	TBD	0.58	5	0.58	5
Bis(2-chloroisopropyl) ether	108-60-1	TBD	TBD	0.48	5	0.48	5
Bis(2-ethylhexyl) phthalate	117-81-7	TBD	TBD	9.03	10	9.03	10
Butyl benzyl phthalate	85-68-7	TBD	TBD	2.10	10	2.10	10
Carbazole	86-74-8	TBD	TBD	0.68	10	0.68	10
Chrysene	218-01-9	TBD	TBD	1.47	5	1.47	5
Dibenz(a,h)anthracene	53-70-3	TBD	TBD	0.88	10	0.88	10
Dibenzofuran	132-64-9	TBD	TBD	0.97	5	0.97	5
Diethyl phthalate	84-66-2	TBD	TBD	1.31	10	1.31	10
Dimethyl phthalate	131-11-3	TBD	TBD	1.31	10	1.31	10
Di-n-butyl phthalate	84-74-2	TBD	TBD	1.16	10	1.16	10
Di-n-octyl phthalate	117-84-0	TBD	TBD	3.55	10	3.55	10
Fluoranthene	206-44-0	TBD	TBD	0.98	10	0.98	10
Fluorene	86-73-7	TBD	TBD	0.70	5	0.70	5
Hexachlorobenzene	118-74-1	TBD	TBD	0.98	5	0.98	5
Hexachlorobutadiene	87-68-3	TBD	TBD	1.20	2.5	1.20	2.5
Hexachlorocyclopentadiene	77-47-4	TBD	TBD	1.13	5	1.13	5
Hexachloroethane	67-72-1	TBD	TBD	0.82	5	0.82	5
Indeno(1,2,3-cd)pyrene	193-39-5	TBD	TBD	3.89	10	3.89	10
Isophorone	78-59-1	TBD	TBD	0.84	5	0.84	5
Naphthalene	91-20-3	TBD	TBD	0.82	2.5	0.82	2.5
Nitrobenzene	98-95-3	TBD	TBD	0.70	5	0.70	5
N-Nitrosodi-n-propylamine	621-64-7	TBD	TBD	1.77	5	1.77	5
Pentachlorophenol	87-86-5	TBD	TBD	1.52	10	1.52	10
Phenanthrene	85-01-8	TBD	TBD	0.93	5	0.93	5
Phenol	108-95-2	TBD	TBD	0.71	2.5	0.71	2.5
Pyrene	129-00-0	TBD	TBD	1.49	10	1.49	10

Reference Limits and Evaluation Table E

Matrix	Air
Analytical Group[1]	TO-17
Concentration Level	Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit µg/L, µg/Kg, µg/Wipe	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Propene	115-07-1	TBD	TBD	0.48	1.00	0.48	1.00
Dichlorodifluoromethane	75-71-8	TBD	TBD	0.22	0.50	0.22	0.50
Freon 114	76-14-1	TBD	TBD	0.15	0.50	0.15	0.50
Chloromethane	74-87-3	TBD	TBD	0.83	2.00	0.83	2.00
1,3-Butadiene	106-99-0	TBD	TBD	0.22	0.50	0.22	0.50
Vinyl Chloride	75-01-4	TBD	TBD	0.16	0.50	0.16	0.50
Bromomethane	74-83-9	TBD	TBD	0.52	2.00	0.52	2.00
Chloroethane	75-00-3	TBD	TBD	0.47	1.00	0.47	1.00
Trichlorofluoromethane	75-69-4	TBD	TBD	0.14	0.50	0.14	0.50
1,1-Dichloroethene	75-34-4	TBD	TBD	0.12	0.50	0.12	0.50
Freon 113	76-13-1	TBD	TBD	0.16	0.50	0.16	0.50
Isopropyl alcohol	67-63-0	TBD	TBD	0.43	1.00	0.43	1.00
Methylene Chloride	75-09-2	TBD	TBD	0.58	2.00	0.58	2.00
Acetone	67-64-1	TBD	TBD	0.72	2.00	0.72	2.00
trans-1,2-Dichloroethene	156-60-5	TBD	TBD	0.14	0.50	0.14	0.50
Hexane	110-54-3	TBD	TBD	0.16	0.50	0.16	0.50
Methyl tert-butyl ether	1634-04-4	TBD	TBD	1.58	5.00	1.58	5.00
1,1-Dichloroethane	75-34-3	TBD	TBD	0.16	0.50	0.16	0.50
cis-1,2-Dichloroethene	156-59-2	TBD	TBD	0.13	0.50	0.13	0.50
Cyclohexane	110-82-7	TBD	TBD	0.14	0.50	0.14	0.50
Chloroform	67-66-3	TBD	TBD	0.13	0.50	0.13	0.50
Carbon Tetrachloride	56-23-5	TBD	TBD	0.13	0.50	0.13	0.50
Ethyl acetate	141-78-6	TBD	TBD	0.11	0.50	0.11	0.50
1,1,1-Trichloroethane	71-55-6	TBD	TBD	0.16	0.50	0.16	0.50
2-butanone	78-93-3	TBD	TBD	0.17	0.50	0.17	0.50
Heptane	14-82-5	TBD	TBD	0.12	0.50	0.12	0.50
Benzene	71-43-2	TBD	TBD	0.14	0.50	0.14	0.50

1,2-Dichloroethane	107-06-2	TBD	TBD	0.15	0.50	0.15	0.50
Trichloroethene	79-01-6	TBD	TBD	0.24	0.50	0.24	0.50
1,2-Dichloropropane	78-87-5	TBD	TBD	0.12	0.50	0.12	0.50
Bromodichloromethane	75-27-4	TBD	TBD	0.08	0.50	0.08	0.50
1,4-Dioxane	123-91-1	TBD	TBD	0.21	0.50	0.21	0.50
Methyl methacrylate	80-62-6	TBD	TBD	0.11	0.50	0.11	0.50
cis-1,3-Dichloropropene	10061-01-5	TBD	TBD	0.14	0.50	0.14	0.50
4-Methyl-2-pentanone	108-10-1	TBD	TBD	0.18	0.50	0.18	0.50
Toluene	108-88-3	TBD	TBD	0.15	0.50	0.15	0.50
trans-1,3-Dichloropropene	10061-02-6	TBD	TBD	0.13	0.50	0.13	0.50
1,1,2-Trichloroethane	79-00-5	TBD	TBD	0.12	0.50	0.12	0.50
Tetrachloroethene	127-18-4	TBD	TBD	0.14	0.50	0.14	0.50
2-Hexanone	591-78-6	TBD	TBD	0.16	0.50	0.16	0.50
Dibromochloromethane	124-48-1	TBD	TBD	0.15	0.50	0.15	0.50
1,2-Dibromoethane	106-93-4	TBD	TBD	0.13	0.50	0.13	0.50
Chlorobenzene	108-90-7	TBD	TBD	0.15	0.50	0.15	0.50
Ethylbenzene	100-41-4	TBD	TBD	0.17	0.50	0.17	0.50
m,p-Xylene	106-42-3/108-38-3	TBD	TBD	0.43	1.00	0.43	1.00
o-Xylene	95-47-6	TBD	TBD	0.17	0.50	0.17	0.50
Styrene	100-42-5	TBD	TBD	0.20	0.50	0.20	0.50
Bromoform	75-25-2	TBD	TBD	0.20	0.50	0.20	0.50
1,1,2,2-Tetrachloroethane	79-34-5	TBD	TBD	0.22	0.50	0.22	0.50
4-Ethyltoluene	622-96-8	TBD	TBD	0.19	0.50	0.19	0.50
1,3,5-Trimethylbenzene	108-67-8	TBD	TBD	0.25	0.50	0.25	0.50
1,2,4-Trimethylbenzene	95-63-6	TBD	TBD	0.22	0.50	0.22	0.50
1,3-Dichlorobenzene	541-73-1	TBD	TBD	0.23	0.50	0.23	0.50
1,4-Dichlorobenzene	106-46-7	TBD	TBD	0.28	1.00	0.28	1.00
Benzyl Chloride	100-44-7	TBD	TBD	0.26	1.00	0.26	1.00
1,2-Dichlorobenzene	95-90-41	TBD	TBD	0.25	0.50	0.25	0.50
Hexachlorobutadiene	87-68-3	TBD	TBD	0.65	2.00	0.65	2.00
1,2,4-Trichlorobenzene	120-82-1	TBD	TBD	0.51	2.00	0.51	2.00
Naphthalene	91-20-3	TBD	TBD	1.06	5.00	1.06	5.00

Reference Limits and Evaluation Table F

Matrix	Wipe
Analytical Group[1]	Opioids methanol extraction
Concentration Level	Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit µg/L, µg/Kg, µg/Wipe	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Heroin	561-27-3	TBD	TBD	0.0708	0.200	0.0708	0.200
Remifentanil	132539-07-2	TBD	TBD	0.0097	0.030	0.0097	0.030
Acetylfentanyl	3258-84-2	TBD	TBD	0.00564	0.030	0.00564	0.030
Fentanyl	437-38-7	TBD	TBD	0.00544	0.030	0.00544	0.030
Carfentanil	61086-44-0	TBD	TBD	0.00663	0.030	0.00663	0.030
Sulfentanil	60561-17-3	TBD	TBD	0.0617	0.030	0.0617	0.030
Alfentanil	69049-06-5	TBD	TBD	0.0101	0.030	0.0101	0.030

Notes:
Extracts run by GCMS Quad MMI LVI

Reference Limits and Evaluation Table G

Matrix	Wipe
Analytical Group[1]	Opioids
Concentration Level	Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit µg/L, µg/Kg, µg/Wipe	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs ug/wipe	QLs
Heroin	561-27-3	TBD	TBD	0.0101	0.030	0.0101	0.030
Remifentanil	132539-07-2	TBD	TBD	0.00192	0.008	0.00192	0.008
Acetylfentanyl	3258-84-2	TBD	TBD	0.00060	0.001	0.00060	0.001
Fentanyl	437-38-7	TBD	TBD	0.00046	0.001	0.00046	0.001
Carfentanil	61086-44-0	TBD	TBD	0.00098	0.001	0.00098	0.001
Sulfentanil	60561-17-3	TBD	TBD	0.00023	0.001	0.00023	0.001
Alfentanil	69049-06-5	TBD	TBD	0.00037	0.001	0.00037	0.001
Xylanzine	7361-61-7	TBD	TBD	0.00033	0.001	0.00033	0.001
Ketamine	6740-88-1	TBD	TBD	0.00867	0.02	0.00867	0.02
Methamphetamine	300-62-9	TBD	TBD	0.01635	0.03	0.01635	0.03
Cocaine	50-36-2	TBD	TBD	0.000891	0.05	0.000891	0.05

Notes:
Extracts analyzed via UPLCMSMS

QAPP Worksheet #16.
Project Schedule/Timeline Table

Activities	Organization	Dates (Month Day, Year)		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
QAPP Preparation	PHILIS	06/18/2024	7/10/24	NA	NA
Instrument Calibrations	PHILIS	Prior to sample analysis	Prior to sample analysis	NA	NA
MDLs and DOCs	PHILIS	Prior to sample analysis	Prior to sample analysis	Prior to Project Start	Prior to Project Start

QAPP Worksheet #17.
Sampling Design and Rationale

Describe and provide a rationale for choosing the sampling approach (e.g., grid system, biased statistical approach):

NA The laboratory does not collect samples.

QAPP Worksheet #18.

Sampling Locations and Methods/SOP Requirements Table

Sampling Location/ ID Number	Matrix	Depth	Analytical Group	Concentration Level	Number of Samples (identify field duplicates)[1]	Sampling SOP Reference[2]	Rationale for Sampling Location
To be determined by the sampling team							

Notes:
[1]MS/MSD and field duplicate samples should be collected at a frequency of 1 for every 20 samples.
[2]Specify the appropriate letter or number from the Project Sampling SOP References table (Worksheet #21).

QAPP Worksheet #19.
Analytical SOP Requirements Table

Matrix	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference[1]	Sample Volume	Containers (number, size, and type)	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)
Soil	CWA	Low	SOP L-A-502 SOP L-P-107	10 g	8 oz. amber jars	0-6 °C	ASAP but within 14 Days
Wipe	CWA	Low	SOP L-A-502 SOP L-P-107	1 Wipe	2 40 mL vials	0-6 °C	ASAP but within 7 Days
Water	8260	Low	SOP L-A-101	40 mL	2 40 mL vials with NO headspace	0-6 °C	ASAP but within 7 Days, unless preserved with HCL then 14 days
Water	8270	Low	SOP L-A-201 SOP L-P 101	100 mL	2 125 mL amber bottles	0-6 °C	ASAP but within 14 Days
Soil	8270	Low	SOP L-A-201 SOP L-P-203	30 g	8 oz amber jar	0-6 °C	ASAP but within 14 Days
Air	TO-17	Low	SOP L-A-601	1 Liter	2 Tubes	4 °C	ASAP but within 30 days
Soil	Opioids	Low	SOP L-P-114 SOP L-A_310	30 g	8 oz amber jars	0-6 °C	ASAP but within 7 Days
Wipe	Opioids	Low	SOP L-P-114 SOP L-A_310	1 Wipe	2 40 mL vials	0-6 °C	ASAP but within 7 Days

Notes:
[1]Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23).
ºC – Degrees Celsius, oz – ounce

QAPP Worksheet #20.

Field Quality Control Sample Summary Table (1)

Matrix	Analytical Group	Concentration Level	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations[2]	No. of Field Duplicates	No. of MS/MSD	No. of Field Blanks	No. of Equip. Blanks	Total No. of Samples to Lab
To be determined by the sampling team									

Notes:
[1]Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23).
[2]If samples will be collected at different depths at the same location, count each discrete sampling depth as a separate sampling location or station.

MS – Matrix Spike
MSD – Matrix Spike Duplicate

QAPP Worksheet #21.
Project Sampling SOP References Table

Reference Number	Title, Revision Date and/or Number	Originating Organization	Equipment Type	Modified for Project Work? (Y/N)	Comments
N/A	To be determined by the sampling team				

QAPP Worksheet #22.

Field Equipment Calibration, Maintenance, Testing, and Inspection Table

Field Equipment	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
To be determined by the sampling team									

QAPP Worksheet #23.
Analytical SOP References Table

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
SOP L-A-502	Analysis of CWAs by GC-MS Rev 0 05/07/2024	Definitive	CWA	GC/MS LVI Quad	PHILIS	N
SOP L-A-201	Semivolatile Organics by Method 8270E Rev 3 06/19/2024	Definitive	Semivolatile Organics	GC/MS Quad	PHILIS	N
SOP L-A-101	Volatile Organics by Method 8260D Rev 3 05/31/2024	Definitive	Volatile Organics	GC/MS Quad	PHILIS	N
SOP L-A-601	Air Analysis by TO-17 Rev 2 09/07/2023	Definitive	Air	GC/MS Quad	PHILIS	N
SOP L-A-310	Opioids on Soil, Water, and Wipes by Altis UPLC/MS/MS Rev 5 01/23/2024	Definitive	Opioids	UPLCMSMS	PHILIS	N
SOP L-A-100	Moisture Determination Rev 1 08/24/2023	Definitive	Soils	Drying Oven	PHILIS	N
SOP L-P-101	Sep Funnel Extraction for SVOA in Water Rev 2 06/21/2024	Definitive	Water	Sep Funnel	PHILIS	N
SOP L-P-203	Microwave Extraction Rev 0. 05/09/2024	Definitive	Water	Microwave	PHILIS	N
SOP L-A-704	Analysis of Opioids by GCMS QUAD LVI	Definitive	Soil, Wipe	GC/MS LVI Quad	PHILIS	N
SOP L-P-200	Pressurized Solvent Extraction (PSE)	Definitive	Soil, Wipe	PSE	PHILIS	N

QAPP Worksheet #24.
Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
GCMS Quad	%RSD, Linear, or Quadratic	As needed	20 % RSD 0.99 Linear 0.995 Quadratic	Check all points for validity or recalibrate	Analyst	SOP L-A-603 Rev 1 SOP L-A-201 Rev 3 SOP L-A-101 Rev 3 SOP L-A-601 Rev 2 SOP L-A-502 Rev 0 SOP L-A-704 Rev 0
UPLC/MSMS	%RSD, Linear, or Quadratic	As needed	20 % RSD 0.99 Linear 0.995 Quadratic	Check all points for validity or recalibrate	Analyst	SOP L-A-310 Rev 5

Notes:
[1]Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23).

QAPP Worksheet #25.

Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table

Instrument/ Equipment	Maintenance Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
GCMS Quad	Per method	CCV-Opening CCV-Closing	Per method	40 % 50 %	Evaluate System, reanalyze CCV, and recalibrate if necessary. Reanalyze affected samples.	Analyst	SOP L-A-603 Rev 0
GCMS Quad	Per method	BFB or DFTPP prior to calibration CCV-Opening	Per method	Passing tune criteria 20%	Evaluate system, reanalyze tune or CCV, and recalibrate if necessary. Reanalyze affected samples	Analyst	SOP L-A-201 Rev 3 SOP L-A-101 Rev 3 SOP L-A-601 Rev 2 SOP L-A-101 Rev 3 SOP L-A-601 Rev 2 SOP L-A-502 Rev 0 SOP L-A-704 Rev 0
UPLCMSMS	Per method	CCV	Per method	±20 %	Evaluate system, reanalyze CCV, and recalibrate if necessary. Reanalyze affected samples	Analyst	SOP L-A-310 Rev 5

Notes:
[1]Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23).

QAPP Worksheet #26.
Sample Handling System

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
• Sample Collection (Personnel/Organization): N/A
• Sample Packaging (Personnel/Organization): N/A
• Coordination of Shipment (Personnel/Organization): N/A
• Type of Shipment/Carrier: N/A
SAMPLE RECEIPT AND ANALYSIS
• Sample Receipt (Personnel/Organization): PHILIS
• Sample Custody and Storage (Personnel/Organization): PHILIS
• Sample Preparation (Personnel/Organization): PHILIS
• Sample Determinative Analysis (Personnel/Organization): PHILIS
SAMPLE ARCHIVING
• Samples: Per SAP/QAPP: PHILIS
• Sample Extracts/Digestate Storage: Per SAP/QAPP: PHILIS
SAMPLE DISPOSAL
• Personnel/Organization: Site Personnel or PHILIS
• Number of Days from Analysis: Site Personnel

QAPP Worksheet #27.
Sample Custody Requirements

Chain-of-Custody Procedures: A Chain-of-Custody (COC) form will be maintained from the time the sample is collected until its delivery to the laboratory. To maintain a record of sample collection, transfer between personnel, shipment, and receipt by the laboratory, a COC record will be filled out for each sample at each sampling location. Each individual in possession of the samples must sign and date the sample COC document. Each time the samples are transferred, the signatures of the persons relinquishing and receiving the samples, as well as the date and time, will be documented. A copy of the COC is retained by the project manager for the site file. When samples (or groups of samples) are not under direct control of the individual responsible for them, they must be stored in a locked container sealed with a custody seal. The COC record will be considered completed upon receipt at the laboratory. The COC record should include (at minimum) the following: NA

- Type (s) of analysis(es) to be performed
- Sample ID number
- Sample information
- Sample station location
- Sample date
- Name(s) and signature(s) of sampler(s)
- Signature(s) of any individual(s) with control over samples

A separate COC form must accompany each cooler in each shipment. Within the laboratory, the person responsible for sample receipt must sign and date the COC form; verify that custody seals are intact on shipping containers; compare samples received against those listed on the COC form; examine all samples for possible shipping damage, leakage, and improper sample preservation; note on the COC record or laboratory receiving documentation that specific samples were damaged; notify sampling personnel as soon as possible so that appropriate samples may be resampled; verify that sample holding times have not been exceeded; maintain laboratory COC documentation; and place the samples in appropriate laboratory storage. If requested, the laboratory may submit internal COC documentation with the data package. Final sample disposition is completed according to laboratory license requirements.

Sample Identification Procedures: All samples for laboratory analysis, including QC samples, will be given a unique sample number that is assigned by the preparing laboratory.

QAPP Worksheet #28.
QC Samples Table

		Concentration Level:	Low
Analytical Group:	CWA	Sampler's Name:	N/A
Analytical Method/ SOP Reference:	SOP L-A-502 Rev 0 05/07/2024	Field Sampling Organization:	N/A
Matrix:	Soil/Water/Wipe/Air	Analytical Organization:	PHILIS
Sampling SOP:	N/A	No. of Sample Locations:	N/A

QC Sample	Frequency / Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	DQI	Measurement Performance Criteria
Laboratory Duplicates	1 DUP or MS/MSD	RPD ≤ 30%	Flag associated data or reprep and reanalyze Samples where possible	Chemist	Laboratory Precision	
Method Blank	1/Prep Batch	No target analyte concentrations above method detection limit Air samples require closing blank also	Flag associated data or reprep and reanalyze Samples where possible	Chemist	Laboratory Contamination	
LCS	1/Prep Batch	50% - 150%	Flag associated data or reprep and reanalyze Samples where possible	Chemist	Laboratory Accuracy	
MS/MSD	1/Prep Batch	50% - 150%	Flag associated data or reprep and reanalyze samples where possible	Chemist	Matrix Interference/ Laboratory Accuracy	

		Concentration Level:	Low Level GCMS QUAD
Analytical Group:	8260D Volatiles, 8270E Semivolatiles	Sampler's Name:	N/A
Analytical Method/ SOP Reference:	SOP L-A-101 Rev 3 05/31/2024 SOP L-A-201 Rev 3 06/19/2024	Field Sampling Organization:	N/A
Matrix:	Water and Soil	Analytical Organization:	PHILIS
Sampling SOP:	N/A	No. of Sample Locations:	N/A

QC Sample	Frequency / Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	DQI	Measurement Performance Criteria
CCV or calibration	Opening	8260D Opening 80-120% 8270E Opening 80-120%	Reanalyze and/or recalibrate system	Chemist		
Method Blank	1/Prep Batch	No target analyte concentrations above method reporting limit	Flag associated data or reprepare and reanalyze samples where possible if data is affected	Chemist	Laboratory Contamination	
LCS	1/Prep Batch	8260D Varies per analyte 8270E Varies per analyte	Reprepare and reanalyze LCS's where possible	Chemist	Laboratory Accuracy	
Laboratory Duplicates	1/Prep Batch	% RSD 30%	Flag associated data or reprepare and reanalyze samples where possible if data is affected	Chemist	Laboratory Precision	
MS/MSD	1/Prep Batch	8260D Varies per analyte 8270E Varies per analyte	Flag associated data or reprepare and reanalyze samples where possible if data is affected	Chemist	Sample Matrix	

			Concentration Level:	Low		
Analytical Group:	Opioids		Sampler's Name:	N/A		
Analytical Method/ SOP Reference:	SOP L-A-310 SOP L-A-704		Field Sampling Organization:	**N/A**		
Matrix:	Wipe, Soil, Water		Analytical Organization:	PHILIS		
Sampling SOP:	N/A		No. of Sample Locations:	N/A		
QC Sample	**Frequency / Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**DQI**	**Measurement Performance Criteria**
Laboratory Duplicates	1 DUP	RPD ≤ 30%	Flag associated data or reprep and reanalyze samples where possible	Chemist	Laboratory Precision	
Method Blank	1/Prep Batch	No target analyte concentrations above method reporting limit	Flag associated data or reprep and reanalyze samples where possible	Chemist	Laboratory Contamination	
LCS	1/Prep Batch	50% - 150%	Flag associated data or reprep and reanalyze samples where possible	Chemist	Laboratory Accuracy	
MS/MSD	1/Prep Batch if sample provided	50% - 150%	Flag associated data or reprep and reanalyze samples where possible	Chemist	Matrix Interference/ Laboratory Accuracy	

QAPP Worksheet #29.
Project Documents and Records Table

Sample Collection Documents and Records	On-site Analysis Documents and Records	Off-site Analysis Documents and Records	Data Assessment Documents and Records	Other
NA	Logbook(s)	NA	Data Review Form	NA
	Final Analytical Data Summary Report			
	LIMS			
	Sample Receipt, Custody, and Tracking Records			
	Preliminary analytical data reports			
	Final Analytical Data Summary Reports			
	Laboratory Electronic Data Deliverables			
	Sample Preparation Logs			
	Run Logs			
	Equipment Maintenance, Testing, and Inspection Logs			
	Instrument printouts (raw data)			
	Quality Control Sample Summary Forms			
	Sample Disposal Records			
	Corrective Action Reports			

QAPP Worksheet #30.
Analytical Services Table

Matrix	Analytical Group	Concentration Level	Sample Locations/ ID Numbers	Analytical SOP	Data Package Turnaround Time	Laboratory/Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/Organization (Name and Address, Contact Person and Telephone Number)
Soil & Wipes	CWA	Low	NA	L-A-502 Rev 0	2 weeks after Prelim results sent	CSS, Attn: Sang Chung 2890 Woodbridge Ave, Bldg 238 Edison, NJ 219-477-8860	CSS, Attn: Crystal Chu 2890 Woodbridge Ave, Bldg 238 Edison, NJ 516-467-9580
Soil & Water	Volatiles	Low	NA	L-A-101 Rev 3	2 weeks after Prelim results sent	CSS, Attn: Sang Chung 2890 Woodbridge Ave, Bldg 238 Edison, NJ 219-477-8860	CSS, Attn: Crystal Chu 2890 Woodbridge Ave, Bldg 238 Edison, NJ 516-467-9580
Soil & Water	Semivolatiles	Low	NA	L-A-201 Rev 3	2 weeks after Prelim results sent	CSS, Attn: Sang Chung 2890 Woodbridge Ave, Bldg 238 Edison, NJ 219-477-8860	CSS, Attn: Crystal Chu 2890 Woodbridge Ave, Bldg 238 Edison, NJ 516-467-9580
Soil, Water, & Wipes	Opioids	Low	NA	L-A-310 Rev 5 L-A-704 Rev 0	2 weeks after Prelim results sent	CSS, Attn: Sang Chung 2890 Woodbridge Ave, Bldg 238 Edison, NJ 219-477-8860	CSS, Attn: Crystal Chu 2890 Woodbridge Ave, Bldg 238 Edison, NJ 516-467-9580

QAPP Worksheet #31.
Planned Project Assessments Table

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 CA (Title and Organizational Affiliation)	Person(s) Responsible for Monitoring Effectiveness of CA (Title and Organizational Affiliation)
Data Review	NA	Internal	PHILIS	CSS QA Manager and/or Lead Chemist	CSS QA Manager and/or Lead Chemist	CSS Lead Chemist and/or Chemists	CSS Lead Chemist and/or Chemists

QAPP Worksheet #32.
Assessment Findings and Response Actions

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
NCR/CAR	P&A or contamination	PHILIS Lead Chemist and QA Manager	ASAP	Data flagging or reprep and reanalyze	PHILIS Lead Chemists and QA Manager	ASAP

QAPP Worksheet #33.
QA Management Reports Table

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)
NA	NA	NA	NA	NA

QAPP Worksheet #34.
Sampling and Analysis Verification (Step I) Process Table

Verification Input	Description	Internal/ External	Responsible for Verification (Name, Organization)
COC Forms	Lists all samples sent to the lab for analysis and received by the lab for analysis	External/ Internal	Sample team/sample receipt team
Laboratory Data	Verify samples prepped, analyzed, reviewed, and reported within holding time and QA limits.	Internal	Sang Chung/ PHILIS Edison Tom Fowler/PHILIS Castle Rock

QAPP Worksheet #35.

Sampling and Analysis Validation (Steps IIa and IIb) Process Table

Step IIa/IIb	Validation Input	Description	Responsible for Validation (Name, Organization)
	Laboratory Data	Verify samples and associated quality control are in place and within limits or addressed in the case narrative.	Tom Antony, PHILIS QA Manager
	Data Package Completeness	Verify samples received have been reported with correct data.	Julia Capri, PHILIS Program Manager

QAPP Worksheet #36.
Sampling and Analysis Validation (Steps IIa and IIb) Summary Table

Step IIa/IIb	Matrix	Analytical Group	Concentration Level	Validation Criteria	Data Validator (title and organizational affiliation)
NA	NA	NA	NA	NA	NA

QAPP Worksheet #37.
Data Usability Assessment

Summarize the usability assessment process and all procedures, including interim steps and any statistics, equations, and computer algorithms that will be used: Data, generated by the laboratory, are tabulated and reviewed for precision, accuracy, representativeness, and completeness by the project manager or QA Manager. The review of these data quality indicators (DQI) will compare the DQI with the DQO detailed in the project-specific QAPP and in the analytical methods used.

Questions about data, as observed during the data review process, are resolved by contacting the respective site personnel and laboratories for resolution. All communications are documented including the resolution to the observed deficiencies. Hard copies of all original data and deliverables are kept in the project file.

When the data does not meet the project DQOs, CSS will investigate the root cause to the deficiency. Reasons may include laboratory operation, such as the laboratory's failure to adjust the extraction weight on high-moisture-content soil, failure of laboratory reporting limits to meet site Action Limits, or poor correlation between field screening and laboratory results. In these situations, CSS will discuss corrective actions with the EPA work assignment manager. These actions may include:

- Resampling for all or some of the parameters
- Preparing a technical memorandum to the site file, detailing limitations to the data
- Validating the data at a higher tier level to better qualify the results
- Preparing a technical memorandum determining the bias of field results

Describe the evaluative procedures used to assess overall measurement error associated with the project: The following specific items will be assessed in the manner described below:

Precision – Results of all laboratory duplicates and field duplicates will be presented in the laboratory data validation report. For each duplicate pair, the RPD will be calculated for each analyte with results greater than or equal to the quantitation limit. The RPDs will be checked against the measurement performance criteria presented on Worksheet #12. The RPDs exceeding criteria will be identified on the tables in the final report with appropriate qualifiers. The analytical report's case narrative will provide a discussion summarizing the results of the laboratory precision.

Accuracy/Bias Contamination – Results for all laboratory method blanks and instrument blanks will be presented in the laboratory data package. The results for each analyte will be checked against the measurement performance criteria presented on Worksheet #12. Results for analytes that exceed criteria will be identified on the tables in the final report with appropriate qualifiers. The analytical report's case narrative will provide a discussion summarizing the results of the laboratory accuracy/bias.

Overall Accuracy/Bias – The results for the continuing calibration standards and laboratory control standards will be presented in the laboratory data report. These results will be compared to the requirements listed on Worksheet #12. The analytical report's case narrative will provide a discussion summarizing overall accuracy/bias.

Sensitivity – All sample results will be presented in tabular format for each analyte. The sample results for each analyte will be checked against the method detection limits. Results for analytes that do not meet the required quantitation limits will be discussed. The analytical report's case narrative will provide any conclusions about the sensitivity of the analyses.

Representativeness – Representativeness will be maintained by following SOPs for sampling anal analyses. Any conclusions about the representativeness of the sampling will be drawn and any limitations on the use of the data will be described in the case narrative.

Completeness – A completeness check will be done on all samples collected in the field and data generated by the laboratory. Completeness criteria are presented on Worksheet #12. Completeness will be calculated as follows. For each sample collected, completeness will be calculated as the number of samples collected and number of analyses performed, divided by the total number of planned sample collection points and analyses. A discussion will follow summarizing the calculation of data completeness.

Reconciliation – Each of the project quality objectives presented on Worksheet #12 will be examined to determine if the objective was met. Each analysis will first be evaluated in terms of the major impacts observed from the data validation, DQIs, and measurement performance criteria assessments. Based on the results of these assessments, the quality of the data will be determined. Based on the quality determined, the usability of the data for each analysis will be determined. Based on the usability of the data from all analyses for an objective, it will be determined if the project quality objective was met. As part of the reconciliation of each objective, conclusions will be drawn and any limitations on the usability of any of the data will be described.

Identify the personnel responsible for performing the usability assessment: The CSS QA Manager will do a compliance check of the data to determine the usability of analytical data. The PM, Julia Capri, will be responsible for the overall usability to meet project objectives.

Describe the documentation that will be generated during usability assessment and how usability assessment results will be presented so that they identify trends, relationships (correlations), and anomalies: Overall usability of data to meet project objectives will be described in the final report.

ATTACHMENT 1 -
PROJECT ROUTINE ANALYSIS LIST

Analyte Type	Sample Collection Method	Analytical Method	Prep Method	Matrix	Required Field QA/QC Samples	Optional Field QA/QC Samples	Container Type & Size	Preservative	Holding Time	EDD Results	Level 4 Data Pkg	Certification	Samples per day (8 hours)	Max samples per day (24 hours)	Comments
CWAs Cyclohexyl Sarin, Sarin, Soman, Sulfur Mustard, VX	125 mL amber jar with PTFE lined septum caps	CWA SAP TOF GC/MS	CWA SAP	Water	MS/MSD	Rinse blank	2 - 125 mL jars with Teflon lined lids	Cool to 4 ± 2° C.	14 days	Per QAPP or project requirement	14 Days from EDD report	None	CR-20 ED-20	CR-40 ED-40	
CWAs Cyclohexyl Sarin, Sarin, Soman, Sulfur Mustard, VX	4 or 8 oz jar with Teflon lined lid	CWA SAP TOF GC/MS	CWA SAP	Soil	MS/MSD	Rinse blank	4 or 8 oz jar	Cool to 4 ± 2° C.	14 days	Per QAPP or project requirement	14 Days from EDD report	None	CR-20 ED-20	CR-40 ED-40	
CWAs Cyclohexyl Sarin, Sarin, Soman, Sulfur Mustard, VX	Wipes	CWA SAP TOF GC/MS	CWA SAP	Wipes	Wipe trip blank		1 wipe	Cool to 4 ± 2° C.	14 days	Per QAPP or project requirement	14 Days from EDD report	None	CR-20 ED-20	CR-40 ED-40	
CWAs Cyclohexyl Sarin, Sarin, Soman, Sulfur Mustard, VX	125 mL amber jar with PTFE lined septum caps	CWA SAP LVI GC/MS	CWA SAP	Water	MS/MSD	Rinse blank	2 - 125 mL jars with Teflon lined lids	Cool to 4 ± 2° C.	14 days	Per QAPP or project requirement	14 Days from EDD report	None	ED-20	ED-50	
CWAs Cyclohexyl Sarin, Sarin, Soman, Sulfur Mustard, VX	4 or 8 oz jar with Teflon lined lid	CWA SAP LVI GC/MS	CWA SAP	Soil	MS/MSD	Rinse blank	4 or 8 oz jar	Cool to 4 ± 2° C.	14 days	Per QAPP or project requirement	14 Days from EDD report	None	ED-20	ED-50	
CWAs Cyclohexyl Sarin, Sarin, Soman, Sulfur Mustard, VX	Wipes	CWA SAP LVI GC/MS	CWA SAP	Wipes	Wipe trip blank		1 wipe	Cool to 4 ± 2° C.	14 days	Per QAPP or project requirement	14 Days from EDD report	None	ED-20	ED-50	
VOC Water	40mL VOA vial with PTFE lined septum caps	8260D	5030C	Water	Trip blank, MS/MSD		3 VOA vials	pH adjusted to <2 with HCl Cool to 4 ± 2° C	14 days	Per QAPP or project requirement	14 Days from EDD report	NELAP	CR-30 ED-30	CR-50 ED-50	

Analyte Type	Sample Collection Method	Analytical Method	Prep Method	Matrix	Required Field QA/QC Samples	Optional Field QA/QC Samples	Container Type & Size	Preservative	Holding Time	EDD Results	Level 4 Data Pkg	Certification	Samples per day (8 hours)	Max samples per day (24 hours)	Comments
VOC Soil	EnCore or preweighed vials with PTFE septum lined caps	8260D	5035A	Soil	Trip blank, MS/MSD		3 VOA vials or 3 En Cores	Cool to 4 ± 2° C	En Cores frozen or extracted upon receipt 14 days	Per QAPP or project requirement	14 Days from EDD report	NELAP	CR-30 ED-30	CR-50 ED-50	
CWA Air (HD)	Sorbent tubes	CWA SAP TOF GC/MS	CWA SAP	Air	Trip blank tube from same tube prep batch		2 TENAX tubes	Cool to < 4° C	30 days	Per QAPP or project requirement	14 Days from EDD report	None	CR-20	CR-40	Need two weeks to set up
SVOC Water	125 mL amber jar with PTFE lined septum caps	8270E	3510C	Water	MS/MSD	Rinse blank	125 mL or larger	Cool to 4 ± 2° C	7 days to extract then 40 days to analysis	Per QAPP or project requirement	14 Days from EDD report	NELAP	CR-20 ED-20	CR-40 ED-40	
SVOC Soil	4 or 8 oz jar with Teflon lined lid	8270E	3545A	Soil	MS/MSD	Rinse blank	4 or 8 oz jar	Cool to 4 ± 2° C	14 days to extract then 40 days to analysis	Per QAPP or project requirement	14 Days from EDD report	NELAP	CR-20 ED-20	CR-40 ED-40	
OPP SVOC Soil	4 or 8 oz jar with Teflon lined lid	8270E	3545A	Soil	MS/MSD	Rinse blank	4 or 8 oz jar	Cool to 4 ± 2° C	14 days to extract then 40 days to analysis	Per QAPP or project requirement	14 Days from EDD report	NELAP	CR-20 ED-20	CR-40 ED-40	
CWA Air (HD) PCD Method	Sorbent tubes	PCD Method TOF	PCD Method	Air	Trip blank tube from same tube prep batch		2 TENAX tubes	Cool to < 4° C	30 days	Per QAPP or project requirement	14 Days from EDD report	None	CR-20	CR-40	Waiting for AMC/CMA approval. DAMMS tubes cannot be run overnight

Analyte Type	Sample Collection Method	Analytical Method	Prep Method	Matrix	Required Field QA/QC Samples	Optional Field QA/QC Samples	Container Type & Size	Preservative	Holding Time	EDD Results	Level 4 Data Pkg	Certification	Samples per day (8 hours)	Max samples per day (24 hours)	Comments
Opioids Fentanyl, Carfentanil, Sulfentanil, Acetylfentanil, Alfentanil, Heroin, Remifentanil, Water	125 mL amber jar with PTFE lined septum caps	8270E LVI QUAD	Micro Extraction	Water	MS/MSD	Rinse blank	4 or 8 oz jar	Cool to 4 ± 2° C	7 days to extract then 40 days to analysis	Per QAPP or project requirement	14 Days from EDD report	None	CR-20	CR-40	
Opioids Fentanyl, Carfentanil, Sulfentanil, Acetylfentanil, Alfentanil, Heroin, Remifentanil, Soil	4 or 8 oz jar with Teflon lined lid	8270E LVI QUAD	Micro Extraction	Soil	MS/MSD	Rinse blank	125 mL or larger	Cool to 4 ± 2° C	14 days to extract then 40 days to analysis	Per QAPP or project requirement	14 Days from EDD report	None	CR-20	CR-40	
Opioids Fentanyl, Carfentanil, Sulfentanil, Acetylfentanil, Alfentanil, Heroin, Remifentanil, Wipes	Wipes	8270E LVI QUAD	Micro Extraction	Wipes	Wipe trip blank		1 wipe	Cool to 4 ± 2° C.	14 days to extract then 40 days to analysis	Per QAPP or project requirement	14 Days from EDD report	None	CR-20	CR-40	
Opioids Fentanyl, Carfentanil, Sulfentanil, Acetylfentanil, Alfentanil, Heroin, Remifentanil, Water	125 mL amber jar with PTFE lined septum caps	LCMS/MS	Micro Extraction	Water	MS/MSD	Rinse blank	4 or 8 oz jar	Cool to 4 ± 2° C	7 days to extract then 40 days to analysis	Per QAPP or project requirement	14 Days from EDD report	None	CR-20	CR-60	Method in development

Analyte Type	Sample Collection Method	Analytical Method	Prep Method	Matrix	Required Field QA/QC Samples	Optional Field QA/QC Samples	Container Type & Size	Preservative	Holding Time	EDD Results	Level 4 Data Pkg	Certification	Samples per day (8 hours)	Max samples per day (24 hours)	Comments
Opioids Fentanyl, Carfentanil, Sulfentanil, Acetylfentanil, Alfentanil, Heroin, Remifentanil, Soil	4 or 8 oz jar with Teflon lined lid	LCMS/MS	Micro Extraction	Soil	MS/MSD	Rinse blank	125 mL or larger	Cool to 4 ± 2° C	14 days to extract then 40 days to analysis	Per QAPP or project requirement	14 Days from EDD report	None	CR-20	CR-60	Method in development
Opioids Fentanyl, Carfentanil, Sulfentanil, Acetylfentanil, Alfentanil, Heroin, Remifentanil, Wipes	Wipes	LCMS/MS	Micro Extraction	Wipes	Wipe trip blank		1 wipe	Cool to 4 ± 2° C.	14 days to extract then 40 days to analysis	Per QAPP or project requirement	14 days from EDD report	None	CR-20	CR-60	
CWA FGAs Soil	4 or 8 oz jar with Teflon lined lid	LCMS/MS	Micro Extraction	Soil	MS/MSD	Rinse blank	4 or 8 oz jar	Cool to 4 ± 2° C.	14 days	Per QAPP or project requirement	14 days from EDD report	None	CR-20	CR-80	Method in development
CWA FGAs Wipes	Wipes	LCMS/MS	Micro Extraction	Wipes	Wipe trip blank		1 wipe	Cool to 4 ± 2° C.	14 days to extract then 40 days to analysis	Per QAPP or project requirement	14 days from EDD report	None	CR-20	CR-80	
VOC in air	Sorbent tubes	TO-17 QUAD	TO-17	Air	Trip blank tube from same tube prep batch		2 TENAX tubes	Cool to < 4° C	30 days	Per QAPP or project requirement	14 days from EDD report	NELAP Certified	ED-12	ED-40	

NELAP - National Environmental Laboratory Accreditation Program National Environmental Laboratory Accreditation Program
SD - Sample Duplicate **MS/MSD** - Matrix Spike/ Matrix Spike Duplicate **EQ** - Equipment Blank **TBD** - To Be Determined
ED - Edison, NJ PHILIS Lab **CR** - Castle Rock, CO PHILIS Lab **N/A** - Not Applicable
See the monthly PHILIS Analysis Methods and Vehicle Mobilization Report for additional information.

APPENDIX A -
PHILIS SOP L-A-502 Rev. 0 05/07/2024
Analysis of CWAs by GC-MS

STANDARD OPERATING PROCEDURE

FOR

ANALYSIS OF CHEMICAL WARFARE AGENTS BY GC/MS

PHILIS SOP L-A-502 Rev. 0

Revision Date: 05-07-2024

EPA Contract No. 68HERH21D0002

PREPARED BY

PHILIS

PREPARED FOR

U.S. Environmental Protection Agency
Office of Emergency Management
Washington, DC 20460

Approvals:

PHILIS, Castle Rock Lead Chemist	**May 7, 2024** **Date**
PHILIS, Edison Lead Chemist	**May 7, 2024** **Date**
PHILIS, Quality Assurance Manager	**May 7, 2024** **Date**
PHILIS, Program Manager	**May 7, 2024** **Date**

Revision History

Revision	Name	Date	Description of Change
A	James Travis	04/01/2021	Transitional Issue
0	James Travis	03/07/2022	Program Issue

SOP REVISION FORM

SOP Name:	**Analysis of Chemical Warfare Agents by GC/MS**		
Purpose: *(Review or Revise)*	*SOP #:*	*Rev. #:* *(Being Reviewed or Revised)*	*Origination / Release Date:*
Program Issue	*SOP No. L-A-502*	A	04/30/2021
Requested by:	James Travis	Date:	03/07/2022

New Document Revision Date:	**05/07/2024**	**New Document Revision #:** *(If Applicable)*	**0**

For *Revision* : Summary of Revisions (specify sections)

1.0 and 2.0	Sections 1.0 and 2.0 removed from document
3.0	Section 3.0 added to QA section
18.0, 19.0, 20.0	Sections added to QA section 9.12, and 9.13 to 9.17
1.2 and 1.4	Added to increase specificity of the scope of the SOP
7.6	Section removed
10.3	Added updated storage requirements for laboratory standards
11.1	Added updated storage requirements for samples
11.4	Added updated holding times for samples
Section 12	EQ numbers updated
12.2.3	Updated IDC criteria
12.3.3.3	Modified method blank criteria (High ND)
12.3.3.5	Modified method blank re-extraction criteria
12.4	Added matrix spike criteria
12.4.3	Added basic limits for recovery and %RPD for matrix spikes
12.5.4	Added basic limits for LCS recovery
13.2.2	Frequency of GC/MS instrument performance check updated.
13.4.5	RRF standards for CCV opening and closing modified
22.13, 22.14, 22.15	References added
Table 3.	All RTs & RRTs updated, some primary/secondary quant ions changed
Table 4 and Table 5	Removed
Table 6	Full Scan removed, SIM & TOF some surrogates and internals removed

Standard Operating Procedure
Analysis of Chemical Warfare Agents by GC/MS
L-A-502 Rev. 0

TABLE OF CONTENTS

TABLES, FIGURES, AND ATTACHMENTS

Standard Operating Procedure
Analysis of Chemical Warfare Agents by GC/MS
L-A-502 Rev. 0

1.0 Scope and Application

1.1 The US Environmental Protection Agency (USEPA) National Homeland Security Center (NHSRC), in collaboration with experts from across USEPA and other federal agencies, has identified analytical methods to be used for the analysis of extractable semivolatile chemical agents in response to a homeland security incident. Summaries of these methods are provided in Standardized Analytical Methods for Environmental Restoration following Homeland Security Events (SAM) (U.S. EPA, *Standard Analytical Methods for Environmental Restoration Following Homeland Security Events* (SAM) document and information are posted at: http://www.epa.gov/sam/). NHSRC is currently using the SAM methods to develop analytical protocols for laboratory identification and measurement of target agents during site remediation. These methods will be used to assist in determining the presence of contamination, the effectiveness of decontamination, and site clearance following decontamination.

1.2 This standard operating procedure (SOP) for CSS is a gas chromatography/mass spectrometry (GC/MS) using Quadrupole (with or without Large Volume Injection) or Time of Flight techniques for analysis CWA'S listed below and in Table 1 at the mid part per trillion (ng/L or ng/Kg) to low part per billion (ug/L or ug/Kg) level in waters and soils. This procedure follows the general guidelines of EPA method 8270E for full scan GC/MS

1.3 Analytical Protocol for Cyclohexyl Sarin, Sarin, Soman and Sulfur Mustard Using Gas Chromatography/Mass Spectrometry (EPA/600/R-16/115 Sept. 2016 and Analytical Protocol for VX Using Gas Chromatography/Mass Spectrometry (EPA/600/R-16/116 Sept. 2016.

Contaminant	CAS Number
Cyclohexyl sarin (GF)	329-99-7
Mustard, sulfur / Mustard gas (HD)	505-60-2
Sarin (GB)	107-44-8
Soman (GD)	96-64-0
VX	50782-69-9

1.4 The procedures in this protocol also may be applicable for the following CWAs; however, evaluation studies have not yet been performed.

Contaminant	CAS Number
Chlorosarin	1445-76-7
Chlorosoman	7040-57-5
1-Methylethyl ester ethylphosphonofluoridic acid (GE)	1189-87-3
Mustard, nitrogen (HN-1)	538-07-8
Mustard, nitrogen (HN-2)	51-75-2
Mustard, nitrogen (HN-3)	555-77-1
R-33 (VR)	159939-87-4
Tabun (GA)	77-81-6
VE	21738-25-0
VG	78-53-5
VM	21770-86-5

1.5 Procedures in this protocol have been tested for the target analytes listed in Section 1.3 in reference matrices (i.e., reagent water, Ottawa sand, dried soils, and wipes) and have not been evaluated in field samples.

2.0 Summary of Method

2.1 The protocol involves solvent extraction of the sample followed by gas chromatography/ mass spectrometry (GC/MS) analysis to determine semivolatile CWAs.

2.2 Prior to analysis, samples must be prepared using sample preparation techniques appropriate for each analyte and matrix type. Aqueous, solid, and wipe samples are extracted by microscale extraction. Extracts may require a concentration step using nitrogen evaporation to achieve appropriate levels of quantitation. NOTE: Procedures for extraction of air samples are undergoing single-laboratory evaluation.

2.3 Development of a successful SIM method requires identifying the ions to be monitored, the ion dwell times, the ions in each group, and the timing for switching between groups. A quantitation ion is selected with a confirmation ion being monitored for identification purposes. Switching times are set where there is adequate resolution (a gap of 1-2 seconds) between peaks. If there is inadequate time between eluting peaks, small retention time shifts may cause peaks to partially or completely disappear as there are changes in the ions monitored. Dwell times will be set by default once the ions per group and the switching times are identified in the method. These can be adjusted manually in order to optimize sensitivity as needed.

2.4 Development of the full scan method follows the same protocol as is used in the SW846 Method 8270E procedure.

3.0 Definitions

3.1 Batch‡: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A Preparation Batch is composed of between 1 and 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and the last sample in the batch to be 24hours. Each Preparation Batch requires; one MB, LCS, and MS/MSD pair. An Analytical Batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

3.2 Holding Time: The maximum amount of time permitted between sampling and sample preparation and/or sample preparation and sample analysis. Also the period of time a sample may be stored prior to analysis when there is no preparation step. See the specific method or SW846 8000D Table 4.1.

3.3 Internal Standards (IS)‡: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

3.4 Ion Dwell Time: Scan time in milliseconds divided by the total ions in the group.

3.5 Laboratory Control Sample (LCS)‡: (however named, such as laboratory fortified blank, blank spike (BS), or QC check sample). A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

The standard source can be the same as the calibration or a second source. The LCS is analyzed exactly like a sample to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.6 Matrix Spike (MS): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The spiking solution may be from the calibration standard or second source, but should be the same as the LCS. The MS is analyzed exactly like a sample, and the analytical result is to determine whether the sample matrix contributes bias to the analytical result. The background concentrations of the analytes in the sample matrix must be determined in separate aliquots and the measured values in the MS corrected from the background concentrations.

3.7 Matrix Spike Duplicate (MSD): Second aliquot of the environmental sample used to prepare the MS, which is fortified, processed, and analyzed identically to the MS. The MSD is used to assess method precision.

3.8 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. Method Blank analytical results are evaluated to determine the presence of contamination in the analytical method process.

3.9 Primary Ion Area: The detector response chosen for quantitation purposes

3.10 Reporting Limit (RL): The reporting limit, also known as the LOQ is the minimum concentration that can be reported as a quantitated value for a target analyte in a sample. This value can be no lower than the concentration of the lowest calibration standard.

3.11 Secondary Ion Area: The detector response chosen for identification and confirmation purposes.

3.12 Selected Ion Monitoring: A mass spectrometry technique that provides lower detection level capability by monitoring fewer mass scans for longer periods of time that is done in full-scan methods.

3.13 Surrogate Standard (SS): Organic compounds which are similar to the target analytes in chemical composition and mimic the behavior of the target analytes throughout the analytical process. Surrogate compounds are not normally found in environmental samples. Each calibration standard, sample, MB, LCS, MS, and MSD is spiked with surrogate standards. Surrogates are used to evaluate analytical efficiency by measuring recovery. See analytical method SOP for a list of specific surrogate compounds that are appropriate for sample-specific analysis.

ǂ EL-V1M2-ISO-2016, 2016 NELAP Standard definition

4.0 Interferences

4.1 Matrix interferences can be caused by contaminants that are extracted from the sample during the extraction process. The amount of matrix interference varies from sample to sample. Cleanup procedures may help eliminate some of the interferences.

4.2 Contaminants in the solvents, reagents, glassware, and other extraction components may lead to matrix interferences. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running MBs with every batch. The data from all GC/MS data for every MB, LCS, MS, MSD, and sample must be evaluated for interferences. If interferences are detected, it is necessary to determine if the source of interference is in the preparation and then take corrective action to eliminate the interference. Using high purity reagents, solvents, and gases helps minimize interference problems.

4.3 Carryover contamination may occur when a sample containing low levels of analytes is injected immediately following a sample containing high levels of analytes or background. If this situation occurs during a non-monitored analysis, the sample containing the low concentration SVOCs may require reanalysis. If the situation occurs during monitored analysis, a solvent blank should be run after the high level sample to ensure that the system is free of contamination. To reduce carryover, the injection syringe must be rinsed with solvent between samples.

4.4 Phthalate contamination is commonly observed in a full scan analysis and its occurrence should be carefully evaluated as an indicator of the contamination problem in the sample preparation step of the analysis. Phthalate does not interfere with the SIM method.

4.5 An interference that is unique to SIM techniques can arise from the presence of an interfering compound which produces the same ion in the same retention time window used for quantitation of one of the CWA's. This event results in a positive interference to the reported value for the compound of interest. This interference is controlled to some degree by acquiring data for a confirmatory ions. If the ion ratios between the quantitation ion and the confirmation ion are not within the specified limits, then interferences may be present. Full scan analysis to identify compounds throughout the mass range is the most reliable assurance against reporting false positives.

5.0 Safety

WARNING: The toxicity of CWAs presents hazards unfamiliar to most experienced laboratory personnel. Special techniques and precautions must be used even for the simplest procedures involving these agents. If CWAs are suspected target analytes, laboratory personnel must be thoroughly trained in appropriate safety procedures prior to using this method.

5.1 There are specific requirements for operations with CWA's. Analysts must have read the PHILIS Chemical Hygiene Plan relating to CWA's and received all required training, including the training for use of Duodote countermeasure kits, prior to conducting the analytical procedures described in this protocol.

5.2 At a minimum, personal protective equipment (PPE) requirements include safety glasses, lab coats, and protective gloves. The availability of emergency response equipment and support personnel should be as indicated in a laboratory Chemical Hygiene Plan.

5.3 Exposure to chemical agent material is possible from contact, and risk is primarily associated with compromise of protective clothing. Respiratory exposure can result from spills or improper use of ventilation controls and PPE.

5.4 At concentrations of CWAs that are within the calibration range of this method, exposure to the solvents and reagents used may present more of a health concern than the target analytes.

5.5 Employees must abide by the policies and procedures in the Chemical Hygiene Plan and this document. This procedure involves hazardous material, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow the appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are hazardous. Standard laboratory safety procedures should be followed when working with unknown samples.

5.6 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded. Non-disposable gloves must be cleaned immediately. Latex and vinyl gloves provide no protection against the organic solvents used in this method, so nitrile or similar must be used.

5.7 The toxicity and/or carcinogenicity of the reagents and analytes used in this method have not been precisely defined; therefore, each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. This entire extraction procedure must be performed in a fume hood.

6.0 Equipment and Supplies

6.1 Glassware

6.1.1 Autosampler vials with Teflon lined crimp tops used for analysis and storage of sample extracts. These may be clear or amber.

6.1.2 Mini inserts with plastic springs used with autosampler vials to allow for smaller extract aliquots.

6.1.3 10-mL/40-mL/60-mL vials used for storage of standards and spiking solutions

6.2 Syringes

Gas-tight micro syringes- various sizes for transferring the concentrated extracts, adding internal standards to extracts, and aliquotting the calibration standards.

6.3 Instrumentation

6.3.1 Gas chromatograph/Mass spectrometer system: an analytical system complete with a temperature-programmable gas chromatograph suitable for split/split-less injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source, and the instrument must be operated in split-less injection mode.

6.3.2 Gas Chromatography Column – Recommended length 30 m x 0.25 mm ID (or 0.32 mm) bonded phase silicon coated fused silica capillary column DB-5 (J&W Scientific); RTX-5, RTX-5Sil MS (Restek); Zebron ZB-5(Phenomenex); SPB-5 (Supelco); AT-5 (Alltech); HP-5 (Agilent); CP-Sil 8 CB (Chrompack); 007-2 (Quadrex); BP-5 (SGE); or equivalent. Although a film thickness of 1.0 micron is recommended because of its larger capacity, a film thickness of 0.25 micron may be used. A capillary column is considered equivalent if:

6.3.2.1 The column does not introduce contaminants that interfere with the identification and quantification of the compounds listed in Table 1.

6.3.2.2 The analytical results generated using the column meet the initial and continuing calibration verification technical acceptance criteria listed in the protocol and the quantitation levels determined as described in Section 9.11.

6.3.2.3 The column provides equal or better resolution of the compounds listed in Table 1, when compared to columns listed in Section 6.3.2.

6.3.3 Mass Spectrometer – Must be capable of scanning from 35 – 500 atomic mass unit (amu) every second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum that meets the tuning acceptance criteria when 50 ng or less of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet. The instrument must be vented to the outside of the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.3.4 Autosampler: Gerstel MPS-2 or equivalent.

6.3.5 GC/MS interface: Any GC/MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.3.6 Data System The data system is equipped with the Agilent Chemstation software for data acquisition, Enviroquant for data processing and Gersel's Maestro for the autosampler. Any equivalent system would work.

6.3.7 Syringe: 10-µL Gerstel syringe, or equivalent.

6.3.8 Carrier gas: ultra-highpurity, equivalent or better helium.

6.3.9 Large Volume Injection system to be used with the quadrupole instruments.

6.3.10 Time of Flight (TOF) mass spectrometer

7.0 Reagents and Standards

7.1 Reagents

Original containers of reagents shall be labeled with expiration date when applicable. All containers of prepared reagents must bear a name, preparation date, and must be linked to the preparation records.

7.1.1 Organic-free Reagent Water – Defined as water in which contamination is not observed at or above the RL for each analyte of interest. Reagent water may be generated by passing tap water through a filter bed containing activated carbon or may be purchased.

7.1.2 Reagent soil – TCL-free sand is used for QC samples.

7.1.3 Helium carrier gas- 99.999% (UHP) or better such as Research Grade, 99.9999%.

7.1.4 Nitrogen- purge gas, 99.999% (UHP) grade.

7.2 Solvents

7.2.1 Methanol –nano grade or equivalent.

7.2.2 Methylene Chloride–nano grade or equivalent.

7.2.3 Acetone–nano grade or equivalent.

7.3 Standards

The laboratory must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the laboratory and presented upon request. Standard solutions purchased from a chemical supply house as extracts in sealed, glass ampules may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the ampulated standard solutions in ampules, if unopened, may be retained and used for two years from the preparation date. The expiration date of the standards, upon the breaking

of the glass seal, is six months (or sooner, if the standard has degraded or evaporated). Note: For many of the target compounds, neat standards may be unavailable; therefore, the laboratory may need to purchase diluted standards.

Store unopened ampules of stock standard solutions at ≤6 °C. If no manufacturer's expiration date is provided, unopened ampuled standard solutions may be retained and used for up to six months after the preparation date (Reference 16.11). Store opened stock standard solutions at ≤6 °C in PTFE-lined screw-cap amber bottles.

Fresh standards should be provided every twelve months (for solutions containing a single target compound) or six months (for solutions containing a mixture of target compounds), or sooner if the expiration date has elapsed.

Store the working standards at ≤ 6 °C in containers with PTFE-lined caps. Certain analytes may degrade in as little as two weeks; therefore, the working standard solution should be checked against CCV standards at least weekly for stability. If stored as singleanalyte solutions, standards containing soman (GD) or cyclohexyl sarin (GF) should be stable to up to 12 months; standards containing sulfur mustard (HD) should be stable for up to six months; and standards containing sarin (GB) should be stable for up to five months. Multi-component working standards should be replaced after five months. Working standard solutions must be replaced if the stock standard solutions have expired or if comparison with CCV samples indicates a problem.

7.3.1 Prepare standards for a calibration curve with a minimum of five points. Five points are valid for average response factor or linear regression curve fitting. Six calibration points are required for quadratic (second-order) curve fits. The low point of the calibration curve must be at or below the reporting limit. The high standard defines the range of the calibration. Two stock standards are prepared, one at 20µg/mL and another at 2 µg/mL. The lower stock is used to prepare the lowest levels of the ICAL. See Table 6 as an example for the preparation of the ICAL levels for the lists.

7.3.2 An internal standard (IS) solution is prepared by dissolving the compounds in DCM or by purchasing a mixture from a commercial source. See Table 2 for a list of the internal standards used. The final concentration in the extract should be 0.5 ng/µL.

7.3.3 Surrogate Standard Spiking Solution: Prepare as instructed in the extraction SOP (PHILIS SOP L-P-107) will result in a concentration of 25 µg/mL. Other concentrations may be used provided the resulting amount in the samples and standards doesn't change. Surrogate compounds are listed in Table 2.

7.3.4 DFTPP GC/MS Tuning Standard: A solution in methylene chloride containing 50 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared.

7.3.5 Laboratory Control Spiking Solution: Prepared as instructed in the extraction SOPs. This solution must contain all target analytes.

7.3.6 Matrix Spike Solution: This is the same as the Laboratory Control Spiking Solution.

7.3.7 The standards must be stored away from any light source at 0 - 6 °C in Teflon lined screw cap amber bottles. The standard solutions expire six months after preparation date or at the earliest expiration date assigned by the vendor to any parent standard, whichever is earlier. Continuing calibration standards and other dilute standards should be checked weekly for degradation or when the standards fail to meet criteria, whichever is first.

7.3.8 Protect all standards from light. Samples, sample extracts, and standards must be stored separately.

7.3.9 The laboratory is responsible for maintaining the integrity of standard solutions and verifying the solution prior to use. The standards must be brought to room temperature prior to use, checked for losses, and checked to ensure that all components have remained in solution. Guidance on standard verification procedures can be found in EPA's Superfund Analytical Services / Contract Laboratory Program, Multi-Media, Multi-Concentration Organics Analysis, SOM01.2, Exhibit E, Section 7, May 2005. (http://www.epa.gov/superfund/programs/clp/download/som/som11e-h.pdf)

8.0 Sample Collection, Preservation, and Storage

8.1 Sample Preservation

Samples must be stored on ice or refrigerated at 4 °C (± 2 °C) immediately after collection until receipt in the laboratory. The presence of chlorine may increase the degradation rate of G-agents in water. If chlorine is suspected to be present in water samples (e.g., treated drinking water or wastewater) that are to be measured for G-agents, add approximately four drops (~0.2 mL) of a 10 % solution of sodium thiosulfate per 35mL sample. If clouding results, add less sodium thiosulfate to a fresh sample aliquot. If sodium thiosulfate is not added during sample collection, it should be added immediately upon sample receipt in the laboratory, prior to sample analysis or extraction. Sample Storage

8.1.1 Samples must be protected from light and refrigerated at 0 - 6°C from the time of receipt until 60 days after delivery of results to the reference agency. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.1.2 Samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.2 Sample Extract Storage

8.2.1 Sample extracts must be protected from light and stored at 0 - 6°C until one year after delivery of results to the reference agency.

8.2.2 Samples, sample extracts, and standards must be stored separately.

8.3 Technical Holding Times

8.3.1 Soil and wipe samples must be extracted within seven days of receipt at the laboratory. Aqueous samples should be analyzed as soon as possible upon receipt in the laboratory. At a minimum, DCM must be added to aqueous samples within 48 hours of receipt (DCM should be added immediately to aqueous samples that will be analyzed for HD), and samples must be completely extracted within seven days of receipt..

8.3.2 Extracts must be analyzed within 14 days following extraction.

9.0 Quality Control

9.1 Initial Demonstration of Capability (IDC)

An initial demonstration of capability (IDC) shall be performed prior to the analysis of any samples and with each significant change in instrument type (e.g., different detection technique), personnel or method. An IDC consists of the following:

9.1.1 An initial demonstration of precision and recovery (IPR) determination (Section 9.2).

9.1.2 A method detection limit (MDL) study (Section 9.7).

9.1.3 A quantitation limit (QL) determination (Section 9.8) on a clean matrix (reagent water, Ottawa sand, pre-cleaned wipes).

The IDC consists of four replicate samples of a clean matrix spiked with CWAs around the midpoint of the calibration curve and carried through the entire analytical process. Prior to performing the IDC it is required that a valid initial calibration (Section 10.3) be established.

9.2 Initial Precision and Recovery (IPR)

9.2.1 For preparation of IDC samples, see PHILIS SOP L-P-107.

9.2.2 Calculations for IDC.

Calculate the percent recovery of each compound in the IDC sample using Equations 4-7 (Section 12.2.6). Calculate an average percent recovery for each compound.

Calculate a percent relative standard deviation (%RSD) for each compound in the IPR samples.

9.2.3 Technical Acceptance Criteria for IDC

The average percent recovery of each compound in the IDC should be within 50 -150%

The % RSD of each compound in the IPR should be less than or equal to 30.

9.2.4 Corrective Action for IDC

If the technical acceptance criteria in 9.2.3 and Table 5 are not met, inspect the system for problems and take corrective actions to achieve the acceptance criteria.

9.3 Method Blanks

A method blank is a volume of a clean reference matrix (e.g., reagent water for water samples, clean inert sand along with purified sodium sulfate or Hydromatrix drying agent for solid samples, clean absorbent for air samples, or clean wipe for wipe samples) spiked with a sufficient amount of surrogate standard spiking solution such that the same amount of surrogate is added as for the associated samples and carried through the entire analytical procedure. Internal standard solution is added just prior to analysis by GC/MS to give a concentration of 0.5 ng/µL for each internal standard for both full scan and SIM modes. The volume or weight of the reference matrix must be approximately equal to the volume or weight of the samples associated with the blank.

9.3.1 Frequency of Method Blanks

A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples [excluding MS/MSDs and Performance Evaluation (PE) samples]. In addition, a method blank shall:

9.3.1.1 Be extracted by the same procedure used to extract samples.

9.3.1.2 Be analyzed on each GC/MS system used to analyze associated samples and conditions (i.e., GC/MS settings).

9.3.1.3 Under no circumstances should method blanks be analyzed at a dilution.

9.3.2 Technical Acceptance Criteria for Method Blank Analysis

9.3.2.1 All blanks must be analyzed at the frequency described in Section 9.3.1 on a GC/MS system meeting the DFTPP tuning criteria in Section 10.2.4 and Table 1, initial calibration in Section 10.3, and continuing calibration verification (CCV) technical acceptance criteria in Section 10.4.5.

9.3.2.2 The Percent Recovery (%Recovery) of each of the surrogates in the blank must be within the acceptance limits listed in Table 5.

9.3.2.3 The blank must meet the sample acceptance criteria listed in Section 9.3.

9.3.2.4 A method blank for solid, water, air, and wipe samples must contain less than the RL of target compounds. Note: In cases where a blank has detects above the RL, but associated samples have detects greater than 10 times the blank, consult the agency to determine if re-extraction is required.

9.3.3 Corrective Action for Method Blanks

9.3.3.1 If a method blank does not meet the technical acceptance criteria for method blank analysis, the laboratory shall consider the analytical system to be out of control.

9.3.3.2 If contamination is the problem, then the source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. It is the laboratory's responsibility to ensure that interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in the GC/MS be eliminated. If possible, an aliquot of any sample associated with the contaminated blank must be re-extracted and reanalyzed.

9.3.3.3 If surrogate recoveries in the method blank do not meet the acceptance criteria listed in Table 6, first reanalyze the method blank. If the surrogate recoveries do not meet the acceptance criteria after reanalysis, the method blank and an aliquot of any sample associated with that method blank must be re-extracted, if possible, and reanalyzed. If a surrogate recovery is high and all corresponding samples had non-detects for the associated target compounds, sample re-extraction and reanalysis are not required.

9.3.3.4 If the method blank does not meet internal standard response requirements listed in Section 9.3, follow the corrective action procedure outlined in Section 9.4. The laboratory shall resolve and document the resolution of the problem before proceeding with sample analysis.

9.3.3.5 If the method blank does not meet the retention time (RT) requirements for internal standards, check the instrument for malfunction and recalibrate. Reanalyze the method blank. If the method blank does not meet the criteria, then all corresponding sample data should be flagged.

9.4 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

To evaluate the effects of the sample matrix on the methods used for analyses, a mixture of target compounds must be spiked into two aliquots of a water or solid sample and analyzed in accordance with the appropriate method. Mixtures should be spiked at levels at a concentration near the midpoint of the calibration range.

An MS/MSD pair is analyzed with each batch of ≤ 20 samples of each water or solid matrix type. MS/MSDs are not performed on wipe samples. As part of EPA's quality assurance/quality control (QA/QC) program, water rinseate samples and/or field blanks (field QC) or PE samples may accompany solid, water, air, and/or wipe samples that are delivered to the laboratory for analysis. The laboratory must not perform MS/MSD analysis on any of the field QC or PE samples.

If the reference agency designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample remaining to perform an MS/MSD, then the laboratory shall choose another sample on which to perform an MS/MSD analysis. At the time the selection is made, the laboratory shall notify the reference agency that insufficient sample was received and identify the reference agency sample selected for the MS/MSD analysis.

If there is insufficient sample remaining in any of the samples in a batch to perform the required MS/MSD, the laboratory will report this in the data narrative.

9.4.1 Dilution of MS/MSD

Before any MS/MSD analysis, analyze the original sample, then analyze the MS/MSD at the same concentration as the most concentrated extract for which the original sample results will be reported.

9.4.2 Calculations for MS/MSD

Calculate the percent recovery of each matrix spike compound in the MS/MSD sample (see EQ. 10 in Section 12.2.9).

Calculate the Relative Percent Difference (RPD) of the concentrations of each compound in the MS/MSD using EQ. 1.

Concentrations of the matrix spike compounds are calculated using the same equations as used for target compounds (Equation 4 for water samples and Equation 5 for solid samples in Section 12.2.6).

EQ. 1 Relative Percent Difference Calculation

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

Where:

C_1 = Measured concentration of the first sample aliquot

C_2 = Measured concentration of the second sample aliquot

9.4.3 Technical Acceptance Criteria for MS/MSD

All MS/MSDs must be analyzed on a GC/MS system meeting DFTPP, initial and continuing calibration verification technical acceptance criteria, and the method blank technical acceptance criteria.

The MS/MSD must be extracted and analyzed within the technical holding time (Section 8.4).

The retention time (RT) shift for each of the internal standards must be within ± 0.50 minutes (30 seconds) between the MS/MSD sample and the most recent CCV standard analysis.

The limits for matrix spike compound recovery and RPD are 50 – 150 % and ≤ 30 %, respectively. For difficult matrices, laboratories are encouraged to collect sufficient data to support development of laboratory-specific criteria.

9.4.4 Corrective Action for MS/MSD

If recovery or RPD limits are not met and the LCS, CCV and method blank are within acceptable limits, this may be an indication of matrix interferences.

If MS/MSD recovery limits cannot be met, flag the results of the associated sample.

9.5 Laboratory Control Sample (LCS)

An LCS consists of an aliquot of clean reference matrix, of the same weight or volume as the corresponding field samples, and spiked with the same compounds at the same concentrations used to spike the MS/MSD. When the results of the MS/MSD analysis indicate matrix interference may be present, the LCS results are used to verify that the interferences are due to the sample matrix and not from artifacts introduced in the laboratory.

9.5.1 Frequency of LCS Analyses

One LCS must be prepared, extracted, analyzed, and reported for every 20 field samples or fewer extracted in a batch of a similar matrix. The LCS must be extracted and analyzed concurrently with the samples, using the same extraction procedure, cleanup procedure (if required), and instrumentation.

9.5.2 Calculations for LCS

Calculate the recovery of each compound in the LCS using Equation 10 (Section 12.2.9).

9.5.3 Technical Acceptance Criteria for LCS Analysis

All laboratory control samples must be extracted and analyzed at the frequency described in Section 9.5.1 on a GC/MS system meeting the tuning, initial and continuing calibration verification, and the method blank technical acceptance criteria.

9.5.4 The limits for LCS compound recovery are 50 – 150 %. Corrective Action for LCS

If LCS recovery limits are not met, inspect the system for problems and take corrective actions to achieve the acceptance criteria.

If LCS recovery limits cannot be met, flag all associated sample and blank data accordingly.

9.6 This method uses a GC/MS in the full scan or the SIM mode to determine method detection limits.

9.7 Method detection limits (mdl) are determined using the procedure outlined in 40 CFR Part 136, Appendix b, Revision 2.

9.8 Method reporting limits are determined using the MDL's determined. Reporting limits may never be below the mdl's.

9.9 Instrument Detection Limit (IDL) Determination

Before any field samples are analyzed, laboratories may determine an IDL for each target compound on each instrument used for analysis. While determining IDLs are not required, IDL results can be helpful in determining an appropriate spike level for use in determining the MDL (Section 9.10). It is recommended that IDLs be verified annually thereafter, or after major instrument maintenance. Major instrument maintenance includes, but is not limited to: cleaning or replacement of the mass spectrometer source, mass filters, electron multiplier, and installing a different GC column type. An IDL is instrument-specific and independent of sample matrices.

9.9.1 An IDL is determined for each compound as the concentration that produces an average signal-to-noise ratio of between 3:1 and 5:1 for at least three replicate injections.

9.9.2 All documentation for the IDL determination shall be maintained at the laboratory and provided to the reference agency or the data user upon request.

9.10 Method Detection Limit (MDL) Determination

Before any field samples are analyzed, laboratory MDLs must be determined for each target analyte in appropriate reference matrices (i.e., reagent water, Ottawa sand, or clean wipes), using the sample preparation and analytical procedures described in this protocol for each specific matrix, and following the instructions and requirements described at 40 CFR Part 136, Appendix B.

9.10.1 The laboratory must use full method procedures to prepare and analyze at least seven replicates.

9.10.2 Spike each replicate sample at concentrations of 1 – 5 times the IDL concentration for each analyte and analyze the samples following protocol procedures.

9.10.3 To determine analyte MDLs, the following equation is applied to the analytical results (Student's t-factor is dependent on the number of replicates used; 3.14 assumes seven replicates):

MDL = 3.14 x sd

Where:

sd = the standard deviation for the analytical results, and

3.14 = the Student's t-value for seven replicate samples

9.10.4 The MDL results calculated using the equation in Section 9.7.3 must meet the following requirements as well as all other requirements specified in 40 CFR Part 136, Appendix B:

9.10.5 MDL result must not be greater than the spiking level used for the MDL determination.

9.10.6 MDL result must not be less than one tenth the spiking level used for the MDL determination.

9.10.7 If either requirement is not met, the laboratory must adjust their spiking level appropriately and repeat the MDL determination.

9.11 Reporting Limit (RL) Determination

Laboratory RLs can be determined by multiplying the standard deviation of the results used to determine the MDL by 10. This approach uses the variability of the results used to determine the MDL, to estimate the concentration that would yield a 10% relative standard deviation (RSD) under ideal conditions. The resulting RL should be evaluated against the criteria listed below. These criteria are provided as guidance. If any of the criteria are not met, the laboratory should consult project managers to determine if the RL is sufficient to address project needs:

9.11.1 Results from spikes at the RL should be above the MDL.

9.11.2 The RL should be at or above the lowest calibration level.

9.11.3 The RL should be at least two times the MDL.

9.11.4 The relative standard deviation of results from spikes at the RL should be less than 30%.

9.11.5 The mean recovery of spikes at the RL must be within 50 – 150%.

9.12 Analytical data generated by the instrument software are reviewed and evaluated by the analyst as follows:

9.12.1 DFTPP, instrument calibration, calibration verifications, IS/SS, QC measures are evaluated and the results documented on the separate forms:

9.12.1.1 For each 12-hour sequence, a tune evaluation report of DFTPP is generated.

9.12.1.2 For each ICAL, an instrument calibration report showing relative and average response factors and percent relative standard deviations is generated.

9.12.1.3 For each CCV, a report showing response factors and percent deviations compared to the associated ICAL is generated.

9.12.1.4 Generate a QA-QC check report for internal standard area counts and percent recoveries for the surrogates.

9.12.1.5 Calculate analyte percent recoveries CCV, LCS, ICV, MS, and RPD for MSD.

9.12.2 All false positives are Q-Deleted, and all positively identified target analytes are reported to LIMS. Include the spectra in the data package for positive results.

9.12.3 Manual integration is applied in cases when the instrument data processing software produces integrated areas that are not valid. The manual adjustments to the chromatographic peak must be performed in a consistent manner for the calibration standards, QC and field samples.

9.12.4 Anytime the analyst alters the instrument generated quantitation report, the hard copies of both reports (original and corrected) must be retained (e.g., manual integration).

9.12.5 Discrepancies in the analytical run are described in the “QC Summary form” and discussed with the Lead Chemist.

9.12.6 Reviewed data is entered into LIMS, hard copies of LIMS reports are printed and compared to the original data.

9.12.7 All records derived from the analytical process are assembled in the analytical data packages that consist of:

9.12.7.1 LIMS work-order list.

9.12.7.2 Analytical run sheet.

9.12.7.3 "QC Summary Form" signed by the Lead Chemist.

9.12.7.4 DFTPP tune evaluation report.

9.12.7.5 QA-QC check report.

9.12.7.6 Quantitation Report for each Sample and QCS.

9.12.7.7 Evaluation reports for CCV, ICV, LCS, MS, and MSD.

9.12.7.8 Initial calibration form.

9.12.7.9 LIMS report of each sample.

9.12.8 Data packages are placed in files and stored in the PHILIS document storage area.

9.13 See the QAPP for the data affected and follow the instructions.

In cases where quality control measures do not meet acceptance criteria, the quality of the analytical data is not acceptable and the analyst does the following:

9.14 When tuning and/or instrument calibration fail to meet acceptance criteria, the analysis does not start. The problem is investigated and the necessary instrument maintenance is performed, followed with reanalysis of DFTPP and/or calibration.

9.15 If after analysis, any of the criteria for quality control are not met, or the sample is not available for reanalysis, the analyst must notify the Lead Chemist. The Lead Chemist will implement the corrective action plan.

9.16 The analyst shall report to the Lead Chemist and indicate any out control event listed on the "QC Summary form". Such events include:

9.16.1.1 Damage to the sample.

9.16.1.2 Holding time exceeded.

9.16.1.3 Inadequate sample preservation.

9.16.1.4 Sample results exceeds agencies Action Limit

9.16.1.5 Samples do not reflect historical data.

9.16.1.6 Upward trending or sample results approaching internal warning limits.

9.16.1.7 Any non-target analyte peak present on the instrument generated chromatogram.

9.17 The Lead Chemist will implement the corrective action plan described in the PHILIS corrective action plan document.

10.0 Calibration and Standardization

10.1 Instrument Operating Conditions

10.1.1 Gas Chromatograph (GC)

The following GC analytical conditions are provided for guidance and may be modified if needed to optimize analytical results. Other conditions may be used, provided that all technical acceptance criteria in Sections 10.2.4, 10.3.4, 10.4.5, and 12.3 are met. Examples of alternate conditions using shorter columns or GC-MS Time of Flight (TOF) are provided in Appendix A.

10.1.1.1 Initial column temperature: 50°C for 0.5 minutes

10.1.1.2 Column temperature program: 50-290°C at 23°C/minute

10.1.1.3 290-320°C at 15°C/minute

10.1.1.4 Final column temperature hold: 320°C

10.1.1.5 Injector temperature: 280°C

10.1.1.6 Injection mode: Pulsed splitless for 0.4 minutes

10.1.1.7 Sample injection volume: 1.0 µL

10.1.1.8 GC column: Agilent HP-5MS, (5%-phenyl)-methylpolysiloxane (see Section 6.4.2 for equivalent columns)

10.1.1.9 Column dimensions: 30 m x 0.25 mm x 0.25 µm

10.1.1.10 Carrier gas: Helium at 32 cm/second

Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, blanks, and MS/MSDs.

10.1.2 Mass Spectrometer (MS)

The following MS full scan analytical conditions are provided in this section to optimize analytical results. Other settings may be used provided they are equivalent or better. Examples of alternate conditions using Time of Flight (TOF) MS are provided in Appendix A.

10.1.2.1 MS transfer line temperature: 280°C

10.1.2.2 Source temperature: 230°C or according to manufacturer's specifications

10.1.2.3 MS quadrupole temperature: 150°C

10.1.2.4 Electron energy: 70 eV (nominal)

10.1.2.5 Scan range: 35 to 500 m/z

10.1.2.6 Ionization mode: Electron Ionization (EI), positive

10.1.2.7 Scan time: 3.15 scan/sec (minimum of 3 scans/second)

10.1.2.8 Library searching: NIST 05 Mass Spectral Data Base

Note: Although SIM may be used in cases when there is a need to address low concentration levels, the procedure is prone to matrix interference effects and false positives. Use of SIM should be limited to sample matrices that present minimal background interferences and cases where a large amount of qualified data is tolerable.

The standard MS conditions using selected ion monitoring (SIM) analyses performed in electron ionization mode are provided:

10.1.2.9 MS transfer line temperature: 280ºC

10.1.2.10 MS source temperature: 230ºC

10.1.2.11 MS quadrupole temperature: 150ºC

10.1.2.12 Solvent delay time: 3 minutes

10.1.2.13 Electron energy: 70 eV

10.1.2.14 Ion dwell time: 100 milliseconds per ion (analytes are assigned different SIM groups based on elution order; depending on the number of ions monitored per group, cycle times ranged from 1.44 – 2.86 cycles/second)

10.1.2.15 Ionization polarity: Electron Ionization (EI), positive

10.2 GC/MS Mass Calibration (Tuning) and Ion Abundance

10.2.1 Summary of GC/MS Instrument Performance Check

The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibration compound such as perfluoro-tri-n-butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.3.4). Prior to the analysis of any samples, including MS/MSDs, blanks, or calibration standards, the laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution (Table 2) containing DFTPP.

10.2.2 Frequency of GC/MS Instrument Performance Check – The instrument performance check solution must be injected once at the beginning of each 24-hour period, during which samples, blanks, or standards are to be analyzed. The 24-hour period begins at the moment of injection of the DFTPP solution. The time period ends after 24 hours have elapsed according to the system clock.

10.2.3 GC/MS Instrument Performance Check

The analysis of the instrument performance check solution may be performed as an injection of 50 ng or less of DFTPP into the GC/MS or by adding a sufficient amount of DFTPP to the calibration standards to result in an on-column amount of 50 ng or less of DFTPP (Section 7.3.4) and analyzing the calibration standard.

10.2.4 Technical Acceptance Criteria for GC/MS Instrument Performance Check

The instrument performance check solution must be analyzed at the frequency described in Section 10.2.2.

Abundance criteria are listed in Table 2 for guidance. The mass spectrum of DFTPP must be acquired in the following manner: three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.

Note 1: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical GC/MS instrument run conditions.

Note 2: The above tuning criteria are suggested when using DFTPP. If alternative tuning methods are used, consult the method or manufacturer notes for guidance on criteria. A DFTPP tune is not necessary when using SIM.

10.2.5 Corrective Action for GC/MS Instrument Performance Check

If the GC/MS instrument performance check technical acceptance criteria are not met, re-tune the GC/MS system. It may be necessary to perform maintenance to achieve the technical acceptance criteria.

The instrument performance check technical acceptance criteria in Section 10.2.4 must be met before any standards, samples, including MS/MSDs, or required blanks are analyzed.

10.3 Initial Calibration

Prior to sample analysis, and after instrument performance check technical acceptance criteria have been met, each GC/MS system must be calibrated at a minimum of five concentrations (Section 10.2.2 and Table 6) to determine instrument sensitivity and the linearity of GC/MS response for the target and surrogate compounds. If the RSD criteria cannot be met, a linear or quadratic curve may be used. Each initial calibration standard contains all the target compounds, surrogates, and internal standards.

10.3.1 Frequency of Initial Calibration

Each GC/MS must be calibrated whenever the laboratory takes corrective action that may change or affect the initial calibration criteria, or if the CCV technical acceptance criteria are not met.

If time remains in the 12-hour period after meeting initial calibration acceptance criteria, samples may be analyzed. It is not necessary to analyze a continuing calibration standard within this period.

10.3.2 Procedure for Initial Calibration

Prepare at least five calibration standards containing all the detected target compounds and associated surrogates at the concentrations described in Table 6.

Add a sufficient amount of internal standard solution (Section 7.3.2) to aliquots of calibration standards to result in 0.5 ng/µL of each internal standard. Standards specified in Section 10.3.1 should permit most of the target compounds to have relative retention times (RRTs) of approximately 0.60 to 1.70, using the assignments of internal standards to target compounds given in Table 2.

Analyze each calibration standard by injecting 1.0 µL of standard.

10.3.3 Calculations for Initial Calibration

Calculate the relative response factors (RRFs) for each analyte and surrogate using Equation 2 and the primary characteristic ions found in Table 3. Assign target compounds and surrogates to internal standards according to Table 2. For internal standards, use the primary ion listed in Table 3 unless interferences are present. Note: Unless otherwise stated, the area response of the primary characteristic ion is the quantitation ion.

EQ. 2 Relative Response Factor Calculation

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured (Table 3)

A_{is} = Area of the characteristic ion for specific internal standard (Table 2)

C_{is} = Amount of the internal standard injected (ng)

C_x = Amount of the target compound or surrogate injected (ng)

The Mean Relative Response Factor ($\overline{RRF}$) for the Initial Calibration RRFs and mean RRFs must be calculated for all compounds. Calculate the percent relative standard deviation (%RSD) of the RRF values for the initial calibration. If linear regression or quadratic curve fitting is needed, consult SW-846 Method 8000D for guidance on the appropriate calculations.

10.3.4 Technical Acceptance Criteria for Initial Calibration

An initial calibration should be performed at the frequency described in Section 10.3.1 on a GC/MS system meeting the instrument performance check technical acceptance criteria (Section 10.2.3).

The RRF for each target compound and surrogate should be greater than or equal to 0.01.

The %RSD of the RRFs over the initial calibration range for each target compound and surrogate should be less than or equal to 20.00. If %RSD for a target analyte or surrogate cannot meet the acceptance criteria, curve fitting by linear or quadratic regression may be used provided the R^2 value is greater than or equal to 0.99 linear) or 0.995 (quadratic). [Note: Percent drift criteria of 40 % will be added to all initial calibration levels.]

Note: Laboratories have experienced difficulty meeting these criteria when calibrating instruments for VX analyses. Calibration criteria specifically for VX may be developed and provided once sufficient multi-laboratory data are available.

10.3.5 Corrective Action for Initial Calibration

If technical acceptance criteria using at least one of the three optional approaches to initial calibration (%RSD of the RRFs, linear regression, or quadratic regression) are not met, inspect the system for problems, take corrective actions, and re-calibrate the system. If criteria are not met with re-calibration, the laboratory will flag all data associated with the calibration.

Initial calibration technical acceptance criteria must be met before any samples, including MS/MSDs or required blanks are analyzed and reported without data qualification.

10.4 Continuing Calibration Verification

10.4.1 Summary of Continuing Calibration Verification

Prior to the analysis of samples, and after instrument performance check technical acceptance criteria and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing a CCV standard to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements. The CCV standard contains all the target compounds, surrogates, and internal standards. The same injection volume must be used for all standards, samples, and blanks.

10.4.2 Frequency of Continuing Calibration Verification – Each GC/MS used for analysis must be checked once every 12-hour time period of operation or after the analysis of 20 samples (whichever comes first). All samples must be bracketed by acceptable CCVs. The 12-hour time period begins with the injection of DFTPP

10.4.3 Procedure for Continuing Calibration Verification

Add a sufficient amount of internal standard solution (Section 7.3.4) to an aliquot of CCV standard to result in a concentration of 0.5 ng/µL for both full scan and SIM analyses.

Analyze the CCV standard by injecting 1.0 µL or 10uL of standard.

10.4.4 Calculations for CCV

Calculate an RRF for each target compound and surrogate using Equation 2 and the primary characteristic ions found in Table 3.

Calculate the Percent Difference (%Difference) between the $\overline{RRF}$ from the most recent initial calibration and the continuing calibration verification RRF for each target compound and surrogate using Equation 3.

EQ. 3 Relative Response Factor Percent Difference Calculation

$$\%\text{Difference}_{RRF} = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

Where:

RRF_i = Mean Relative Response Factor from the most recent initial calibration meeting technical acceptance criteria.

RRF_c = Relative Response Factor from CCV standard.

10.4.5 Technical Acceptance Criteria for CCV

The CCV standard must be analyzed at or near the mid-point concentration level, at the frequency described in Section 10.4.2, on a GC/MS system meeting the instrument performance check and the initial calibration technical acceptance criteria.

The RRF for each target compound and surrogate should be ≥ 0.01.

For the opening CCV, the PD or percent difference of RRFs for each target compound should be within the range of ±40. For the closing CCV, the PD or percent difference of RRFs for each target compound should be within the range of ±50.

EQ. 3a Percent Drift (PD) Calculation for CCV

$$PD = \frac{\text{CalculatedConcentration} - \text{Theoretical Concentration}}{\text{Theoretical Concentration}} \text{x} 100\%$$

The percent drift (PD) for each target compound should be within the range of ±50.

Excluding those ions in the solvent front, no quantitation ion may saturate the detector.

10.4.6 Corrective Action for CCV

If the CCV technical acceptance criteria in Section 10.4.5 are not met, recalibrate the GC/MS instrument according to Section 10.3.

CCV technical acceptance criteria should be met before any samples MS/MSDs, or required blanks, are analyzed. If CCV criteria are not met, flag associated samples and blanks accordingly.

10.5 Instrument Blank

10.5.1 Summary of Instrument Blank

An instrument blank is comprised of DCM spiked with internal standards at the same concentration used for associated samples. The purpose of the instrument blank is to minimize the impact of carryover.

10.5.2 Frequency of Instrument Blank

An instrument blank is recommended for analysis following suspected carry-over or during analysis of samples containing suspected high concentrations.

10.5.3 Procedure for Instrument Blank Analysis

Add sufficient amount of internal standard solution (Section 7.3.4) to an aliquot of CCV standard to result in a concentration of 0.5 ng/µL. Analyze each calibration standard by injecting 1.0 µL of standard.

10.5.4 Calculations for Instrument Blank

Calculate the concentrations of any observed target analyte using Equation 4, setting V_t, V_o, and DF all equal to 1.

10.5.5 Technical Acceptance Criteria for Instrument Blank

If an instrument blank is analyzed, the concentration of all target analytes in the instrument blank should be less than the concentration of the target analytes in the low calibration standard. The area response of the internal standards should be within 50 – 150% of the associated CCV or mid-level concentration of the initial calibration.

10.5.6 Corrective Action for Instrument Blank

If an instrument blank is analyzed and the instrument blank technical acceptance criteria are not met, analyze an additional instrument blank. If the problem persists, inspect the system for problems and take corrective actions to achieve the acceptance criteria. Instrument blank technical acceptance criteria should be met before samples are analyzed. Samples that are analyzed with corresponding instrument blanks that do not meet the instrument blank criteria should be reanalyzed, or the corresponding data should be flagged.

11.0 Procedure

11.1 Sample Analysis

11.1.1 Analysis is performed using an automated injection GC/MS instrument.

11.1.2 In ChemStation, load the sequence from the previous run and enter in the sequence information for the day. A typical sequence will have one or two rinses, the DFTPP tune, the CCV, an instrument blank, the QC from the batch, then extracts of the samples.

11.1.3 Calibrate the instrument as described in Section 10.3.2. All instrument tuning and calibration criteria must be met prior to the analysis of samples.

11.1.4 All samples must be analyzed using the same instrument conditions as the preceding ICAL, and CCV standards.

11.1.5 Add internal standard to the sample extract to result in a 0.5 ng/µL concentration of internal standard. Mix thoroughly before injection into the instrument. The internal standard amount is the same for full scan or SIM analysis.

11.1.6 If samples are to be diluted, add the internal standard after the dilution is made.

11.1.7 Inject the sample aliquot into the GC/MS using the sample injection technique as used for the standards. Injection amount is 1 µL.

11.1.8 The data system will determine the concentration of each analyte in the extract using calculations based on the initial calibration, not the continuing calibration verification.

11.1.9 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst. The minimum documentation required is a hard copy of the original data peak integration and a copy showing the manual integration with the analyst initials and date and explanation of why the manual integration was performed.

11.1.10 The internal standard response in the sample must be within 50- 200% of the response in the CCV.

11.2 Dilutions

11.2.1 If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for an analysis at a lesser dilution, the sample

must be re-analyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.2.2 Add the internal standard to the diluted extract for a resulting concentration of 0.5 ng/µL of each internal standard (for both full scan and SIM analyses), and analyze the diluted extract.

11.2.3 Reporting Dilutions

The most concentrated dilution with no target analytes above the calibration range will be reported. Other dilutions will be reported only at the client's request.

12.0 Data Analysis and Calculations

12.1 Qualitative Identification of Target Compounds

12.1.1 The compounds listed in Table 1 must be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of the standard of the suspected compound. Two criteria must be satisfied to verify the identifications:

12.1.1.1 Elution of the sample analyte within the GC RRT unit window established from the 12-hour calibration standard

12.1.1.2 Correspondence of the sample analyte and calibration standard component mass spectra

12.1.2 For establishing correspondence of the GC RRT, the sample component must compare within ±0.06 RRT units of the standard component. For samples analyzed during the same 24 hour time period as the initial calibration standards, compare the analyte RTs to those from the midpoint initial calibration standard. Otherwise, use the corresponding CCV standard. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using EICPs for ions unique to the component of interest.

12.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained from a calibration standard on a GC/MS meeting the daily instrument performance requirements for DFTPP are required. Once obtained, these standard spectra may be used for identification purposes only if the GC/MS meets the DFTPP daily instrument performance requirements.

12.1.4 For full scan analyses, all ions present in the standard mass spectrum at a relative intensity greater than 10% (the most abundant ion in the spectrum equaling 100%) must be present in the sample spectrum. The relative intensities of ions specified in Table 3 must agree within ± 20% between the standard and sample spectra (e.g., for an ion with an abundance

of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 – 70%). Ions greater than 10% in the sample spectrum, but not present in the standard spectrum, must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. When target compounds are below LOQs but the spectrum meets the identification criteria, report the concentration with a "J". For example, if the LOQ is 5.0 g/L and concentration of 3.0 g/L is calculated, report as "3.0 J".

For SIM or TOF analysis, the signals for the ions in Table 3 must be present and must maximize within the same two seconds. The signal-to-noise ratio (S:N) for the GC peak at each ion must be greater than or equal to 2.5 for each target compound and surrogate detected in a sample extract, and greater than or equal to 10 for all target compounds and surrogates in the CCV standard.

12.1.5 If a compound cannot be verified by all of the spectral identification criteria in Sections 12.1.1 – 12.1.4, but in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the laboratory must report the identification and proceed with quantitation.

12.2 Data Analysis and Calculations of Target Compounds

12.2.1 Target compounds identified shall be quantitated by the internal standard method. The internal standard used shall be the one assigned to that analyte for quantitation (Table 2). The EICP area of primary characteristic ions of analytes listed in Table 3 are used for quantitation.

12.2.2 It is expected that situations will arise when the automated quantitation procedures in the GC/MS software provide inappropriate quantitation. This normally occurs when there is compound coelution, baseline noise, or matrix interferences. In these circumstances, the laboratory must perform a manual quantitation. Manual integrations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific target compound. The area integrated must not include baseline background noise. The area integrated must not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system.

12.2.3 In all instances where the data system report has been edited or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report, and shall include the integration scan range. The GC/MS operator must also mark each integrated area on the quantitation report. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data.

12.2.4 The requirements listed in Sections 12.2.1 – 12.2.3 apply to all standards, samples, and blanks.

12.2.5 The $\overline{RRF}$ from the initial calibration is used to calculate the concentration in the sample. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. If linear regression is used, a regression curve must be used to calculate the concentration in samples. Refer to Section 12.2.7 for calculating sample concentration using linear regression techniques.

12.2.6 Calculate the concentration in the sample using the $\overline{RRF}$ and Equations 4-7.

EQ. 4 Concentration of Water Sample

$$\text{Concentration (ug/L)} = \frac{(A_x)(I_s)(V_t)(DF)}{(A_{is})(\overline{RRF})(V_o)(V_i)}$$

Where:

A_x = Area of the characteristic ion for the target compound

A_{is} = Area of the characteristic ion for the internal standard

I_s = Amount of internal standard injected in ng

V_o = Volume of water extracted in mL

V_i = Volume of extract injected in µL

V_t = Volume of the extract in µL

(Note: Extraction of water samples does not include concentration, and V_t is equal to the sum of the volumes added for extraction and addition of surrogates, internal standards, and any spiked target compounds.)

$\overline{RRF}$ = Mean Relative Response Factor determined from the initial calibration standard

DF = Dilution Factor. If no dilution is performed, DF = 1.0. The DF for analysis of water samples is defined as:

$$DF = \frac{\text{µL most conc. extract used to make dilution + µL clean solvent}}{\text{µL most conc. extract used to make dilution}}$$

EQ. 5 Concentration of Solid Sample

Note: Equation 5 includes a %moisture (D) factor for those cases when data is to be reported on the basis of dry sample weight. In cases where results are reported in terms of sample weight, this factor is deleted from the equation.]

$$\text{Concentration } \mu g/Kg \text{ (Dry weight basis)} = \frac{(A_x)(I_s)(V_t)(DF)}{(A_{is})(V_i)(\overline{RRF})(W_s)(D)}$$

Where:

A_x, I_s, A_{is}, V_i are as given for water, above.

V_t = Volume of concentrated extract in µL

$$D = \frac{100 - \%\text{Moisture}}{100}$$

W_s = Weight of sample extracted in g

$\overline{RRF}$ = Mean Relative Response Factor determined from the initial calibration standard

DF = Dilution Factor

EQ. 6 Concentration of Air Sample

$$\text{Concentration } ng/\text{std } m^3 = \frac{(A_x)(I_s)(V_t)(DF)}{(A_{is})(V_o)(V_i)(\overline{RRF})}$$

Where:

A_x = area response for the compound to be measured, counts

A_{is} = area response for the internal standard, counts

I_s = amount of internal standard, ng

$\overline{RRF}$ = the mean RRF from the most recent initial calibration, dimensionless

V_o = volume of air sampled, std m^3

V_t = volume of concentrated extract, µL

V_i = volume of extract injected, µL

DF = dilution factor for the extract. If there was no dilution, DF equals 1. If the sample was diluted, DF is greater than 1.

EQ. 7 Concentration of Wipe Sample

$$\text{Concentration } \mu g/\text{std } cm^2 = \frac{(A_x)(I_s)(V_t)(DF)}{(A_{is})(V_o)(V_i)(\overline{RRF})}$$

Where:

A_x = area response for the compound to be measured, counts

A_{is} = area response for the internal standard, counts

I_s = amount of internal standard, µg

$\overline{RRF}$ = the mean RRF from the most recent initial calibration, dimensionless

Area = area of surface wiped, cm^2

V_t = volume of concentrated extract, µL

V_i = volume of extract injected, µL

DF = dilution factor for the extract. If there was no dilution, DF equals 1. If the sample was diluted, DF is greater than 1.

12.2.7 Calculate the concentration in the sample using linear regression.

Set y = (Peak Area of Target/Peak Area of Internal Standard) and x = (Theoretical Concentration of Target/Theoretical Concentration of Internal Standard).

Plot (Peak Area of Target/Peak Area of Internal Standard [Y-axis]) vs. (Theoretical Concentration of Target/Theoretical Concentration of Internal Standard).

Determine the slope of the line (m) and the y-intercept (b).

Rearrange the line equation to solve for x: x = (y-b)/m.

Multiply x by the concentration of the internal standard to get the concentration of target in extract.

Multiply the concentration of target analyte in the extract by the extract volume, and divide by the sample volume to get concentration of target analyte in sample.

12.2.8 Adjusted LOQ Calculations

EQ. 8 Aqueous Adjusted LOQ

$$\text{Adjusted LOQ} = \text{Method LOQ} \times \frac{(V_x)(V_t)(DF)}{(V_o)(V_c)}$$

Where:

V_t, DF, and V_o are as given in Equation 4.

V_x = Method sample volume

V_c = Method concentrated extract volume

EQ. 9 Solid Adjusted LOQ

$$\text{Adjusted LOQ} = \text{Method LOQ} \times \frac{(W_x)(V_t)(DF)}{(W_s)(V_c)(D)}$$

Where:

V_t and DF are as given in Equation 4.
W_s and D are as given in Equation 5.
W_x = Method sample weight
V_c = Method concentrated extract volume

12.2.9 Surrogate Recoveries

Calculate surrogate recoveries for all samples, blanks, and MS/MSDs. Determine if recovery is within limits (Table 5).

Calculate the concentrations of the surrogates using the same equations as used for the target compounds. Calculate the recovery of each surrogate using EQ. 10.

EQ. 10 Percent Recovery

$$\text{Recovery} = \%R = \frac{C_s}{C_n} \times 100$$

Where:

C_s = Measured concentration of the spiked sample aliquot.

C_n = Nominal (theoretical) concentration increase that results from spiking the sample, or the nominal concentration of the spiked aliquot (for LCS).

12.3 Technical Acceptance Criteria for Sample Analysis

12.3.1 The samples must be analyzed on a GC/MS system meeting the instrument performance check, initial calibration, CCV, and blank technical acceptance criteria.

12.3.2 The sample must be extracted and analyzed within the technical holding times.

12.3.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.

12.3.4 The percent recoveries of the surrogates in a sample should be within the recovery limits listed in Table 5. These limits are based on a CWA workgroup consensus and will be updated following method validation. Note: The surrogate recovery requirements do not apply to samples that have been diluted.

12.3.5 The instrumental response (EICP area) for each of the internal standards in the sample must be within the range of 50.0 – 200% of the response of the internal standard in the most recent CCV standard analysis.

12.3.6 The RT shift for each internal standard must be within ± 0.50 minute (30 seconds) between the sample and the most recent CCV standard analysis.

12.3.7 Excluding those ions in the solvent front, no ion may saturate the detector. If a target compound concentration exceeds the upper limit of the initial calibration range, a more dilute aliquot of the sample extract must also be analyzed.

12.4 Corrective Action for Sample Analysis

12.4.1 The sample technical acceptance criteria must be met before data are reported. If the corrective actions described in this section did not solve the problem, all associated sample and blank data must be flagged accordingly.

12.4.2 Corrective action for failure to meet instrument performance checks and initial and continuing calibration verification must be completed before the analysis of samples. If the corrective actions described in Sections 10.2.5 (instrument performance check), 10.3.5 (initial calibration), or 10.4.6 (CCV) did not solve the problem, all associated sample and blank data must be flagged accordingly.

12.4.3 Corrective action for surrogate recoveries in a sample fail to meet the acceptance criteria specified in Section 12.3.4, check calculations, sample preparation logs, surrogate standard spiking solutions, and the instrument operation.

12.4.3.1 If the calculations were incorrect, correct them and verify that the surrogate recoveries meet their acceptance criteria.

12.4.3.2 If the sample preparation logs indicate that the incorrect amount of surrogate standard spiking solution was added to the sample, then re-extract (if possible) and reanalyze the sample after adding the correct amount of surrogate standard spiking solution.

12.4.3.3 If the surrogate standard spiking solution was improperly prepared, concentrated, or degraded, re-prepare the solution, re-extract (if possible), and reanalyze the samples.

12.4.3.4 If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. Verify that the surrogate recoveries meet their acceptance criteria.

12.4.3.5 If the instrument malfunction affected the calibrations, recalibrate the instrument before reanalyzing the sample extract.

12.4.3.6 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

12.4.3.7 Re-extract (if possible) and reanalyze the sample. EXCEPTION: If surrogate recoveries in a sample used for a matrix spike/matrix spike duplicate (MS/MSD) were considered unacceptable, then it should be re-extracted/reanalyzed only if surrogate recoveries met the acceptance criteria in both the MS/MSD analyses.

12.4.3.8 If the surrogate recoveries meet acceptance criteria in the re-extracted/reanalyzed sample, then the problem was within the laboratory's control.

12.4.3.9 Submit data from both analyses. Distinguish between the initial analysis and the extraction/reanalysis on all deliverables.

12.4.4 Corrective action for internal standards in a sample that fail to meet their acceptance criteria, check calculations, internal standard solutions, and instrument operation.

12.4.4.1 If the calculations were incorrect, correct them, and verify that the internal standard responses meet their acceptance criteria.

12.4.4.2 If the internal standard solution was improperly prepared, concentrated, or degraded, re-prepare solutions and reanalyze another aliquot of the sample extract (if possible) after adding the correct amount of the freshly prepared internal standard solution.

12.4.4.3 If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract.

12.4.4.4 If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

12.4.4.5 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

12.4.4.6 Reanalyze the sample extract.

EXCEPTION: If internal standard responses in a sample used for an MS and/or MSD were outside the acceptance windows, then the sample should be reanalyzed only if internal standard compound recoveries met the internal standard acceptance criteria in both the MS/MSD analysis.

12.4.4.7 If the internal standard responses meet acceptance criteria in the reanalyzed sample extract, then the problem was within the laboratory's control.

12.4.4.8 Submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables.

13.0 Method Performance

13.1 Laboratory accuracy and precision will be those listed in the single and multiple lab studies from the CWA protocol in the 2013 draft.

13.2 Other specific Quality Assurance Objectives (QAO) may be found in the appropriate statement-of-work or Quality Assurance Project Plan (QAPP) for specific projects.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477.

15.0 Waste Management

15.1 The waste produced from this procedure consists of waste collected from the extraction equipment, excess sample, Standards, Methylene Chloride, Acetone, and Methanol.

15.2 Excess reagents are disposed following the MSDS instructions.

15.3 Glass pipettes are disposed in the lab scraps waste.

15.4 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

15.5 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.6 The Environmental Protection Agency requires that laboratory waste management practices conducted are consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society.

16.0 References

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16.9 U.S. Environmental Protection Agency, Office of Research and Development, *Battelle Draft Final Report – Evaluation of Sample Preparation and Analytical Methodologies*, April 17, 2008.

16.10 U.S. Environmental Protection Agency, *Standard Analytical Methods for Environmental Restoration Following Homeland Security Events* (SAM) document and information are posted at: http://www.epa.gov/sam/

16.11 "Extraction of VX from Soils", Bellier B. et al, *Anal. Chem.* 2004, 76, 2791-2797.

16.12 EPA's Superfund Analytical Services / Contract Laboratory Program, Multi-Media, Multi-Concentration Organics Analysis, SOM01.2, Exhibit E, Section 7, May 2005. (http://www.epa.gov/superfund/programs/clp/download/som/som11e-h.pdf)

16.13 Analytical Protocol for Cyclohexyl Sarin, Sarin, Soman and Sulfur Mustard Using Gas Chromatography/Mass Spectrometry (EPA/600/R-16/115 Sept. 2016

16.14 Analytical Protocol for VX Using Gas Chromatography/Mass Spectrometry (EPA/600/R-16/116 Sept. 2016.

17.0 Tables, Figures, and Attachments

Table 1. Decafluorotriphenylphosphine (DFTPP) Key Ions and Ion Abundance Recommendations

These recommendations are from "Analytical Protocol for Chemical Warfare Agents using GCMS"

Mass	Ion Abundance Criteria	
	Quadrupole	Time of Flight (TOF)
51	10.0 – 80.0% of mass 198	10.0 – 85.0% of mass 198
68	Less than 2.0% of mass 69	Less than 2.0% of mass 69
69	Present	Not used
70	Less than 2.0% of mass 69	Less than 2.0% of mass 69
127	10.0 – 80.0% of mass 198	10.0 – 80.0% of mass 198
197	Less than 2.0% of mass 198	Less than 2.0% of mass 198
198	Base peak 100% relative abundance (see Note below)	Base peak 100% relative abundance
199	5.0 – 9.0% of mass 198	5.0 – 9.0% of mass 198
275	10.0 - 60.0% of mass 198	10.0 - 60.0% of mass 198
365	Greater than 1.0% of mass 198	Greater than 0.5% of mass 198
441	Present but less than mass 443	Less than 150% of mass 443
442	Greater than 50.0% of mass 198	Greater than 30.0%
443	15.0 – 24.0% of mass 442	15.0 – 24.0% of mass 442

Note: All ion abundances MUST be normalized to m/z 198.

Table 2. Internal Standards and Surrogates

CWA	Surrogate Compounds	Internal Standards
Sarin (GB)	Nitrobenzene-d_5	1,4-Dichlorobenzene-d_4
Soman (GD1)	Nitrobenzene-d_5	1,4-Dichlorobenzene-d_4
Soman (GD2)	Nitrobenzene-d_5	1,4-Dichlorobenzene-d_4
Cyclohexyl Sarin (GF)	Triphenyl phosphate or Terphenyl-d_{14}	Naphthalene-d_8
Mustard, sulfur (HD)	Triphenyl phosphate or Terphenyl-d_{14}	Naphthalene-d_8
VX	Triphenyl phosphate	Phenanthrene-d_{10}

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Table 3. Example Retention Times, Relative Retention Times and Characteristic Ions for Target Compounds, Surrogate Compounds, and Internal Standards

Contaminant	Retention Time (sec)	Relative Retention Time	Full Scan and SIM	
			Primary Quantitation Ion	Secondary Quantitation Ions
Cyclohexyl sarin (GF)	322.192	1.02	99	**67**, **81, 137**, **82**
Mustard, sulfur / Mustard gas (HD)	316.592	0.98	109	158, 160, **63**, **111**
Sarin (GB)	195.399	0.63	99	**125, 81**
Soman (GD1)	272.194	1.05	99	**126**, **82,** 69
Soman (GD2)	273.394	1.06	99	**126**, **82,** 69
VX	429.263	0.94	114	**127**, 79, **72**
Triphenyl phosphate (S)	558.476	1.64	326	**325, 215**
Nitrobenzene-d_5	291.593	1.1	82	
Terphenyl-d_{14} (S)	524.478	1.57	244	**122**
1,4-Dichlorobenzene-d_4 (IS)	268.895		152	**150, 115,** 78
Napthalene-d_8 (IS)	322.192		136	**68, 108**
Phenanthrene-d_{10} (IS)	452.983		188	**94, 80**

Notes:
Bold quantitation ions indicate the secondary quantitation ions used during single-laboratory testing.
(S) = Surrogate
(IS) = Internal Standard

Table 4. Surrogate Recovery

Nitrobenzene-d5	50 - 150
Nitrobenzene-d5	50 - 150
Nitrobenzene-d5	50 - 150
Nitrobenzene-d5	50 - 150
Nitrobenzene-d5	50 - 150
Triphenyl phosphate	50 - 150
p-Terphenyl-d14 p-Terphenyl-d14	50 - 150
Nitrobenzene-d5	50 - 150
Triphenyl phosphate p-Terphenyl-d14	50 - 150
p-Terphenyl-d14	50 - 150

Table 5. Example Calibration Standard Concentrations (ng/µL) used during Laboratory Method Development

GC/MS – Selective Ion Monitoring or TOF/LVI Quadrupole								
Analyte	**CAS RN**	**Cal 1**	**Cal 2**	**Cal 3**	**Cal 4**	**Cal 5**	**Cal 6**	**Cal 7**
Sarin (GB)	107-44-8	0.01	0.05	0.08	0.1	0.25	0.5	1.0
Soman (GD1 and GD2)	96-64-0	0.005	0.025	0.04	0.05	0.125	0.25	0.5
Cyclohexyl Sarin (GF)	329-99-7	0.01	0.05	0.08	0.1	0.25	0.5	1.0
Mustard, sulfur (HD)	505-60-2	0.005	0.025	0.04	0.05	0.125	0.25	0.5
VX	50782-69-9	.01	0.05	0.08	0.1	0.25	0.5	1.0
Nitrobenzene-d_5 (S)	4165-60-0	0.01	0.05	0.08	0.1	0.25	0.5	1.0
	321-60-8	0.01	0.05	0.08	0.1	0.25	0.5	1.0
Terphenyl-d_{14} (S)	1718-51-0	0.01	0.05	0.08	0.1	0.25	0.5	1.0
Triphenyl phosphate (S)	115-86-6	0.01	0.05	0.08	0.1	0.25	0.5	1.0
1,4-Dichlorobenzene-d_4 (IS)	3855-82-1	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Naphthalene-d_8 (IS)	1146-65-2	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	15067-26-2	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Phenanthrene-d_{10} (IS)	1517-22-2	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	1719-03-5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	1520-96-3	0.5	0.5	0.5	0.5	0.5	0.5	0.5

Note: * These surrogates or internal standards are not required for the compounds being addressed by this protocol, but may be used if they are already included in solutions that will be used by the laboratory.

APPENDIX A: EXAMPLE INSTRUMENT CONDITIONS

The conditions provided in this appendix can be used to increase sample throughput and have been used by laboratories implementing the procedures described in the protocol. Unless modifications are specified below, the instrument operating conditions are equivalent to what is provided in Sections 10.1.1 and 10.1.2.

A-1.0 GC conditions using a quadrupole mass spectrometer

A.1.1 Using a 30-m column

GC conditions splitless mode (Agilent 6890/5973 instrument operated in SIM mode):

Injector Temp:	280°C
Carrier Gas Flow:	64.4 mL/minute
GC Oven Program:	50°C for 0.5 minutes, 23°C/minute to 290°C, 15 °C/minute to 320 °C hold for 0.1 minutes
Total Runtime:	13 minutes

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APPENDIX B -
PHILIS SOP L-A-201
Semivolatile Organics by Method 8270E Rev. 3 06/19/2024

STANDARD OPERATING PROCEDURE

FOR

SEMIVOLATILE ORGANICS BY METHOD 8270E

PHILIS SOP L-A-201 Rev. 3

Revision Date: 06-19-2024

EPA Contract No. 68HERH21D0002

PREPARED BY

PHILIS

PREPARED FOR

U.S. Environmental Protection Agency
Office of Emergency Management
Washington, DC 20460

Approvals:

PHILIS, Castle Rock Lead Chemist	**June 19, 2024** **Date**
PHILIS, Edison Lead Chemist	**June 19, 2024** **Date**
PHILIS, Quality Assurance Manager	**June 19, 2024** **Date**
PHILIS, Program Manager	**June 19, 2024** **Date**

Revision History

Revision	Name	Date	Description of Change
A	James Travis	04/01/2021	Transitional Issue
0	James Travis	03/21/2022	Program Issue
1	James Travis	06/09/2022	Revision
2	James Travis	10/14/2022	Revision
3	James Travis Tom Antony	12/07/2023	Revision

SOP REVISION FORM

SOP Name:	**Semivolatile Organics by Method 8270E**		
Purpose: *(Review or Revise)*	*SOP #:*	*Rev. #:* *(Being Reviewed or Revised)*	*Origination / Release Date:*
Revision	*SOP No. L-A-201*	2	10/26/2022
Requested by:	James Travis	Date:	12/07/2023

New SOP Revision Date:	**06/19/2024**	**New SOP Revision #:** *(If Applicable)*	**3**

For *Revision* : Summary of Revisions (specify sections)

2.2, 2.3, 2.4, 2.5	Microwave added as an extraction method
2.6	Method number 3546 added
16.8	Microwave method 3546 added to references
Section 17.0	Updated QA-017 form (Figure 1)

For *Review*: Comments

Standard Operating Procedure
Semivolatile Organics by Method 8270E
L-A-201 Rev. 3

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TABLES AND APPENDIX

Standard Operating Procedure
Semivolatile Organics by Method 8270E
L-A-201 Rev. 3

1.0 Scope and Application, and Components to be Analyzed

1.1 This SOP is executed in accordance with the U.S. Environmental Protection Agency and National Environmental Laboratory Accreditation Program (NELAP).

1.2 This procedure can be used to determine presence and concentration of analytes listed in Section 17 Tables 2 and 3 in aqueous, solid, sludge and wipe samples.

1.3 This Standard Operating Procedure (SOP) documents the PHILIS Program application of EPA Method SW846 8270E, "Determination of the Concentration of Semivolatile Organic Compounds in Aqueous and Soil Samples by Gas Chromatography/Mass Spectrometry", which will be used in the PHILIS Mobile Labs.

1.4 This method can be used to detect and quantitate most pH neutral, acidic, and basic organic compounds that are soluble in methylene chloride (or other suitable solvents provided that the desired performance data can be generated) and are capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, halo ethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. In most cases, this method is not appropriate for the quantitation of multi-component analytes, e.g. Aroclors, Toxaphene, Chlordane, etc. This is due to the limited sensitivity for the above mentioned analytes.

Note that the compounds are listed in approximate retention time order. Additional compounds may be added to this list, as long as they are validated prior to sample analysis. This validation would be performed by conducting Method Detection Limit (MDL) and Precision & Accuracy (P&A) studies.

CAUTION: Compounds that are documented as being difficult to analyze using this analytical method are listed in Section 17 Table 4. These compounds may require special treatment when being determined by this method.

Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use of gas chromatograph/ mass spectrometers and skilled interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of Method

2.1 Aqueous samples are extracted with methylene chloride using automated solid phase extraction (SPE), separatory funnel, or by micro-extraction techniques. The extract is typically concentrated to 1mL, and internal standards are added prior to analysis by GC/MS. Other final volumes for extract concentration are allowed based on data requirements.

2.2 Soil or solid samples are extracted using pressurized solvent extraction (PSE), microwave extraction or a micro extraction. Table 1 below is an example of amounts of soil or solid extracted and an approximate expected analyte range that may be used to determine the amount of soil to extract if estimated concentrations of analytes are available.

2.3 For low level soil samples, 30 grams of soil are extracted with 50:50 methylene chloride/acetone using pressurized solvent extraction (PSE) or microwave extraction. The extract is concentrated to 1.0 mL, and internal standards are added prior to analysis by GC/MS. Anticipated analyte concentration range for this process is 0.083 mg/Kg to 5.0 mg/Kg.

2.4 For medium level soil samples, 15 grams of soil is extracted with 50:50 methylene chloride/acetone using pressurized solvent extraction (PSE) or microwave extraction. The extract is concentrated to 10 mL, and internal standards are added prior to analysis by GC/MS. Anticipated analyte concentration range for this process is 1.66 mg/Kg to 100 mg/Kg.

2.5 For high level soil samples, 1 gram of soil is extracted with 50:50 methylene chloride/acetone using pressurized solvent extraction (PSE) or microwave extraction. The extract is concentrated to 10 mL, and internal standards are added prior to analysis by GC/MS. Anticipated analyte concentration range for this process is 24.9 mg/Kg to 1500 mg/Kg.

2.6 Extraction procedures are described in PHILIS specific extraction SOPs and they are based on SW 846 Methods 3510, 3511, 3535A, 3545A, 3546 and 3570. Other extraction procedures are acceptable provided the procedure is validated prior to use on samples.

2.7 Qualitative identification of compounds detected by this method is based on retention times and on comparison of the sample mass spectrum with characteristic ions in a reference mass spectrum. Once a target compound has been identified, quantitation of that compound is based on the integrated area of the primary characteristic ion relative to the integrated area of the primary characteristic ion of the nearest internal standard.

3.0 Definitions

3.1 Batch‡: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A Preparation Batch is composed of between 1 and 20 environmental samples of the same matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and the last sample in the batch to be 24hours. An Analytical Batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

All batches require one MB, LCS, and MS/MSD pair or MS and Sample Duplicate when possible.

3.2 Chain of Custody (COC) ‡: Record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers; the mode of collection; the collector, the time of collection, preservation, and requested analyses. See also Legal Chain of Custody Protocols.

Each time the samples are transferred, the document should be signed by the person releasing the samples and by the person receiving the samples. A date and time must also be recorded.

3.3 Holding Time: The maximum amount of time permitted between sampling and sample preparation and/or sample preparation and sample analysis. Also the period of time a sample may be stored prior to analysis when there is no preparation step. See the specific method or SW846 8000B table 4.1.

3.4 Internal Standards (IS) ‡: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

3.5 Laboratory Control Sample (LCS) ‡: (however named, such as laboratory fortified blank, blank spike (BS), or QC check sample). A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

The standard source can be the same as the calibration or a second source. The LCS is analyzed exactly like a sample to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.6 Matrix Spike (spiked sample of fortified sample)‡: A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of the sample for which an independent test results of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

3.7 Matrix Spike Duplicate (spiked sample or fortified sample duplicate)‡: A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

3.8 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. Method Blank analytical results are evaluated to determine the presence of contamination in the analytical method process. The method blank should not contain analytes of interest that are ½ the Reporting Limit or greater.

3.9 Method Detection Limit (MDL): The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined by analyzing seven or more replicates of a spiked analyte free matrix and the resulting statistical calculation, in accordance with 40 CFR 136, Appendix B, Revision 2.0.

3.10 Required Detection Limit (RDL): Detection limits established by a regulatory authority for certain analytes. The laboratory MDL values must be equal or lower than the RDL. This is also known as the CRQL, the contract-required quantitation limit.

3.11 Reporting Limit (RL): The reporting limit, also known as the LOQ is the minimum concentration that can be reported as a quantitated value for a target analyte in a sample. This value can be no lower than the concentration of the lowest calibration standard.

3.12 Second Source Calibration Verification (SCV): A solution prepared from a source that is different from the calibration standards. The SCV is immediately following the ICS, and is used to verify calibration standard accuracy.

3.13 Selected Ion Monitoring: A mass spectrometry technique that provides lower detection level capability by monitoring fewer mass scans for longer periods of time than is done in full-scan methods.

3.14 Surrogate Standard (SS): Organic compounds which are similar to the target analytes in chemical composition and mimic the behavior of the target analytes throughout the analytical process. Surrogate compounds are not normally found in environmental samples. Each calibration standard, sample, MB, LCS, MS, and MSD is spiked with surrogate standards. Surrogates are used to evaluate analytical efficiency by measuring recovery. See analytical method SOP for a list of specific surrogate compounds that are appropriate for sample-specific analysis.

ǂ EL-V1M2-ISO-2016, 2016 NELAP Standard definition.

4.0 Interferences

4.1 Positive matrix interferences can be caused by contaminants that are extracted from the sample during the extraction process. Negative matrix interference can occur when samples contain materials that have a strong affinity for the analyte compounds. The amount of matrix interference varies from sample to sample. Cleanup procedures may help eliminate some of the interferences.

4.2 Contaminants in the solvents, reagents, glassware, and other extraction components may lead to matrix interferences. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running MBs with every batch. GC/MS data for every MB, LCS, MS, MSD, and sample must be evaluated for interferences. If interferences are detected, the lab should attempt to determine the source of interference and take corrective action to eliminate it.

4.3 High purity reagents, solvents, and gases must be used to minimize interference problems with the sample analysis.

4.4 Carryover contamination may occur when a sample containing low levels of SVOCs is analyzed immediately following a sample containing high levels of SVOCs. If this situation occurs during a non-monitored analysis, the sample containing the low concentration SVOCs may require reanalysis. If the situation occurs during monitored analysis, a blank should be run after the high level sample to ensure that the system is free of contamination. To reduce carryover, the injection syringe must be rinsed with solvent between samples.

4.5 Phthalate contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis. Sample preparation equipment used for sample preparation shall not be composed of plastic materials.

5.0 Health and Safety Warnings

5.1 This method does not address all safety issues associated with its use. Laboratory personnel are responsible for maintaining a safe work environment and a current awareness of the Chemical Hygiene Plan regarding the safe handling of the chemicals listed in this method.

WARNING: This procedure involves working with hazardous materials. It is the responsibility of the analyst to follow the appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are hazardous.

5.2 Specific Safety Concerns or Requirements

WARNING: Standard laboratory personal protective equipment (PPE) for routine laboratory functions will include safety glasses with side shields, disposable nitrile gloves, laboratory coat, and closed-toe non-absorbent shoes. Additional PPE may be required as based on increased hazards of the work task performed or abnormal event such as spill clean-up. Disposable gloves that have been contaminated must be removed and discarded. Non-disposable gloves must be cleaned immediately. Latex and vinyl gloves provide no protection against the organic solvents used in this method, so nitrile or similar material must be used.

WARNING: GC/MS instruments and other equipment may have heated zones which can cause severe burns if contacted. Prior to working on any equipment containing a heated source, the equipment will be cooled to a safe temperature.

WARNING: The MS is under vacuum pressure. It must be vented and brought up to atmospheric pressure and cooler temperatures prior to working on the source.

WARNING: GC/MS instruments have high voltage areas. Instrument power must be turned off and the instrument unplugged prior to performing source maintenance. The power source of the equipment will be lock-out and/or a tag placed at or near the source to prevent inadvertent operation during a maintenance function.

WARNING: The toxicity and/or carcinogenicity of the reagents and analytes used in this method have not been precisely defined; therefore, each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Procedures involving primary standards and sample preparation must be performed in a fume hood.

WARNING: All preparation of standards and sample preparation are required to be conducted in an operating fume hood. Acetone and methanol are highly flammable and require handling caution near any heated source and required storage only in a flammable storage cabinet. Methylene chloride is a highly volatile chemical that poses a significant inhalation hazard if spilled. Methanol can be absorbed through the skin and methylene chloride is very corrosive to the skin and eyes, therefore extreme care is needed and strict hygiene practices.

5.3 A Material Safety Data Sheet (MSDS) and PHILIS Chemical Hazard Summary sheet are available for each analyte and reagent used in the mobile laboratory to all employees and are required reading/understanding prior to working with the chemical. Special safety precautions for sample preparation (e.g. solvent extraction equipment and methods) are provided in the sample preparation SOPs.

6.0 Equipment and Supplies

6.1 Glassware

6.1.1 Small glass vials (1mL or 2 mL) are used for storage of sample extracts, calibration standards and stock standards.

6.1.2 4mL, 10 mL, 40 mL, or 60 mL vials are used for storage of standards and spiking solutions.

6.2 Solvents

6.2.1 Acetone—Capillary GC, GC/MS, pesticide or equivalent grade

6.2.2 Methylene Chloride—Capillary GC, GC/MS, pesticide or equivalent grade

6.2.3 Methanol—Capillary GC, GC/MS, pesticide or equivalent grade

6.3 Syringes

6.3.1 Gas-tight micro syringes- various sizes for transferring the concentrated extracts, diluting samples, adding internal standards to extracts, and preparing calibration standards.

6.4 Instrumentation

6.4.1 Gas chromatograph/mass spectrometer system: an analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly interfaced to the source.

6.4.2 Column: PHILIS Castle Rock uses 30m x 0.25mm ID, 0.25-µ m film thickness fused-silica capillary column coated with 5% diphenyl/95% dimethyl polysiloxane (Restek RTX-5MS or equivalent). PHILIS Edison uses RXI-5 Sil MS 30 m x 0.25 mm. Alternate columns are acceptable if they provide acceptable performance.

6.4.3 Mass Spectrometer: Capable of scanning from 35 to 500 amu every one second or less, using 70eV in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for DFTPP that meets all the criteria in Table 7, when 50 ng or less of the tuning standard is injected.

6.4.4 Auto sampler: Gerstel MPS-2 rail system or equivalent.

6.4.5 GC/MS interface: Capillary column direct into the ion source.

6.4.6 Data System: The data system is equipped with the Agilent Chemstation software for data acquisition, Enviroquant for data processing and Gerstel's Maestro for the autosampler. Mass Hunter is used on the newer instruments. Other equivalent software may be used.

6.4.7 Syringe: 10 µL Gerstel syringe, or equivalent.

7.0 Reagents and Standards

7.1 Reagents

Note: Original containers of reagents shall be labeled with expiration dates in accordance with the OSHA Hazard Communication Program. All containers of prepared reagents must bear a name, preparation date, and must be linked to the preparation records.

7.1.1 Reagent water can be Milli-Q water, tap water, distilled water or any other water provided no interferences are noted.

7.1.2 Reagent soil is TCL-free sand and is used for QC samples. Ottawa Sand that has been processed through the Fast PSE may also be used for QC samples.

7.1.3 Helium carrier gas is 99.999% (UHP) or greater such as Research Grade, 99.9999%.

7.1.4 Nitrogen- gas is 99.999% (UHP) grade.

7.2 Standards

A minimum five-point calibration curve is prepared for establishing average response factors or linear regression curve fitting. Six calibration points are required for quadratic (second-order) curve fits. The low point of the calibration curve must be equal to or less than the reporting limit. The high standard defines the calibration range. See Section 17 Tables 8 and 9 for examples of the preparation of the ICAL levels for the Full List and the PAH lists. Other amounts of the standards listed below may be used based on the sensitivity of the instrument.

7.2.1 An internal standard (IS) solution is purchased at a concentration of 2000 µg/mL. The list of internal standards for this method is provided in Section 17 Table 4. Other concentrations of IS may be used provided the amount in the standards and samples remain constant.

7.2.2 Internal standards are added to all standards and extracts, resulting in a final concentration of 40 µg/mL.

7.2.3 Surrogate Standard Spiking Solution is purchased or prepared so that the resulting concentration in samples and quality control is at 40 µg/mL. Surrogate compounds for this method are listed in Section 17 Table 6.

7.2.4 DFTPP GC/MS Tuning Standard is used for determining acceptable instrument performance. The methylene chloride solution contains 50 µg/mL of decafluorotriphenylphosphine (DFTPP). Pentachlorophenol, benzidine, and DDT should also be included in the Tuning Standard at 50 µg/mL. Preparation in alternate solvents may result in degradation of DFTPP. The instrument is only required to pass the tuning standard when a calibration in analyzing.

7.2.5 Laboratory Control Spiking Solution is purchased or prepared so that the resulting concentration is at 40 µg/mL. The LCS shall include all compounds of interest. The LCS may be prepared from a source different than used for the instrument calibration or the same source as the calibration. Other levels could be used as long as the resulting concentration of the LCS is near the midpoint of the calibration curve.

7.2.6 Matrix Spike Solution is the same as the Laboratory Control Spiking Solution.

7.2.7 The levels are defined with a final volume of 1000 µL, although there is actually 1020 µL after the addition of the internal standard mix. Thus, compound concentrations (including internal standards and surrogates) are all 1.96% lower in absolute terms than stated. However, since every extract (standards, samples and QC) contains 1020 µL (2% more than the stated volume) after the addition of the IS mix, the deviation of concentrations from true values is offset by the deviation in final extract volumes from true values. Other final volumes may be used based on reporting requirements.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Samples are collected by field sampling teams in 1000-mL amber bottles or 8-oz amber jars and are put on ice to maintain a temperature of 0-6°C and submitted to the laboratory. See SOP sample login procedures, for sample acceptance criteria. Other containers may be used provided the size is adequate for the reporting limits required, are clean, and do not add any interferences.

8.2 Samples received on the collection day shall be considered acceptable if there is evidence that the chilling process has begun such as arrival on ice. In such cases, sample temperatures that are in excess of 6 °C upon receipt are acceptable.

8.3 Samples are maintained at the temperature of 0-6°C.

8.4 Sample extraction holding time is 7 days for aqueous samples and 14 days for soil samples. The sample extracts must be analyzed within 40 days of extraction.

9.0 Quality Control and Acceptance Criteria

QC requirements include the Initial Demonstration of Capability and ongoing QC requirements that must be met when preparing and analyzing samples.

9.1 Initial Demonstration of Capability (IDOC) is an evaluation that must be successfully performed by an analyst prior to analyzing any field samples and any time major method modifications are made. The following is done to demonstrate laboratory capability to perform this method:

9.1.1 Prior to conducting the IDOC study, the analyst tunes the instrument and generates an acceptable instrument calibration following the procedure outlined in Section 10 of this SOP. A MB is analyzed to demonstrate that the background contamination is low enough to not interfere with analytes.

9.1.2 Method precision and accuracy is demonstrated by analyzing four (4) replicate LCSs fortified at a known concentration (e.g. 40µg/mL) typically around the midpoint of the calibration. Precision and accuracy are calculated.

9.1.3 Recovery limits are established using instrument generated data. The acceptable range will be set using the control charts at three standard deviations and updated every six months or sooner.

9.1.4 MDLs are established by analyzing a minimum of seven replicates of a known concentration and a minimum of seven blanks extracted and analyzed over a three-day period.

9.1.5 MDL verification is performed at the time of initial method development, each time the MDL study is performed, and on an annual basis.

9.1.6 RL's are established by the lowest point in the calibration curve.

9.2 Ongoing QC is applied when performing this method and includes analyzing an acceptable instrument calibration, verification standard, MB, LCS, MS, MSD, with samples. Every batch must contain at least one MB, LCS, MS, and MSD. If there is not enough volume for an MS/MSD pair, then a sample DUP or an LCSD must be performed for precision data Control Limits.

9.2.1 Control limits are determined for surrogates, laboratory control samples, matrix spike samples and precision and accuracy. Limits can be calculated when 15 – 20 data points are available and monitored every 20 – 30 data points thereafter. They should be evaluated at least every 6 months. The recovery limits are the mean recovery ±3 standard deviations for surrogates, MS, and LCS. Precision limits for the MS/MSD or LCS/LCSD pair are the absolute value of the mean relative percent difference (RPD) ±3 standard deviations.

9.2.2 These limits do not apply to dilutions, but the surrogate and matrix spike recoveries will be reported unless the dilution is 4x or more.

All surrogates, LCS, and MS recoveries (except for dilutions) must be entered into Element so that historical control limits can be generated. For multiple dilutions, reported from the same extract, surrogates will be reported for all dilutions of less than 4x.

9.3 MDL Procedure

MDLs and RLs are established by analyzing a minimum of seven replicates of a standard at or near the estimated MDL and seven blank replicates. Tabulation of results and MDL calculations are performed by the method in 40 CFR, Part 136, Method Update Rule Revision 2.

9.3.1 Initial MDLs

9.3.1.1 Initial MDLs are established by analyzing a minimum of seven replicates of the low-level calibration standard and a minimum of seven blanks prepped and analyzed over three separate days. The MDL should be spiked 1 to 5 times the estimated MDL. Extract and analyze the MDL standards and blanks with the same procedure as regular samples.

9.3.1.2 For each compound, calculate the mean and standard deviation of the replicates in micrograms per liter (µg/L). Then calculate the MDL by multiplying the standard deviation by the Student's t value. The one-sided (single-tailed) Student's t values at the 99% confidence levels are used (e.g., t = 3.143 at the 99% confidence level for n = 7). MDL studies are repeated annually and verified each time they are prepared. MDL results are stored in Element each time they are calculated. MDL blanks are calculated using the above formula and then adding the mean of the blank results provided that the analyte is detected in all MDL blank analyses. If the mean of the blank results in a negative number then use 0 in place of the mean. The sum of these two numbers is the blank MDL. The larger of the two values will be used as the MDL. If all MDL blanks show no analyte detection, then the spiked MDL determination is used. If there is a mixture of analyte detections and non-detections, then the largest method blank detection is used as the MDL blank. Again, the larger of the MDL spike and MDL blank is used as the analyte MDL.

9.3.2 Ongoing MDL Data Collection

9.3.2.1 Ongoing MDL's are determined by preparing and analyzing two spiked standards at 1-5 times the estimated md and two blanks once per quarter for a minimum of seven determinations. The blanks and spikes may be analyzed in the same prep batch, but is not required. If the instruments are being used regularly, the MDL spikes may be added to the routine batches and the regular blanks used. All blanks analyzed during the evaluation period should be used.

9.3.2.2 At least once per year re-evaluate the MDL by calculating as above in 12.3.1.2. Use the larger of the spiked determinations and blank determinations for the MDL value. If all blanks are non-detect, then the MDL Blank is not calculated. If all blanks have detection, then the MDL Blank is calculated as a regular MDL. If there are less than 100 blank determinations, and there is a mixture of detects and non-detects, then use the highest value to determine the MDL.

9.4 MDL Verification (MDLV)

9.4.1 At least once every thirteen months, re-calculate the MDL spike and MDL blank from the collected spiked samples and method blank results.

9.4.2 Include data generated within the last twenty four months, but only data with the same spiking level. Only documented instances of gross failures (instrument malfunctions, mislabeled samples, cracked vials, etc.) may be excluded from the calculations.

9.5 Method Blank (MB)

9.5.1 For aqueous samples, the method blank is reagent water, and for soil samples it is Ottawa sand or an analyte-free sand. The method blank is free of the analytes of interest and is spiked with the surrogates. At least one method blank must be prepared with every batch.

9.5.2 Acceptance Criteria: The result for the method blank must be less than one half the RL or less than 10% of the analyte concentration found in the associated samples, whichever is higher, to report definitive results. If the analyte result is not less than ½ the RL then the associated samples must be greater than 10 times the blank to report definitive results.

9.5.3 Corrective Action: If a compound fails to meet these criteria, the lead chemist will be informed. In general, batch samples, other than those that are non-detect for the contaminant compounds will be re-extracted. However, if the analyte in the method blank was not detected in any of the associated samples, the data can still be reported.

9.6 Instrument Blank (IB)

Instruments must be evaluated for contamination during every 12-hour analytical run. This can be accomplished by analysis of a MB. If a MB is unavailable, an instrument blank must be analyzed. An instrument blank consists of methylene chloride with the internal standards added. It is evaluated the same way as a method blank.

9.7 Laboratory Control Sample (LCS)

The LCS is prepared using reagent water for aqueous samples or analyte-free sand for soil samples. A laboratory control sample is prepared and analyzed with every batch of samples. The compounds must be spiked at a concentration that falls within the working range of the calibration. See Section 6.0 of this SOP.

9.7.1 Acceptance Criteria: All analytes must be within the control limits to report definitive data. Example control limits are in Table 2. Current control limits are stored in the LIMS and are updated every six months.

9.7.2 Corrective Action: If any analyte in the LCS is outside the established control limits, a corrective action must be performed. A corrective action may consist of a data evaluation to determine the effect on data, to complete reprep and reanalysis. All corrective actions must be documented.

9.7.3 If the batch is not re-extracted or re-analyzed, the reasons for accepting the batch must be clearly presented in the report. An example of acceptable reasons for this might be that the MS/MSD are acceptable and sample surrogate recoveries are within control limits, showing that the problem was just on the LCS. This is also applicable if the analyte that failed is not a target analyte for the project, or if the analyte recovered above the control limit, but was not detected in the associated samples.

9.7.4 If re-extraction and re-analysis of the batch are not possible due to limited sample volume, the LCS is reported, all associated samples are flagged accordingly, and the appropriate comments are made in the report.

9.8 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

The matrix spike is a second aliquot of one of the samples in the batch, and the matrix spike duplicate is a third aliquot of the same sample. The MS/MSD are spiked with the same analytes and concentration as the LCS. The MS and MSD samples are prepared with every batch. See Section 6 of this SOP.

9.8.1 Acceptance Criteria: The percent recovery must be within the control limits. The RPD for the pair must be less than or equal to the control limit.

9.8.2 Corrective Action: If the recovery or RPD of an analyte is outside of its control limits, or if an RPD fails, then a corrective action must be performed. Typically, if the recoveries of the MS/MSD are similar but not within control limits and the recoveries of the LCS are within control limits, then the analysis can continue. This is documented as matrix interference.

9.8.3 If there are recovery failures in the MS/MSD and the LCS, then the batch must be re-extracted and/or re-analyzed. Or, all associated data must be qualified and a reason must be included in the data package detailing the batch was not re-extracted and re-analyzed.

9.8.4 If re-extraction is not possible due to limited sample volume, then a duplicate LCS (LCSD) may be run with the re-extraction batch. The RPD of the LCS/LCSD must be less than or equal to the established control limit.

9.9 Surrogates

9.9.1 Each sample, MB, and QC sample is spiked with the surrogate standards. The surrogates must be spiked within the working range of the ICAL. The surrogates are listed in Table 6. After analysis, if any of the surrogates fail to meet criteria, the sample must be re-extracted or re-analyzed. If the re-extraction fails in the same manner, it can be documented in the report that the failure is due to matrix interference.

9.9.2 If a sample has a surrogate failure and it has an associated MS/MSD, and the surrogate recoveries in the pair also fail, then the sample and the MS/MSD do not require re-extraction. This indicates matrix interference.

9.9.3 If the sample is re-extracted and the surrogates in the re-analysis are acceptable, the re-analysis should be reported. This indicates the failure was within the control of the analyst. However, if the sample is re-extracted outside of the hold time, both sets of results should be reported.

9.9.4 If the re-extraction confirms the surrogate failure, the original results should be reported and the matrix interference should be documented in the report.

9.9.5 Method precision and accuracy are demonstrated by analyzing 4 replicate LCS's fortified at concentration listed in Table 5 according to the procedure described in Section 13 of this SOP. Precision and accuracy are calculated using an EXCEL Spreadsheet.

9.9.5.1 Acceptable precision for RSD is ≤ 30%. Once adequate points are available, laboratory limits will be established.

9.9.5.2 Once adequate points are available, laboratory acceptance limits will be established.

9.9.6 Ongoing QC applied when performing this method includes analyzing acceptable instrument calibration/calibration verification standards, method blanks, LCS, and MS/ MSD. Internal standards and surrogates must be acceptable with all QC samples and with test samples.

9.10 Lower limit of quantitation (LLOQ)

9.10.1 The LLOQ is the lowest concentration at which the laboratory has demonstrated target analytes can be reliably measured and reported with a certain degree of confidence. The LLOQ must be greater than or equal to the lowest point in the calibration curve. The laboratory shall establish the LLOQ at concentrations where both quantitative and qualitative requirements can consistently be met. The laboratory shall verify the LLOQ at least annually, and whenever significant changes are made to the preparation and/or analytical procedure, to demonstrate quantitation capability at lower analyte concentration levels. The verification is performed by the extraction and/or analysis of an LCS (or matrix spike) at 0.5 - 2 times the established LLOQ. Additional LLOQ verifications may be useful on a project-specific basis if a matrix is expected to contain significant interferences at the LLOQ. The verification may be accomplished with either clean control material (e.g., reagent water, solvent blank, Ottawa sand, diatomaceous earth) or a representative sample matrix, free of target compounds.

9.10.2 The LLOQ verification is prepared by spiking a clean control material with the analyte(s) of interest at 0.5 - 2 times the LLOQ concentration level(s). Alternatively, a representative sample matrix free of targets may be spiked with the analytes of interest at 0.5 - 2 times the LLOQ concentration levels. The LLOQ check is carried through the same preparation and analytical procedures as environmental samples and other QC samples. It is recommended to analyze the LLOQ verification on every instrument where data is reported; however, at a minimum, the lab should rotate the verification among similar analytical instruments such that all are included within three years.

9.10.3 Recovery of target analytes in the LLOQ verification should be within established in-house limits or within other such project-specific acceptance limits to demonstrate acceptable method performance at the LLOQ. Until the laboratory has sufficient data to determine acceptance limits, the LCS criteria ± 20% (i.e., lower limit minus 20% and upper limit plus 20%) may be used for the LLOQ acceptance criteria. This practice acknowledges the potential for greater uncertainty at the low end of the calibration curve. Practical, historically based LLOQ acceptance criteria should be determined once sufficient data points have been acquired.

10.0 Calibration and Standardization

Instruments are tuned to meet DFTPP acceptance criteria, calibrated with an ICAL of at least four levels, and confirmed every twelve-hour shift with a continuing calibration verification standard (CCV). Recommended instrument conditions are listed in Table 10.

Allow all standards and sample extracts to warm to room temperature prior to injection.

10.1 DFTPP Tune Checks

10.1.1 Instruments must be checked to verify that the acceptance criteria are met for DFTPP (decafluorotriphenylphosphine) prior to the ICAL. See Table 7 for DFTPP acceptance criteria. The mass spectrum is acquired with three scans (the peak apex scan and the scans immediately preceding and following the apex) and averaged. Background subtraction is required and must be accomplished using a single scan acquired within 20 scans of the elution of DFTPP. The background subtraction should be designated only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or any other discrete peak that does not co-elute with DFTPP.

10.1.2 Inject 50 ng of the tuning standard. Collect the mass spectra of the DFTPP (background-corrected) and confirm that all of the m/z criteria, listed in Table 7, are met. If the tune check does not meet the criteria, the analyst may need to perform maintenance on the instrument and retune the mass spectrometer. The DFTPP tune must pass all criteria before any standards, samples, or blanks are analyzed.

10.1.3 The analysis of the tune check solution is also used to evaluate the inertness of the chromatographic system. If the peak tailing factor for benzidine and/or pentachlorophenol is >2.0 or the degradation for DDT is >20%, it indicates that the chromatographic system needs maintenance to improve the inertness of the system. Degradation and tailing factor checks are performed to verify injection port inertness and are important when the target list includes a broad range of analyte chemistries, especially reactive phenols and pesticides. These checks are optional when the analytes of interest are not subject to the same chromatography or reactivity problems.

10.2 Initial Calibration (ICAL)

10.2.1 Compounds are typically assigned to the internal standard that has the closest retention time to that analyte. Consistent internal standard references across the different instruments should be utilized.

10.2.2 Setting Retention Times, Retention Time Windows and Integration Parameters

Once the purge and trap and GC cycle have finished for the midpoint or other calibration standard, load the quantitation file. Review each peak to make sure that the processing software identified the correct peak. If not, manually integrate the peak. Save all of the retention times. Quantify the calibration file and go through each ion profile of the target list, take note of the ion ratios, verify that the spectrum and profile match the standard spectrum.

The relative retention time (RRT) of the target analytes in every calibration level should be within 0.06 RRT units.

10.2.3 A minimum five-point calibration curve is prepared. This is valid for average response factors or linear regression curve fitting. A minimum of six calibration points is required for quadratic curve fits. The low point of the calibration curve must be at or below the reporting limit. The high standard defines the range of the calibration. See Tables 8 and 9 for the preparation of the ICAL levels.

10.2.4 Acceptance criteria for the Instrument Calibration and CCVs, and the required frequency of their analysis are summarized in Table 10.

10.2.5 Rejection of Calibration Points

10.2.5.1 It is not generally acceptable to remove internal points from a calibration curve. Typically, instrument maintenance and the accuracy of the calibration standards should be examined if the calibration acceptance criteria are not met.

10.2.5.2 If no problems are found, then a point can be rejected as long as it meets the following criteria:

The rejected point is the highest or lowest point in the ICAL. This may be done by analyte. An internal calibration point may also be removed if the reason is obvious. Examples are; a bad injection, internal standards left out, gross contamination, etc. In these cases, the entire point, including all analytes, must be removed and the reason documented.

10.2.6 The lowest remaining calibration point is still at or below the reporting limit. If the calibration point is higher, then the reporting limit must be raised.

10.2.7 The highest remaining calibration point defines the upper concentration of the working range, and all samples above this concentration must be diluted and re-analyzed.

10.2.8 The calibration must still have the minimum number of calibration levels required by the method. [Five levels for average response factors and linear curve-fits, six levels for quadratic (second-order) curve-fits].

10.2.9 The internal standard is added to produce a 40µg/mL (40 ng on column – 1µL inj.) final concentration.

10.2.10 Analyze each calibration level. Calculate the response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in the calculation section of this SOP. Samples may not be analyzed unless the ICAL meets the following criteria:

10.2.11 The RSD must be <20% for each compound of interest.

10.2.12 If the RSD for a compound in the initial calibration is >20%, then the calibration points may be fit to a linear or a nonlinear curve, such as a second-order polynomial. A curve fit should not be employed in lieu of the average RF to compensate for instrumentation problems or needed maintenance.

10.2.13 Linear curve-fits may be used if there are five (5) or more ICAL levels. Quadratic (second-order) curve-fits may be used if there are 6 or more ICAL levels. The use of a weighted linear regression is recommended to improve accuracy of quantitation at the low end of the curve. Curve-fits can be used if it is determined that the curve will generate accurate results across the calibration range. If a curve-fit is used, a re-quantitation of the low point of the ICAL against the ICAL must show acceptable accuracy.

10.2.14 If a linear curve-fit is used, the coefficient of determination (r^2) must be greater than 0.990. For quadratic curve-fits, the intercept and degree of curvature should be examined to be sure that the results will be reliable throughout the working range and the coefficient of determination is greater than 0.990. There must not be two levels that would produce the same value. Quadratic curve-fits should not be used to compensate for detector saturation or to avoid proper instrument maintenance.

10.2.15 The second source calibration verification (SCV) standard, made from a different source than the ICAL (an alternate vendor or a unique lot from the same vendor) must be analyzed immediately after the calibration. The value determined from the second source check should be within 30% of the expected concentration. An alternative recovery limit may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding that these results could be used for screening purposes and would be considered estimated values.

10.2.16 If more than 10% of the compounds in the ICAL are greater than 20%RSD and do not meet the coefficient of determination criteria for curve-fits, then the instrument is not acceptable to analyze samples. Maintenance must be performed and the instrument ICAL must be performed again.

10.2.17 The minimum response factor for the most common target analytes should be met. See Table 11.

10.2.18 Weighting of Calibration Data Points.

In a linear regression curve-fit, the lower points of the ICAL have a significant bias over the higher points in determining the generated curve. This is not seen in quadratic regression. However, in environmental analysis, accuracy at the low end is very important. For this reason, use 1/Concentration^2or 1/Concentration weighting. This will improve accuracy at the low end of the ICAL and should be used for curve-fits. All compounds should be recalculated using the final calibration curve. The recalculated concentration of the low calibration point should be within +/- 50% of the standard's true concentration, and the concentration of the middle point standard should be within +/- 30%.

Quantitation is performed using the calibration curve or average response factor from the initial curve, not the continuing calibration.

10.2.19 The Relative Error of the calibration curve is determined by processing the lowest point and the midpoint of the calibration against the curve. The % difference in true value is the Relative Error.

10.3 Continuing Calibration Verification (CCV)

10.3.1 The CCV standard must contain all target analytes and surrogates to be reported. The level for the CCV is approximately in the middle of the ICAL. Daily analysis of the GC/MS tune check solution is no longer required as part of the CCV. The analyst should, however, closely monitor chromatography as well as target and IS responses in the CCV for deterioration in the system.

10.3.2 The percent difference/drift for each analyte must be less than or equal to 20%. Due to the long list of compounds that may be analyzed by this method, it is expected that some compounds will fail to meet the criterion. If the criterion is not met for more than 20% (13 compounds for Full List, 3 compounds for PAH) of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when the failed compound is present, the concentrations must be reported as estimated values.

10.3.3 The IS responses for the CCV must be within a factor of 2 (50-200%) of the responses in the mid-point of the corresponding ICAL.

10.3.4 If any IS retention time in the CCV changes by more than 30 seconds from the retention time of the mid-point of the corresponding ICAL, the chromatographic system must be inspected for malfunctions and corrections must be made.

10.3.5 Sample analysis may begin if the CCV passes the above criteria. If the CCV does not pass the criteria, perform an evaluation of the system, are there any obvious problems, was the correct method used, or do routine maintenance. Re-inject the CCV and if this solves the problem, then continue with the sequence. If not, more extensive maintenance may be required or analyze a new calibration curve.

10.3.6 A CCV may be omitted if samples are analyzed within 12 hours of ICAL, and the injection of the last ICAL standard may be used as the starting time reference for evaluation.

10.3.7 The minimum response factors for the most common target analytes should be met in the CCV. If they are not met, maintenance must be performed before sample analysis can begin. Possible problems that would cause this are: standard mix degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

11.0 Procedure

11.1 Sample extraction

See specific extraction SOPs.

11.2 Sample Preparation

11.2.1 Remove samples from the laboratory refrigerator.

11.2.2 Verify that the samples have been logged into LIMS, and are within holding time. If the sample exceeds holding time, notify the Lead Chemist and follow the corrective action plan.

11.2.3 Batch up to 20 environmental samples for extraction.

11.2.4 For samples to be analyzed as MS/MSD follow the procedure below:

The client must provide enough volume for a parent sample and the MS/MSD. If performing a 1L extraction, this means the client must provide 3L of sample.

11.2.5 For the MS/MSD samples, transfer the samples into their appropriately marked containers (1L bottles, 40mL VOA vials, Microwave extraction vessels or PSE metal tubes).

11.2.6 Spike the MS/MSD with the appropriate amount of surrogates and spikes.

11.2.7 Refer to the extraction SOPs for the preparation procedures.

11.3 Standard Preparation

Follow the example procedure listed in Tables 8 and 9.

11.4 Sample Analysis

11.4.1 Analysis is performed using an automated injection GC/MS instrument.

11.4.2 In Chemstation (or Gerstel software), load the sequence from the previous run and enter in the sequence information for the day. A typical sequence will have one or two rinses, the DFTPP tune, the CCV, an instrument blank, the QC from the batch, then the samples. A tune is only required with a calibration but may be analyzed if desired. If the samples being analyzed are suspicious or possibly high in non-target analytes, running a rinse pattern of H_2O, MeOH, and $MeCl_2$ at the end of the sequence will help maintain the quality of your instrument.

11.5 Calibrate the instrument as described in Section 13.

11.5.1 All samples must be analyzed using the same mass spectrometric conditions as the preceding DFTPP analysis. Add internal standard to the sample extract to result in a 40µg concentration (for example, 100µL of IS solution (at 400µg/mL) in a 1000µL extract). Mix thoroughly before injection into the instrument.

11.5.2 Inject 1µL of the extract using the sample injection technique as used for the standards.

11.5.3 The data system will determine the concentration of each analyte in the extract using calculations in Section 15. Quantitation is based on the initial calibration, not the continuing calibration verification.

11.5.4 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst. The minimum documentation required is a copy of the original data peak integration and a copy showing the manual integration with the analyst initials and date and explanation of the reason for the manual integration.

11.5.5 Tentatively Identified Compounds (TICs) may be requested by the client. Perform a library search on the unknown peaks present in the chromatogram if TICs are requested.

11.5.6 The internal standard response in the sample must be between 50-200% of the response of the internal standard in the daily CCV.

11.6 Identification of Analytes

11.6.1 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. See Table 15 for a listing of characteristic ions that may be used for compound identification. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum 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. Compounds are identified when the following criteria are met.

11.6.1.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other.

11.6.1.2 Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

11.6.1.3 The Relative Retention Time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

11.6.1.4 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%.)

11.6.1.5 Use professional judgment in interpretation where interferences are observed.

11.6.2 Structural isomers that produce very similar mass spectra 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 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported (e.g., benzo[b]fluoranthene and benzo[k]fluoranthene). The above calculations are only for laboratory standards. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

11.6.3 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.6.4 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:

11.6.4.1 Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

11.6.4.2 The relative intensities of the major ions should agree within ± 30%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20 and 80%.)

11.6.4.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

11.6.4.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Samples that are diluted must have the internal standard concentration replenished to the level originally in the sample. This may be accomplished by diluting the sample with a solution of methylene chloride containing the proper amount of IS, or by diluting with methylene chloride and then adding the proper amount of IS.

Once surrogates are diluted to a level where accurate quantitation is not possible then surrogates should be reported as diluted out.

11.6.5 If the response for any compound exceeds the current calibration range, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initially diluted extract has no hits or hits below 20% of the calibration range and the matrix allows for an analysis at a lesser dilution, the sample should be re-analyzed at a dilution to bring the most abundant analyte above 50% of the calibration range.

11.6.6 Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are significantly less than two times the height of the internal standards, the sample should be reanalyzed at a lesser dilution. This requirement is approximate and subject to analyst judgment. For example, samples containing organic acids may need to be analyzed at a higher dilution to avoid damaging the column.

11.6.7 Reporting Dilutions

The least dilute sample with no target analytes above the calibration range will be reported. Other dilutions will be reported only at the client's request.

11.6.8 Retention Time Criteria for Samples

The retention times of the internal standards in the CCV must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 0.5 minutes from that in the midpoint of the ICAL, then the chromatographic system must be inspected for malfunctions and corrections must be made. Re-analysis of the samples analyzed while the system was malfunctioning is required.

If the retention time of any internal standard in any sample varies by more than 0.5 minutes from the preceding CCV, the data must be carefully evaluated to ensure that no analytes have shifted outside of their retention time windows.

11.7 Percent Moisture

Analytical results of soil or solid samples may be reported as a dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as a dry weight.

One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented by the analyst and included in the final report.

12.0 Data Analysis and Calculations

12.1 The concentration of each analyte is calculated using Agilent MSD Chemstation software using the multipoint average response factor method established in Section 13 of this SOP. Response factors and analyte concentrations are calculated by the equations below:

12.2 Relative response factor (RRF):

$$RRF = \frac{(A_x)(C_{IS})}{(A_{IS})(C_x)}$$

where:
Ax = Area of the quantitation ion for the surrogate or compound being measured.
Ais = Area of the quantitation ion for the specific internal standard.
Cis = Concentration of the specific internal standard.
Cx = Concentration of the surrogate or compound being measured.

12.3 Average RRF:

Average RRF $(\overline{RRF})$: $\overline{RRF} = \frac{\sum_1^n RRF}{n}$

where
n = number of initial calibration standards

12.4 Percent relative standard deviation (%RSD):

$$\%RSD = (^{S}/_{\overline{x}})100$$

where:
$\overline{x} = \overline{RRF}$: $\overline{RRF} = \frac{\sum_1^n RRF}{n}$
where:
s = standard deviation: $= \sqrt{\frac{(\sum_{i=1}^{n}(x_i - \overline{x})^2)}{n-1}}$

12.5 Sample concentration using RRF:

$$\text{Conc.}\left(\frac{\mu g}{L}\right) = \frac{(A_x)(I_x)(D)}{(\overline{RRF})(V_o)(A_{IS})}$$

where :
A_x = area of quantitation ion for compound being measured
I_x = amount of internal standard injected (ng)
A_{is} = area of quantitation ion for the internal standard
$\overline{RRF}$ = mean relative response factor for compound being measured
V_o = volume of water extracted (mL) accounting for dilutions
D = Dilution Factor

12.6 Percent recovery for CCV, SCV, LCS, and MS are performed using the following equation:

$$\%R = \left[\frac{(C_{spk-}\ C_x)}{C_t}\right] \times 100$$

where:
C_{spk} = the concentration of the analyte in the spiked sample
C_x = the concentration of the analyte in the reference (parent) sample; (C_x = 0 for CCV, LCS and SCV.)
C_t = the theoretical spike concentration.

12.7 Relative percent difference for duplicate is calculated using the following equation:

$$RPD = \left[\frac{|C_1 - C_2|}{(C_1 + C_2)/_2}\right] 100$$

where:
C_1 = concentration of the first sample C_2 = concentration of the second sample

13.0 Method Performance

13.1 Data Assessment and Acceptance Criteria for Quality Control Measures

Instrument generated data goes through a series of reviews prior to being submitted to the client. First the analyst reviews the data to ensure method and client requirements are met. Then the instrument data goes through a peer review covering the same items as the analyst. Both reviews are documented on the attached Form QA-017, which is provided in Figure 1. The Quality Assurance Manager also reviews a minimum of 10 % of data to evaluate the QA process.

13.2 Analytical data generated by the instrument software is reviewed and evaluated by the analyst as follows: DFTPP, instrument calibration, calibration verifications, IS/SS, QC measures are evaluated and the results documented on the separate forms:

13.2.1 Generating the tune evaluation of DFTPP.

13.2.2 Generating the instrument calibration relative response factors and percent relative standard deviations.

13.2.3 Generating QA-QC check report for internal standard area counts and percent recoveries for the surrogates.

13.2.4 Calculating analyte percent recoveries CCV, LCS, SCV, MS, and RPD for MSD.

13.3 In order for the analytical data to be acceptable, the calibration standards and quality control measures must meet the criteria listed in this SOP.

13.4 Anytime that an analyst alters an instrument generated quantitation report, the hardcopies of both reports (original and analyst's corrected) must be retained (e.g., manual integration). The altered report must be initialed and dated by the analyst with the reason for altering. The corrected report must also be reviewed, initialed, and dated by a peer or supervisor.

13.5 All false positives are Q-Deleted, with an explanation of the Q-deletion included in the raw data and all positively identified target analytes are reported to LIMS. Include the spectra in the data package.

13.5.1 Manual integration is applied in cases when the instrument data processing software produces integrated areas that are not valid. The manual adjustments to the chromatographic peak must be performed in a consistent manner for the calibration standards, QC and field samples. Please see the Manual Integration SOP.

13.5.2 Chromatograms of all field samples are examined to detect additional peaks, which were not identified as target analytes. If such peaks are present, generate a Library Search Report and report a tentatively identified compound (TIC) if the percent match is greater than 50%. The Lead Chemist should be notified immediately in that case. This is only done if TICs are requested by the client. TICS are usually requested by next 10 largest, etc.

13.5.3 Discrepancies in the analytical run are described in "Data Review Form QA-017 and discussed with the Lead Chemist.

13.6 Reviewed data is entered into LIMS, hard copies of the LIMS report is printed and compared to the original data. All records derived from the analytical process are assembled in the analytical data files. Files can be electronic on the servers or hard copy in file cabinets. Each data file consists of:

13.6.1 Analytical run sheet (sequence log)

13.6.2 DFTPP tune evaluation report

13.6.3 QA-QC check report

13.6.4 Quantitation Report for each Sample

13.6.5 Evaluation reports for CCV, SCV, LCS, MS, and MSD.

13.6.6 Initial calibration form

13.7 Data files are placed in boxes or file cabinets marked EPA Method 8270E and stored in the PHILIS document storage area. Electronic data, including reports are maintained on servers in multiple locations.

13.8 Demonstration of laboratory accuracy, precision, and MDLs are presented in Tables 2 and 3.

13.9 Other specific Quality Assurance Objectives (QAO) may be found in the appropriate statement-of-work or Quality Assurance Project Plan (QAPP) for specific projects.

13.10 Corrective Action for Out of Control

In cases where quality control measures do not meet acceptance criteria, the quality of the analytical data is not acceptable and the analyst does the following:

13.10.1 When tuning and instrument calibration fail to meet acceptance criteria, the analysis does not start. The problem is investigated and the necessary instrument maintenance is performed, followed with tuning and calibration.

13.10.2 If after analysis, any of the criteria for quality control are not met, or the sample is not available for reanalysis, the analyst must notify the Lead Chemist. The Lead Chemist will implement the corrective action plan.

13.10.3 The analyst shall report to the Lead Chemist and indicate of the "Data Review Form QA-017" any out control event. Such events include:

13.10.3.1 Damage to the sample.

13.10.3.2 Holding time exceeded.

13.10.3.3 Inadequate sample preservation.

13.10.3.4 Sample results exceeds the Agency's action limit

13.10.3.5 Samples do not reflect historical data.

13.10.3.6 Upward trending or sample results approaching interval warning limits.

13.10.3.7 Any non-target analyte peak present on the instrument generated chromatograms that interfere with regular analysis. Tentative identification compounds (TICs) may also be requested by the client.

13.11 The Lead Chemist will implement the corrective action plan described in the PHILIS corrective action plan document (SOP A-C-101).

13.12 When tuning and instrument calibration fail to meet acceptance criteria, the analysis does not start. The problem is investigated and the necessary instrument maintenance is performed, followed with tuning and calibration.

13.13 See Table 14 for a summary of corrective action taken when QC samples or client sample QC does not meet acceptance criteria.

13.14 Contingencies for Handling Out of Control or Unacceptable Data

See the QAPP that the samples were analyzed under for guidance.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. The EPA places pollution prevention as the management option of first choice with regard to laboratory waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 The Environmental Protection Agency requires that laboratory waste management practices be compliant with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult the PHILIS Chemical Hygiene Plan.

14.3 The waste produced from EPA Method 8270E consist of waste collected from the extraction process, extracts, excess sample, standards (stock mixes, PDS, WS), methylene chloride, and methanol.

14.4 Excess reagents are disposed in accordance with MSDS and laboratory waste management plan requirements.

14.5 Glass pipettes are disposed in the glassware waste container.

14.6 Refer to EPA Method 8270E, sections 14.0 and 15.0 for additional guidance

14.7 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036.

15.0 Waste Management

Waste management procedures are specified in the Hazardous Waste Management Plan.

16.0 References

16.1 EPA Method 8270E Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Revision 6, June 2018; U.S. EPA Office of Solid Waste.

16.2 40 CFR 136, Appendix B, Revision 2. Definition and Procedure for the Determination of the Method Detection Limit – December, 2016.

16.3 U.S. EPA Contract Laboratory Program Statement of Work OLM 04.2.

16.4 U.S. EPA National Functional Guidelines, Superfund Organic Methods Data Review, June, 2008.

16.5 2003, 2009, and 2016 NELAP manuals.

16.6 EPA Method 3500C, Organic Extraction and Sample Preparation, Revision 3, May 2003; U.S. EPA Office of Solid Waste.

16.7 EPA Method 3545A Pressurized Fluid Extraction (PFE), Revision 1, February 2007; U.S. EPA Office of Solid Waste.

16.8 EPA Method 3546 Microwave Extraction, Revision 1, February 2007; U.S. EPA Office of Solid Waste

17.0 Tables, Diagrams, Flowcharts and Validation Data

Table 1. Example Extraction and Analyte Range

Soil Sample Type	Analytical Range	RL Range, mg/Kg	Sample Mass	Final Extract Volume
Trace analysis of clean soil sample; clean conformational analysis	Low Level	0.083 – 5.0	30 grams	1.0 mL
Moderate soil contamination; extent of contamination evaluation project	Medium Level	1.66 - 100	15 grams	10 mL
Heavy contamination of soil, waste characterization	High Level	24.9 - 1500	1 gram	10 mL

Table 2. Example Analytes Determined by EPA Method 8270E
Method Detection Limits (MDLs) and Precision & Accuracy (P&A)

8270 Method List		MDL	MDL	MDL	MDL	RPD	Control Limits	RPD	Control Limits
Compound	CAS No.	Water (SPE) (ug/L)	25 mL Water (Micro-extract) (ug/L)	100 mL Water (Sep Funnels) (ug/L)	Soil (ug/Kg)	SPE (%)	SPE (% Recovery)	Micro (%)	Micro Ext (% Recovery)
N-Nitrosodimethylamine	62-75-9	11	34.1	7.6	40	20	1 - 63	20	1 - 97
Phenol	108-95-2	1.7	30.5	4.3	29	20	1 - 91	20	1 - 63
Aniline	62-53-3	0.4	97.9	17.0	25	20	1 - 97	20	23 - 92
Bis(2-chloroethyl) ether	111-44-4	1.4	80.6	12.8	37	20	1 - 114	20	43 - 91
2-Chlorophenol	95-57-8	1.8	83.6	11.4	42	20	8 - 93	20	15 - 96
1,3-Dichlorobenzene	541-73-1	1.1	63.5	12.4	39	20	1 - 84	20	35 - 90
1,4-Dichlorobenzene	106-46-7	1.1	68.0	12.4	38	20	1 - 89	20	38 - 84
Benzyl alcohol	100-51-6	2.5	40.8	9.8	40	20	1 - 86	20	1 - 130
1,2-Dichlorobenzene	95-50-1	2.1	68.3	12.9	40	20	1 - 90	20	38 - 87
2-Methylphenol	95-48-7	2.1	47.2	9.2	38	20	4 - 107	20	12 - 89
Bis(2-chloroisopropyl) ether	39638-32-9	1.2	76.3	12.8	41	20	3 - 139	20	36 - 123
3/4-Methylphenol	106-44-5	0.9	39.8	9.2	40	20	14 - 82	20	1 - 93
N-Nitrosodi-n-propylamine	621-64-7	2.2	66.0	13.1	35	20	1 - 136	20	46 - 99
Hexachloroethane	67-72-1	1.4	62.1	10.6	36	20	1 - 81	20	29 - 85
Nitrobenzene	98-95-3	1.7	62.4	8.4	35	25	1 - 145	25	37 - 99
Isophorone	78-59-1	2.0	57.5	8.6	34	20	1 - 121	20	41 - 96
2-Nitrophenol	88-75-5	2.0	69.7	7.2	31	20	1 - 79	20	7 - 113
2,4-Dimethylphenol	105-67-9	2.3	60.2	22.4	26	20	4 - 105	20	39 - 82
Bis(2-chloroethoxy)methane	111-91-1	2.0	72.0	11.6	40	20	1 - 125	20	39 - 99
2,4-Dichlorophenol	120-83-2	2.4	80.6	6.7	34	20	8 - 91	20	1 - 123
1,2,4-Trichlorobenzene	120-82-1	1.3	63.8	24.6	36	20	5 - 97	20	44 - 90
Naphthalene	91-20-3	1.4	67.6	10.2	37	20	3 - 97	20	40 - 94
4-Chloroaniline	106-47-8	1.2	79.1	11.6	34	20	1 - 74	20	32 - 104
Hexachlorobutadiene	87-68-3	1.1	58.8	11.2	40	20	5 - 84	20	26 - 93
4-Chloro-3-methylphenol	59-50-7	1.8	47.6	5.1	22	20	1 - 136	20	1 - 125
2-Methylnaphthalene	91-57-6	1.7	65.0	7.3	35	20	3 - 110	20	40 - 100
Hexachlorocyclopentadiene	77-47-4	1.8	31.7	5.6	42	20	1 - 71	20	21 - 97
2,4,6-Trichlorophenol	88-06-2	1.8	108	7.1	39	20	1 - 76	20	7 - 131
2,4,5-Trichlorophenol	95-95-4	2.1	91.7	7.4	36	20	1 - 74	20	18 - 132
2-Chloronaphthalene	91-58-7	1.9	64.2	10.2	32	20	1 - 100	20	48 - 94
2-Nitroaniline	88-74-4	1.8	44.6	5.7	32	20	1 - 54	20	45 - 119
Dimethyl phthalate	131-11-3	1.8	68.5	34.7	33	20	1 - 112	20	57 - 113
2,6-Dinitrotoluene	606-20-2	2.0	43.3	6.0	35	20	1 - 115	20	54 - 114
Acenaphthylene	208-96-8	2.2	65.0	8.5	28	20	1 - 76	20	54 - 102
Acenaphthene	83-32-9	1.7	71.1	6.7	35	20	9 - 83	20	53 - 102
3-Nitroaniline	99-09-2	1.4	60.5	6.9	32	20	1 - 58	20	55 - 112
2,4-Dinitrophenol	51-28-5	5.5	53.0	12.1	83	20	1 - 49	20	6 - 133
4-Nitrophenol	100-02-7	1.6	54.1	8.8	27	20	8 - 81	20	1 - 250
Dibenzofuran	132-64-9	1.7	68.4	7.5	29	20	1 - 106	20	59 - 102
2,4-Dinitrotoluene	121-14-2	1.6	3.0	4.5	31	20	1 - 99	20	31 - 126
Diethyl phthalate	84-66-2	1.4	65.7	7.6	36	20	6 - 111	20	54 - 118
4-Chlorophenyl phenyl ether	7005-72-3	1.6	66.3	8.6	31	20	2 - 104	20	45 - 117
Fluorene	86-73-7	1.4	71.3	7.0	30	20	2 - 105	20	53 - 112
4-Nitroaniline	100-01-6	1.7	48.1	3.4	39	20	1 - 62	20	65 - 114
4,6-Dinitro-2-methylphenol	534-52-1	1.5	35.5	4.3	16	20	1 - 44	20	12 - 147
4-Bromophenyl phenyl ether	101-55-3	1.5	70.7	6.4	30	20	1 - 500	20	52 - 116
Hexachlorobenzene	118-74-1	1.0	71.8	7.7	38	20	1 - 101	20	55 - 120
Pentachlorophenol	87-86-5	1.3	51.0	4.0	37	20	1 - 56	20	14 - 132
Phenanthrene	85-01-8	0.8	72.8	6.5	30	20	2 - 105	20	63 - 115
Anthracene	120-12-7	1.0	64.7	4.6	20	20	1 - 85	20	63 - 115
Malathion	121-75-5								

Table 3. Analytes Determined by EPA Method 8270E with Example Detection Limits and Precision & Accuracy (P&A) -PAHs only

PAH by 8270		MDL	MDL	MDL	MDL		RPD	Control Limits
Compound	CAS No.	Water ug/L	Soil ug/Kg	Water, Low-Level SIM Method ug/L	Soil, ug/Kg		(%) Water	(% Recovery) Soil
Acenaphthylene	208-96-8	1.0	4.8	0.2	1.8		20	31 - 120
1-Methylnaphthalene	90-12-0	1.5	14	0.2	2.1		20	45 - 115
2-Methylnaphthalene	91-57-6	1.7	11	0.2	2.2		20	41 - 118
Pyrene	129-00-0	1.8	18	0.4	2.1		20	55 - 119
Benz[a]anthracene	56-55-3	1.7	13	0.2	1.8		20	29 - 125
Benzo[a]pyrene	50-32-8	1.4	16	0.4	4.3		20	21 - 109
Fluoranthene	206-44-0	1.5	23	0.2	1.4		20	60 - 115
Benzo[b]fluoranthene	205-99-2	0.7	14	0.3	2.1		20	15 - 96
Fluorene	86-73-7	1.4	5.0	0.3	1.7		20	45 - 119
Dibenzo[a,h]anthracene	53-70-3	3.2	22	0.2	2.6		20	7 - 108
Anthracene	120-12-7	1.3	11	0.2	1.2		20	52 - 113
Acenaphthene	83-32-9	1.5	6.0	0.2	1.8		20	57 - 111
Chrysene	218-01-9	1.5	18	0.3	1.6		20	68 - 109
Phenanthrene	85-01-8	1.2	12	0.3	1.0		20	67 - 111
Indeno[1,2,3-cd]pyrene	193-39-5	1.0	11	0.2	3.7		20	44 - 111
Benzo[g,h,i]perylene	191-24-2	0.9	9.0	0.2	2.0		20	33 - 116
Benzo[k]fluoranthene	207-08-9	0.9	27	0.5	2.3		20	48 - 126
Naphthalene	91-20-3	1.4	9.0	0.2	2.0		20	50 - 114

Table 4. Difficult Compounds to Analyze

Compound	Analysis Problem and Treatment
Hexachlorocyclopentadiene	Subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
N-Nitrosodiphenylamine	Decomposes in the gas chromatograph inlet and cannot be distinguished from diphenylamine.
Pentachlorophenol 2,4-dinitrophenol 4-nitrophenol 4,6-dinitro-2-methylphenol 4-chloro-3-methylphenol 2-nitroaniline 3-nitroaniline 4-chloroaniline benzyl alcohol	Subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
3-methylphenol & 4-methylphenol	Due to inadequate chromatographic resolution compounds are reported as 3&4-methylphenol.
1,2-diphenylhydrazine	Compound is reported as azobenzene, which is formed by decomposition.
N-Nitrosodimethylamine	Difficult to separate from the solvent under the chromatographic conditions used.
Pyridine	Compound degrades at the GC injection port temperatures in this method. Lowering the injection port temperature may affect other compounds in this method adversely; therefore, a different method should be considered if pyridine is required. Pyridine may be evaporated off during sample concentration.

Table 5. Internal Standards used for EPA Method 8270E

Compound	Applicable Methods for IS	Example Spiking Level in ng
Acenapthene-d_{10}	Full List, PAH	40
Chrysene-d_{12}	Full List, PAH	40
1,4-Dichlorobenzene-d_4	Full List	40
Napthalene-d_8	Full List, PAH	40
Perylene-d_{12}	Full List	40
Phenanthrene-d_{10}	Full List, PAH	40

Table 6. Surrogate Standards Used for EPA Method 8270E

Compound	Applicable Methods	Example Spiking Level in ng
Nitrobenzene-d_5	Full List, PAH	40
2-Fluorobiphenyl	Full List, PAH	40
Terphenyl-d_{14}	Full List, PAH	40
Phenol-d_5	Full List	40
2-Fluorophenol	Full List	40
2,4,6-Tribromophenol	Full List	40

Table 7. DFTPP Key Ions and Ion Abundance Criteria

m/z	8270E Ion Abundance Criteria
68	<2% of mass 69
69	Present
70	<2% of mass 69
197	<2% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
365	>1% of mass 198
441	< 150 % of mass 443
442	Base peak or present
443	15-24% of mass 442

Alternate tuning criteria may be employed (e.g., CLP or Method 625), provided that method performance is not adversely affected.

Table 8. 8270E Calibration Levels

Example Full List 8270 Calibration Levels - 1000/2000µg/mL Stocks										
	Level (ng)									
Stock Concentration (ng/µL)	2.5	5	10	20	50	80	120	160	SCV - 50	2.5
B/N Surrogates (µL)	2.5	5	10	20	50	80	120	160	50	2.5
Acid Surrogates (µL)	1.25	2.5	5	10	20	40	60	80	20	1.25
MegaMix (µL)	2.5	5	10	20	50	80	120	160	0	2.5
SCV Stock (µL)	0	0	0	0	0	0	0	0	50	0
Total (µL)	6.25	12.5	25	50	120	200	300	400	120	6.25
MeCl2	993.75 µL	987.5µL	975 µL	950 µL	880 µL	800 µL	700 µL	600 µL	880 µL	993.75 µL
Internal Standard	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL
Final Volume	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL

Table 9. Example PAH 8270 Calibration Levels

PAH Only 8270 Calibration Levels - 1000/2000µg/mL Stocks										
	Level (ng)									
Stock Concentration (ng/µL)	2.5	5	10	20	40	80	120	160	SCV - 40	2.5
B/N Surrogates (µL)	2.5	5	10	20	40	80	120	160	40	2.5
PAH Standard (µL)	1.25	2.5	5	10	20	40	60	80	0	1.25
MegaMix (µL)	0	0	0	0	0	0	0	0	40	0
Total (µL)	3.75	7.5	15	30	60	120	180	240	80	3.75
MeCl2	996.25 µL	992.5µL	985 µL	970 µL	940 µL	880 µL	820 µL	760 µL	920 µL	996.25 µL
Internal Standard	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL
Final Volume	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL
Stock Concentration (ng/µL)	2.5	5	10	20	40	80	120	160	SCV - 40	2.5

Table 10. Example EPA Method 8270E Analysis Sequence with QC and Instrument Calibration Frequency and Acceptance Criteria

Analysis #	Sample Name	QC and Instrument Calibration Acceptance Criteria	QC and Instrument Calibration Frequency
1	DFTPP	1. DFTPP see Table 6	Analyzed prior to instrument calibration.only
2	Cal 1	1. Instrument Calibration must have %RSD ≤ 20%. If greater than 10% of analytes cannot meet the RSD or regression curve criteria (RSD < 20% or r^2 > 0.99), then instrument may need maintenance or curve evaluation (dropping upper or lower points), trying different curve fits, etc. 2. Should meet 8270E recommended minimum RRF or be able to see standard at the reporting limit. 3. Must have relative retention time = 0.06 RR	Calibration Analyzed anytime CCV fails criteria for analytes of interest. And system evaluation, minor maintenance, etc. will not produce an acceptable CCV.
3	Cal 2		
4	Cal 3		
5	Cal 4		
6	Cal 5		
7	Cal 6		
8	Cal 7		
9	MB	Must be free from contamination that could prevent determination of target analytes at the RL. Must be <1/2 RL.	Find problem and reanalyze all associated samples and QC.
10	SCV	1. Determination of target analytes 2. Concentration of target analytes must be within +/- 30% of true value. 3. IS Response 50 – 150% of Cal 3 or Cal midpoint 4. IS RT's ± 30 seconds	Analyzed immediately after Cal curve
		Daily sequences require a CCV and should have a method or instrument blank. After that, any or all of the items that were included in the preparation batchs may be analyzed as long as the 12 hour CCV window is not exceeded. Sample number is not limited. Below is an example sequence that includes all the preparation batch components.	
11	DFTPP	1. Same as Above	1. Same as above

Analysis #	Sample Name	QC and Instrument Calibration Acceptance Criteria	QC and Instrument Calibration Frequency
12	CCV	1. Percent Recovery of Target Analytes ± 20% 2. SS Percent Recovery--meet in-house limits. 3. Should meet 8270E recommended minimum RRF or evaluate to determine if the reporting limit can be achieved.	1. Analyzed initially with each batch of samples or QC within 12 hour period.
13	MB	1. Same as Above	1. Same as above. Prepared with each batch of samples. This can also be an instrument blank.
14	LCS	1. Percent Recovery of Target--meet in-house limits or data flagged.2. SS Percent Recovery --meet in-house limits or data flagged. 3. IS Response 50 - +100% of CCV	1. Prepared with each batch of samples.
15	Sample 1	1. IS/SS see at the bottom of this table	
16	MS	1. Percent Recovery of Target Analytes--meet in-house limits or data flagged 2. SS Percent Recovery--meet in-house limits or data flagged 3. IS Response 50 - +100% of CCV	1. Prepared with each batch of samples.
18	MSD	1 - 3 same as above %RSD (section 12) --meet in-house limits or data flagged	1. Prepared with each batch of samples.
19	Sample 2	See statements below for IS and SS.	Reanalyze at a dilution
20	Sample 3		
20	Sample 4		
21	Samples 5-20		
Internal Standard (IS) and Surrogate Standard (SS) in all samples and QCs must meet the following acceptance criteria: 1 IS Response 50 - 200 % of the midpoint of the most recent calibration or the daily CCV. 2 SS must meet in-house limits or data flagged			

Table 11. Example GC/MS Instrument Conditions PHILIS-Castle Rock, CO

GC Conditions	
Inlet	Split at 280°C,
Capillary Column	Restek RX-5MS, 30M length, 0.25mm ID, 0.5um film thickness
Column Mode	Constant flow, 3.4mL/min
Temperature Program	Initial temp = 50°C, Initial time = 1.50 min
	25°C/min ramp to 170°C
	12°C/min ramp to 320°C and hold for about one minute past the elution of the last compound.
Run Time	About 20 minutes with a new column,
Carrier Gas	Helium
	Pulsed split 20.0mL/min, 3.00 min
	Total flow ≈ 34mL/min
Injection Volume	1.0µL
Split Ratio	3:1
Split Flow	≈ 24mL/min
Transfer line	280°C
MS Conditions	
MS Source	230°C or 240°C
MS Quadrupole	200°C

NOTE: The conditions listed above are subject to final fine adjustments to maximize instrument sensitivity. Changes to the above conditions are acceptable as long as method criteria are met.

Table 12. Example GC/MS Instrument Conditions PHILIS-Edison, NJ

GC Conditions	
Inlet	280°C,
Capillary Column	Restek RX-5silMS, 30M length, 0.25mm ID, 0.25um film thickness
Column Mode	Constant flow, 1.2 mL/min
Temperature Program	Initial temp = 40°C, Initial time = 1.0 min
	25°C/min ramp to 280°C, hold 0 min.
	35°C/min ramp to 320°C and hold 2.0 minutes to end of run.
Run Time	About 28 minutes injection to injection.
Carrier Gas	Helium
	Pulsed split = 20 psi to 0.20 minutes
	Total flow ≈ 24mL/min
Injection Volume	1.0µL
Split Ratio	5:1
Split Flow	≈ 6 mL/min
Transfer line	300°C
MS Conditions	
MS Source	230°C
MS Quadrupole	150°C

Table 13. Recommended Minimum Response Factor Criteria for Initial and Continuing Calibration Verification Using the Suggested Primary Quant Ions

Suggested Semivolatile Compounds Minimum Response Factor (RF)			
Compound	**RF**	**Compound**	**RF**
Benzaldehyde	0.010	2,4-Dinitrophenol	0010
Phenol	0.800	4-Nitrophenol	0.010
Bis(2-chloroethyl)ether	0.700	Dibenzofuran	0.800
2-Chlorophenol	0.800	2,4-Dinitrotoluene	0.200
2-Methylphenol	0.700	Diethyl phthalate	0.010
2,2'-Oxybis-(1-chloropropane)	0.010	1,2,4,5-Tetrachlorobenzene	0.010
Acetophenone	0.010	4-Chlorophenyl-phenyl ether	0.400
4-Methylphenol	0.600	Fluorene	0.900
N-Nitroso-di-n-propylamine	0.500	4-Nitroaniline	0.010
Hexachloroethane	0.300	4,6-Dinitro-2-methylphenol	0.010
Nitrobenzene	0.200	4-Bromophenyl-phenyl ether	0.100
Isophorone	0.400	N-Nitrosodiphenylamine	0.010
2-Nitrophenol	0.100	Hexachlorobenzene	0.100
2,4-Dimethylphenol	0.200	Pentachlorophenol	0.050
Bis(2-chloroethoxy)methane	0.300	Phenanthrene	0.700
2,4-Dichlorophenol	0.200	Anthracene	0.700
Naphthalene 0.700	0.700	Carbazole	0.010
4-Chloroaniline	0.010	Di-n-butyl phthalate	0.010
Hexachlorobutadiene	0.010	Fluoranthene	0.600
Caprolactam	0.010	Pyrene	0.600
4-Chloro-3-methylphenol	0.200	Butyl benzyl phthalate	0.010
2-Methylnaphthalene	0.400	3,3'-Dichlorobenzidine	0.010
Hexachlorocyclopentadiene	0.050	Benzo(a)anthracene	0.800
2,4,6-Trichlorophenol	0.200	Chrysene	0.700
2,4,5-Trichlorophenol	0.200	Bis-(2-ethylhexyl)phthalate	0.010
1,1'-Biphenyl	0.010	Di-n-octyl phthalate	0.010
2-Chloronaphthalene	0.800	Benzo(b)fluoranthene	0.700
2-Nitroaniline	0.010	Benzo(k)fluoranthene	0.700
Dimethyl phthalate	0.010	Benzo(a)pyrene	0.700
2,6-Dinitrotoluene	0.200	Indeno(1,2,3-cd)pyrene	0.500
Acenaphthylene	0.900	Dibenz(a,h)anthracene	0.400
3-Nitroaniline	0.010	Benzo(g,h,i)perylene	0.500
Acenaphthene	0.900	2,3,4,6-Tetrachlorophenol	0.010

Table 14. 8270E Method Criteria

Item	Measure	Action
Instrument Tune	Outside 8270E Acceptance Criteria	Re-Tune-- Repeated failure indicates a need for system adjustment or maintenance. Perform system maintenance and re-tune the instrument. No analysis should be performed until the system is tuned correctly.
Instrument Tailing or Breakdown	Pentachlorophenol or Benzidine tailing above 2 or DDT Breakdown above 20 %.	**Advisory Only--**Evaluate the need for system maintenance/perform maintenance if needed and re-tune.
Internal Standard(s)—(IS)	50-200% of the mid-point of the initial calibration standard or daily CCV.	If the problem is a calibration sample, evaluate the system (repair) and reanalyze. Remake the standard if an error is suspected. If the problem is a prepped QC sample or field sample, re-analyze. If the re-analysis is within limits, report the results within limits. If the problem is a prepped QC sample, evaluate, the batch may need to be reprepped. If the reanalysis of a field sample is outside limits, dilute and reanalyze. Report the diluted results. Flag data that does not meet acceptance criteria.
Response Factors	See Table 11 for a list of recommended minimum response factors.	If the response factor is below acceptance criteria, then the system must be evaluated to make sure the analyte can be seen at the reporting limit. Recalibrate and reanalyze affected samples.
Initial Calibration (ICAL)	Average Response Factor >20.0 % RSD.	Evaluate points in the curve for use of linear or quadratic regression (r2 must be ≥0.990). Also evaluate upper and lower points for removal..Internal calibration points may be removed if there is an obvious reason, then the entire calibration point must be removed. Criteria still not met, recalibrate if compound is an analyte of interest.
ICAL Point Eval. all compounds and all levels	Not within ±50% of True Value for low point and ±30% for all others	Recalibrate if % deviation or drift is not met and compound is an analyte of interest.
Initial Calibration Verification	Not within ±30% of true value for deviation or drift.	Recalibrate if % deviation is not met and the compound is an analyte of interest.
Continuing Calibration Verification (CCV)—Analyzed if ICAL is not analyzed.	Not within ±20% of true value for deviation	If the CCV is not within ±20 % of the true value, then perform routine maintenance, such as verify all instrument settings, method used, front end maintenance, etc. Reinject a CCV and if passes, continue sequence. If not further maintenance or a new ICAL is required. Further maintenance would also require two passing CCV's to show the problem is solved.
Method Blank	Analyte(s) of interest at or above ½ reporting limit.	If the associated samples are non-detect, no action is required. If the analyte(s) is/are detected in the sample, flag with a "b" or reanalyze. If the analyte level in the sample is 10 time greater than the blank contamination, the results are not affected. Locate the source of the contamination.
Laboratory Control Spike (LCS)	% recovery outside laboratory acceptance criteria	If the LCS % recovery is high and the sample is non-detect, no action is required. If the LCS is high and the sample(s) have detects, reanalyze the sample. If the LCS is low, the samples should be reanalyzed. Flag data that does not meet laboratory acceptance criteria
Laboratory Control Spike Duplicate (LCSD)	% Recovery outside laboratory acceptance criteria. RPD acceptance criteria is 20%.	% recovery same as the LCS. If the RPD value is above the acceptance criteria in the LIMS, then evaluate the system for possible problems. Reprep and reanalyze samples as necessary and if possible. Flag data that does not meet laboratory acceptance criteria
Matrix Spike (MS)	% Recovery outside laboratory acceptance criteria.	If the % Recovery is outside laboratory acceptance criteria, evaluate the LCS. If the LCS is in control, then there is the possibility of matrix effect. The sample should be flagged appropriately.
Matrix Spike Duplicate (MSD)	% Recovery outside laboratory acceptance criteria. RPD acceptance criteria is 20%.	% recovery same as the MS. If the RPD value is above the acceptance criteria in the LIMS, then evaluate the system for possible problems. Reanalyze samples if possible or flag results.
Surrogate(S)	% Recovery outside laboratory acceptance criteria.	If the % recovery is outside laboratory acceptance criteria on a QC sample, evaluate the system. Surrogate recalibration may be necessary. If the % recovery is on a client sample, reprep and reanalyze if possible. If the % recovery is within criteria, report the sample within limits. If % recovery is outside criteria and is confirmed, then there is a matrix effect. Flag the results as estimated and report the initial result.

Table 15. Example Characteristic Quantitation Ions for SVOA*

Compound	Primary Quant Ion	Secondary Quant Ions
Phenol	94	65,66
Aniline	93	66,65
Bis(2-chloroethyl) ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene	146	148, 111
Benzyl alcohol	108	79, 77
1,2-Dichlorobenzene	146	148, 111
2-Methylphenol	108	107, 77, 79, 90
Bis(2-chloroisopropyl)ether	45	77, 121
3/4-Methylphenol	107	108, 77, 79, 90
N-Nitrosodi-di-n-propylamine	70	42, 101, 130
Hexachloroethane	201	117, 199
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	109, 65
2,4-Dimethylphenol	122	107, 121
Bis(2-chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 127
4-Chloroaniline	127	129, 65, 92
Hexachlorobutadiene	225	223, 227
4-Chloro-3-methylphenol	142	107, 144
2-Methylnaphthalene	142	141
1-Methylnaphthalene	142	141, 115
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 97, 132, 99
2-Chloronaphthalene	162	127, 164
2-Nitroaniline	65	92, 138
Dimethylphthalate	163	194, 164
2,6-Dinitrotoluene	165	63, 89
Acenaphthylene	152	151, 153

Compound	Primary Quant Ion	Secondary Quant Ions
Acenaphthene	153	154, 152
3-Nitroaniline	138	108, 92
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	65	139, 109
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 89
Diethylphthalate	149	177, 150
4-Chlorophenyl phenyl ether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	65, 108, 92, 80, 39
Azobenzene	77	182, 51, 105
2-Methyl-4,6-dinitrophenol	198	51, 105
Diphenylamine	169	168, 167
4-Bromophenyl phenyl e...	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	176, 179
Carbazole	167	166, 139
Di-n-butyl phthalate	149	150, 104
Fluoranthene	202	101, 203
Pyrene	202	200, 203
Butyl benzyl phthalate	149	91, 206
Benzo[a]anthracene	228	229, 226
Chrysene	228	226, 229
Bis(2-ethylhexyl)phthalate	149	167, 279
Di-n-octyl phthalate	149	167, 43
Benzo[b]fluoranthene	252	253, 125
Benzo[k]fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 277
Dibenzo(a,h)anthracene	278	139, 279
Benzo(ghi)perylene	276	138, 277

* Other semivolatile compounds may be analyzed using Method 8270E

Figure 1. Example GC/MS Data Review Form

PHILIS Program

CSS

DATA REVIEW FORM – GC/MS

Instrument and Date: _____ **Sequence #:** _____

Analysis: *(Select One)* ☐ Semivolatiles ☐ Volatiles ☐ Other

	Yes	No	Peer Rvw	QA Rvw	Comments
Analyst Report					
PHILIS narrative is complete	☐	☐	☐	☐	
Reported data matches the raw data	☐	☐	☐	☐	
Reporting limits and qualifiers are correct	☐	☐	☐	☐	
Sample Receiving					
Samples received in acceptable condition and compliant with COC	☐	☐	☐	☐	
Samples properly preserved	☐	☐	☐	☐	
Sample receipt checklist filled out	☐	☐	☐	☐	
Instrument Tune and Calibration					
Instrument met tuning criteria, where required, and analyses were completed within the 12 hour clock	☐	☐	☐	☐	
ICAL average response factor % RSD is <20 or applied curve fit meets criteria	☐	☐	☐	☐	
The ICAL has an adequate number of points	☐	☐	☐	☐	
Response factors meet minimum criteria for ICAL and CCV	☐	☐	☐	☐	
ICAL low point is within 50% of known value and the mid-point is within 30% of the known value or SOP listed levels	☐	☐	☐	☐	
SCV is within 30 % of true values for deviation or drift	☐	☐	☐	☐	
CCV compounds meet acceptance criteria	☐	☐	☐	☐	
Method Blank					
Analytes detected at or above their reporting limits are flagged	☐	☐	☐	☐	
Samples					
Samples prepared and extracts analyzed within holding time limits	☐	☐	☐	☐	
Target compound report included and chromatograms provided	☐	☐	☐	☐	
Manual integration/Q-Deletion is initialed and dated by analyst and reviewer on ion profiles	☐	☐	☐	☐	
All target quantitation ion integrations and spectral identifications are included	☐	☐	☐	☐	
Calculations have been verified—see calculations sheet.	☐	☐	☐	☐	
Internal standard summary					
Is area between 50%-200% of the ICAL midpoint or daily CCV	☐	☐	☐	☐	
Retention times are within 0.5 minutes of the midpoint of the ICAL	☐	☐	☐	☐	
Surrogate recovery report					
Surrogate recovery meets acceptance criteria	☐	☐	☐	☐	
Sample results are properly flagged	☐	☐	☐	☐	
Preparation batch summary					
All samples are accounted for	☐	☐	☐	☐	
Results reflect sample mass/volume prepared	☐	☐	☐	☐	
Solid results are provided dry weight basis	☐	☐	☐	☐	
Matrix spike/matrix spike duplicate					
MS/MSD percent recoveries are within limits	☐	☐	☐	☐	
Relative percent differences are within limits	☐	☐	☐	☐	
Sample results been flagged appropriately	☐	☐	☐	☐	
Laboratory control spike/laboratory control spike duplicate					
LCS/LCSD recoveries are within limits	☐	☐	☐	☐	
Relative percent differences are within limits	☐	☐	☐	☐	
Have sample results been flagged appropriately	☐	☐	☐	☐	

Analyst review signature Date | Peer review signature Date | QA review signature Date

PHILIS2 Form ID#: QA-017 / Release Date: 09/18/2023

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APPENDIX C -
PHILIS SOP L-A-101
Volatile Organics by Method 8260D Rev. 3 05/31/2024

STANDARD OPERATING PROCEDURE

FOR

VOLATILE ORGANICS BY METHOD 8260D

PHILIS SOP L-A-101 Rev. 3

Revision Date: 05-31-2024

EPA Contract No. 68HERH21D0002

PREPARED BY

PHILIS

PREPARED FOR

U.S. Environmental Protection Agency
Office of Emergency Management
Washington, DC 20460

Approvals:

PHILIS, Castle Rock Lead Chemist	**May 31, 2024** **Date**
PHILIS, Edison Lead Chemist	**May 31, 2024** **Date**
PHILIS, Quality Assurance Manager	**May 31, 2024** **Date**
PHILIS, Program Manager	**May 31, 2024** **Date**

Revision History

Revision	Name	Date	Description of Change
A	James Travis	04/01/2021	Transitional Issue
0	James Travis	03/21/2022	Program Issue
1	James Travis	06/09/2022	Revision
2	James Travis	10/14/2022	Revision
3	James Travis	12/07/2023	Revision

SOP REVISION FORM

SOP Name:	**Volatile Organics by Method 8260D**		
Purpose: *(Review or Revise)*	*SOP #:*	*Rev. #:* *(Being Reviewed or Revised)*	*Origination / Release Date:*
Revision	*SOP No. L-A-101*	2	10/26/2022
Requested by:	James Travis	Date:	12/07/2023

New SOP Revision Date:	**05/31/2024**	**New SOP Revision #:** *(If Applicable)*	**3**

For *Revision* : Summary of Revisions (specify sections)

6.1	Corrected formatting Issues
7.1	Corrected formatting Issues
7.4	Corrected formatting Issues
7.1.3	Expiration passage removed from this section
7.1.13	Expiration passage removed from this section
7.5.2	Specific reagent amounts modified to reflect current procedure
7.5.5	Archon IS/SS is no longer used with this method, so passage was removed
7.5.6, 7.5.7	Passages removed due to redundancy with section 7.5.3 and 7.5.4
10.1.2.1	Masshunter added
11.3.10, 11.3.13	Specific reagent amounts modified to reflect current procedure
11.3.11	Autosampler name removed
17.0	Updated Figure 2 to current version of form

For *Review*: Comments

Standard Operating Procedure
Volatile Organics by Method 8260D
L-A-101 Rev. 3

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TABLES AND FIGURES

Standard Operating Procedure
Volatile Organics by Method 8260D
L-A-101 Rev. 3

1.0 Scope and Application, Including Components to be Analyzed

1.1 This method can be used to determine the presence and concentration of the volatile analytes listed in Section 17 Tables 1 & 2 in aqueous samples: groundwater, surface water, wastewater, soil, solid, and waste samples.

1.2 This SOP is applied for purgeable organic analytes from aqueous or solid matrices except where a specific Quality Assurance Project Plan (QAPP) overrides this method's quality control and acceptance criteria.

1.3 This standard operating procedure (SOP) documents CSS's application of EPA Method 8260D, Revision 4, dated June 2018, EPA Method 5030C, Revision 3, May 2003-Determination of Volatile Organic Compounds in aqueous samples by Purge-and-Trap Gas Chromatography/Mass Spectrometry and EPA Method 5035A, Revision 1, July, 2002-Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, and EPA Method 3585, Revision 0, dated December 1996 that are used in the PHILIS Mobile Labs. This SOP may also be used with EPA Methods 5031, 5032, and 5041 which are not currently used in the PHILIS Mobile Labs.

1.4 This SOP is executed in accordance with the U.S. Environmental Protection Agency and National Environmental Laboratory Accreditation Program (NELAP).

1.5 Example detection limits for analytes determined by EPA Method 8260D are listed in Section 17 Tables 1 & 2 for waters and soils.

2.0 Summary of Method

2.1 Aqueous Samples (Based on SW846 Method 5030C): Helium is bubbled through 10 mL of water in a purge and trap sparge vessel. The purgeables are efficiently transferred from the liquid phase to the gaseous phase. The vapor is swept on a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with the helium to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

2.2 Soil Samples (Based on SW846 Method 5035A): Samples are collected and prepared in accordance with methods based on the potential level of volatile organic contaminants that are estimated to be present. Methods for low level VOCs are considered for samples that will generally fall in the 0.5 to 200 µg/kg range. Methods for High VOC concentrations (methanol extractions) are designed for samples estimated to contain VOC levels greater than 200 µg/kg.

2.2.1 Volatile Organic Compounds at low levels in soil samples are determined by collecting a 5-g sample, weighed in the field at the time of collection, and placing it in a pre-weighed 40 mL VOA vial with a septum sealed screw-cap that already contains a stirring bar and sodium bisulfate preservation solution. The vial is sealed and transported to the PHILIS mobile labs. The entire vial is then placed, unopened, into the soil/water autosampler. Prior to analysis, organic-free reagent water, surrogates, and internal standards are automatically added to the sample by the OI 4100 soil/water autosampler without opening the vial. The vial is then heated to 40 °C, stirred and purged onto an adsorbent trap using helium carrier gas. When purging is then complete, the trap is then backflushed with helium and thermally desorbed onto the GC column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

2.2.2 An alternative to field preservation is the use of Encore Samplers (or equivalent) as collection and storage devices. Samples collected in this device must be preserved by the laboratory or analyzed within 48 hours of collection. The soil sample is removed with the use of an extrusion tool and analyzed or preserved. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer. Refer to Section 17 Table 8 for holding time and preservation requirements.

2.2.3 High level soils are extracted with methanol and analyzed as an aqueous sample. Typically, this would be approximately 5 grams of soil extracted with 5 mL of Methanol. A maximum of 100 uL (or 1mL spiked into 50mL – and 10mL of the 50mL purged) of methanol extract added to 5 mL reagent water should be purged in the system, as described above.

2.3 Oily Samples (SW 846 Method 3585): Samples that contain oily material are assessed to determine water-miscibility. Samples that are soluble in methanol may be weighed and diluted with methanol for analysis as in 5.1. Samples that are not soluble in water miscible solvents are prepared by dilution with hexadecane, or other suitable solvent, and directly injected for analysis. The gas chromatograph is temperature programmed to separate the components which are then detected with a mass spectrometer.

3.0 Definitions

3.1 Batch‡: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A Preparation Batch is composed of between 1 and 20 environmental samples of the same matrix, meeting the above criteria and with a maximum time between the start of processing of the first and the last sample in the batch to be 24hours. An Analytical Batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples

An 8260 volatiles analytical batch will consist of no more than twenty (20) environmental samples in addition to the SOP Quality Control requirements.

All batches require one MB, LCS, and MS/MSD pair or MS and Sample Duplicate where possible.

3.2 BFB: 4-bromofluorobenzene or a solution that contains the analyte, 4-bromofluorobenzene, which is used to evaluate the tuning and the performance of the mass spectrometer. The BFB tune is required to be analyzed at the beginning of each 12-hour period during which a calibration is analyzed. A tune is not required for a sequence where a calibration is not performed but may be analyzed at the analysts discretion.

3.3 Chain of Custody (COC) ‡: Record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers; the mode of collection; preservation; and requested analyses.

Each time the samples are transferred, the document should be signed by the person releasing the samples and by the person receiving the samples. A date and time must also be recorded.

3.4 Continuing Calibration Verification (CCV): A standard analyzed at the beginning of each analytical sequence that contains all method analytes at a concentration near the mid-range of the calibration curve. Each analyte must have a recovery within a percentage range specified in the method to validate that analyte in the calibration curve. A CCV is not required if a calibration curve is analyzed at the start of an analysis sequence. Some methods require additional CCV's. The CCV frequency will be stated in the method SOP.

3.5 Holding Time: The maximum amount of time permitted between sampling and sample preparation and/or sample preparation and sample analysis. Also the period of time a sample may be stored prior to analysis when there is no preparation step. See the specific method or SW846 8000B Table 4.1.

3.6 Initial Demonstration of Proficiency (IDP): Also known as a Demonstration of Capability (DOC). A procedure involving the analysis of a calibration and QC samples to demonstrate precision and accuracy after method development, significant changes in instrumentation or after training a new analyst. Procedure outlined in Section 12.1.

3.7 Instrument Calibration Standards (ICS): A solution prepared from the primary dilution standard solution or stock standard solutions, internal standards and surrogate analytes. The ICS solutions are used to calibrate the instrument response with respect to analyte concentration.

3.8 Internal Standards (IS)[∓]: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

3.9 Laboratory Control Sample (LCS)[∓]: (however named, such as laboratory fortified blank, blank spike (BS), or QC check sample). A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

The standard source can be the same as the calibration or a second source. The LCS is analyzed exactly like a sample to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.10 Laboratory Duplicate (LD): Two sample aliquots taken in the laboratory and analyzed separately with identical procedures. Analyses of the aliquots indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.11 Lower Limit of Quantitation (LLOQ): The LLOQ is the lowest concentration at which the laboratory has demonstrated target analytes can be reliably measured and reported with a certain degree of confidence, which must be greater than or equal to the lowest point in the calibration curve. The laboratory shall establish the LLOQ at concentrations where both quantitative and qualitative criteria can consistently be met. Procedures for LLOQ verification are outlined in section 12.3.

3.12 Matrix Spike (spiked sample or fortified sample)[∓]: A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of the sample for which an independent test results of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

3.13 Matrix Spike Duplicate (spiked sample or fortified sample duplicate)‡: A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

3.14 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples of the same batch. Method Blank analytical results are evaluated to determine the presence of contamination in the analytical method process. A blank analyte result must be < ½ the LLOQ for the blank to be acceptable or results above the LLOQ must be greater than 10 times the blank concentration not to be flagged.

3.15 Method Detection Limit (MDL): The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined by analyzing seven or more replicates of a spiked analyte free matrix and the resulting statistical calculation, in accordance with 40 CFR 136, Appendix B, Revision 2.

3.16 Primary Dilution Standard (PDS): A solution of one or several analytes prepared in the laboratory from SSS and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.17 Quality Control Sample (QCS)‡: A sample used to assess the performance of all or a portion of the measurement system. One of any number of samples, such as Certified Reference materials, a quality system matrix fortified by spiking, or actual samples fortified by spiking, intended to demonstrate that a measurement system or activity is in control.

3.18 Reporting Limit (RL): The reporting limit, also known as the LOQ is the minimum concentration that can be reported as a quantitated value for a target analyte in a sample. This value can be no lower than the concentration of the lowest calibration standard.

3.19 Required Detection Limit (RDL): Detection limits established by a client or regulatory authority for analytes of concern. The laboratory MDL values must be equal or lower than the RDL. This is also known as the CRQL, the contract-required quantitation limit.

3.20 Second Source Calibration Verification (SCV): A solution prepared from a source that is different from the calibration standards. The SCV is immediately following the ICS, and is used to verify calibration standard accuracy.

3.21 Stock Standard Solution (SSS): A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased as certified from a reputable commercial source.

3.22 Surrogate Standard (SS): Organic compounds which are similar to the target analytes in chemical composition and mimic the behavior of the target analytes throughout the analytical process. Surrogate compounds are not normally found in environmental samples. Each calibration standard, sample, MB, LCS, MS, and MSD is spiked with surrogate standards. Surrogates are used to evaluate analytical efficiency by measuring recovery. See analytical method SOP for a list of specific surrogate compounds that are appropriate for sample-specific analysis.

3.23 Working Standards (WS): Instrument calibration/calibration verification standards and quality control standards used in an analytical sequence such as BFB, ICS, CCV, SCV, MS, and MSD.

3.24 Trip Blank: An aliquot of reagent water placed in a VOA vial that travels with the cooler to determine if contaminants or interferences were introduced into the samples during sampling or transportation of the containers and samples

‡ EL-V1M2-ISO-2016, 2016 NELAP Standard definition.

4.0 Interferences

4.1 Samples for volatile organics analyses (VOA) are susceptible to laboratory chemical contaminants (e.g.: methylene chloride, acetone). Samples may become contaminated by diffusion of volatile organics through the septum seal into the sample during shipment and storage.

4.2 Carryover contamination may occur when a sample containing low levels of VOCs is analyzed immediately following a sample containing high levels of VOCs. If this situation occurs during a non-monitored analysis, the sample containing the low concentration VOCs may require reanalysis. If the situation occurs during monitored analysis, a blank should be run to ensure that the system is free of contamination, and in addition, the sample should be re-analyzed at a higher dilution factor.

4.3 Other contamination or interferences could be present in laboratory glassware, chemicals, and reagents used.

4.4 Soil samples that contain carbonate minerals (either from natural sources or applied as an amendment) may effervesce upon contact with the acidic preservative solution option in the low concentration sample vial. If the amount of gas generated is very small (i.e., several mL), any loss of volatiles as a result of such effervescence may be minimal if the vial is sealed quickly. However, if larger amounts of gas are generated, not only may the sample lose a significant amount of analyte, but the gas pressure may shatter the vial if the sample vial is sealed. Therefore, when samples are known or suspected to contain high levels of carbonates, a test sample should be collected, added to a vial, and checked for effervescence. If a rapid or vigorous reaction occurs, discard the sample and collect

low concentration samples in vials without chemical preservation. Samples of different preservation should be batched separately in the lab with QC reflecting the same preservation. Preservation should be documented accordingly on COC's and in LIMS.

4.5 Water samples may also effervesce upon addition of HCL preservative. Non-preserved samples, should be stored and batched separately from other samples and properly documented.

4.6 Mobile laboratories with volatile analysis areas must be kept at positive pressure to keep from drawing contaminants into the area and instruments.

5.0 Health and Safety Warnings

5.1 This method does not address all safety issues associated with its use. Laboratory personnel are responsible for maintaining a safe work environment and a current awareness of the Chemical Hygiene Plan regarding the safe handling of the chemicals listed in this method.

WARNING: The following VOCs have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, and vinyl chloride.

5.2 The toxicity and/or carcinogenicity of the other reagents and analytes used in this method have been defined; however, each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Procedures involving primary standards and sample preparation should be performed in a fume hood.

5.3 Safety Data Sheets (SDS) for each analyte and reagent used in the mobile laboratory are available to all employees. SDS should be consulted prior to handling chemicals.

5.4 Laboratory personnel are required to be familiar with the general laboratory safety including the location and proper use of safety/emergency equipment.

5.5 Acid preservatives and preserved samples are corrosive and should be handled and disposed of accordingly.

6.0 Equipment and Supplies

6.1 Sampling Equipment for Aqueous Samples

6.1.1 40 mL pre-cleaned VOA vials fitted with Teflon-lined screw caps.

6.1.2 40 mL VOA vials preserved with HCl and fitted with Teflon-lined screw caps.

6.1.3 40 mL VOA vials preserved with 100 ul of 0.25 mg/ul ascorbic acid solution and fitted with Teflon-lined screw caps. 1:1 HCL to be added in the field.

6.1.4 40 mL VOA vials preserved with 50ul of 0.07 mg/ul Na2s3O3 solution and fitted with Teflon-lined screw caps.

6.2 Sampling Equipment for Soil/Solid Samples

6.2.1 Pre-weighed 40 mL pre-cleaned VOA vials containing 5 mL of 20% sodium bisulfate solution and magnetic stir bar fitted with Teflon-lined screw caps.

6.2.2 Pre-weighed 40 mL pre-cleaned VOA vials containing 5 mL of methanol and a magnetic stir bar fitted with Teflon-lined screw caps.

6.2.3 Pre-weighed 40 mL pre-cleaned VOA vials containing 5 mL of Tri-sodium phosphate solution and magnetic stir bar fitted with Teflon-lined screw caps for fuel oxygenates.

6.2.4 Pre-weighed 40 mL pre-cleaned VOA vials containing 5 mL of reagent water and a magnetic stir bar, fitted with Teflon-lined screw caps.

6.2.5 Encore® sampler.

6.2.6 4-oz or 8-oz soil jars for moisture determination.

6.3 Glassware

6.3.1 Volumetric flask- class A, various sizes.

6.3.2 Disposable Pasteur pipettes.

6.3.3 Mininert vials (2 mL or 5 mL) and Mininert valves or 2mL screw cap vials.

6.3.4 1-L or 2-L Erlenmeyer Flask(s).

6.3.5 OI Analytical 50mL or 25-mL sparge vessel.

6.3.6 OI 5mL or 10mL loop.

6.3.7 5 mL measuring pipette (for analyses of soils/solids).

6.4 Syringes

Gas-tight micro syringes – various sizes.

6.5 Instrumentation

6.5.1 Agilent 6890N Gas Chromatograph or equivalent.

6.5.2 Agilent 5973 Mass Spectrometer- electron impact only (70 eV) or equivalent.

6.5.3 OI Analytical Eclipse 4760 Purge and Trap Concentrator or equivalent.

6.5.4 OI Analytical 4100 sample processor or equivalent.

6.5.5 Agilent MSD ChemStation G1701 DA software (or higher revision) or equivalent.

6.5.6 Restek, RTX-VMS 20 m (L) x 0.18 mm (id) x 1.0 µm (d_f) gas chromatographic column or equivalent.

6.5.7 OI Analytical Trap #10 or equivalent.

6.5.8 NIST 2002 Mass Spectral library (or higher revision) or equivalent.

6.6 Equipment

6.6.1 Heated Stirrer.

6.6.2 Nitrogen purge line for reagent water.

6.6.3 Drying oven (for analyses of dry weight for soils /solids).

6.6.4 Moisture analyzer (for analyses of soils/solids).

6.7 Supplies

6.7.1 Magnetic stir bars.

7.0 Reagents and Standards

Records are retained for all standards and reagents including the manufacturer/vendor, the Manufacture's Certificate of Analysis or purity, the date of receipt, recommended storage conditions, and an expiration date. Standard and reagent preparations are documented in the LIMS system, which will track dilutions and trace them to purchased stocks by lot numbers or neat compounds, reference to the method of preparation, date of preparation, expiration date of prepared solution and preparer's initials.

7.1 Reagents

Original containers of reagents must be labeled with an expiration date. All containers of prepared reagents must bear a name, preparation date, and must be recorded in the LIMS system or in a preparation log

7.1.1 Organic Free Reagent Water – water that does not contain analytes of interest or interferences that would prevent detection of analytes of interest at the reporting limit.

Deionized water with resistivity of 18.2 MΩ-cm or greater, treated with heated nitrogen purge for at least 1 hour to eliminate organic contaminants

7.1.2 HCl 37% ACS Grade. For preparation of 1:1 HCl for sample preservation in the field, and batch QC preparation for samples that are preserved in the field.

7.1.3 Preparation of 1:1 HCl. Add 15 mL of reagent water to a 40mL vial. Carefully add 15mL 37%HCL to the water. Purge with Nitrogen for one hour. Two or three drops from a pastuer pipette per vial for field samples not undergoing dechlorination. Samples dechlorinated in the field with ascorbic acid must be acidified after adding to the vial with ascorbic acid. Retain vials with acid or a portion of the field added HCl for batch QC.

7.1.4 L Ascorbic Acid > 99%- For dechlorination of aqueous samples in the field where field acid preservation will be done in the field. 3mg solid ascorbic acid added to 40ml vials before shipment or use aqueous solution.

7.1.5 Preparation of 0.25 mg/uL aqueous solution of ascorbic acid: Add 62.5g ascorbic acid to a 250mL beaker. Add 100mL reagent water and stir to dissolve powder. Decant the liquid a 250mL volumetric and add water in smaller portions and stir until powder is completely dissolved. Decant portions into volumetric flask and bring up to mark with reagent water. Invert and decant into a 250mL amber wide mouth jar. Purge with Nitrogen for one hour, create LIMD ID and label. 100uL into a 40ml vial. 80uL per 50Ml volumetric flask for QC preparation.

7.1.6 Sodium Thiosulfate (Na2S2O3) ACS Grade: Added to vials for aqueous samples as solid (3mg) or in solution form for dichlorination of samples where dichlorination and cooling are the only preservation options chosen. Prepare batch QC using the same lot used to preserve the samples.

7.1.7 Preparation of 0.07 mg/uL NaS2O3 solution. Weigh 17.5 g of NaS2O3 into a clean beaker, add 100mL reagent water and stir to dissolve powder. Decant the liquid a 250 mL volumetric and add water in smaller portions and stir until powder is completely dissolved. Decant portions into volumetric flask and bring up to mark with reagent water. Invert and decant into a 250 mL amber wide mouth jar. Purge with Nitrogen for one hour, create LIMD ID and label. 50 uL of solution per 40mL vial. Retain at least 4 vials per 20 samples for QC preparation.

7.1.8 Methanol- Purge and Trap grade only. 5ml of methanol are added to 40ml vials where approximately 5 g of solid/soil samples are added in the field or collected in Encore sampler and added in the lab. In the case of field preservation in methanol, vials with solvent are tared in the lab where tare weights are recorded in a logbook and on the vial label in indelible ink. A balance check of calibration weights is done and recorded in the same log within a 12 hour time frame.

7.1.9 Hexadecane – ACS Reagent Grade

7.1.10 Helium carrier gas: 99.999% (UHP) grade or better.

7.1.11 Nitrogen- purge gas, 99.999% (UHP) grade or better.

7.1.12 Sodium bisulfate monohydrate (NaHSO4), 97% (or better) for acid preservation of soil/solid samples in the field or added to the contents of an Encore sampler in the lab.. One gram of solid NaHSO4 + 5ml reagent water per approximately 5g of sample in a 40ml vial with a magnetic stir bar or use 5ml of a 20% aqueous solution with a stir bar to the same.

7.1.13 Preparation of an aqueous 20% NaHSO4 solution: Carefully add 57.6 g of solid NaHSO4 crystals to 100ml reagent water in a clean 250 mL beaker with a plastic spoon or spatula.

Note: NaHSO4 crystals are acidic and highly corrosive. Stir until most of the crystals have dissolved and decant the liquid into a 250 mL volumetric flask. Add smaller amounts of water, stir and decant smaller portions of water until all the crystals have dissolved. Bring the solution to the 250 mL mark with reagent water, Invert flask and decant into s 250 mL wide mouth amber jar and purge with nitrogen for an hour. Check and periodically check the solution for interferences. Use 5 mL with a stir bar per 5 g of sample or blank sand.

7.1.14 Ottawa Sand- Reagent Grade (for analyses of soils/solids). Other sands may be used provided they do not contain analytes of interest or interferences that would prevent reporting analytes at their reporting limits. Purchased sand may require cleaning before use as reagent (blank) sand.

7.1.14.1 Preparation of Reagent Sand option 1 (Edison/preferred)- Check lab in building 209 for muffle furnace availability. Add raw Ottawa sand into a one liter beaker or multiple one liter beakers. Bake for four hours or overnight in the muffle furnace at 400 C. The muffle furnace is programmed for cool down to handling temperature. Transfer warm sand into 8 oz jars with minimal headspace. Wrap parafilm around the lids. Log into LIMS with a six month expiration date. Label and periodically run blanks to assure that it is interference free. Store away from interfering solvents.

7.1.14.2 Preparation of Reagent Sand option 2- Slowly add Ottawa sand into a one liter beaker half filled with reagent water while stirring. Let settle and decant the water to waste. Scoop wet sand into second beaker half filled with water while stirring. Repeat twice more. Spread wet sand out on a flat pan and dry in a drying oven over night or longer. Transfer warm sand into 8oz jars with minimal headspace. Wrap parafilm around the lids. Log into LIMS with a six month expiration date. Label and periodically run blanks to assure that it is interference free. Store away from interfering solvents.

7.1.14.3 Preparation of Reagent Sand option 3—Take a sample size of reagent sand and use 5 grams of the material as a blank. Analyze the sand the same as a reagent blank. If the sand is clean (all detection at least less than ½ the reporting limit) then the sand does not need further cleaning to be used for the method blank.

7.2 Standards

Stock Standard Solutions (SSS) – certified standards are purchased from approved vendors. The standards listed in this SOP are examples. SSS are used to prepare primary dilution standards (PDS), Working Standards (WS), and second source calibration verification standards (SCV). The source and composition of the SSS used to prepare a particular PDS, IS, or LCS is given in Section 17 Tables 3 & 4 of this SOP. Stock solutions are transferred from a flame sealed ampule to a 2 mL vial via a chilled Pasteur pipette, care must be taken avoid bubbling air through the liquid when transferring. Immediately cap the vial. The opening date is documented in LIMS and the expiration date is changed based on the guidelines provided in section 12.2.6 but are not to exceed the original manufacturer's expiration listed on the COA. Print a new label for the storage vial. The following SSS are used:

7.2.1 Target Analyte Mixes.

7.2.2 Surrogate Standard Mixes (SS).

7.2.3 Internal Standard Analyte Mixes (IS).

7.2.4 BFB Tuning Solution.

7.2.5 Labeled SSS solutions are stored in the freezer, refrigerator, or cabinet depending on manufacture's recommendations until they expire.

7.2.6 Frequency of Standard Preparation

Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases may need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented.

Dichlorodifluoromethane and chloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases may need to be replaced after one month for working standards and three months for opened stocks or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently

7.2.7 Original Certificates of Analysis (CofA's) of SSS are maintained in binders dedicated for the Certificates of Analysis and are available to personnel. CofA's may also be stored on servers that are available to personnel. A pdf of the CofA is attached to the standard in LIMS for easy reference. The certificates shall be used each time the method standards are prepared to confirm the concentration of analytes.

7.2.8 IS/SS are prepared as described in Section 17 Table 4 and immediately transferred to the OI 4100 standard vessel.

7.2.9 Labeled PDSs are stored in the freezer and replaced every 2-3 weeks or sooner when analytical results indicate a problem. Each Mininert vial containing the PDS shall be labeled in a standard format as described in section 9.1.5 including the expiration date.

7.3 Working Standards (WS) for water

Working Standards are prepared according to Section 17 Table 5. Working Standards are used for the initial calibration, initial and continuing calibration verification, LCS and LCSD.

7.3.1 MS's are prepared by taking a 49.95 mL aliquot of an environmental sample and spiking it with 50 µL of PDS.

7.3.2 The OI 4100 fills a 10 mL sampling loop via peristaltic pump, adds 2.0 ul of IS/SS PDS and transfers the aqueous solution to a 25ml purge vessel.

7.4 Working Standards for Medium Level Soils:

7.4.1 Working standard for medium level soils are prepared similarly to Section 17 Table 5 for ICAL, CCV, and SCV working standards except that a constant ratio of 1ml of purge & trap methanol to 50 mL of water is maintained in every standard. For example, CAL1 with the addition of 2mL of standard would include 998uL of blank methanol to 50mL of H2O and CAL7, 100 uL of PDS + 900 uL of methanol in 50 mL H2O.

7.4.2 A medium soil blank is prepared by weighing 5 +/-.04 g of reagent sand into 5 mL of methanol

7.4.3 LCSs for medium soils are spiked as follows. Create a 100ug/ml standard (100ul of the 4 Restek stocks listed in order at the top of Section 17 Table 3) + 1600 ul of methanol in a 2mL vial., Spike with 500 uL of the 100 ug/mL PDS and quickly add 4.5 mL of methanol. Invert no more than 3x. If methanol extracts were prepared in the field, weigh 5 g of reagent sand into retained methanol vial, remove 500 uL of methanol from the blank extract and then add the spike. This results in a 1000 ug/Kg spike.

7.4.4 Matrix spikes are prepared similarly to LCSs except for using sample instead of blank sand.

7.5 Working Standards (WS) for low level soils

7.5.1 Working Standards are prepared as per Section 17 Table 6. They are used for the instrument performance check, calibration, and calibration verification.

As per Section 17 Table 4, known amounts of methanolic PDS's are spiked directly to a 40 mL VOA bottle that contains 5.0 (±0.5 g) of Ottawa sand, 5 mL of 20% sodium bisulfate preservative and a magnetic stir bar.

7.5.2 All analysis samples and QC are automatically spiked with a consistent aliquot of IS/SS – usually between 1 and 5 uL by the autosampler directly to the sample while adding 10ml of reagent water resulting in a concentration of 50 µg/Kg. Concentration is based on the concentration in 5 g of soil. The addition of water does not affect the stated concentration of the standard or sample.

7.5.3 Retain records for all standards and reagents including the manufacturer/vendor, the Manufacture's Certificate of Analysis or purity, the date of receipt, recommended storage conditions, and an expiration date.

7.5.4 Document standards and reagents preparation in the LIMS System-indicate traceability to purchased stocks or neat compounds, reference to the method of preparation, date of preparation, expiration date of prepared solution and preparer's initials.

7.5.5 Preservation of low level soils or aqueous samples can vary by project. Calibration for low level standards can be done without sodium bisulfite preservative as long as batch QC is preserved with the same amount and lot of preservatives in order to document their affect on recovery.

8.0 Sample Collection, Preservation, Shipment and Storage

PHILIS personnel do not take field samples, however proper samples containers and preservatives are listed in Section 17 Table 8.

PHILIS PT and QC samples should be treated exactly as actual samples. Use the date received as the sample date and allow LIMS to assign the standard hold times as per the method being analyzed. If the holding time is exceeded, document that it is a PT or QC sample that was received in a sealed ampoule and not opened until analysis. Once extracted or opened, normal holding times would be used and if times were exceeded, then the results would not be used.

8.1 Aqueous samples are collected in multiple 40 mL pre-cleaned VOA bottles.

8.1.1 Soil/Solid samples are collected in multiple 40 mL pre-cleaned VOA vials containing 5 mL of 20 % $NaHSO_4$ solution or 5 mL of methanol (for high level solids) and a magnetic stir bar.

8.1.2 Soil/Solid samples may also be taken in multiple Encore Samplers.

8.2 If there is a site specific sampling procedure as a part of the QAPP, then it automatically supersedes this SOP.

8.3 Samples are delivered to the PHILIS or appropriate field refrigerator for shipment to the lab for analysis within holding time.

8.4 The samples delivered to the PHILIS on the collection day must be transported in coolers containing ice to demonstrate the cooling process has begun. Samples shipped overnight to PHILIS must have temperatures that do not exceed 6 °C.

8.5 Samples are maintained at the temperature range from just above freezing to 6 °C

8.6 Temperature blanks should be included in the shipment with samples.

8.7 Trip blanks must be included with any volatile sample shipment.

8.8 If reagents are added in the field (e.g. 1:1 HCl), the same lot should be available to the lab for QC preparation.

9.0 Quality Control and Acceptance Criteria

QC requirements include the Demonstration of Capability and ongoing QC requirements that must be met when preparing and analyzing samples.

9.1 DEMONSTRATION OF CAPABILITY (DOC) – must be successfully performed by the analyst prior to analyzing any field samples and any time major method modifications are made. The following is done to demonstrate laboratory capability to perform this method:

9.1.1 Prior to conducting the DOC study, the analyst tunes the instrument, when required, and generates or verifies an acceptable instrument calibration following the procedure outlined in Section 10 of this SOP. A MB is analyzed to demonstrate that the background contamination is low enough to not interfere with analytes.

9.1.2 Method precision and accuracy are demonstrated by analyzing 4 replicate LCS's fortified at concentration listed in Section 17 Tables 5 or 6 and analyzed according to the procedure described in Section 11 of this SOP. Precision and accuracy limits are re-established every six months. Use current limits.

9.2 Ongoing QC applied when performing this method includes analyzing acceptable instrument calibration/calibration verification standards, method blanks, LCS, and MS/ MSD. Internal standards and surrogates must be acceptable with all QC samples and with test samples.

9.3 Lower limit of quantitation (LLOQ) – The LLOQ is the lowest concentration at which the laboratory has demonstrated target analytes can be reliably measured and reported with a certain degree of confidence, which must be greater than or equal to the lowest point in the calibration curve. The verification is performed by the preparation and/or analysis of an LCS (or matrix spike) at 0.5 - 2 times the established LLOQ.

Recovery of target analytes in the LLOQ verification should be within established in-house limits or within other such project-specific acceptance limits to demonstrate acceptable method performance at the LLOQ. Until the laboratory has sufficient data to determine acceptance limits, the LCS criteria of ±20% (i.e., lower limit minus 20% and upper limit plus 20%) may be used for the LLOQ acceptance criteria. This practice acknowledges the potential for greater uncertainty at the low end of the calibration curve. Practical, historically based LLOQ acceptance criteria should be determined once sufficient data points have been acquired.

9.4 MDL Procedure

MDLs and RLs are established by analyzing a minimum of seven replicates of a standard at or near the estimated MDL. Tabulation of results and MDL calculations are performed by the method in 40 CFR, Part 136, Method Update Rule Revision 2.

9.4.1 Initial MDLs

9.4.1.1 Initial MDLs are established by analyzing a minimum of seven replicates of the low-level calibration standard and a minimum of seven blanks prepped and analyzed over three separate days. The MDL should be spiked 0.5 to 2 times the estimated MDL. Extract and analyze the MDL standards and blanks with the same procedure as regular samples.

9.4.1.2 For each compound, calculate the mean and standard deviation of the replicates in micrograms per liter (µg/L). Then calculate the MDL by multiplying the standard deviation by the Student's t value. The one-sided (single-tailed) Student's t values at the 99% confidence levels are used (e.g., t = 3.143 at the 99% confidence level for n = 7). MDL results are stored in Element each time they are calculated. This calculation must be performed separately for the spikes and blanks. If all blanks do not have analyte detection, then the largest blank value is taken for the blank MDL. If all blanks do have detection, use them to calculate the MDL with the formula above and add the mean of the blank result. If the mean of the blank results is a negative number then use 0 in place of the mean. The sum of these two numbers is the blank MDL. The larger of the MDL spike and MDL blank values is the MDL.

9.4.2 Ongoing MDL Data Collection

9.4.2.1 Ongoing MDL's are determined by preparing and analyzing two spiked standards at 1-5 times the estimated MDL and two blanks once per quarter for a minimum of seven determinations. The blanks and spikes may be analyzed in the same prep batch but is not required. If the instruments are being used regularly, the MDL spikes may be added to the routine batches and the regular blanks used. All blanks analyzed during the evaluation period should be used.

9.4.2.2 If no samples are analyzed during a quarter, then no ongoing MDLs are required. When this is the situation, MDLs, both spiked and blank, are analyzed with the PT samples analyzed every six months.

9.4.3 Annual calculations

At least once per year or a minimum of 13 months, evaluate the MDL by, calculating as above in 9.4.1.2. Use the larger of the spiked determinations and blank determinations for the mdl value. Include all data generated during the last twenty four months.

10.0 Calibration and Standardization

10.1 Prior to the analysis of samples, performance of the instrument is optimized, and an instrument calibration curve is developed. BFB is analyzed prior to instrument calibration, in order to verify that the mass abundance acceptance criteria specified in Section 17 Table 9 have been achieved. Tune checks are only required prior to ICAL, Alternatively, other published tuning criteria may be used provided that method performance is not adversely affected.

10.1.1 In order for data to be acceptable, all samples must be analyzed within a 12 hour window from the injection of the tune or CCV.

10.1.2 BFB (50 nanograms or less) can either be direct injected or purged into the system

10.1.2.1 Prepare a 50ug/ml standard in methanol by adding 1960ul of methanol to a 2mL screw cap vial. Add 40uL of a Restek Surrogate standard (Cat#30004) mix at 2500ug/mL.

For BFB injection using an autosampler, the maximum standard concentration shall be 50 µg/mL with a 1 µL injection. Using a purge and trap method, an aqueous standard at 10 µg/mL shall be used (inject 10 µL into a 50 mL vol flask), with a 10 mL purge to deliver 50 nanograms of BFB into the system. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required and must be accomplished using a single scan acquired within 20 scans of the elution of the BFB. Do not subtract part of the BFB peak or other discrete peak that does not coelute with the BFB. All calculations are performed by ChemStation Enviroquant or by MassHunter. BFB acceptance criteria are in Section 17 Table 9.

10.2 Setting Retention Times, Retention Time Windows and Integration Parameter

Once the purge and trap and GC cycle have finished for the midpoint or other calibration standard, load the quantitation file. Review each peak to make sure that the processing software identified the correct peak. If not, manually integrate the peak. Save all of the retention times. Quantify the calibration file and go through each ion profile of the target list, take note of the ion ratios, verify that the spectrum and profile match the standard spectrum.

10.3 The instrument is calibrated using standards at the seven (7) concentrations (given in Section 17 Tables 5, 6, or 7 based on the matrix) in the following manner: Cal1 – Cal 7 are used to generate the calibration curve for all target analytes. Average response factor or a linear regression curve can be used with five points, but a quadratic regression requires a minimum of six points. More or less standard points may be used provided required QA criteria can be met.

10.4 Rejection of calibration points

10.4.1 It is not generally acceptable to remove points from a calibration curve. Typically instrument maintenance and the accuracy of the calibration standards should be examined if the calibration acceptance criteria are not met.

10.4.2 If no problems are found, then a point(s) can be rejected as long as it meets the following criteria.

10.4.3 If the rejected point is the highest or lowest point in the ICAL, then the rejection may be done by analyte. If the rejected point is an internal point on the ICAL, it may be removed if the reason is obvious and the entire level (all analytes) is removed with the reason documented. Examples for level removal are; a bad injection, internal standards low or missing, contamination, etc.

10.5 The CAL1 standard contains the analytes at the RL of the analytical method. The lowest concentration included in the calibration curve is the reporting limit.

10.6 A response factor calibration curve is generated for each target analyte by plotting the response factor as a function of concentration ratio. If the analyte does not meet the 20% variability acceptance criteria, then a regression fit should be used. If linear or quadratic regression is used, the resulting curve fit must be 0.99 or greater.

10.7 All calibration points must be recalculated (not reanalyzed) using the final calibration curve in which this standard is used (i.e., re-fitting the response from the calibration standard back into the curve). The recalculated concentration of the calibration standard corresponding to the LLOQ must be within ±50% of the standard's true concentration and within ±30% for all others (i.e. above the low standard).

10.8 Recommended initial and continuing calibration relative response factors (RRFs) for the volatile compounds are listed in Section 17 Table 10. If the response is below the recommended limit, then the calibration must be evaluated to determine that the lowest point on the calibration curve may be distinguished from the baseline.

10.9 The instrument calibration curve is initially verified by the SCV and continuously verified every 12 hours by the CCV. The concentration of the CCV is ≤ the midlevel of the calibration curve.

10.10 The Relative Error of the calibration curve is determined by processing the lowest point and the midpoint of the calibration against the curve. The % difference in true value is the Relative Error.

10.11 Acceptance criteria for the Instrument Calibration and CCVs, and the required frequency of their analysis are summarized in Section 17 Table 11.

11.0 Procedure

Samples can be prepared after passing an SVC, after an ICAL or CCV from the same matrix as the samples. An instrument blank may be run after a CCV or LCS if carryover at the CCV level is anticipated.

11.1 Sample Preparation for Aqueous Samples based on SW846 Method 5030C

11.1.1 Remove samples from the laboratory refrigerator and allow to equilibrate to ambient temperature.

11.1.2 Prepare and analyze the batch blank and LCS from with the same amount and lot of reagents and preservatives as the samples.

11.1.3 Verify that they have been logged into the LIMS and are within the holding time. If the sample exceeds holding time notify the Lead Chemist and follow the corrective action plan.

11.1.4 Transfer the internal custody of the container being analyze to APL01 or PAL and mark as Active Out from sample receiving or the refrigerator where sample are stored. Verify that you are logged into your own LIMS account.

11.1.5 Ensure that the 40 mL sampling bottles are free of headspace. If headspace is noticed, notify the Lead Chemist and follow the corrective action plan. Headspace is considered a problem is the bubble is greater than ¼ inch in diameter (the size of a pea).

11.1.6 Analyze no more than 20 samples per batch.

11.1.7 Load vials on the sampling tray and run the water program on the auto sampler. Verify that the correct standard addition vessel is being used. 10ml of the water samples will be added to the sparge vessel while adding 2ul of the internal standard surrogate solution

11.1.8 Once analyzed, the pH and total and residual chlorine level of the spent container can be determined by test strip and recorded into the special info section of the batch bench sheet.

11.1.9 For samples to be analyzed as MS/MSD follow the procedure below:

11.1.9.1 The client must provide four (4) additional samples to be analyzed as MS/MSD in addition to the original 40 mL VOA bottle.

11.1.9.2 To create an MS sample, transfer approximately 44 mL of the sample to a 50 mL volumetric flask.

11.1.9.3 Spike 50 µL of LCS PDS to the volumetric flask and dilute to the 50 mL mark with the sample only, not reagent water.

11.1.9.4 For MSD samples, repeat the procedure for the MS sample

11.2 Sample preparation for Medium Level Soil Samples based on SW846 Method 5035A.

11.2.1 Verify the calibration of a top loading using certified weight which cover the range of the samples to be weighed. Check off the serial number of the weights and balance in the sample weight log look. The top loading balance in APL01 and SPA01 read to the hundredth of a gram. It is a NELAP requirement that sample weights for 8260D and calibration weights be recorded to the same number of significant figures. Record the calibration weights accordingly.

11.2.2 Remove the sample samples from the refrigerator or sample receiving and transfer the internal custody of the containers removed appropriately.

11.2.3 Samples from 5g Encore samples must be extracted or frozen on the day of receipt. Tare a 40ml vial on a top loading balance. Extrude the contents of the Encore sampler into the vial and. Record the weight in the logbook. Add 5ml of purge and trap methanol and cap the vial. Allow the methanol to moisten the core and gently shake to break up the core and/or mix the vial contents. Agitate the extracts periodically over the course a half an hour. vials Allow to settle until methanol on top is clear. If the sample does not settle samples may be loaded into a centrifuge (balance the load when adding to a centrifuge) and spin briefly at a low setting to settle out the contents

11.2.4 Samples preserved with methanol in the field are prepared by recording the tare weight determining the final weight and logging into a sample weight log.

11.2.5 Batch QC is by adding weighing 5+/- 0.04g of reagent sand to the 5ml methanol in 40ml vials that were retained by the lab when preparing sample kits or adding 5ml methanol to 5+/- 0.04g of reagent sand in the lab.

11.2.6 The LCS blank extract is spiked as follows: Create a 100ug/ml standard (100ul of the 4 Restek stocks listed in order at the top of Section 17 Table 3) + 1600ul of methanol in a 2ml vial. Remove 500ul of methanol from the extract. Spike with 500ul of the 100ug/ml PDS. Invert no more than 3x.

11.2.7 Final weights are all recorded in the batch bench sheet,

11.2.8 Methanol extracts can be screened by headspace prior to analyses. See SOP-L-A-102 for this procedure.

11.2.9 Extracts are analyzed at a default dilution of x50 by transferring 1.0ml of the sample or QC extract via gas tight syringe to a 50ml volumetric flask containing approximately 48ml of reagent water and then bring up to the mark with reagent water via pasteur pipette. If a dilution is being run with a lesser aliquot of extract add additional methanol to bring the total volume of methanol in 50mL of water to 1.0 mL.

11.2.10 Load vials on the sampling tray and run the water program on the OI 4100. Verify that the correct standard addition vessel is being used. 10ml of the dilutions will be added to the sparge vessel while adding 2uL of the internal standard surrogate solution.

11.3 Preparation and analysis of Low Level Soil Samples

11.3.1 Remove the samples from the refrigerator or sample receiving.

11.3.2 Verify that they have been logged into LIMS and are within holding time. If the sample exceeds holding time, notify the Lead Chemist and follow the corrective action plan.

11.3.3 Edit the internal custody log in LIMS for the containers that you are working with.

11.3.4 Batch no more than 20 samples to be analyzed.

11.3.5 Reweigh the samples and ensure the original tare weight was recorded. If it was lost, damaged or destroyed, notify the Lead Chemist and follow the corrective action plan.

11.3.6 Weigh the samples, record the weights in the sample weight log Determine the final weight and log into the batch bench sheet in LIMS.

11.3.7 The contents of Encore samples are extruded into a tared 40ml vial. Weights are recorded and 5ml of reagent water or 5ml of 20% Sodium bisulfate are added depending on when the samples are to analyzed and or the QAPP. Also add a magnetic stir bar.

11.3.8 Batch blanks are prepared in retained vials with water or sodium bisulfate if the samples were added in the field.5.0 +/- .04 g of reagent sand are weighed int the vial.

11.3.9 Batch blanks for Encore samples prepared in the lab. 5. +/- -0.04g of reagent sand is weighed int a 40ml tared vial, a stir bar and 5 ml of reagent water or 20% sodium bisulfate solution from the sample preparation lot is added along with a magnetic stir bar.

11.3.10 LCS and matrix spikes are spiked with a known concentration of PDS directly into the prepared sample or QC sample and swirled to mix in the spike.

11.3.11 Sample and QC are loaded on the auto sampler tray. A soil program is chosen for analysis after verifying the correct standard vessel is being used.

11.3.12 Fresh reagent water is added to the instrument reservoir.

11.3.13 10ml of water is added to vial while adding 1-5 uL of a known concentration of internal standard/surrogate mix. The sample is preheated to 40C and purged through a multistage needle while stirring.

11.4 Standard Preparation

Follow the procedure listed in Section 17 Table 5 for waters, Section 17 Table 6 for low level soils, and Section 17 Table 7 for high level soils.

11.5 Sample Analysis- Sections 11,1, 11,2, and 11.3 cover the loading of the OI 4100 for various matrices. Example Purge and Trap and GC/MS acquisition parameter

11.5.1 In ChemStation, load the "default" or previous day's sequence. Make sure the sequence ties the correct method and tune settings for the samples being analyzed. Make the changes as necessary to reflect the QC and samples that you will be analyzing. A typical sequence would start with the tune (only required if calibrating), CCV, MB, and LCS. It would then contain samples and an MS/MSD or MS/Sample Dup. Save the sequence with the instrument ID and the date of analysis. Instrument blanks after standards or LCS sample if carryover contamination is anticipated.

11.5.2 Check the helium supply, water supply, and IS/SS to make sure an adequate amount is available to complete the sequence.

11.5.3 Start the sequence.

11.6 Identification of Analytes

11.6.1 The analyte is identified by comparison of its mass spectrum to a reference spectrum updated in the instrument method. The major ions (greater than 10% of the most abundant ion should be present in the spectra. The relative % of the major ions should be within ±20% of the expected abundance.

11.6.2 The analyte is also identified by its retention time compared to the retention time observed for the same analyte in the most recent retention time update. The retention time must be within 10 seconds of the midpoint of the calibration curve or most recent CCV for that compound. An RRT value may also be used. If retention time criteria fails and judgement from qualitative MS data indicate a positive hit notify the lead chemist to see if the data should be reported with a flag.

11.7 Quantitation of Analytes

Analytes are quantified by comparing the response to that in the calibration curve and multiplied by any dilution or sample preparation factor. A list of the analytes and quant ions is listed in Section 17 Table 13.

12.0 Data Analysis and Calculations

12.1 The concentration of each analyte is calculated using Agilent MSD ChemStation software using an average response factor or linear regression curve as established in Section 10 of this SOP. Response factors and analyte concentrations are calculated by the equations below:

12.2 Relative response factor (RRF):

$$RRF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

where:
A_x = Area of the quantitation ion for the surrogate or compound being measured.
A_{is} = Area of the quantitation ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard.
C_x = Concentration of the surrogate or compound being measured.

12.3 Average RRF:

$$\overline{RRF} = \frac{\sum_{1}^{n} RRF}{n}$$

where
n = number of initial calibration standards

12.4 Percent relative standard deviation (%RSD):

$$\%RSD = \left(\frac{s}{\bar{x}}\right)100$$

where:
s = standard deviation: $s = \sqrt{\frac{\left(\sum_{i=0}^{n}(\bar{x} - x_i)^2\right)}{n-1}}$

12.5 $\bar{x} = \overline{RRF}$:

$$\overline{RRF} = \frac{\sum_{1}^{n} RRF}{n}$$

12.6 Sample concentration using RRF:

$$\text{Conc.}\left(\frac{\mu g}{L}\right) = \frac{(A_x)(I_s)(D)}{(\overline{RRF})(V_o)(A_{IS})}$$

where :
A_x = area of quantitation ion for compound being measured
I_s = amount of internal standard injected (ng)
A_{is} = area of quantitation ion for the internal standard
$\overline{RRF}$ = mean relative response factor for compound being measured
V_o = volume of water extracted purged (mL) accounting for dilutions
D = Dilution Factor

12.7 Percent recovery for CCV, ICV, LCS, and MS are performed using the following equation:

$$\%R = \left[\frac{(C_{spk} - C_x)}{C_t}\right]100$$

where:
C_{spk} = the concentration of the analyte in the spiked sample
C_x = the concentration of the analyte in the reference (parent) sample; (Cx = 0 for CCV, LCS and ICV.)
C_t = the theoretical spike concentration.

12.8 Relative percent difference for duplicate is calculated using the following equation:

$$RPD = \left[\frac{|C_1 - C_2|}{(C_1 + C_2)/2}\right]100$$

where:
C_1 = concentration of the first sample
C_2 = concentration of the second sample

12.9 Instrument generated data goes through a series of reviews prior to being submitted to the client. First the analyst reviews the data to ensure method and client requirements are met. Then the instrument data goes through a peer review covering the same items as the analyst. Both reviews are documented on Form QA-017, which is provided in Figure 2. The Quality Assurance Manager also reviews a minimum of 10 % of data to evaluate the QA process.

12.10 Analytical data generated by the instrument software is reviewed and evaluated by the analyst and peer as follows:

12.10.1 BFB, instrument calibration, calibration verifications, IS/SS, QC measures are evaluated and the results documented on the separate forms.

12.10.2 The tune evaluation of BFB.

12.10.3 The instrument calibration relative response factors and percent relative standard deviations.

12.10.4 QA-QC check report for internal standard area counts and percent recoveries for the surrogates.

12.10.5 Analyte percent recoveries CCV, LCS, SCV, MS, and RPD for MSD.

12.11 In order for the analytical data to be acceptable, the calibration standards and quality control measures must meet the criteria listed in Sections 9 and 10 of this SOP including Section 17 Tables 9 - 11 and 14.

12.12 All false positives are Q-Deleted, and all positively identified target analytes are reported to LIMS.

12.13 Manual integration is applied in cases when the instrument data processing software produces integrated areas that are not valid. The manual adjustments to the chromatographic peak must be performed in a consistent manner for the calibration standards, QC and field samples.

Manual integration should not be substituted for proper maintenance of the instrument or setup of the method (e.g. retention time updates), integration parameter files, etc.

The analyst should seek to minimize manual integrations by proper instrument maintenance, retention time updates, and configuring peak integration parameters.

12.14 If the QAPP requires it, chromatograms of all field samples are examined to detect additional peaks, which were not identified as target analytes. If such peaks are present, generate a Library Search Report and report a tentatively identified compound (TIC) if the percent match is greater than the 50%. The Lead Chemist should be notified

immediately in that case. An example chromatogram is shown in Figure 1. Method 8260D Revision 4 Section 11.6.2 provides guidelines for tentative identification of non target peaks.

12.15 Anytime the analyst alters the instrument generated quantitation report, the hardcopies of both reports (original and analyst's corrected) must be retained (e.g., manual integration). The altered report must be initialed and dated by the analyst with a reason for altering. The corrected report must also be reviewed, initialed, and dated by a peer or supervisor.

12.15.1 Discrepancies in the analytical run are documented on the "Data Review Form, QA-017" and discussed with the Lead Chemist. "Data Review Form QA-017" is signed by the Level 1 reviewer, the Level II reviewer, and Quality Assurance.

12.16 Reviewed data is entered into LIMS, hard copies of LIMS report is printed and compared to the original data or may be reviewed in LIMS.

12.17 All records derived from the analytical process are assembled in the analytical data packages that consist of:

12.17.1 Analytical run sheet.

12.17.2 BFB tune evaluation report, if analyzed.

12.17.3 QA-QC check report.

12.17.4 Quantitation Report for each Sample and QCS.

12.17.5 Evaluation reports for CCV, SCV, LCS, MS, and MSD.

12.17.6 Initial calibration form.

12.18 Data packages are maintained electronically on servers in multiple locations.

12.19 Corrective Actions for Out of Control

In cases where quality control measures do not meet acceptance criteria, the quality of the analytical data is not acceptable, and the analyst does the following:

12.19.1 When tuning and instrument calibration fail to meet acceptance criteria, the analysis does not start. The problem is investigated, and the necessary instrument maintenance is performed, followed with tuning and calibration. Instrument tuning is only required prior to calibration.

12.19.2 If the acceptance criteria listed in Section 17 Tables 11 & 14 of this SOP are not met for ICAL, SCV, CCV, MB, LCS, MS, MSD, internal standards, and surrogates, then the affected QCs and associated samples should be treated as per laboratory or QAPP protocols.

12.19.3 If after analysis, any of the criteria for quality control are not met, or the sample is not available for reanalysis, the analyst must notify the Lead Chemist. The Lead Chemist will implement the corrective action plan.

12.20 The analyst shall report to the Lead Chemist and indicate on the "Data Review Form QA-017" any out of control event. Such events include:

12.20.1 Damage to the sample.

12.20.2 Headspace in the sample bottle.

12.20.3 Holding time exceeded.

12.20.4 Inadequate sample preservation.

12.20.5 Sample results exceeds the Agency's action limit

12.20.6 Samples do not reflect historical data.

12.20.7 Upward trending or sample results approaching interval warning limits.

12.20.8 Any non-target analyte peak present on the instrument generated chromatogram that interferes with target analyte peaks.

12.21 The Lead Chemist will implement the corrective action plan described in the PHILIS corrective action plan document.

12.22 See the QAPP that the samples were analyzed under for contingencies or guidance on handling out of control or unacceptable data.

13.0 Method Performance

13.1 Demonstration MDL data is presented in Section 17 Tables 1 & 2. MDLs are analyzed at least annually or with instrumentation changes. Lab Accuracy and Precision data are used to calculate lab specific acceptance criteria. Precision and Accuracy data are recalculated and evaluated every six months. Limit acceptance criteria will be established no tighter than 80 % to 120 % for accuracy and 20% for precision.

13.2 Other specific Quality Assurance Objectives (QAO) may be found in the appropriate statement-of-work or Quality Assurance Project Plan (QAPP) for specific projects.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. The EPA places pollution prevention as the management option of first choice with regard to laboratory waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 The Environmental Protection Agency requires that laboratory waste management practices be compliant with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult the PHILIS Chemical Hygiene Plan.

14.3 The waste produced from EPA Method 5030C or 5035A/8260D consist of waste collected from the purge and trap system, excess sample, standards (stock mixes, PDS, WS), and methanol.

14.4 Waste from the purge and trap system from field samples are disposed in the Hazardous Waste container.

14.5 Excess reagents are disposed following the MSDS instructions.

14.6 Glass pipettes are disposed in the glassware waste.

14.7 Refer to EPA Method 8260D, section 14.0 and 15.0 for additional guidance.

14.8 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036.

15.0 Waste Management

Waste management procedures are specified in the Hazardous Waste Management Plan.

16.0 References

16.1 EPA Method 8260D, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Revision 4, June 2018; U.S. EPA Office of Solid Waste.

16.2 EPA Method 8260C, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Revision 3, August 2006; U.S. EPA Office of Solid Waste.

16.3 EPA Method 5030C, Purge-And-Trap of Aqueous Samples, Revision 3, May 2003; U.S. EPA Office of Solid Waste.

16.4 EPA Method 5035A, Closed System Purge and Trap and Extraction for Volatile Organics in Soil and Waste Samples, Revision 1, July 2002.

16.5 2003, 2009, and 2016 NELAP manuals.

16.6 40 CFR 136, Appendix B, Revision 2. Definition and Procedure for the Determination of the Method Detection Limit – December, 2016

16.7 U.S. EPA Contract Laboratory Program Statement of Work OLM 04.2.

16.8 U.S. EPA National Functional Guidelines, Superfund Organic Methods Data Review, June, 2008.

17.0 Tables, Diagrams, Flowcharts and Validation Data

Table 1. Examples of Analytes, MDLs, and RLs for Water using EPA Method 8260D

Analyte	CAS #	MDL (µg/L)	RL (µg/L)
Dichlorodifluoromethane	75-71-8	0.3	5.0
Chloromethane	74-87-3	0.6	5.0
Vinyl Chloride	75-01-4	0.7	5.0
Bromomethane	74-83-9	1.1	5.0
Chloroethane	75-00-3	0.8	5.0
Trichlorofluoromethane	75-69-4	0.5	5.0
1,1-Dichloroethene	75-35-4	1.4	5.0
t-Butyl alcohol	75-65-0	10.1	25
Carbon disulfide	75-15-0	0.7	5.0
Iodomethane	74-88-4	0.4	5.0
Methylene chloride	75-09-2	0.6	10.0
Methyl-tert-Butyl ether	1634-04-4	0.3	5.0
Acetone	67-64-1	8.4	25.0
trans-1,2-Dichloroethene	156-60-5	1.4	5.0
Di isiopropyl ether	108-20-3	0.3	5.0
1,1-Dichloroethane	75-34-3	0.5	5.0
cis-1,2-Dichloroethene	156-59-2	0.6	5.0
2,2-Dichloropropane	594-20-7	2.0	10.0
Bromochloromethane	74-97-5	0.7	5.0
Chloroform	67-66-3	0.6	5.0
Carbon tetrachloride	56-23-5	1.0	5.0
1,1,1-Trichloroethane	71-55-6	1.7	5.0
t-Amyl methyl ether	994-05-8	.3	5.0
1,1-Dichloropropene	563-58-6	0.5	5.0
2-Butanone	78-93-3	4.7	25.0
Ethyl tert-butyl ether	637-92-3	.2	5.0
Benzene	71-43-2	0.4	1.0
1,2-Dichloroethane	107-06-2	0.5	5.0
Trichloroethene	79-01-6	0.6	5.0
Dibromomethane	74-95-3	0.6	5.0
1,2-Dichloropropane	78-87-5	0.5	5.0
Bromodichloromethane	75-27-4	0.5	5.0
cis-1,3-Dichloropropene	10061-01-5	1.0	5.0
Toluene	108-88-3	0.5	5.0
Tetrachloroethene	127-18-4	0.3	5.0

Analyte	CAS #	MDL (µg/L)	RL (µg/L)
trans-1,3-Dichloropropene	10061-02-6	0.8	5.0
1,1,2-Trichloroethane	79-00-5	0.6	5.0
Dibromochloromethane	124-48-1	0.3	10.0
1,3-Dichloropropane	142-28-9	0.6	5.0
1,2-Dibromoethane	106-93-4	0.8	5.0
2-Hexanone	591-78-6	7.1	25.0
Chlorobenzene	108-90-7	0.6	5.0
Ethyl benzene	100-41-4	0.3	5.0
1,1,1,2-Tetrachloroethane	630-20-6	0.5	5.0
m,p-Xylenes	1330-20-7	0.4	10.0
o-Xylene	95-47-6	0.5	5.0
Bromoform	75-25-2	0.4	5.0
Styrene	100-42-5	0.4	5.0
Isopropylbenzene	98-82-8	0.3	5.0
Bromobenzene	108-86-1	0.5	5.0
n-Propylbenzene	103-65-1	0.4	5.0
1,1,2,2-Tetrachloroethane	79-34-5	1.0	5.0
2-Chlorotoluene	95-49-8	0.3	5.0
1,2,3-Trichloropropane	96-18-4	0.9	5.0
1,3,5-Trimethylbenzene	108-67-8	0.3	5.0
4-Chlorotoluene	106-43-4	0.4	5.0
tert-Butylbenzene	98-06-6	0.3	5.0
1,2,4-Trimethylbenzene	95-63-6	0.4	5.0
sec-Butylbenzene	135-98-8	0.3	5.0
1,3-Dichlorobenzene	541-73-1	0.5	5.0
p-Isopropyltoluene	99-87-6	0.4	5.0
Butylbenzene	104-51-8	0.4	5.0
1,4-Dichlorobenzene	106-46-7	0.5	5.0
1,2-Dichlorobenzene	95-50-1	0.7	5.0
1,2-Dibromo-3-chloropropane	96-12-8	0.6	5.0
1,2,4-Trichlorobenzene	120-82-1	1.0	5.0
Hexachlorobutadiene	87-68-3	0.8	5.0
Naphthalene	91-20-3	1.1	5.0
1,2,3-Trichlorobenzene	87-61-6	1.0	5.0
4-Methyl-2-Pentanone	108-10-1	7.0	25.0

Table 2. Examples of Analytes, MDLs, and RLs for Soils using EPA Method 8260D

Analyte	CAS #	MDL (µg/kg)	RL (µg/kg)
Dichlorodifluoromethane	75-71-8	2.2	5.0
Chloromethane	74-87-3	1.0	5.0
Vinyl Chloride	75-01-4	1.2	5.0
Bromomethane	74-83-9	1.0	5.0
Chloroethane	75-00-3	1.0	5.0
Trichlorofluoromethane	75-69-4	2.3	5.0
1,1-Dichloroethene	75-35-4	2.0	5.0
t-Butyl alcohol	75-65-0	9.5	20.0
Carbon disulfide	75-15-0	1.7	5.0
Iodomethane	74-88-4	1.2	5.0
Methylene chloride	75-09-2	2.1	20.0
Methyl-tert-Butyl ether	1634-04-4	1.0	5.0
Acetone	67-64-1	16.3	20.0
trans-1,2-Dichloroethene	156-60-5	1.7	5.0
Di isiopropyl ether	108-20-3	0.8	5.0
1,1-Dichloroethane	75-34-3	0.8	5.0
cis-1,2-Dichloroethene	156-59-2	0.7	5.0
2,2-Dichloropropane	594-20-7	1.8	5.0
Bromochloromethane	74-97-5	0.7	5.0
Chloroform	67-66-3	0.7	5.0
Carbon tetrachloride	56-23-5	1.7	5.0
1,1,1-Trichloroethane	71-55-6	1.2	5.0
t-Amyl methyl ether	994-05-8	2.0	5.0
1,1-Dichloropropene	563-58-6	2.7	5.0
2-Butanone	78-93-3	2.4	10.0
Ethyl tert-butyl ether	637-92-3	1.6	5.0
Benzene	71-43-2	1.1	5.0
1,2-Dichloroethane	107-06-2	0.7	5.0
Trichloroethene	79-01-6	2.4	5.0
Dibromomethane	74-95-3	0.7	5.0
1,2-Dichloropropane	78-87-5	0.8	5.0
Bromodichloromethane	75-27-4	0.7	5.0
cis-1,3-Dichloropropene	10061-01-5	1.1	5.0
Toluene	108-88-3	1.9	5.0
Tetrachloroethene	127-18-4	4.7	10.0

Analyte	CAS #	MDL (µg/kg)	RL (µg/kg)
trans-1,3-Dichloropropene	10061-02-6	0.7	5.0
1,1,2-Trichloroethane	79-00-5	0.6	5.0
Dibromochloromethane	124-48-1	0.7	5.0
1,3-Dichloropropane	142-28-9	0.8	5.0
1,2-Dibromoethane	106-93-4	0.8	5.0
2-Hexanone	591-78-6	5.0	10.0
Chlorobenzene	108-90-7	1.8	5.0
Ethyl benzene	100-41-4	2.4	5.0
1,1,1,2-Tetrachloroethane	630-20-6	0.8	5.0
m,p-Xylenes	1330-20-7	2.7	5.0
o-Xylene	95-47-6	2.0	5.0
Bromoform	75-25-2	1.0	5.0
Styrene	100-42-5	2.6	5.0
Isopropylbenzene	98-82-8	2.6	5.0
Bromobenzene	108-86-1	1.7	5.0
n-Propylbenzene	103-65-1	3.1	5.0
1,1,2,2-Tetrachloroethane	79-34-5	2.1	5.0
2-Chlorotoluene	95-49-8	2.6	5.0
1,2,3-Trichloropropane	96-18-4	1.6	5.0
1,3,5-Trimethylbenzene	108-67-8	3.1	5.0
4-Chlorotoluene	106-43-4	2.9	5.0
tert-Butylbenzene	98-06-6	2.4	5.0
1,2,4-Trimethylbenzene	95-63-6	3.3	5.0
sec-Butylbenzene	135-98-8	3.1	5.0
1,3-Dichlorobenzene	541-73-1	2.6	5.0
p-Isopropyltoluene	99-87-6	3.1	5.0
Butylbenzene	104-51-8	3.3	5.0
1,4-Dichlorobenzene	106-46-7	2.7	5.0
1,2-Dichlorobenzene	95-50-1	2.1	5.0
1,2-Dibromo-3-chloropropane	96-12-8	1.6	5.0
1,2,4-Trichlorobenzene	120-82-1	3.0	5.0
Hexachlorobutadiene	87-68-3	2.7	5.0
Naphthalene	91-20-3	1.5	5.0
1,2,3-Trichlorobenzene	87-61-6	2.4	5.0
4-Methyl-2-Pentanone	108-10-1	4.6	10.0

Table 3. Example Preparation of PDS, IS/SS, SCV-PDS in Methanol for Analyses of Aqueous Samples and Methanol Extractions

PDS Name	SSS Mix Used				Solvent	PDS description		
	Source/catalog#	Analytes	Conc. µg/mL	Volume µL	Volume mL	Conc. µg/mL	Final Volume mL	Application
PDS	Restek/30633	Mega Mix	2,000	500	MeOH 1.8	50	2.00	ICS, CCV, MS, MSD, LCS, LCSD
	Restek/30042	Gases	2,000	50		50		
	Restek/30006	Ketones	5,000	50		125		
	Restek/30465	Oxygenates	2,000	50		50		
IS/SS	Restek/30241	IS	2,500	1,000	MeOH	250	10.00	All Samples & Standards
	Restek/30004	SS	2,500	1,000	8.0	250		
SCV-PDS	AccuStandard/ M-502B-10X	Gases	2000	50	MeOH 1.725	50	2.00	SCV
	AccuStandard/ M-502A-R-10X	Liquids	2000	50		50		
	Accustandard CLP-22K-10X	Ketones	2000	125		125		
	Accustandard OGAD-001	Oxygenates	2000	50		50		

Note: tert-Butyl alcohol is 5x, ketones are 2.5x and m+p-Xylene is 2x the concentration stated in all preparations.

Table 4. Example Preparation of PDS, IS/SS, SCV-PDS methanol standards for Analyses of Soil/Solids

PDS Name	SSS Mix Used				Solvent	PDS description		
	Source/catalog#	Analytes	Conc. µg/mL	Volume µL	Volume mL	Conc. µg/mL	Final Volume mL	Application
PDS 50	Restek/30633	Mega Mix	2,000	50	MeOH 1.8	50	2.00	ICS, CCV, MS, MSD, LCS, LCSD
	Restek/30042	Gases	2,000	50		50		
	Restek/30006	Ketones	5,000	50		125		
	Restek/30465	Oxygenates	2,000	50		50		
PDS 5	PDS 50	All above.	50	200	MeOH 1.8	5	2.00	CAL/MRL
IS/SS	Restek/30241	IS	2,500	500	MeOH	125	10.00	All Samples & Standards
	Restek/30004	SS	2,500	500	8.0	125		
SCV-PDS	AccuStandard/ M-502B-10X	Gases	2000	50	MeOH 1.725	50	2.00	SCV
	AccuStandard/ M-502A-R-10X	Liquids	2000	50		50		
	Accustandard CLP-22K-10X	Ketones	2000	125		125		
	Accustandard OGAD-001	Oxygenates	2000	50		50		

Note: tert-Butyl alcohol is 5x, ketones are 2.5x and m+p-Xylene is 2x the concentration stated in all preparations.

Table 5. Example Preparation of Aqueous Working Standards in Edison

Working Standard Name	WS Conc. (µg/L) Analytes	Vol (µL)		Final Volume Water (mL)
		PDS	SCV-PDS	
Cal 1	2.0	2.0	-	50.00
Cal 2	5.0	5.0	-	50.00
Cal 3	10.0	10.0	-	50.00
Cal 4	20.0	20.0	-	50.00
Cal 5	50.0	50.0	-	50.00
Cal 6	80.0	80.0	-	50.00
Cal 7	100.0	100.0	-	50.00
CCV	20.	20.		50.00
SCV	50.	-	50	50.00
LCS	20.	20	-	50.00

Note: tert-Butyl alcohol is 5x, ketones are 2.5x and m+p-Xylene is 2x the concentration stated in all preparations.

Table 6. Example Preparation of Working Standards for Analyses of Low Level Soil/Solids

Working Standard Name	WS Conc. (µg/kg) Analytes	Vol (µL)			Mass Sand (g)	Vol 20% $NaHSO_4$ (mL)
		PDS-5	PDS-50	SCV-PDS		
Cal 1	5	5	-	-	5.0	5.0
Cal 2	10	10	-	-	5.0	5.0
Cal 3	20	20	-	-	5.0	5.0
Cal 4	50	-	5	-	5.0	5.0
Cal 5	80	-	8	-	5.0	5.0
Cal 6	100	-	10	-	5.0	5.0
Cal 7	150	-	15	-	5.0	5.0
CCV	50	-	5	-	5.0	5.0
SCV	50	-	-	5	5.0	5.0
LCS	50	-	5	-	5.0	5.0

Note: tert-Butyl alcohol is 5x, ketones are 2.5x and m+p-Xylene is 2x the concentration stated in all preparations.

Table 7. Example Preparation of Aqueous Working Standards for Analyses of High Level Soils

Working Standard Name	WS Conc. (µg/kg) Analytes	Vol (µL)		Final Volume Water (mL)
		PDS	SCV-PDS	
Cal 1	100.	2.0	-	50.00
Cal 2	250.	5.0	-	50.00
Cal 3	500.	10.0	-	50.00
Cal 4	1000	20.0	-	50.00
Cal 5	2500	50.0	-	50.00
Cal 6	4000	80.0	-	50.00
Cal 7	5000	100.0	-	50.00
CCV	1000	20.0	-	50.00
SCV	2500	-	50	50.00
LCS	1000	20.0		50.00

Note: tert-Butyl alcohol is 5x, ketones are 2.5x and m+p-Xylene is 2x the concentration stated in all preparations.

Table 8. Recommended VOC Sample Preservation Techniques and Holding Times taken from SW 846 Method 5035A and Chapter 4 Table 4-1

Sample Matrix	Preservative	Holding Time	Comment
Aqueous Samples No Residual Chlorine Present	Cool to 4 ± 2° C.≤ 6 °C	7 days	If MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples. If aromatic and biologically active compounds are analytes of interest, acid preservation is necessary and the holding time is extended to 14 days.
Aqueous Samples No Residual Chlorine Present	Cool to ≤ 6 °C and adjust pH to less than 2 with HCl or solid NaHSO4.	14 days[1]	Reactive compounds such as 2-chloroethylvinyl either readily break down under acidic conditions. If these types of compounds are analyst of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.
Aqueous Samples Residual Chlorine Present	Collect sample in a pre-preserved container containing either 25 mg ascorbic acid or 3 mg of sodium thiosulfate per 40-mL of chlorinated sample volume containing less than 5 mg/L of residual chlorine. Cool to ≤ 6 °C.	7 days	Samples containing greater than 5 mg/L of residual chlorine may require additional amounts of dechlorinating agents. If MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples. If aromatic and biologically active compounds are analytes of interest, acid preservation is necessary and the holding time is extended to 14 days.
Aqueous Samples Residual Chlorine Present	Collect sample in a pre-preserved container containing e 25 mg ascorbic acid per 40-mL of chlorinated sample volume containing less than 5 mg/L of residual chlorine. Cool to ≤ 6 °C and adjust pH to less than 2 with HCl	14 days[1]	Samples containing greater than 5 mg/L of residual chlorine may require additional amounts of dechlorinating agents. Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible. Caution: never add acid preservative directly to a dechlorinating agent prior to sample collection.
Solid Samples[2]	Sample is extruded into an empty sealed vial and frozen on-site to < -7° C.	14 days[1]	Sample vials should not be frozen below -20° C due to potential problems with vial seals and the loss of constituents upon sample thawing.
Solid Samples[2]	Sample is extruded into an empty sealed vial and cooled to ≤ 6 °C for no more than 48 hours then frozen to < -7° C upon laboratory receipt.	14 days[1]	Analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48 hour period. Sample vials should not be frozen below -20° C due to potential problems with vial seals and the loss of constituents upon sample thawing.
	Sample is extruded into an empty sealed vial and cooled to ≤ 6 °C for no more than 48 hours then preserved with methanol upon laboratory receipt.	14 days[1]	Analysis must be completed within 48 hours if samples are not preserved with methanol prior to the expiration of the 48 hour period.

Sample Matrix	Preservative	Holding Time	Comment
Solid Samples[2]	Sample is extruded into an empty sealed vial and cooled to ≤ 6 °C.	48 hours	
	Cool to ≤ 6 °C the coring tool used as a transport device.	48 hours	The holding time may be extended to 14 days if the sample is extruded to a sealed vial and either frozen to < -7° C or chemically preserved. Coring tools should not be frozen below -20° C due to the potential problems with tool seals and the loss of constituents upon sample thawing.
	Freeze to < -7° C the coring tool used as a transport device	48 hours	The holding time may be extended to 14 days if the sample is extruded to a sealed vial and either frozen to < -7° C or chemically preserved. Coring tools should not be frozen below -20° C due to the potential problems with tool seals and the loss of constituents upon sample thawing.
Solid Samples[2]	Sample is extruded into a vial containing reagent water and frozen on-site to < -7° C.	14 days[1]	Sample vials should not be frozen below -20° C due to potential problems with vial seals and the loss of constituents upon sample thawing.
	Sample is extruded into a vial containing reagent water and cooled to ≤ 6 °C for 48 hours or less then frozen to < -7° C upon laboratory receipt.	14 days[1]	Analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48 hour period. Sample vials should not be frozen below -20° C due to potential problems with vial seals and the loss of constituents upon sample thawing.
Solid Samples[2]	Sample is extruded into a vial containing reagent water and 1 g $NaHSO_4$ and cooled to ≤ 6 °C.	14 days[1]	Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.
	Sample is extruded into a vial containing methanol and cooled to ≤ 6 °C.	14 days[1]	Additional methanol extract storage time beyond 14 days may be acceptable if the desired VOC constituent stability can be demonstrated from appropriate performance data.

Notes:

1 A longer holding time may be appropriate if it can be demonstrated that the reported VOC concentrations are not adversely affected from preservation, storage and analyses performed outside the recommended holding times.

2 For biologically active soils, immediate chemical or freezing preservation is necessary due to the rapid loss of BTEX compounds within the first 48 hours of sample collection.

Table 9. BFB Relative Abundance Suggested Criteria

* BFB Relative Abundance Criteria	
m/z	**Relative Abundance Criteria**
95	50 to 200% of mass 174
96	5 to 9% of 95 with Helium carrier gas
173	<2% of 174
174	50-200% or mass of 95
175	5 to 9% of 174
176	95 to 105% of m/z 174
177	5 to 10% of m/z 176

Note: * Criteria based on EPA Method 524.4 (Reference 17), with modified m/z 95 and m/z 174 abundance criteria.

Table 10. Example Relative Response Factor Criteria for Initial and Continuing Calibration Verification

Compounds	Minimum Response Factor	Compounds	Minimum Response Factor
Dichlorodifluoromethane	0.100	1,2-Dichloropropane	0.100
Chloromethane	0.100	Bromodichloromethane	0.200
Vinyl Chloride	0.100	Cis-1,3-Dichloropropene	0.200
Bromomethane	0.100	Trans-1,3-Dichloropropene	0.100
Chloroethane	0.100	4-Methyl-2-pentanone	0.100
Trichlorofluoromethane	0.100	Toluene	0.400
1,1-Dichloroethene	0.100	1,1,2-Trichloroethane	0.100
1,1,2-Trichloro-1,2,2-trifluroethane	0.100	Tetrachloroethane	0.200
Acetone	0.010	2-Hexanone	0.100
Carbon disulfide	0.100	Dibromochloromethane	0.100
Methyl Acetate	0.100	1,2-Dibromoethane	0.100
Methylene chloride	0.100	Chlorobenzene	0.500
Trans-1,2-Dichloroethene	0.100	Ethylbenzene	0.100
Cis-1,2-Dichloroethene	0.100	Meta-/para-Xylene	0.100
Methyl tert-Butyl Ether	0.100	Ortho-Xylene	0.300
1,1-Dichloroethane	0.200	Styrene	0.300
2-Butanone	0.01	Bromoform	0.100
Chloroform	0.200	Isopropylbenzene	0.100
1,1,1-Trichloroethane	0.100	1,1,2,2-Tetrachloroethane	0.300
Cyclohexane	0.100	1,3-Dichlorobenzene	0.600
Carbon tetrachloride	0.100	1,4-Dichlorobenzene	0.500
Benzene	0.500	1,2-Dichlorobenzene	0.400
1,2-Dichloroethane	0.100	1,2-Dibromo-3-chloropropane	0.050
Trichloroethene	0.200	1,2,4-Trichlorobenzene	0.200
Methylcyclohexane	0.100		

Table 11. Example EPA Method 8260D Analysis Sequence with QC and Instrument Calibration Frequency and Acceptance Criteria

Analysis #	Sample Name	QC and Instrument Calibration Acceptance Criteria	QC and Instrument Calibration Frequency
1	BFB	1. BFB see Section 17 Table 9	Required prior to instrument calibration only
2	Cal 1	1. Instrument Calibration must have %RSD ≤ 20%. If greater than 10% of analytes cannot meet the RSD or regression curve criteria (RSD < 20% or r^2 > 0.99), then instrument is out of control, and needs maintenance and recalibration. 2. Should meet 8260D recommended minimum RRF or be able to see standard at the reporting limit. 3. Must have relative retention time ± 017 RRT or ± 10 seconds	Calibration analyzed anytime CCV fails criteria and no obvious instrument problems can be found.
3	Cal 2		
4	Cal 3		
5	Cal 4		
6	Cal 5		
7	Cal 6		
8	Cal 7		
9	MB	Must be free from contamination that could prevent determination of target analytes at the RL. Must be < ½ the Project RL or < ½the LOQ,	Find problem and reanalyze all associated samples and QC.
10	SCV	1. Determination of target analytes 2. Concentration of target analytes must be within +/- 30% of true value. 3. IS Response 50 – 200% of Cal 3 or Cal midpoint 4. IS RT's ± 30 seconds	Analyzed immediately only after Cal curve
11		Jump to 13 after SCV.	SCV injection starts 12-hour clock
12	CCV	1. Percent Deviation of Target Analytes ± 20% 2. SS Percent Recovery--meet in-house limits. 3. Should meet 8260D recommended minimum RRF or evaluate to determine if the reporting limit can be achieved. 4. 3. IS Response 50 – 200% of o Cal midpoint 5. IS RT is within 30 seconds of calibration midpoint.	1. Analyzed initially with each batch of 20 samples within 12-hour work shift
13	MB	1. Same as Above	1. Same as above
14	MB Methanol	1. Same as Above	1. Same as Above
15	LCS/LCSD	1. Percent Recovery of Target analytes--meet in-house limits or data flagged. 2. SS Percent Recovery --meet in-house limits or data flagged. 3. IS Response 50 - +200% of CCV 4. RPD must meet in house limits	1. LCS is analyzed with each batch of 20 within a 12-hour work shift 2. LCSD analyzed only if no MS/MSD is in batch.
16	Sample 1	1. IS/SS see at the bottom of this table	
17	MS	1. Percent Recovery of Target Analytes--meet in-house limits or data flagged 2. SS Percent Recovery--meet in-house limits or data flagged 3. IS Response 50 - +200% of CCV	1. Analyzed with each batch of 20 within a 12-hour work shift
18	MSD	1 - 3 same as above %RSD (section 12) --meet in-house limits or data flagged	1. Analyzed with each batch of 20 within a 12-hour work shift
19	Samples 2-20	See statements below for IS and SS.	Reanalyze at a dilution until recoveries meet acceptance criteria.
Internal Standard (IS) and Surrogate Standard (SS) in all samples and QCs must meet the following acceptance criteria: 1 IS Response 50 - 200 % of the midpoint of the most recent calibration or the daily CCV. 2 SS must meet in-house limits or data flagged			

Table 12. Example Purge and Trap-GC/MS Settings for EPA Method 8260D

GC/MS Settings for EPA Method 8260				
OI 4100 Autosampler			OI 4760 Eclipse Purge and Trap	
	Water Only	Soil Only	Trap:	10
Needle Rinses	1	1	Sparge Mount	40
SAMA (ul)	2	0	Sample (purge):	35
SAMB (ul)	0	2	Sample (bake)	40
SAMC (ul)	0	0	Prepurge Time	Off
SAMD (ul)	0	0	Preheat Time	Off
Purge Time	11	11	Purge Time:	11
Desorb Time	0.7	0.7	Dry Purge	Off
P & T Rinses	1	1	Trap Temp	20
Rinse Water	Hot	Hot	Water Mgmt Temps:	
WSettle Time	5sec			
W Stir Time		0	Purge	120
Soil Preheat Stir	na	yes	Desorb	0
Soil PreheatTime	na	0.5min	Bake	240
Soil PH/PG Temp	na	40	Bake Time	4
Soil Stir	na	yes	Bake Temp	210
Lop Size	10	10	Desorb Time	0.7
GC ReadyPol.	Inverted	Inverted	Desorb Temp	190
			Desorb Preheat Temp	180
			Transfer Line Temp	140
			Valve Oven Temp	140
			Sparger	25ml
			Options	
			Drain on Start Up	On
			Purge on Bake	On
			Drain After Abort	On
			Sample Introduction	4100
			GC Ready	Normal
			SAMLV20 Pressure	8
GC Inlet			Column	
Front Inlet			Column 1	
Mode:		Split 75:1	Capillary Column	
Initial Temp:		185°C	Model Number:	RTX-Volatiles
Pressure:		7.91 psi	Max Temp:	280 °C
Total flow:		78.6 mL/min	Nominal Length:	30 m
Gas Type:		He	Nominal diameter:	0. mm
			Nominal film thickness:	1.0 µm
			Initial flow:	1.0 mL/min
			Mode:	Constant flow
			Inlet:	Front Inlet
			Outlet:	MSD
			Outlet pressure:	Vacuum

GC/MS Settings for EPA Method 8260				
GC Oven				
Oven:		Ramps:		
Initial Temp:	50°C	#Rate	Final Temp	Final Time
Initial Time:	0 min	1. 10°C/min	100°C	1.0 min
Maximum Temp:	280°C	2. 40°C/min	220°C	5.0 min
Equilibration Time:	0.5 min	Run Time:	14.00 min	
		Aux Temp:	230°C	
Mass Spectrometer				
Tune File:	bfb.u	scan rate:	3	
Acquisition Mode:	Scan			
MS Method:	8260 2019.M	MS Zone		
		MS Quad:		150°C
Scan Parameters		MS Source (detector):		250°C
Low Mass:	35	Transfer Line		230°C
High Mass:	270	Solvent delay:		0.5 min

Table 13. Example Quantitation Ions and Qualifiers

Analyte	RT (min)	Quant Ion	Q1	Q2	Q3
Fluorobenzene IS	3.99	96	77	/	/
Dichlorodifluoromethane	0.90	85	87	/	/
Chloromethane	0.98	50	52	/	/
Vinyl Chloride	1.02	62	64	/	/
Bromomethane	1.16	94	96	/	/
Chloroethane	1.22	64	66	/	/
Trichlorofluoromethane	1.28	101	103	/	/
1,1-Dichloroethene	1.51	96	61	63	/
Acetone	1.83	58	43	/	/
Iodomethane	1.59	142	127	/	/
Carbon Disulfide	1.54	76	78	/	/
Methylene Chloride	1.80	84	86	49	/
Methyl tert-Butyl Ether	1.84	73	41	57	43
trans-1,2-Dichloroethene	1.89	96	61	98	/
Di isopropyl ether	1.95	45	43	87	59
1,1-Dichloroethane	2.27	63	65	83	/
cis-1,2-Dichloroethene	2.67	96	61	98	/
2,2-Dichloropropane	2.76	77	97	/	/
2-Butanone	3.20	72	43	/	/
Ethyl tert Butyl Ether	3.25	59	87	57	41
Bromochloromethane	2.83	128	130	50	/
Chloroform	2.90	83	85	/	/
1,1,1-Trichloroethane	3.09	97	99	61	/
Tert Amyl methyl ether	3.13	73	55	43	87
1,1-Dichloropropene	3.22	75	110	77	/
Carbon Tetrachloride	3.02	117	119	121	/
1,2-Dichloroethane-*d*4	3.63	65	102	/	/
Benzene	3.48	78	/	/	/
1,2-Dichloroethane	3.72	62	98	/	/
Chlorobenzene-d_5 IS	7.27	117	/	/	/
Trichloroethene	4.21	95	97	130	132
1,2-Dichloropropane	4.84	63	65	112	/
Dibromomethane	4.72	93	95	174	/
Bromodichloromethane	4.93	83	85	127	/
cis-1,3-Dichloropropene	5.63	75	77	39	/
4-Methyl-2-pentanone	6.29	43	58	85	100
Toluene-d_8	5.82	98	/	/	/
trans-1,3-Dichloropropene	6.31	75	77	39	/

Analyte	RT (min)	Quant Ion	Q1	Q2	Q3
1,1,2-Trichloroethane	6.46	83	97	85	/
Tetrachloroethene	6.25	164	129	131	166
1,3-Dichloropropane	6.71	76	78	/	/
2-Hexanone	7.08	43	58	57	100
Dibromochloromethane	6.61	129	127	/	/
1,2-Dibromoethane	6.81	107	109	188	/
Chlorobenzene	7.29	112	77	114	/
1,1,1,2-Tetrachloroethane	7.32	131	133	119	/
Ethylbenzene	7.33	91	106	/	/
m,p-Xylene	7.43	106	91	/	/
o-Xylene	7.71	106	91	/	/
1,4-Dichlorobenzene-*d*4 IS	8.69	152	115	150	/
Styrene	7.75	104	78	103	/
Bromoform	7.75	173	175	254	/
Isopropylbenzene	7.92	105	120	77	/
BFB	8.07	95	174	176	/
n-Propylbenzene	8.16	91	120	/	/
Bromobenzene	8.13	156	77	158	/
1,1,2,2-Tetrachloroethane	8.21	83	131	85	/
1,2,3-Trichloropropane	8.27	75	77	/	/
2-Chlorotoluene	8.24	91	126	/	/
4-Chlorotoluene	8.34	91	126	/	/
1,3,5-Trimethylbenzene	8.28	105	120	/	/
tert-Butylbenzene	8.64	119	91	134	/
1,2,4-Trimethylbenzene	8.49	105	120	/	/
sec-Butylbenzene	8.54	105	134	/	/
1,3-Dichlorobenzene	8.65	146	111	148	/
4-Isopropyltoluene	8.62	119	134	91	/
1,4-Dichlorobenzene	8.69	146	111	148	/
1,2-Dichlorobenzene	8.9	146	111	148	/
n-Butylbenzene	8.83	91	92	134	/
1,2-Dibromo-3-Chloropropane	9.29	75	155	157	/
Hexachlorobutadiene	9.58	225	223	227	/
1,2,4-Trichlorobenzene	9.6	180	182	145	/
Naphthalene	9.74	128	/	/	/
1,2,3-Trichlorobenzene	9.83	180	182	145	/
Toluene	5.87	92	91	/	/

Table 14. 8260D Method Acceptance Criteria

Item	Measure	Action
Instrument Tune	Outside Acceptance Criteria	Re-tune.
	Repeated failure indicates a need for system maintenance.	Perform system maintenance and re-tune the instrument. No analyses should be performed until the system is tuned correctly. Tune with calibration only.
Internal Standard(s)--(IS)	50-200 % of the mid-point of the initial calibration standard or the daily CCV	If the nonconformance is on a calibration or QC sample, evaluate the system (repair) and reanalyze. Remake the standard if an error is suspected.
		If the nonconformance is on a field sample, reanalyze. If the reanalysis is within limits, report the results within limits. If the reanalysis is outside limits, dilute and reanalyze. Report the diluted results.
Response Factor(s)	≥ 0.01 for problem analytes such as ketones, and ≥ 0.05 for all other target analytes.	If a response factor is below acceptance criteria, then the system must be evaluated to make sure the analyte can be seen at the reporting limit. Recalibrate and reanalyze affected samples.
Initial Calibration (ICAL)	Average Response Factor > 20.0 % RSD	Evaluate points in the curve for use of linear or quadratic regression (r2 must be ≥ 0.99). Also evaluate upper and lower points for removal. Criteria still not met, recalibrate if compound is an analyte of interest.
ICAL Low Point Eval	Not within ± 50 % of True Value	Recalibrate if % deviation or drift is not met and compound is an analyte of interest.on recalculation with new curve
All ICAl points except low point	Not within +/- 30% of true value	Recalibrate if % deviation or drift is not met and compound is an analyte of interest.on recalculation with new curve
Second Source Calibration Verification (SCV)	Not within ± 30% of true value for deviation or drift	Recalibrate if % deviation or drift is not met and the compound is an analyte of interest.
Continuing Calibration Verification (CCV)	Not within ± 20 % of True Value	Evaluate the system for problems, correct method or standard, perform routine maintenance, etc. Reanalyze standard and if failure repeats, then analyze a new ICAL
Method Blank	Analyte concentration must be <1/2 the reporting limit for the project or <1/2 the LLOQ.	If the associated samples are non detect, no action is required. If the analyte(s) is detected in the sample, flag with a "b" or reanalyze. If the analyte level in the sample is 10 times or greater than the blank contamination, the results are not affected. Locate the source of the contamination.
Laboratory Control Spike (LCS)	% Recovery. Laboratory acceptance criteria are evaluated every six months. Acceptable values are stored in LIMS.	If the LCS % Recovery is high and the sample is non detect, no action is required. If the LCS is high and the sample has detects, renalyze the sample. If the LCS is low, the sample(s) should be reanalyzed.
Laboratory Control Spike Duplicate (LCSD)	Same criteria as the LCS with the addition of RPD. RPD acceptance criteria is evaluated every six months with values stored in LIMS.	% Recovery same as the LCS. If the RPD value is above the acceptance criteria in LIMS, then evaluate the system for possible problems. Reanalyze samples as necessary.
Matrix Spike(MS)	% Recovery. Laboratory acceptance criteria are evaluated every six months. Acceptable values are stored in LIMS.	If the % Recovery is outside laboratory acceptance criteria, evaluate the LCS. If the LCS is in control, then there is a possible matrix effect. The sample should be flagged appropriately.
Matrix Spike Duplicate (MSD)	Same criteria as the MS with the addition of RPD. Acceptance criteria are evaluated every six months with values stored in LIMS.	% Recovery same as the MS. If the RPD value is above the acceptance criteria in LIMS, then evaluate the system for possible problems. Reanalyze the MS/MSD samples if possible or flag the results.
Surrogate(s)	% Recovery. Laboratory acceptance criteria are evaluated every six months. Acceptable values are stored in LIMS.	If the % Recovery is outside laboratory acceptance criteria on a QC sample, evaluate the system. Surrogate recalibration may be necessary. Reanalyze the QC samples.
		If the % Recovery is on a client sample, reanalyze. If the % Recovery is within criteria, report the sample within limits. If the % Recovery outside criteria is confirmed, there is a matrix effect. Flag the results as estimated and report both results.

Figure 1. 50 µg/L 8260D Total Ion Chromatogram

```
File       :C:\MSDChem\1\DATA\073009\073009004.D
Operator   : AG
Acquired   : 30 Jul 2009  12:13 pm using AcqMethod 8260B2.M
Instrument :   APL01B
Sample Name: VSTD025
Misc Info  :
Vial Number: 4
```

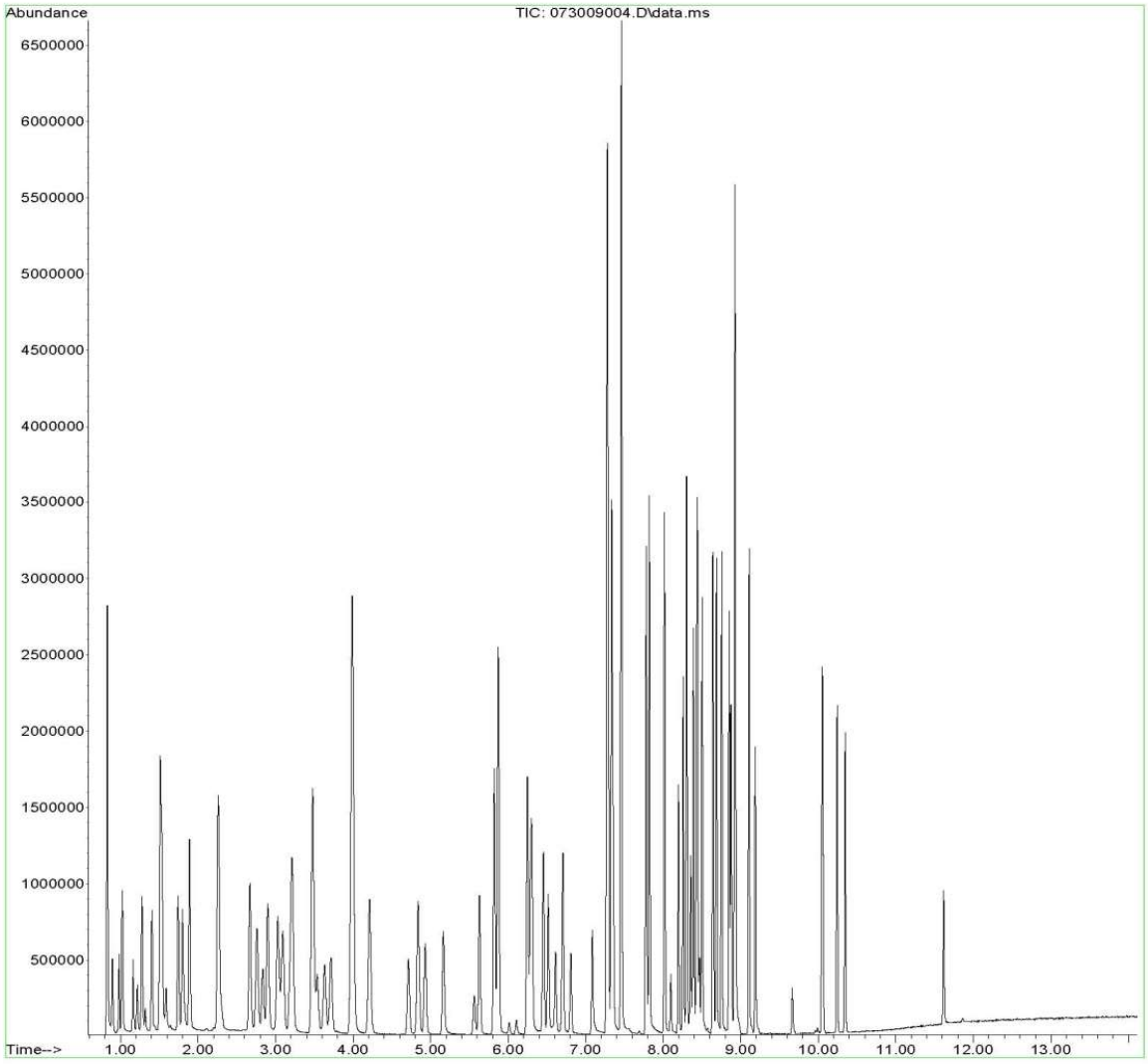

Figure 2. Example GC/MS Data Review Form

PHILIS Program

CSS

DATA REVIEW FORM – GC/MS

Instrument and Date: _____ **Sequence #:** _____

Analysis: *(Select One)* ☐ Semivolatiles ☐ Volatiles ☐ Other _____

	Yes	No	Peer Rvw	QA Rvw	Comments
Analyst Report					
PHILIS narrative is complete	☐	☐	☐	☐	
Reported data matches the raw data	☐	☐	☐	☐	
Reporting limits and qualifiers are correct	☐	☐	☐	☐	
Sample Receiving					
Samples received in acceptable condition and compliant with COC	☐	☐	☐	☐	
Samples properly preserved	☐	☐	☐	☐	
Sample receipt checklist filled out	☐	☐	☐	☐	
Instrument Tune and Calibration					
Instrument met tuning criteria, where required, and analyses were completed within the 12 hour clock	☐	☐	☐	☐	
ICAL average response factor % RSD is <20 or applied curve fit meets criteria	☐	☐	☐	☐	
The ICAL has an adequate number of points	☐	☐	☐	☐	
Response factors meet minimum criteria for ICAL and CCV	☐	☐	☐	☐	
ICAL low point is within 50% of known value and the mid-point is within 30% of the known value or SOP listed levels	☐	☐	☐	☐	
SCV is within 30 % of true values for deviation or drift	☐	☐	☐	☐	
CCV compounds meet acceptance criteria	☐	☐	☐	☐	
Method Blank					
Analytes detected at or above their reporting limits are flagged	☐	☐	☐	☐	
Samples					
Samples prepared and extracts analyzed within holding time limits	☐	☐	☐	☐	
Target compound report included and chromatograms provided	☐	☐	☐	☐	
Manual integration/Q-Deletion is initialed and dated by analyst and reviewer on ion profiles	☐	☐	☐	☐	
All target quantitation ion integrations and spectral identifications are included	☐	☐	☐	☐	
Calculations have been verified—see calculations sheet.	☐	☐	☐	☐	
Internal standard summary					
Is area between 50%-200% of the ICAL midpoint or daily CCV	☐	☐	☐	☐	
Retention times are within 0.5 minutes of the midpoint of the ICAL	☐	☐	☐	☐	
Surrogate recovery report					
Surrogate recovery meets acceptance criteria	☐	☐	☐	☐	
Sample results are properly flagged	☐	☐	☐	☐	
Preparation batch summary					
All samples are accounted for	☐	☐	☐	☐	
Results reflect sample mass/volume prepared	☐	☐	☐	☐	
Solid results are provided dry weight basis	☐	☐	☐	☐	
Matrix spike/matrix spike duplicate					
MS/MSD percent recoveries are within limits	☐	☐	☐	☐	
Relative percent differences are within limits	☐	☐	☐	☐	
Sample results been flagged appropriately	☐	☐	☐	☐	
Laboratory control spike/laboratory control spike duplicate					
LCS/LCSD recoveries are within limits	☐	☐	☐	☐	
Relative percent differences are within limits	☐	☐	☐	☐	
Have sample results been flagged appropriately	☐	☐	☐	☐	

Analyst review signature Date | Peer review signature Date | QA review signature Date

PHILIS2 Form ID#: QA-017 / Release Date: 09/18/2023

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APPENDIX D -
PHILIS SOP L-A-601
Air Analysis by TO-17 Rev. 2 09/07/2023

STANDARD OPERATING PROCEDURE

FOR

AIR ANALYSIS BY TO-17

PHILIS SOP L-A-601 Rev. 2

Revision Date: 09-07-2023

EPA Contract No. 68HERH21D0002

PREPARED BY

PHILIS

PREPARED FOR

U.S. Environmental Protection Agency
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Approvals:

PHILIS, Castle Rock Lead Chemist	**September 7, 2023** **Date**
PHILIS, Edison Lead Chemist	**September 7, 2023** **Date**
PHILIS, Quality Assurance Manager	**September 7, 2023** **Date**
PHILIS, Program Manager	**September 7, 2023** **Date**

Revision History

Revision	Name	Date	Description of Change
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0	Sang Chung Kevin Makuskie	05/17/2021	Program Issue
1	James Travis	06/09/2022	Revision
2	James Travis Sang Chung	08/11/2023	Annual Review

SOP REVISION FORM

SOP Name:	**Air Analysis by TO-17**		
Purpose: *(Review or Revise)*	*SOP #:*	*Rev. #:* *(Being Reviewed or Revised)*	*Origination / Release Date:*
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For *Revision* : Summary of Revisions (specify sections)

Title Page	Changed Project Manager to Program Manager
Document	Changed from NELAP to EPA format

For *Review*: Comments

Standard Operating Procedure
Air Analysis by TO-17
L-A-601 Rev. 2

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Standard Operating Procedure
Air Analysis by TO-17
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1.0 Scope and Application

1.1 This standard operating procedure (SOP) documents PHILIS application of EPA TO-17, dated January 1999 "Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling On Sorbent Tubes", that will be used in the PHILIS Mobile Labs.

1.2 This SOP is executed in accordance with the U.S. Environmental Protection Agency and National Environmental Laboratory Accreditation Program (NELAP).

1.3 Referenced method reporting limit is 0.5 ppb when using 1.0 liter of sample, however reporting limits may vary depending on compound performance. Referenced method reporting limit is 0.5 ppb when using 1.0 liter of sample, however reporting limits may vary depending on compound performance.

1.4 PHILIS utilizes this method for the determination of subsets of the analytes listed in Table 1 in air & emissions. Not all analytes listed in Table 1 have been monitored by the use of solid sorbents. This method provides performance criteria to demonstrate acceptable performance of the method (or modifications of the method) for monitoring a given compound or set of compounds. Startup data was generated using the Markes Ultra and Unity system and Instrument APL01A in Edison using Universal Absorbent tubes (packed with Tenax TA 35/60, Carbograph 1TD 40/60, and Carboxen 1003 40/60) on a specific subset of compounds.

1.5 This SOP is applied for volatile organic analytes from air & emissions matrices except where a specific Quality Assurance Project Plan's (QAPP) override this method's quality assurance plan.

1.6 Atmospheric Pollutants not Suitable for Analysis by this Method

1.6.1 Inorganic gases not suitable for analysis by this method are oxides of carbon, nitrogen and sulfur, O3 and other permanent gases. Exceptions include C2S and N2O.

1.6.2 Other pollutants not suitable are particulate pollutants, (i.e., fumes, aerosols and dusts) and compounds too labile (reactive) for conventional GC analysis.

2.0 Summary of Method

2.1 The monitoring procedure involves transferring or direct collection a known volume of air onto a sorbent packed tube, thermal desorption onto a cold trap followed by desorption of the cold trap into a GC/MS for analysis. Samples can be collected directly on the tube with the use of a calibrated pump, collected in a Tedlar bag, Summa canister, or mini can. Summa canisters and MiniCans are received at pressures of less than one atmosphere and must be diluted to a positive pressure with moisturized zero air prior for syringe extraction of a measured aliquot of sample through a septa port. Transfer of samples via syringe is accomplished by injection onto the tube followed by running nitrogen through the tube on a special loading rig.

2.2 Regardless of the collection method, key steps of this method are listed below.

2.2.1 Selection of a sorbent or sorbent mix tailored for a target compound list, data quality objectives and sampling environment.

2.2.2 Screening the sampling location for VOCs by taking single tube samples to allow estimates of the nature and amount of sample gases.

2.2.3 Initial sampling sequences with two tubes at 1 and 4 liter nominal sample volumes or appropriate proportional scaling of these volumes to fit the target list and monitoring objectives.

2.2.4 Analysis of the samples and comparison to performance criteria.

2.2.5 Acceptance or rejection of the data.

2.2.6 If rejection, then review of the experimental design and repeat analysis or repeat analysis.

2.3 Key steps in sample analysis are listed below.

2.3.1 Dry purge of the sorbent tube with dry, inert gas before analysis to remove water vapor and air. The sorbent tube can be held at temperatures above ambient for the dry purge.

2.3.2 Thermal desorption of the sorbent tube (primary desorption).

2.3.3 Analyte refocusing on a secondary trap.

2.3.4 Rapid desorption of the trap and injection/transfer of target analytes into the gas chromatograph (secondary desorption).

2.3.5 Separation of compounds by high resolution capillary gas chromatography (GC).

2.3.6 Quantitation by mass spectrometry (MS) or conventional GC detectors (only the MS approach is explicitly referred to in Compendium Method TO-17).

3.0 Definitions

3.1 Batch‡: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A Preparation Batch is composed of between 1 and 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and the last sample in the batch to be 24hours. An Analytical Batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

All batches require one MB, LCS, and MS/MSD pair or MS and Sample Duplicate when possible.

3.2 BFB: 4-bromofluorobenzene or a solution that contains the analyte, 4-bromofluorobenzene, which is used to evaluate the tuning and the performance of the mass spectrometer. The BFB tune is analyzed at the beginning of each 12-hour period during which samples or calibration standards are analyzed.

3.3 Breakthrough Volume (BV): Volume of air containing a constant concentration of analyte which may be passed through a sorbent tube before a detectable level (typically 5%) of the analyte concentration elutes from the non-sampling end. Alternatively, the volume sampled when the amount of analyte collected in a back-up sorbent tube reaches a certain percentage (typically 5%) of the total amount collected by both sorbent tubes. These methods do not give identical results. For purposes in the document the former definition will be used.

3.4 Chain of Custody (COC) ‡: Record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers; the mode of collection; preservation; and requested analyses.

Each time the samples are transferred, the document should be signed by the person releasing the samples and by the person receiving the samples. A date and time must also be recorded.

3.5 Continuing Calibration Verification (CCV): A standard analyzed at the beginning of each analytical sequence that contains all method analytes at a concentration near the mid-range of the calibration curve. Each analyte must have a recovery within a percentage range specified in the method to validate that analyte in the calibration curve. A CCV is not required if a calibration curve is analyzed at the start of an analysis sequence. Some methods require additional CCV's. The CCV frequency will be stated in the method SOP.

3.6 Cryogen: (Also referred to as 'cryogenic fluid'). Typically liquid nitrogen, liquid argon, or liquid carbon dioxide. In the present context, cryogens are used in some thermal desorption systems to cool the focusing tube. The Markes Unity System utilizes a Peltier cooler.

3.7 Duplicates (Field): Identical samples collected at the same time, in the same way, and contained, preserved, and transported in the same manner to determine the reproducibility of the sampling.

3.8 Field Blank: A TD tube of the same tube type and from the same conditioning batch as sample tubes. This tube remains capped with brass Swagelok caps and is carried into the field by sampling team and is stored in the same containment vessel as the sample tube.

3.9 Focusing Tube: Narrow (typically <3mm I.D.) tube containing a small bed of sorbent, which is maintained near or below ambient temperature and used to refocus analytes thermally desorbed from the sorbent tube. Once all the VOCs have been transferred from the sorbent tube to the focusing tube, the focusing tube is heated very rapidly to transfer the analytes into the capillary GC analytical column in a narrow band of vapor.

3.10 High Resolution Capillary Column Chromatography: Conventionally describes fused silica capillary columns with an internal diameter of 320 μm or below and with a stationary phase film thickness of 5 μm or less.

3.11 Holding Time: The maximum amount of time permitted between sampling and sample preparation and/or sample preparation and sample analysis. Also the period of time a sample may be stored prior to analysis when there is no preparation step. See the specific method or SW846 8000B table 4.1.

3.12 Instrument Calibration Standards (ICS): A solution prepared from the primary dilution standard solution or stock standard solutions, internal standards and surrogate analytes. The ICS solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 Internal Standards (IS)[‡]: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

3.14 Laboratory Control Sample (LCS)‡: (however named, such as laboratory fortified blank, blank spike (BS), or QC check sample). A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

The standard source can be the same as the calibration or a second source. The LCS is analyzed exactly like a sample to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.15 Laboratory Duplicate (LD): Two sample aliquots taken in the laboratory and analyzed separately with identical procedures. Analyses of the aliquots indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.16 LIMS: Acronym for the Laboratory Information Management System. PHILIS utilizes Promium Element, LIMS software. This system is used to receive, track, and report sample results.

3.17 Method Blank (MB): A TD tube of the same tube type and from the same conditioning batch as sample tubes. This tube retained by the lab and taken out of containment just prior to analysis.

3.18 Method Detection Limit (MDL): The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined by analyzing seven or more replicates of a spiked analyte free matrix and the resulting statistical calculation, in accordance with 40 CFR 136, Appendix B, Revision 2.

3.19 MS-SCAN: Mode of operation of a GC mass spectrometer detector such that all mass ions over a given mass range are swept over a given period of time.

3.20 MS-SIM: Mode of operation of a GC mass spectrometer detector such that only a single mass ion or a selected number of discrete mass ions are monitored.

3.21 Primary Dilution Standard (PDS): A solution of one or several analytes prepared in the laboratory from SSS and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.22 Reporting Limit (RL): The reporting limit, also known as the LOQ is the minimum concentration that can be reported as a quantitated value for a target analyte in a sample. This value can be no lower than the concentration of the lowest calibration standard.

3.23 Retention Volume (RV): The volume of carrier gas required to move an analyte vapor plug through the short packed column which is the sorbent tube. The volume is determined by measuring the carrier gas volume necessary to elute the vapor plug through the tube, normally measured at the peak response as the plug exits the tube.

3.24 Safe Sampling Volume (SSV): Calculated by halving the retention volume (indirect method) or taking two-thirds of the breakthrough volume (direct method), although these two approaches do not necessarily give identical results. The latter definition is used in this document.

Safe Sampling volume will be determined on a project-specific basis and specified in the QAPP. This information is confirmed with the sampling team prior to the sampling event.

3.25 Sample Custodian: The person assigned to be responsible for receiving samples in compliance with all standard procedures. This individual must be trained in entry of data into Promium Element and know all the functions and checks for sample receiving.

3.26 Sample Delivery Group (SDG): A unit within a single project that is used to identify a group of samples for delivery to the laboratory for chemical analysis. An SDG is a group of 20 or fewer field samples within a project, received over a period of up to 14 calendar days (depending on turnaround time requirements). Data from all samples in an SDG are due concurrently.

3.27 Second Source Calibration Verification (SCV): A solution prepared from a source that is different from the calibration standards. The SCV is immediately following the ICS, and is used to verify calibration standard accuracy.

3.28 Selected Ion Monitoring: A mass spectrometry technique that provides lower detection level capability by monitoring fewer mass scans for longer periods of time that is done in full-scan methods.

3.29 Sorbent Strength: Term used to describe the affinity of sorbents for VOC analytes. A stronger sorbent is one which offers greater safe sampling volumes for most/all VOC analytes relative to another, weaker sorbent. Generally speaking, sorbent strength is related to surface area, though there are exceptions to this. The SSVs of most, if not all, VOCs will be greater on a sorbent with surface area “10n” than on one with a surface area of ?n”. As a general rule, sorbents are described as “weak” if their surface area is less than 50 m2g-1 (includes Tenax®, Carbopack™/trap C, and Anasorb® GCB2), “medium strength” if the surface area is in the range 100-500 m2g-1 (includes Carbopack™/trap B, Anasorb® GCBI and all the Porapaks and Chromosorbs listed in EPA Method TO-17 and “strong” if the surface area is around 1000 m2g-1 (includes Spherocarb®, Carbosieve™ S-III, Carboxen™ 1000, and Anasorb® CMS series sorbents.)

3.30 Sorbent Tube: (Also referred to as 'tube' and 'sample tube') Stainless steel, glass or glass lined (or fused silica lined) stainless steel tube, typically 1/4 inch (6 mm) O.D. and of various lengths, with the central portion packed with greater than 200 mg of solid adsorbent material, depending on density and packing bed length. Used to concentrate VOCs from air.

3.31 Standard Sorbent (Sample) Tube: Stainless steel, glass or glass lined (or fused silica lined) stainless steel tube, 1/4 inch (6 mm) O.D. and of various lengths, with the central portion packed with 200 mg of solid adsorbent material depending on sorbent density. Tubes should be individually numbered and show the direction of flow.

3.32 Stock Standard Solution (SSS): A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased as certified from a reputable commercial source.

3.33 Temperature Blank: An aliquot of water placed in the sample cooler to aid in determining the temperature of samples at receipt.

3.34 Thermal Desorption: The use of heat and a flow of inert (carrier) gas to extract volatiles from a solid or liquid matrix directly into the carrier gas and transfer them to downstream system elements such as the analytical column of a GC. No solvent is required.

3.35 Time Weighted Average (TWA) Monitoring: If air is sampled over a fixed time period - typically 1, 3, 8, or 24 hours, the time weighted average atmospheric concentration over the monitoring period may be calculated from the total mass of analyte retained and the specific air volume sampled. Constraints on breakthrough volumes make certain combinations of sampling time and flow rates mutually exclusive.

3.36 Total Ion Chromatogram (TIC): Chromatogram produced from a mass spectrometer detector operating in full scan mode.

3.37 Two-stage Thermal Desorption: The process of thermally desorbing analytes from a solid or liquid matrix, reconcentrating them on a focusing tube and then rapidly heating the tube to inject" the concentrated compounds into the GC system in a narrow band of vapor compatible with high resolution capillary gas chromatography.

ǂ EL-V1M2-ISO-2016, 2016 NELAP Standard definition.

4.0 Interferences

4.1 Minimizing Artifact Interference.

4.1.1 Stringent tube conditioning and careful tube capping and storage procedures are essential for minimizing artifacts. System and sorbent tube conditioning must be carried out using more stringent conditions of temperature, gas flow and time than those required for sample analysis.

4.1.2 Reduce artifacts to 10% or less of individual analyte masses retained during sampling. If this level of reduction is not possible then measure levels and document conditions.

4.1.3 Typical artifact levels for 1/4 inch O.D. tubes of 3.5" length range from 0.01 ng and 0.1 ng for carbonaceous sorbents and Tenax® respectively. These levels compare well with the masses of analytes collected, even from sub-ppb atmospheric concentrations. Artifact levels are typically around 10 ng for Chromosorb® Century series and other porous polymer sorbents. However, these types of sorbents can still be used for air monitoring at low ppb levels if selective or mass spectrometer detectors are used or if the blank profile of the tube demonstrates that none of the sorbent artifacts interfere analytically with the compounds of interest.

4.1.4 Some varieties of charcoal contain metals which will catalyze the degradation of certain organic analytes during thermal desorption at elevated temperatures thus producing additional artifacts and resulting in low analyte recoveries.

4.1.5 Artifacts can be formed from long-term storage of blank tubes. Literature reports of the levels of artifacts on (a) Carbotrap/pack™ C, Carbotrap/pack™ B and Carbosieve™ SIII multi-bed tubes and (b) Tenax® GR tubes, by workers sealing the tubes using metal Swagelok®-type caps and PTFE ferrules with multi-tube, glass storage jars are reported to be between 0.01 ng [after 1-2 months and 0.1 ng [after 6 months] for (a) and (b) respectively. Artifact levels reported for other porous polymers are higher; for example 5 ng for Chromosorb 106 after 1 week. More information is given in the Technical Assistance Document (TAD) referred to in EPA Method TO-17.

4.1.6 Artifacts can also be generated during sampling and sample storage. Benzaldehyde, phenol and acetophenone artifacts are reported to be formed via oxidation of the polymer Tenax® when sampling high concentration (100-500 ppb) ozone atmospheres. Tenax® should thus be used with an ozone scrubber when sampling low levels (<10 ppb) of these analytes in areas with appreciable ozone concentrations. Carbotrap™ type sorbents have not been reported to produce this level of artifact formation. Once retained on a sorbent tube, chemically stable VOCs, loaded in laboratory conditions, have been shown to give good recoveries, even under high ozone concentrations for storage of a year or more.

4.2 Minimizing Interference from water. There are three preferred approaches to reducing water interferences during air monitoring using sorbent tubes.

4.2.1 The first is to minimize water collection by selecting, where possible, a hydrophobic sorbent for the sample tube. This is possible for compounds ranging in volatility from n-C5. Tenax®, Carbotrap™ or one of the other hydrophobic sorbents listed in EPA Method TO-17 should be used.

Note: It is essential to ensure that the temperature of the sorbent tube is the same and certainly not lower than ambient temperature at the start of sampling or moisture will be retained via condensation, however hydrophobic the sorbent.

4.2.2 If the sample loading contains a large amount of water, it is usually possible to eliminate sufficient water to prevent analytical interference by using sample splitting. Samples may be split either between the focusing trap and the capillary column (single splitting) during trap (secondary) desorption or between both the tube and the focusing trap during primary (tube) desorption and between the focusing trap and the column during secondary (trap) desorption (double splitting). It may, in fact, be necessary to split the sample in some cases to prevent overloading the analytical column or detector.

4.2.3 The third water management method is to "dry purge" either the sorbent tube itself or the focusing trap or both. Dry purging the sample tube or focusing trap simply involves passing a volume of pure, dry, inert gas through the tube from the sampling end, prior to analysis.

The tube can be heated while dry purging at slightly elevated temperatures. A trap packing combination and a near ambient trapping temperature must be chosen such that target analytes are quantitatively retained while water is purged to vent from either the tube or trap.

5.0 Safety

Laboratory personnel are required to be familiar with the general laboratory safety plan including the location and proper use of safety/emergency equipment

5.1 Employees must abide by the policies and procedures in the Chemical Hygiene Plan and this document. This procedure involves hazardous material, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow the appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are hazardous. Standard laboratory safety procedures should be followed when working with all samples.

5.2 Specific Safety Concerns or Requirements

Eye protection that satisfies ANSI Z87.1, laboratory coat, and disposable nitrile or Silver-Shield gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded. Non-disposable gloves must be cleaned immediately. Latex and Vinyl gloves provide no protection against some organic solvents.

5.3 Each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Procedures involving primary standards and sample preparation must be performed in a fume hood.

5.4 Material Safety Data Sheets (MSDS) for each analyte and reagent used in the mobile laboratory are available to all employees. The MSDS and the PHILIS Chemical Hazard Summary Sheet must be read and understood by the analyst prior to initial use of a chemical.

6.0 Equipment and Supplies

6.1 Sampling equipment

6.1.1 Thermal desorption tubes- based on the analytes to be determined.

6.1.2 Calibrated sampling pump

6.1.3 Pressure gauge

6.1.4 Mass flow meter

6.2 Glassware

6.2.1 Class A volumetric flask – used if liquid calibration standards will be prepared

6.3 Syringes

6.3.1 Gas tight syringes – various sizes

6.4 Instrumentation

6.4.1 Agilent 8890 Gas Chromatograph

6.4.2 Agilent 5977B Mass Spectrometer

6.4.3 Markes International Unity-xr Thermal Desorption platform – or equivalent

6.4.4 Markes International Ultra-xr Thermal Desorption Tube autosampler—or equivalent

6.4.5 Agilent MSD ChemStation G1701 DA or higher version

6.4.6 Markes Instrument Contol Software 2.0 or equvalent.

6.4.7 Alternate instrument LECO Time of Flight (TOF) Mass Spectrometer

6.4.8 Gerstel Thermal Desorption Unit

6.4.9 LECO Chromatography software

6.4.10 NIST spectral library

6.4.11 Restek RTX-VMS capillary column, 20 m x 1.8 mm x 1.0 µm- column used for VOA analysis. Other columns may be used provided required quality assurance parameters can be met.

6.4.12 TDU tube conditioner

6.5 Equipment for Standard Preparation

6.5.1 Markes International Calibration Loading Rig- used to load standards in either the liquid or gas phase.

7.0 Reagents and Standards

7.1 Reagents

7.1.1 Helium- UHP grade or higher

7.1.2 Nitrogen- UHP grade or higher

7.1.3 Methanol-Purge and Trap grade or equivalent

7.2 Gas Standards

Below is a list of suggest gas standards. Other standards than those listed may be used provided they meet analytical requirements. Gas standards used in the Edison application are listed in 10.2.4 and 10.2.5,

7.2.1 Restek TO-14A Internal Standard/Tuning mix, cat#34408- 1 ppmv in nitrogen

7.2.2 Restek BTEX mix, cat#34414- 1 ppmv in nitrogen

7.2.3 Restek TO-15 mix, 65 components, cat#34436- 1 ppmv in nitrogen

7.2.4 Air Liquide Custom 4 component Internal Standard Mix Sales order:2814370 (1ppmv in nitrogen).

7.2.5 Air Liquide Custom 65 component target compound mix Item TQ15-6276 (1ppm in nitrogen).

7.3 Liquid Standards

Below is a list of suggest liquid standards. Standards from other manufacturers may be used provided they meet analytical requirements. 10.3.4 was used in Edison method development for MS performance evaluation

7.3.1 Restek Mega Mix

7.3.2 Restek Internal Standard (optional)

7.3.3 AccuStandard Liquid and Gas mix

7.3.4 Restek Surrogate Mix. 2500ug/ml Catalog #3004. Diluted (40ul diluted in 2ml Purge and Trap grade methanol) to 50ng/ul of 4-Bromofluorobenzene. 1ul loaded onto Markes Universal tube.

7.4 Calibration Standards are listed in Table 2.

7.4.1 Edison start-up data used the following levels 0.5, 1.0, 2.0, 5.0,10,20,30 50 100 and a 5ml ICV. The 80 and 100 levels were removed from individual compounds in the curve where saturation was present in particular, all aromatic compounds eluting after toluene

8.0 Sample Collection, Preservation, and Storage

PHILIS staff typically does not collect samples, but the information below should be considered when setting up a project.

If the field sampling crew does not have a sample collection form to transfer the sampling information to the laboratory, Figure 1 is an example form that may be used.

8.1 Selection of Tube Dimensions and Materials

8.1.1 The laboratory will be providing and conditioning the same tube type for sampling that is used for the instrument calibration.

8.1.2 As an approximate measure, the breakthrough volume for sorbents contained in equal diameter tubes is proportional to the bed-length (weight) of sorbent. Accordingly, doubling the bed-length would approximately double the SSV (15). SSV for specific analytes are listed in Figure 3. SSV's for analytes not listed in Figure 3 may be available in "Application Notes" from tube manufacturers, or will need to be determined. An "Application Note" from Markes gives a detailed description on a procedure to determine SSVs. Safe Sampling volume will be determined for analytes in the QAPP. This is information will be transmitted to the sampling team prior to sampling. Figure 2 lists some sorbent types and Figure 3 lists SSVs.

8.1.3 Stainless steel (304 or "GC" grade) is the most robust of the commonly available tube materials which include, in addition, glass, glass-lined, and fused silica lined tubing. Tube material must be chosen to be compatible with the specifics of storage and transport of the samples. For example, careful attention to packaging is required for glass tubes.

8.1.4 The Edison method for volatile air toxics utilizes 3.5" x .25"O.D treated stainless steel tubes packed with 380mg of Tenax TA 35/60, Carbograph ITD 40/60, and Carboxen 1003 40/60 which are packed and preconditioned by Markes. All tubes are also preconditioned in lab prior to sampling and are traceable to conditioning batch.

8.2 Tube Labeling

Tubes are engraved with a 6 digit serial number which is logged into a spreadsheet containing a batch ID. This batch ID is added to the LIMS batch and the ChemStation sequence log and the sequence log of the instrument control software. so that the conditioning batch is traceable to all standard, QC and samples. Example log book pages for a conditioning batch log can be found in Figure 4. Markes tubes are also engraved with a bar code which will enter the six digit code into a chemStation sequence or the Markes sequence table via bar code scanner.

8.3 Blank and Sampled Tube Storage

8.3.1 Seal clean, blank sorbent tubes and sampled tubes using inert, Swagelok®-type fittings and PTFE ferrules. Use clean, sealable glass jars or metal cans labelled with the conditioning batch designation and containing a small packet of activated charcoal or activated charcoal/silica gel for storage and transportation of multiple tubes. Store the multi-tube storage container in a clean environment at 4°C, or use within 24 hours.

8.3.2 Keep the sample tubes inside the storage container during transportation and only remove them at the monitoring location after the tubes have reached ambient temperature. Store sampled tubes in a refrigerator at 4°C inside the multi-tube container until ready for analysis.

8.3.3 After sampling remove the sampling tubes with clean gloves, recap the tubes with Swagelok® fittings using PTFE ferrules and place the tubes in a clean, airtight container. If not to be analyzed during the same day, place the container in a clean, cool (<4C) organic solvent free environment and leave there until time for analysis. Section 10.10 of compendium method TO-17 January 1999 allows for a holding time of up to 30 days. Based on this the PHILIS holding time will be officially set at 30 days. Due to the unknown nature of the stability of analytes under long term storage and the nature of the sorbent tubes in the current PHILIS developed method (multiple sorbents) it would be prudent for analysis to proceed as soon as possible after collection.

8.4 Samples may be taken in Tedlar® bags and would have a 72 hour holding time. The air from these bags can be transferred to a sorbent tube using a gastight syringe. The volume transferred must be recorded.

9.0 Quality Control

QC requirements include the Demonstration of Capability and ongoing QC requirements that must be met when preparing and analyzing samples.

9.1 DEMONSTRATION OF CAPABILITY (DOC) – must be successfully performed by the analyst prior to analyzing any field samples. This DOC study must be performed every three months or after every 10^{th} series of runs whichever comes first and any time major method modifications are made. DOC result must be provided with the final data package for the project.

9.1.1 Prior to conducting the DOC study, the analyst tunes the instrument and generates an acceptable instrument calibration following the procedure outlined in Section 13 of this SOP. An MB (blank tube) is analyzed to demonstrate that the background contamination is low enough to not interfere with analyte.

9.1.2 Method precision and accuracy are demonstrated by analyzing six replicate LCS's fortified at concentration near the mid-point of the calibration curve and analyzed according to the procedure described in Section 14 of this SOP. Precision and accuracy are calculated using an EXCEL Spreadsheet.

9.1.2.1 Acceptable precision is RSD ≤ 20%. Once adequate points are available, laboratory limits will be established. Analytical precision below 20% for MTBE has been difficult to achieve due to the reactive nature of this compound. RSD limits have been set to 30% for this compound.

9.1.2.2 Acceptable accuracy is mean percent recovery within ± 50%. Once adequate points are available, laboratory limits will be established.

9.1.2.3 Table 3 represents example DOC data for the Edison application of this method.

9.2 MDL Procedure

MDLs and RLs are established by analyzing a minimum of seven replicates of a standard at or near the estimated MDL. Tabulation of results and MDL calculations are performed by the method in 40 CFR, Part 136, Method Update Rule Revision 2.

9.2.1 Initial MDLs

9.2.1.1 Initial MDLs are established by analyzing a minimum of seven replicates of the low-level calibration standard and a minimum of seven blanks prepped and analyzed over three separate days. The MDL should be spiked 1 to 5 times the estimated MDL. Extract and analyze the MDL standards and blanks with the same procedure as regular samples.

9.2.1.2 For each compound, calculate the mean and standard deviation of the replicates in micrograms per liter (µg/L). Then calculate the MDL by multiplying the standard deviation by the Student's t value. The one-sided (single-tailed) Student's t values at the 99% confidence levels are used (e.g., t = 3.143 at the 99% confidence level for n = 7). MDL studies are repeated annually and verified each time they are prepared. MDL results are stored in Element each time they are calculated.

9.2.1.3 Blank MDL's are calculated according to the procedure listed in 40CFR 136 Appendix B After determination of a blank mdl and a mdl based on a low level spike study, use the larger of the two values.

9.2.2 Ongoing MDL Data Collection

9.2.2.1 Ongoing MDL's are determined by preparing and analyzing two spiked standards at 1-5 times the estimated md and two blanks once per quarter for a minimum of seven determinations. The blanks and spikes may be analyzed in the same prep batch, but is not required. If the instruments are being used regularly, the mdl spikes may be added to the routine batches and the regular blanks used. All blanks analyzed during the evaluation period should be used. If samples are not analyzed during a quarter, it is not required to analyze the Ongoing MDLs for that quarter.

9.2.2.2 At least once per year re-evaluate the mdl by, calculating as above in 12.9.1.2. Use the larger of the spiked determinations and blank determinations for the mdl value.

9.2.3 Ongoing MDL Annual Verification

9.2.3.1 At least once every thirteen months, re-calculate the MDL spike and MDL blank from the collected spiked samples and method blank results per 12.9.1.2.

9.2.3.2 Include data generated within the last twenty four months, but only data with the same spiking level. Only documented instances of gross failures (instrument malfunctions, mislabeled samples, cracked vials, etc.) may be excluded from the calculations.

9.2.3.3 Include the initial MDL spiked samples if the data were generated within the last twenty four months.

9.2.3.4 The verified MDL is the larger of the MDL Blank and MDL Spiked samples.

9.2.4 Using MDLs for Multiple Instruments

9.2.5 If the same MDL is to be used for multiple instruments, then MDL spiked samples and MDL blanks from the included instruments must be pooled prior to the mdl calculation. All MDL spiked samples must be at the same prepared level to be included. The same rules for calculations and data gathering that is used for individual instruments are used for the multiple instruments.

9.3 Ongoing QC applied when performing this method includes analyzing acceptable instrument calibration/calibration verification standards, method blanks, duplicates, LCS's, and closing method blanks. Requirements are listed in Table 4. Internal standards and surrogates must be acceptable with all QC samples and with test samples. Example MDL's are listed in Table 5.

10.0 Calibration and Standardization

10.1 Prior to the analysis of samples, performance of the instrument is optimized and an instrument calibration curve is developed. BFB is analyzed prior to instrument calibration and with each analysis batch processed within 24 hours in order to verify that the mass abundance acceptance criteria specified in Table 6 have been achieved.

All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 % that of m/z 95.

10.1.1 Calibration curve regression model and the range of calibration level used in the performance validation (Demonstration of Capability, Section 11) must be used in all routine sample analysis. Either external or internal standard calibration may be used, as long as the same calibration method is used for all project and QC and samples.

10.1.2 Setting Retention Times Extraction Windows and Integration Parameters.

10.1.2.1 Once data has been acquired for the calibration, absolute retention times must be set for the calibration by quantitation of the midpoint followed by qualitative review of the spectral hits and manual setting of the retention times and ion ratios by selecting and integrating the peaks using EasyID.

10.1.2.2 Global updating of the ion extraction windows must be done for first time calibration and after maintenance where a large retention time shift occurs. A default setting of 0.3 minutes is acceptable for most targets in this method. Some compounds will require narrowing of the extraction windows by placement of flags in EasyID where there are peaks with the same ions that elute in close proximity. Widening of retention time windows may be necessary in the case of broader peaks or tailing. Relative ion extraction windows will be maintained when setting retention time on subsequent calibrations.

10.1.2.3 When setting up a calibration curve the RTE integrator should be used with a default parameter file of RTEINT.P for the Edison method. After retention time settings and extraction windows have been properly set recalculate the file and review each compound for accuracy in integration. Some compounds may have choppy peaks or baseline issues where the setting of compound specific integration parameters can be used to assure proper integration. Manual integration is permitted but a reasonable effort to set the proper parameters in the calibration can result in consistent integrations and save time in processing data later.

10.1.3 The instrument is calibrated using a minimum of five concentrations in the following manner: Cal1 – Cal N (number of last calibration standard) are used to generate the calibration curve for all target analytes. The average response factor or a linear regression curve can be used with five points, but a quadratic regression requires a minimum of six points. Calibration points may be dropped from either end of the calibration curve, but a minimum of five points is required for a curve. Calibration points may also be dropped from the middle of a calibration curve for an obvious reason (low internal standards, standard made wrong, etc.). The reason must be documented and the entire point must be removed. The calibration point may be reanalyzed within 24 hours.

10.1.4 The reporting limit (RL) of the analytical method must be at or above lowest point in the initial calibration.

10.1.5 A response factor calibration curve is generated for each target analyte by plotting the response factor as a function of concentration ratio. If the analyte does not meet the 30% variability acceptance criteria, then a regression fit should be used. If linear or quadratic regression is used, the resulting curve fit must be 0.99 or greater.

10.1.6 Response for each of the internal standards in the calibration curve cannot vary more than 40 % when compared to their average responses. The use of internal standards is optional for this procedure.

10.1.7 Retention time for the internal standards may not vary more than 20 seconds in the calibration or subsequent analyses. The use of internal standards is optional for this procedure.

10.1.8 The instrument calibration curve is initially verified by the SCV and continuously verified by the CCV. The concentration of the calibration checks is at or near the midlevel of the calibration curve.

10.1.9 The low and mid points of the curve must be recalculated with the results documented on an "evaluate data file as continuing calibration" report. All target compound calculated values should return an accuracy of 70-130 of the true value,

10.2 Relative Error

If the calibration curve is a Response Factor curve, then the Relative Error is the Average Response Factor.

If the calibration curve is Linear Regression or Quadratic Regression, then run the lowest and midpoint calibration points against the curve and calculate the % difference from the true value. These are the Relative Errors.

10.3 Acceptance criteria for BFB, Instrument Calibration and CCVs, and the required frequency of their analysis are summarized in Table 6.

11.0 Procedure

11.1 Thermal Desorption Tube Conditioning

This procedure must be performed prior to sampling.

11.1.1 Place the TDU tubes into the tube conditioner

11.1.2 Turn on Nitrogen

11.1.3 Markes Universal tubes are loaded into the TC2 Gerstel Tube or TC20 Markes conditioning system, a nitrogen flow of 100ml/min is established and new or newly packed tubes are conditioned at each of the following temperatures in succession for one hour (100C, 200C, 300C) followed by a half hour at 335C. Reconditioning can be done at 15 minutes at the previously mentioned temperatures. For small batches tubes can also be conditioned by running as a blank on the Ultra/Unity system provided that conditioning is documented the same way as if it was conditioned using the Gerstel TC2,

and they are not included in the same conditioning batch. Allow the tube conditioner to cool down to ambient temperature, and then remove the tubes and cap them with Swagelok fittings and PTFE ferrules. An example of the Tube Conditioning Log is Figure 4.

11.1.4 Tube serial numbers from the same conditioning method on the same day must be documented into a conditioning batch log (Figure 4). All samples and QC including method blanks, field blanks, LCS/LSCD's must originate from the same tube conditioning batch.

11.1.5 Stored in a sealed glass or tin container (labelled with the conditioning batch ID containing a silica gel and adsorbent package. Unless used on the same day they must be stored in a refrigerator at less than 4C. Due to the contraction of metal at lower temperatures the Swagelok fittings must be retightened upon cooling.

11.2 Sample Preparation

11.2.1 Remove the sample TDU tubes from the refrigerator.

11.2.2 Verify that the sample has been logged into LIMS and within holding time. If the sample exceeds the holding time, notify the Lead Chemist and follow the corrective action plan.

11.2.3 The sample can now be placed on the Markes International Ultra 2 autosampler or Gerstel TDU.

11.3 Standard Preparation for Tedlar Bags, SUMMA Cannisters, and MiniCans

11.3.1 An aliquot of sample is extracted via gas tight syringe from a Tedlar bag and transferred to a preconditioned sorbent tube attached to a loading rig. The nitrogen valve is turned on prior to removal of the syringe needle from the rig and UHP Nitrogen is allowed to flow though the tube at 100cc/min for 2 min. Tube is removed from the rig and capped with Diff-lock caps and transferred to the Ultra tray for analysis.

11.3.2 A gauge is attached to a summa canister or MiniCan to determine the pressure. The determined pressure is usually less than 1 atmosphere, Moisturized zero air is added through a secondary port on the canister to raise to a positive (relative to atmospheric pressure) pressure. The new pressure is recorded and a dilution factor is calculated.

11.3.3 An aliquot of sample is extracted via gas tight syringe from a septum fitting on the canister and transferred to a preconditioned sorbent tube attached to a loading rig. The nitrogen valve is turned on prior to removal of the syringe needle from the rig and UHP Nitrogen is allowed to flow though the tube at 100cc/min for 2 min. Tube is removed from the rig and capped with Diff-lock caps and transferred to the Ultra tray for analysis.

11.3.4 Follow the procedure listed in Table 2 using the Markes calibration loading rig or other acceptable procedures.

11.3.5 The Edison method uses a standard mix in a large gas cylinder. Appropriate technique is essential for reproducible results. Prior to tube loading tap the cylinders repeatedly for one or two minutes with a wrench or similar metal object to sonically mix the gases in the cylinder. Using a 250ml syringe withdraw two aliquots (500ml of standard and discard), this is to evacuate the gas in the regulator. Attach the tube to the loading rig and finger tighten nut. For each tube turn on the loading rig open nitrogen valve and attach a flow meter, observe the flow rate and adjust to 100mL +/- 10mL. Turn off valve and remove flow meter. Using the appropriate syringe withdraw gas standard to a mark greater than the desired volume and shut the stopcock on the syringe. Place the syringe under the hood and slowly slide plunger to the point where the syringe barrel is on the desired volume being careful to maintain no pressure on the plunger before closing the luer lock stopcock. Insert the needle into the loading rig and push the needle to just the point you can feel the packing material. Open the syringe stopcock and slowly slide the syringe plunger to load the standard onto the tube taking care to load at a rate no more than 100ml/min. After all of the standard has been loaded and before withdrawing the syringe needle, turn on the nitrogen flow and slowly withdraw the needle. Maintain nitrogen flow for one minute before removing the tube from the loading rig. Cap the inlet end of the tube with an inert end cap, and the outlet end with an untreated end cap. As with all laboratory procedures wear gloves. Handling TD tubes with bare hands can create artifacts which may interfere with analysis.

11.4 Sample Analysis

11.4.1 Analysis is performed using a Thermal Desorption (TD)-GC/MS programmed based on the sorbent tubes and analytes being determined. The program used to generate the calibration must be used for all sample and quality control analyses.

11.4.2 Samples are allowed to equilibrate to room temperature before recapping with Diff -lok caps and being loaded into the Ultra tray. (wear clean gloves when handling tubes to avoid contaminating the tubes with artifacts)

11.4.3 Analysis sequence for EPA Method TO-17 is tune, calibration or CCV, MB, FB, LCS, LCSD. Samples including duplicate and a closing method blank with a different tube from the same conditioning batch.

11.4.4 In the software, ensure that the correct sequence and controlling method is loaded.

11.4.5 In ChemStation, load the “default” sequence and enter the pertinent information into the sequence, making sure the same method used for calibration has been used for analysis. In the Maverick software load the appropriate method and sequence making sure it is the same method used for calibration.

11.4.6 Start the Markes sequence. Tubes are loaded into the Ultra system into and leak checked. Leak check failure results in the trigger of the chemStation sequence to keep the sequence matching the sample. Three leak check failures on separate tube in a row aborts the sequence.

11.4.7 After passing leak check tubes are dry purged for 1 minute followed by the introduction of internal standard through a 1ml standard loop fed by an external cylinder containing 1.00 ppmV each of 1,4-Difluorobenzene, Bromochloromethane, and Chlorobenzene-d5 in Nitrogen. The tube is the desorbed onto a cold trap which is in turn is desorbed into the GC/MS.

11.4.8 After analysis tubes are stored in a sealed glass or tin container (labelled with the condoning batch ID containing a silica gel and adsorbent package Due to the contraction of metal at lower temperatures the Swagelok fittings must be retightened upon cooling

11.4.9 All tubes are subjected to at least one mid-level calibration analysis before being put into circulation, if a large percentage of compounds fail this "CCV" it is retested and if it fails again the tube is taken out of circulation. According to the Markes manual tube lifetime is about 100 cycles which include both analysis and conditioning cycles. The number of cycles will be tracked in the conditioning batch log and tubes will be sent to Markes for repacking.

11.5 Identification of Analytes

11.5.1 The analyte is identified by comparison of its mass spectrum to a reference spectrum in the instrumental method and comparing its retention time to the retention time observed for the same analyte in the most recent CCV or calibration.

11.5.2 Analytes above the calibration range are flagged and reported as estimated.

12.0 Data Analysis and Calculations

12.1 Identification of Analytes

12.2 Percent recovery for LCS and LCSD are calculated using the following equation:

$$\%R = \left[\frac{\left(C_{spk} - C_x\right)}{C_t}\right]100$$

where:
C_{spk} = the concentration of the analyte in the spiked sample
C_x = the concentration of the analyte in the reference (parent) sample; (Cx = 0 for LCS.)
C_t = the theoretical spike concentration.

The concentration of each analyte is calculated using Agilent MSD ChemStation software using an average response factor or linear regression curve as established in Section 13 of this SOP. Response factors and analyte concentrations are calculated by the equations below when internal standards are not used:

12.3 Calibration factor (CF):

$$CF = \frac{(A_x)}{mass\ of\ std}$$

where:
A_x = Area of the Analyte being measured
Mass of std = Total mass of standard injected in nanograms

Average CF ($\overline{\mathrm{CF}}$): $\overline{CF} = \frac{\sum_1^n CF}{n}$

where
n = number of initial calibration standards

12.4 Percent relative standard deviation (%RSD):

$$\%RSD = (^{S}/_{\overline{x}})100$$

where:
$\overline{\mathrm{x}} = \overline{\mathrm{CF}}$: $\overline{\mathrm{CF}} = \frac{\sum_1^{\mathrm{n}} \mathrm{CF}}{\mathrm{n}}$
where:

s = standard deviation: $= \sqrt{\frac{\sum_{\mathrm{i}=1}^{\mathrm{n}}(\mathrm{x_i} - \bar{\mathrm{x}})^2}{\mathrm{n}-1}}$

12.5 Sample concentration using CF:

$$Conc\left(\frac{\mu g}{m^3}\right) = \frac{A_x}{(\overline{CF})(V_o)}$$

where :
A_x = peak area for compound being measured
$\overline{CF}$ =mean calibration factor for compound being measured
V_o = volume of air collected in L

The concentration of each analyte is calculated using Agilent MSD ChemStation software using an average response factor or linear regression curve as established in Section 13 of this SOP. Response factors and analyte concentrations are calculated by the equations below when internal standards are used:

12.6 Relative response factor (RRF):

$$RRF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

where:
A_x = Area of the quantitation ion for the surrogate or compound being measured.
A_{is} = Area of the quantitation ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard.
C_x = Concentration of the compound being measured.

12.7 Average RRF $\left(\overline{RRF}\right)$:

$$\overline{RRF} = \frac{\sum_{1}^{n} RRF}{n}$$

where,
n = number of initial calibration standards

12.8 Percent relative standard deviation (%RSD):

$$\%RSD = \left(\frac{s}{\bar{x}}\right)100$$

where:

$\bar{x} = \overline{RRF}$: $\overline{RRF} = \frac{\sum_{1}^{n} RRF}{n}$

s = standard deviation: $s = \sqrt{\frac{\left(\sum_{i=0}^{n}(\bar{x}-x_i)^2\right)}{n-1}}$

12.9 Sample concentration using RRF:

$$C(ppbv) = \frac{I_s A_x}{\overline{RRF} A_{Is} V_o}$$

where :
A_x = area of quantitation ion for compound being measured
I_s = amount of internal standard injected onto the tube (nL)
A_{is} = area of quantitation ion for the internal standard
$\overline{RRF}$ = mean relative response factor for compound being measured
V_o = volume of air sampled on the tube (L) accounting for dilutions

12.10 Percent recovery for CCV, and, LCS are calculated using the following equation:

$$\%R = \left[\frac{\left(C_{spk} - C_x\right)}{C_t}\right]100$$

where:
C_{spk} = the concentration of the analyte in the spiked sample
C_x = the concentration of the analyte in the reference (parent) sample;
(C_x = 0 for CCV and LCS.)
C_t = the theoretical spike concentration.

12.11 Relative percent difference for duplicate is calculated using the following equation:

$$RPD = \left[\frac{\left|C_1 - C_2\right|}{\left(C_1 + C_2\right)/2}\right]100$$

where:
C_1 = concentration of the first sample
C_2 = concentration of the second sample

13.0 Method Performance

13.1 MDL's are analyzed on an annual basis. Lab Accuracy and Precision data are used to calculate lab specific acceptance criteria. Precision and Accuracy data are recalculated and evaluated every six months. Limit acceptance criteria will be established no tighter than 50 % to 150 %. Precision and Accuracy data and acceptance limits will be evaluated based on ongoing QC produced over time.

Other specific Quality Assurance Objectives (QAO) may be found in the appropriate statement-of-work or Quality Assurance Project Plan (QAPP) for specific projects.

13.2 Analytical data generated by the instrument software is reviewed and evaluated by the analyst as follows:

13.2.1 BFB, instrument calibration, calibration verifications, IS/SS, QC measures are evaluated and the results documented on the separate forms:

13.2.2 The tune evaluation of BFB.

13.2.3 The instrument calibration relative response factors and percent relative standard deviations.

13.2.4 QA-QC check report for internal standard area counts and percent recoveries for the surrogates.

13.2.5 Analyze percent recoveries for the SCV, CCV, LCS, and % RPD for the sample duplicate.

13.2.6 In order for the analytical data to be acceptable, the calibration standards and quality control measures must meet the criteria listed in Sections 12 and 13 of this SOP.

13.2.7 All false positives are Q-Deleted, and all positively identified target analytes are reported to LIMS.

13.3 Manual integration is applied in cases when the instrument data processing software produces integrated areas that are not valid. The manual adjustments to the chromatographic peak must be performed in a consistent manner for the calibration standards, QC and field samples.

Manual integration should not be substituted for proper maintenance of the instrument or setup of the method (e.g. retention time updates), integration parameter files, etc.

The analyst should seek to minimize manual integrations by proper instrument maintenance, retention time updates, and configuring peak integration parameters.

13.4 If the QAPP requires it, chromatograms of all field samples are examined to detect additional peaks, which were not identified as target analytes. If such peaks are present, generate a Library Search Report and report a tentatively identified compound (TIC) if the percent match is greater than the 50%. The Lead Chemist should be notified immediately in that case.

13.5 Anytime the analyst alters the instrument generated quantitation report, the hardcopies of both reports (original and analyst corrected) must be retained (e.g., manual integration). The altered report must be initialed and dated with a reason for altering.

13.6 Discrepancies in the analytical run are described in “QC Summary Form” and discussed with the Lead Chemist.

13.7 Reviewed data is entered into LIMS, hard copies of LIMS report is printed and compared to the original data.

13.8 All records derived from the analytical process are assembled in the analytical data packages that consist of:

13.8.1 LIMS work list.

13.8.2 Analytical run sheet.

13.8.3 BFB tune evaluation report.

13.8.4 QA-QC check report.

13.8.5 Quantitation Report for each Sample and QCS.

13.8.6 Evaluation reports for CCV, SCV, LCS and Initial calibration form.

13.9 Data is stored on the server and is backed up.

13.10 In cases where quality control measures do not meet acceptance criteria, the quality of the analytical data is not acceptable and the analyst does the following:

13.10.1 When tuning and instrument calibration fail to meet acceptance criteria, the analysis does not start. The problem is investigated and the necessary instrument maintenance is performed, followed with tuning and calibration.

13.10.2 If the acceptance criteria listed in Table 4 of this SOP are not met for MB, CCV, FB, LCS/LCSD, ICV, internal standards, and surrogates, the affected QCs and associated samples should be treated as per laboratory or QAPP protocols.

13.10.3 If after analysis, any of the criteria for quality control are not met, or the sample is not available for reanalysis, the analyst must notify the Lead Chemist. The Lead Chemist will implement the corrective action plan.

13.11 The analyst shall report to the Lead Chemist and indicate on the "QC Summary form" any out of control event. Such events include:

13.11.1 Damage to the sample.

13.11.2 Holding time exceeded.

13.11.3 Inadequate sample preservation.

13.11.4 Sample results exceeds the Agency's action limit

13.11.5 Samples do not reflect historical data.

13.11.6 Upward trending or sample results approaching interval warning limits.

13.11.7 Any non-target analyte peak present on the instrument generated chromatogram, if required.

13.12 The Lead Chemist will implement the corrective action plan described in the PHILIS corrective action plan document or the associated SAPP.

13.13 Contingencies for Handling Out of Control or Unacceptable Data

See the QAPP that the samples were analyzed under for guidance.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. The EPA places pollution prevention as the management option of first choice with regard to laboratory waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 The Environmental Protection Agency requires that laboratory waste management practices be compliant with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult the PHILIS Chemical Hygiene Plan.

14.3 The waste produced from EPA Method TO-17 consists of waste collected from excess sample, standards (stock mixes, PDS, WS), and methanol.

14.4 Excess reagents are disposed following the MSDS instructions or the site waste disposal plan.

14.5 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036.

15.0 Waste Management

Waste management procedures are specified in the Hazardous Waste Management Plan.

16.0 References

16.1 EPA Method TO-15, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, January, 1999.

16.2 EPA Method TO-17, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, January, 1999.

17.0 Tables, Figures, and Attachments

Table 1. Title III Clean Air Act Amendment Compounds and Characteristic Masses (M/Z) Used for Quantifying

Compound	CAS#	Primary Ion	Secondary Ion
Methyl chloride (chloromethane); CH3Cl	74-87-3	50	52
Carbonyl sulfide; COS	463-S8-1	60	62
Vinyl chloride (chloroethene); C2H3Cl	7S-01-4	62	64
Diazomethane; CH2N2	334-88-3	42	41
Formaldehyde; CH2O	50-00-0	29	30
1,3-Butadiene; C4H6	106-99-0	39	54
Methyl bromide (bromomethane); CH3Br	74-83-9	94	96
Phosgene; CCl2O	75-44-5	63	65
Vinyl bromide (bromoethene); C2H3Br	593-60-2	106	108
Ethylene oxide; C2H4O	75-21-8	29	44
Ethyl chloride (chloroethane); C2H5Cl	75-00-3	64	66
Acetaldehyde (ethanal); C2H4O	75-07-0	44	29, 43
Vinylidene chloride (1,1-dichloroethylene);	75-35-4	61	96
Propylene oxide; C3H6O	75-56-9	58	57
Methyl iodide (iodomethane); CH3I	74-88-4	142	127
Methylene chloride; CH2Cl2	75-09-2	49	84, 86
Methyl isocyanate; C2H3NO	624-83-9	57	56
Allyl chloride (3-chloropropene); C3H5Cl	107-05-1	76	41, 78
Carbon disulfide; CS2	75-15-0	76	44, 78
Methyl tert-butyl ether; C5H12O	1634-04-4	73	41, 53
Propionaldehyde; C2H5CHO	123-38-6	58	29, 57
Ethylidene dichloride (1,1-dichloroethane);	75-34-3	63	65, 27
Chloroprene (2-chloro-1,3-butadiene);	126-99-8	88	53, 90
Chloromethyl methyl ether; C2H5ClO	107-30-2	45	29, 49
Acrolein (2-propenal); C3H4O	107-02-8	56	55
1,2-Epoxybutane (1,2-butylene oxide);	106-88-7	42	41, 72
Chloroform; CHCl3	67-66-3	83	85, 47
Ethyleneimine (aziridine); C2H5N	151-56-4	42	43
1,1-Dimethylhydrazine; C2H8N2	57-14-7	60	45, 59
Hexane; C6H14	110-54-3	57	41, 43
1,2-Propyleneimine (2-methylazindine);	75-55-8	56	57, 42
Acrylonitrile (2-propenenitrile); C3H3N	107-13-1	53	52
Methyl chloroform (1,1,1 trichloroethane);	71-55-6	97	99, 61
Methanol; CH4O	67-56-1	31	29
Carbon tetrachloride; CCl4	56-23-5	117	119

Compound	CAS#	Primary Ion	Secondary Ion
Vinyl acetate; C4H6O2	108-05-4	43	86
Methyl ethyl ketone (2-butanone); C4H8O	78-93-3	43	72
Benzene; C6H6	71-43-2	78	77,50
Acetonitrile (cyanomethane); C2H3N	75-05-8	41	40
Ethylene dichloride (1,2-dichloroethane);	107-06-2	62	64, 27
Triethylamine; C6H15N	121-44-8	86	58, 101
Methylhydrazine; CH6N2	60-34-4	46	31, 45
Propylene dichloride (1,2-dichloropropane);	78-87-5	63	41, 62
2,2,4-Trimethyl pentane; C8H18	540-84-1	57	41, 56
1,4-Dioxane (1,4 Diethylene oxide);	123-91-1	88	58
Bis(chloromethyl) ether; C2H4Cl2O	542-88-1	79	49, 81
Ethyl acrylate; C5H8O2	140-88-5	55	73
Methyl methacrylate; C5H8O2	80-62-6	41	69, 100
1,3-Dichloropropene; C3H4Cl2 (cis)	542-75-6	75	39, 77
Toluene; C7H8	108-88-3	91	92
Trichloethylene; C2HCl3	79-01-6	130	132, 95
1,1,2-Trichloroethane; C2H3Cl3	79-00-5	97	83, 61
Tetrachloroethylene; C2Cl4	127-18-4	166	164, 131
Epichlorohydrin (l-chloro-2,3-epoxy	106-89-8	57	49, 62
Ethylene dibromide (1,2-dibromoethane);	106-93-4	107	109
N-Nitrso-N-methylurea; C2H5N3O2	684-93-5	60	44, 103
2-Nitropropane; C3H7NO2	79-46-9	43	41
Chlorobenzene; C6H5Cl	108-90-7	112	77, 114
Ethylbenzene; C8H10	100-41-4	91	106
Xylenes (isomer & mixtures); C8H10	1330-20-7	91	106
Styrene; C8H8	100-42-5	104	78, 103
p-Xylene; C8H10	106-42-3	91	106
m-Xylene; C8H10	108-38-3	91	106
Methyl isobutyl ketone; C6H12O	108-10-1	43	58, 100
Bromoform (tribromomethane); CHBr3	75-25-2	173	171, 175
1,1,2,2-Tetrachloroethane; C2H2Cl4	79-34-5	83	85
o-Xylene; C8H10	95-47-6	91	106
Dimethylcarbamyl chloride; C3H6ClNO	79-44-7	72	107
N-Nitrosodimethylamine; C2H6N2O	62-75-9	74	42
Beta-Propiolactone; C3H4O2	57-57-8	42	43
Cumene (isopropylbenzene); C9H12	98-82-8	105	120
Acrylic acid; C3H4O2	79-10-7	72	45, 55
N,N-Dimethylformamide; C3H7NO	68-12-2	73	42, 44

Compound	CAS#	Primary Ion	Secondary Ion
1,3-Propane sultone; C3H6O3S	1120-71-4	58	65, 122
Acetophenone; C8H8O	98-86-2	105	77,120
Dimethyl sulfate; C2H6O4S	77-78-1	95	66,96
Benzyl chloride (a-chlorotoluene); C7H7Cl	100-44-7	91	126
1,2-Dibromo-3-chloropropane; C3H5Br2Cl	96-12-8	57	155, 157
Bis(2-Chloroethyl)ether; C4H8Cl2O	111-44-4	93	63, 95
Chloroacetic acid; C2H3ClO2	79-11-8	50	45, 60
Aniline (aminobenzene); C6H7N	62-53-3	93	66
1,4-Dichlorobenzene (p-); C6H4Cl2	106-46-7	146	148, 111
Ethyl carbamate (urethane); C3H7NO2	51-79-6	31	44, 62
Acrylamide; C3H5NO	79-06-1	44	55, 71
N,N-Dimethylaniline; C8H11N	121-69-7	120	77, 121
Hexachloroethane; C2Cl6	67-72-1	201	199, 203
Hexachlorobutadiene; C4Cl6	87-68-3	225	227, 223
Isophorone; C9H14O	78-59-1	82	138
N-Nitrosomorpholine; C4H8N2O2	59-89-2	56	86, 116
Styrene oxide; C8H8O	96-09-3	91	120
Diethyl sulfate; C4H10O4S	64-67-5	45	59, 139
Cresylic acid (cresol isomer mixture);	1319-77-3		
o-Cresol; C7H8O	95-48-7	108	107
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	110	64
Phenol; C6H6O	108-95-2	94	66
1,2,4-Trichlorobenzene; C6H3Cl3	120-82-1	180	182, 184
Nitrobenzene; C6H5NO2	98-95-3	77	51, 123
Naphthalene	91-20-3	128	

Table 2. Example of Preparation of Working Standards

Working Standard Name	Vol Gas Std Primary Lot (mL)	Vol Gas Std. Alt Lot (mL)	Amt spiked (nL)	Conc. In 1L air (ppbv)
L1	0.50	x	0.50	0.50
L2	1.00	x	1.00	1.00
L3	2.00	x	2.00	2.00
L4	5.00	x	5.00	5.00
L5	10.0	x	10.0	10.0
L6	25.0	x	25.0	25.0
L7	50.0	x	50.0	50.0
CCV	5.00	x	5.00	5.00
LCS	X	5.00	5.00	5.00

Table 3. Example Precision and Accuracy for Six 5nl injections Into Markes Universal TD Tubes Using APL01A

EPA Method TO-17: Precision and Accuracy Data for APL01A

Prep Date: 10/03/17
Analysis Date: 10/03/17
Analyst: Kevin Makuskie
Matrix: Air
Limits: Mean Recovery 50 to 150%, RSD ≤= 20% MTBE ≤= 30%
Batch: E7J0303
Preparation: LCS 10ml E17D115 injected over 30 seconds into Universal Tube. Nitrogen turned on after injection and run at 100ml/min for 1minute.

Instrument: **APL01A**

Analyte	Data Files:	1A100317017.D	1A100317018.D	1A100317019.D	1A100317020.D	1A100317021.D	1A100317022.D	Mean Amt. (nl)	Mean Recovery (%)	STDEV	Precision as RSD (%)
	Spiked Amt. (nl)	LCS 1 (nl)	LCS 2 (µnl)	LCS3 (nl)	LCS 4 (nl)	LCS 5 (nl)	LCS 6 (nl)				
Propene	10.0	9.27	9.29	9.20	9.44	8.94	9.32	9.2	92.4	0.1	1.1
Dichlorodifluoromethane	10.0	9.41	9.54	9.28	9.53	9.24	9.31	9.4	93.9	0.1	1.3
Freon 114	10.0	9.29	9.79	9.31	9.47	9.39	9.16	9.4	94.0	0.2	2.5
Chloromethane	10.0	11.18	9.78	12.04	10.80	8.80	11.10	10.6	106.2	0.9	8.8
1,3-Butadiene	10.0	10.72	9.12	10.80	10.36	8.73	10.62	10.1	100.6	0.8	7.7
Vinyl chloride	10.0	9.64	9.79	9.62	9.50	9.38	9.55	9.6	95.8	0.1	1.2
Chloroethane	10.0	9.88	9.63	9.99	9.66	8.64	9.66	9.6	95.8	0.2	1.8
Trichlorofluoromethane	10.0	9.43	9.58	9.30	9.46	9.03	9.04	9.3	93.1	0.1	1.2
1,1-Dichloroethene	10.0	9.53	9.45	9.29	9.52	9.30	9.14	9.4	93.7	0.1	1.2
Freon 113	10.0	9.46	10.90	9.41	9.48	9.15	9.08	9.6	95.8	0.7	7.6
Acrolein	10.0	10.14	9.95	9.72	10.11	9.29	9.53	9.8	97.9	0.2	2.0
Isopropyl alcohol	10.0	9.50	10.12	9.25	9.03	9.65	8.40	9.3	93.3	0.5	5.1
Methylene Chloride	10.0	9.21	9.05	9.07	9.16	8.85	8.92	9.0	90.4	0.1	0.8
Acetone	10.0	9.56	8.98	9.36	9.64	8.54	9.30	9.2	92.3	0.3	3.2
trans-1,2-Dichloroethene	10.0	9.58	9.68	9.51	9.58	9.30	9.17	9.5	94.7	0.1	0.7
Hexane	10.0	9.53	10.37	9.32	9.68	10.11	9.45	9.7	97.4	0.5	4.7
Methyl tert-butyl Ether	10.0	9.10	14.79	9.13	9.29	15.93	11.29	11.6	115.9	2.8	24.2
1,1-Dichloroethane	10.0	9.75	9.36	9.68	9.72	9.40	9.37	9.5	95.5	0.2	1.9
Vinyl acetate	10.0	9.97	9.70	9.80	9.82	9.41	9.63	9.7	97.2	0.1	1.1
cis-1,2-Dichloroethene	10.0	9.61	9.67	9.48	9.66	9.29	9.28	9.5	95.0	0.1	0.9
Cyclohexane	10.0	9.47	9.67	9.19	9.48	9.14	9.15	9.4	93.5	0.2	2.1
Chloroform	10.0	9.69	9.37	9.48	9.74	9.36	9.29	9.5	94.9	0.2	1.8
Carbon Tetrachloride	10.0	9.75	9.86	9.85	10.13	9.23	9.66	9.7	97.5	0.2	1.7
Tetrahydrofuran	10.0	9.86	9.63	9.48	9.62	9.46	9.28	9.6	95.6	0.2	1.6
Ethyl Acetate	10.0	9.67	9.49	9.49	9.67	9.25	9.15	9.5	94.5	0.1	1.1
1,1,1-Trichloroethane	10.0	9.70	9.31	9.50	9.66	9.42	9.35	9.5	94.9	0.2	1.9
2-Butanone	10.0	9.93	9.47	9.55	9.59	9.54	9.67	9.6	96.3	0.2	2.1
Heptane	10.0	9.72	9.74	9.52	9.99	9.35	9.44	9.6	96.3	0.2	2.0
Benzene	10.0	9.41	9.36	9.09	9.46	9.11	9.00	9.2	92.4	0.2	1.8
1,2-Dichloroethane	10.0	9.80	9.62	9.50	9.76	9.42	9.17	9.5	95.5	0.1	1.4
Trichloroethene	10.0	9.56	9.49	9.34	9.55	9.08	9.13	9.4	93.6	0.1	1.1

Analyte	Data Files:	1A100317017.D	1A100317018.D	1A100317019.D	1A100317020.D	1A100317021.D	1A100317022.D	Mean Amt. (nl)	Mean Recovery (%)	STDEV	Precision as RSD (%)
	Spiked Amt. (nl)	LCS 1 (nl)	LCS 2 (µnl)	LCS3 (nl)	LCS 4 (nl)	LCS 5 (nl)	LCS 6 (nl)				
1,2-Dichloropropane	10.0	9.86	8.96	9.60	9.55	9.05	9.34	9.4	93.9	0.4	4.0
Bromodichloromethane	10.0	9.81	9.09	9.75	9.77	9.20	9.45	9.5	95.1	0.3	3.6
1,4-Dioxane	10.0	9.27	8.39	9.32	9.10	9.05	8.94	9.0	90.1	0.4	4.8
Methyl Methacrylate	10.0	10.29	9.23	10.02	10.00	9.55	9.75	9.8	98.1	0.5	4.7
cis-1,3-Dichloropropene	10.0	10.20	9.24	9.86	9.92	9.44	9.61	9.7	97.1	0.4	4.2
4-Methyl-2-pentanone	10.0	10.56	9.50	10.06	9.95	9.82	9.93	10.0	99.7	0.4	4.4
Toluene	10.0	10.07	9.27	9.79	9.88	9.21	9.51	9.6	96.2	0.3	3.6
trans-1,3-Dichloropropene	10.0	11.06	9.91	10.74	10.72	9.94	10.36	10.5	104.6	0.5	4.7
1,1,2-Trichloroethane	10.0	10.35	9.47	10.08	10.03	9.39	9.76	9.8	98.5	0.4	3.8
Tetrachloroethene	10.0	10.26	9.29	9.78	9.80	9.22	9.48	9.6	96.4	0.4	4.1
2-Hexanone	10.0	11.36	9.97	11.07	10.96	10.60	10.83	10.8	108.0	0.6	5.6
Dibromochloromethane	10.0	10.38	9.54	10.10	10.13	9.44	9.68	9.9	98.8	0.4	3.6
1,2-Dibromoethane	10.0	10.56	9.57	10.24	10.21	9.75	9.95	10.0	100.5	0.4	4.1
Chlorobenzene	10.0	10.40	9.31	9.90	9.88	9.36	9.73	9.8	97.6	0.4	4.6
Ethylbenzene	10.0	10.39	9.33	9.82	10.19	9.07	9.78	9.8	97.6	0.5	4.8
m,p-Xylene	20.0	20.86	18.59	19.71	20.50	18.17	19.47	19.6	97.8	1.0	5.1
o-Xylene	10.0	10.42	9.22	9.79	10.10	8.94	9.67	9.7	96.9	0.5	5.3
Styrene	10.0	11.23	9.84	10.57	10.85	9.59	10.52	10.4	104.3	0.6	5.6
Bromoform	10.0	10.45	9.26	9.81	10.01	9.09	9.68	9.7	97.2	0.5	5.1
1,1,2,2-Tetrachloroethane	10.0	10.91	9.52	10.10	10.50	9.33	10.19	10.1	100.9	0.6	5.9
4-Ethyltoluene	10.0	11.01	9.55	10.07	10.54	9.49	10.29	10.2	101.6	0.6	6.2
1,3,5-Trimethylbenzene	10.0	10.63	9.23	9.82	10.25	9.22	9.96	9.9	98.5	0.6	6.1
1,2,4-Trimethylbenzene	10.0	10.78	9.34	9.89	10.37	9.39	10.17	10.0	99.9	0.6	6.2
1,3-Dichlorobenzene	10.0	11.47	9.64	10.28	10.69	9.80	10.76	10.4	104.4	0.8	7.3
1,4-Dichlorobenzene	10.0	11.44	9.53	10.19	10.70	9.75	10.48	10.3	103.5	0.8	7.8
Benzyl Chloride	10.0	11.82	9.84	10.68	10.93	10.13	10.99	10.7	107.3	0.8	7.6
1,2-Dichlorobenzene	10.0	11.25	9.30	9.99	10.51	9.56	10.59	10.2	102.0	0.8	8.1
Hexachlorobutadiene	10.0	11.63	9.46	9.95	11.19	10.27	11.60	10.7	106.8	1.0	9.6
1,2,4-Trichlorobenzene	10.0	12.09	9.67	10.36	11.38	10.67	11.99	11.0	110.3	1.1	9.7
Naphthalene	10.0	12.53	9.94	10.74	11.65	10.98	12.41	11.4	113.8	1.1	9.9

Table 4. TO-17 Method Criteria

Item	Measure	Action
Instrument Tune	Outside Acceptance Criteria	Re-tune.
	Repeated failure indicates a need for system maintenance.	Perform system maintenance and re-tune the instrument. No analyses should be performed until the system is tuned correctly.
Internal Standard(s)—(IS) Optional	± 40 % of the average of the most recent initial calibration	If the nonconformance is on a calibration or QC sample, evaluate the system (repair) and reanalyze. Remake the standard if an error is suspected.
		If the nonconformance is on a field sample, reanalyze. If the reanalysis is within limits, report the results within limits. If the reanalysis is outside limits, dilute and reanalyze. Report the diluted results.
Internal Standard(s)—(IS) Optional	Retention times of the internal standards may not vary more than ± 20 seconds from the ICAL average retention time.	Evaluate the system for leaks or other problems. Affected samples must be reanalyzed.
Initial Calibration (ICAL) for both internal and external calibration	Average Response Factor > 30.0 % RSD. Recalculation of low and midpoint of the curve must return an accuracy of 70-130% of the true value for regression fits.	Evaluate points in the curve for use of linear or quadratic regression (r2 must be ≥ 0.99). Also evaluate upper and lower points for removal. Criteria still not met, recalibrate if compound is an analyte of interest.
Initial Calibration Verification	Not within ± 30% of true value for deviation or drift	Reanalyze and or recalibrate if % deviation or drift is not met and the compound is an analyte of interest.
Continuing Calibration Verification	Not within ± 30% of true value for deviation or drift.	Reanalyze and or recalibrate if % deviation or drift is not met and the compound is an analyte of interest
Method Blank and closing Method blank	Analyte(s) at or above reporting limit	If the associated samples are non-detect, no action is required. If the analyte(s) is detected in the sample, flag with a "b" or reanalyze. If the analyte level in the sample is 10 times or greater than the blank contamination, the results are not affected. Locate the source of the contamination.
Laboratory Control Spike (LCS)	% Recovery ± 50 %	If the LCS % Recovery is high and the sample is non detect, no action is required. If the LCS is high and the sample has detects, reanalyze the sample. If the LCS is low, the sample(s) should be reanalyzed.
Surrogate(s) Optional	% Recovery. Laboratory acceptance criteria are evaluated every six months. Acceptable values are stored in LIMS.	If the % Recovery is outside laboratory acceptance criteria on a QC sample, evaluate the system. Surrogate recalibration may be necessary. Reanalyze the QC samples.
		If the % Recovery is on a client sample, reanalyze. If the % Recovery is within criteria, report the sample within limits. If the % Recovery outside criteria is confirmed, there is a matrix effect. Flag the results as estimated and report both results.
Laboratory Duplicate (LD)	Acceptance criteria is 20% for RPD	If the RPD value is above 20%, then evaluate the system for possible problems. Reanalyze samples as necessary.
Field blank	Analyte(s) at or above reporting limit	If the associated samples are non-detect, no action is required. If the analyte(s) is detected in the sample then notify the client and flag the any results associated with false positive with “b” in final report

Table 5. Example Compound List and MDL Results from Seven 0.5nl Spikes onto Markes Universal TD Tubes Using APL01

Analyte	CAS #	RL (ppbv)*	Calculated MDL (ppbv)*	Precision as RSD (%)
Propene	115-07-1	0.5	0.10	5.1
Dichlorodifluoromethane	75-71-8	0.5	0.08	5.1
Freon 114	76-14-1	0.5	0.1	4.4
Chloromethane	74-87-3	0.5	0.2	11.4
1,3-Butadiene	106-99-0	0.5	0.1	5.8
Vinyl Chloride	75-01-4	0.5	0.10	6.5
Bromomethane	74-83-9	0.5	0.41	24.8
Chloroethane	75-00-3	1.0	0.28	16.7
Trichlorofluoromethane	75-69-4	0.5	0.08	5.0
1,1-Dichloroethene	75-34-4	0.5	0.09	6.1
Acrolein	107-02-8	0.5	0.18	10.6
Freon 113	76-13-1	0.5	0.10	6.8
Isopropyl alcohol	67-63-0	0.5	0.17	11.8
Methylene Chloride	75-09-2	1.0	0.47	22.0
Acetone	67-64-1	0.5	0.29	13.3
trans-1,2-Dichloroethene	156-60-5	0.5	0.14	10.3
Hexane	110-54-3	0.5	0.15	11.1
Methyl tert-butyl ether	1634-04-4	0.5	0.33	32.1
1,1-Dichloroethane	75-34-3	0.5	0.10	6.8
Vinyl acetate	108-05-4	0.5	0.2	13.3
cis-1,2-Dichloroethene	156-59-2	0.5	0.12	8.3
Cyclohexane	110-82-7	0.5	0.10	7.3
Chloroform	67-66-3	0.5	0.13	9.1
Carbon Tetrachloride	56-23-5	0.5	0.11	8.0
Tetrahydrofuran	109-99-9	0.5	0.24	18.0
Ethyl acetate	141-78-6	0.5	0.20	15.5
1,1,1-Trichloroethane	71-55-6	0.5	0.13	9.5
2-butanone	78-93-3	0.5	0.13	9.5
Heptane	14-82-5	0.5	0.13	10.1
Benzene	71-43-2	0.5	0.16	12.0
1,2-Dichloroethane	107-06-2	0.5	0.15	10.3

Analyte	CAS #	RL (ppbv)*	Calculated MDL (ppbv)*	Precision as RSD (%)
Trichloroethene	79-01-6	0.5	0.13	10.1
1,2-Dichloropropane	78-87-5	0.5	0.18	12.6
Bromodichloromethane	75-27-4	0.5	0.14	11.1
1,4-Dioxane	123-91-1	0.5	0.27	18.6
Methyl methacylate	80-62-6	0.5	0.19	15.7
cis-1,3-Dichloropropene	10061-01-5	0.5	0.17	14.1
4-Methyl-2-pentanone	108-10-1	0.5	0.19	14.8
Toluene	108-88-3	0.5	0.18	13.8
trans-1,3-Dichloropropene	10061-02-6	0.5	0.20	18.2
1,1,2-Trichloroethane	79-00-5	0.5	0.19	14.8
Tetrachloroethene	127-18-4	0.5	0.15	11.6
2-Hexanone	591-78-6	0.5	0.24	18.3
Dibromochloromethane	124-48-1	0.5	0.14	12.5
1,2-Dibromoethane	106-93-4	0.5	0.17	14.4
Chlorobenzene	108-90-7	0.5	0.17	13.7
Ethylbenzene	100-41-4	0.5	0.18	14.2
m,p-Xylene	106-42-3	1.0	0.33	13.3
o-Xylene	95-47-6	0.5	0.20	14.7
Styrene	100-42-5	0.5	0.14	13.5
Bromoform	75-25-2	0.5	0.13	7.0
1,1,2,2-Tetrachloroethane	79-34-5	0.5	0.18	14.4
4-Ethyltoluene	622-96-8	0.5	0.19	16.2
1,3,5-Trimethylbenzene	108-67-8	0.5	0.19	14.6
1,2,4-Trimethylbenzene	95-63-6	0.5	0.22	16.9
1,3-Dichlorobenzene	541-73-1	0.5	0.22	18.6
1,4-Dichlorobenzene	106-46-7	0.5	0.21	18.4
Benzyl Chloride	100-44-7	0.5	0.19	9.9
1,2-Dichlorobenzene	95-90-41	0.5	0.17	13.3
Hexachlorobutadiene	87-68-3	0.5	0.27	20.3
1,2,4-Trichlorobenzene	120-82-1	0.5	0.27	18.9
Naphthalene	91-20-3	0.5	0.32	22.4

*Based on a one Liter sample volume.

Table 6. BFB Relative Abundance Criteria (From EPA Method TO 17)

BFB Relative Abundance Criteria	
m/z	**Relative Abundance Criteria**
50	8 to 40 % of 95
75	30 to 66% of 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of 95
173	<2% of 174
174	50 to 100% of 95
175	4 to 9% of 174
176	93 to 101% of 174
177	5 to 9% of 176

Figure 1. Compendium Method TO-17
Field Test Data Sheet (FTDS)

VOCs — Method TO-17

COMPENDIUM METHOD TO-17
FIELD TEST DATA SHEET (FTDS)

I. GENERAL INFORMATION

PROJECT:_____ DATE(S) SAMPLED:_____
SITE:_____ TIME PERIOD SAMPLED:_____
LOCATION:_____ OPERATOR:_____
INSTRUMENT MODEL NO.:_____ CALIBRATED BY:_____
PUMP SERIAL NO.:_____ RAIN: ____YES _____NO

ADSORBENT CARTRIDGE INFORMATION:

	Tube 1	Tube 2
Type:		
Adsorbent:		
Serial No.:		
Sample No.:		

II. SAMPLING DATA

Tube Identification	Sampling Location	Ambient Temp., °F	Ambient Pressure, in Hg	Flow Rate (Q), mL/min		Sampling Period		Total Sampling Time, min.	Total Sample Volume, L
				Tube 1	Tube 2	Start	Stop		

III. FIELD AUDIT

	Tube 1	Tube 2
Audit Flow Check Within 10% of Set Point (Y/N)?	_ pre- / post-	_ pre- / post-

CHECKED BY:_____
DATE:_____

Figure 1. Compendium Method TO-17 Field Test Data Sheet.

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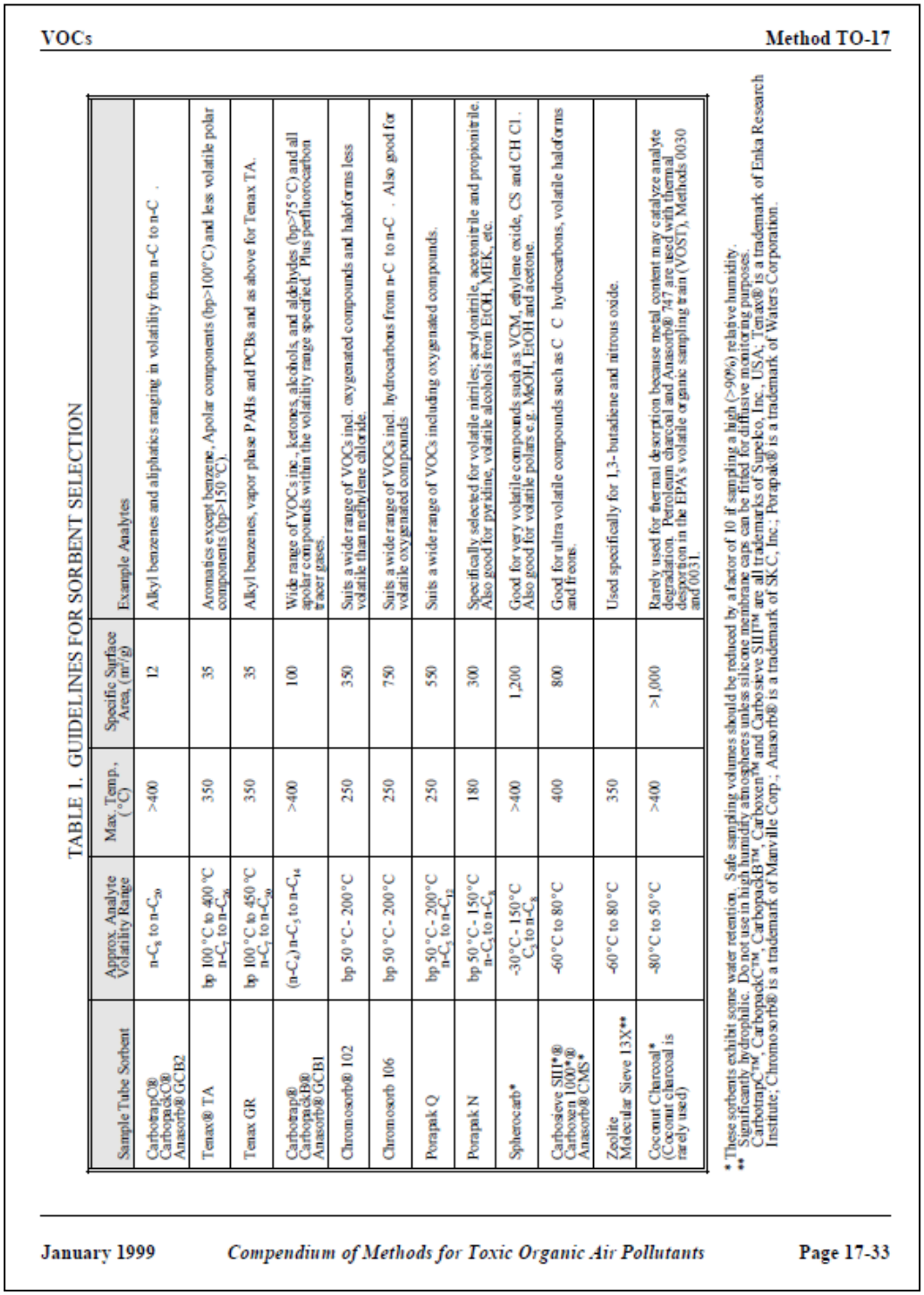
Figure 2. Guidelines for Sorbent Selection



VOCs — Method TO-17

TABLE 1. GUIDELINES FOR SORBENT SELECTION

Sample Tube Sorbent	Approx. Analyte Volatility Range	Max. Temp., (°C)	Specific Surface Area, (m^2/g)	Example Analytes
Carbotrap®C® CarbopackC® Anasorb® GCB2	n-C_4 to n-C_{20}	>400	12	Alkyl benzenes and aliphatics ranging in volatility from n-C to n-C .
Tenax® TA	bp 100 °C to 400 °C n-C_7 to n-C_{30}	350	35	Aromatics except benzene, Apolar components (bp>100°C) and less volatile polar components (bp>150 °C).
Tenax GR	bp 100 °C to 450 °C n-C_7 to n-C_{30}	350	35	Alkyl benzenes, vapor phase PAHs and PCBs and as above for Tenax TA.
Carbotrap® CarbopackB® Anasorb® GCB1	(n-C_4) n-C_5 to n-C_{14}	>400	100	Wide range of VOCs inc. ketones, alcohols, and aldehydes (bp>75°C) and all apolar compounds within the volatility range specified. Plus perfluorocarbon tracer gases.
Chromosorb® 102	bp 50 °C - 200 °C	250	350	Suits a wider range of VOCs incl. oxygenated compounds and haloforms less volatile than methylene chloride.
Chromosorb 106	bp 50 °C - 200 °C	250	750	Suits a wider range of VOCs incl. hydrocarbons from n-C to n-C . Also good for volatile oxygenated compounds
Porapak Q	bp 50 °C - 200 °C n-C_5 to n-C_{12}	250	550	Suits a wider range of VOCs including oxygenated compounds.
Porapak N	bp 50 °C - 150 °C n-C_5 to n-C_8	180	300	Specifically selected for volatile nitriles; acrylonitrile, acetonitrile and propionitrile. Also good for pyridine, volatile alcohols from EtOH, MEK, etc.
Spherocarb*	-30°C - 150°C C_3 to n-C_8	>400	1,200	Good for very volatile compounds such as VCM, ethylene oxide, CS and CH Cl . Also good for volatile polars e.g. MeOH, EtOH and acetone.
Carbosieve SIII*® Carboxen 1000*® Anasorb® CMS*	-60 °C to 80 °C	400	800	Good for ultra volatile compounds such as C C hydrocarbons, volatile haloforms and freons.
Zeolite Molecular Sieve 13X**	-60°C to 80°C	350		Used specifically for 1,3- butadiene and nitrous oxide.
Coconut Charcoal* (Coconut charcoal is rarely used)	-80°C to 50°C	>400	>1,000	Rarely used for thermal desorption because metal content may catalyze analyte degradation. Petroleum charcoal and Anasorb® 747 are used with thermal desorption in the EPA's volatile organic sampling train (VOST), Methods 0030 and 0031.

* These sorbents exhibit some water retention. Safe sampling volumes should be reduced by a factor of 10 if sampling a high (>90%) relative humidity.
** Significantly hydrophilic. Do not use in high humidity atmospheres unless silicone membrane caps can be fitted for diffusive monitoring purposes.
CarbotrapC™, CarbopackC™, CarbopackB™, Carboxen™ and Carbosieve SIII™ are all trademarks of Supelco, Inc., USA; Tenax® is a trademark of Enka Research Institute; Chromosorb® is a trademark of Manville Corp., Anasorb® is a trademark of SKC, Inc., Porapak® is a trademark of Waters Corporation.

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Figure 3. Safe Sample Volumes

APPENDIX 1.

The following list includes safe sampling volume data generated by the UK Health and Safety Executive (4) on single sorbent bed 1/4 inch O.D. stainless steel tubes and compatible with a thermal desorption - capillary GC analytical procedure. It is provided as a resource to readers only. The recommendation for Tube Style 2 is based on the specific tube referenced in Section 6.1.2 and Table 3. Where tubes are not listed with safe sample volumes they have not been tested and their inclusion represents a suggestion only. Application to air sampling is subject to criteria listed in Section 14 of Compendium Method TO-17.

[Note: Combination tubes 1, 2, and 3 referenced in this Appendix are those adsorbent tubes described in Section 9.1.3.]

Compound	Suitable sorbents and SSV's where available
Hydrocarbons	
This procedure is suitable for all aliphatic, aromatic and cyclic hydrocarbons less volatile than ethane and more volatile than n-C20. These include:	
n-Butane	CS III, C 1000, Combination Tubes 2 or 3 or Spherocarb (SSV 820L).
n-Pentane	CS III, C 1000, Spherocarb (SSV 30,000L), Combination Tubes 2 or 3 or Chromosorb 106 (SSV 5.5L).
n-Hexane	Carbopack™ B, Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 30L).
Benzene	Carbopack™ B, Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 26L) or Tenax (SSV 6L).
n-Heptane	Carbopack™ B, Tenax (SSV 17L), Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 160L).
Toluene	Carbopack™ B, Tenax (SSV 38L), Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 80L).
n-Octane	Carbopack™ B, Tenax (SSV 700L) Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 1000L).
Ethylbenzene	Carbopack™ B, Tenax (SSV 180L), Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 360L).
all Xylenes	Carbopack™ B, Tenax (SSV 300L), Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 770L).
n-Nonane	Carbopack™ C/B, Tenax (SSV 700L), Combination Tubes 1, 2 or 3 or Chromosorb 106 (SSV 7000L).
Styrene	Carbopack™ C/B, Tenax (SSV 300L) or Combination Tubes 1, 2 or 3.
Isopropylbenzene	Carbopack™ C/B, Tenax (SSV 480L) or Combination Tubes 1, 2 or 3.
n-Propylbenzene	Carbopack™ C/B, Tenax (SSV 850L) or Combination Tubes 1, 2 or 3.
1-Methyl-3-ethylbenzene	Carbopack™ C/B, Tenax (SSV 1000L) or Combination Tubes 1, 2 or 3.
1-Methyl-4-ethylbenzene	Carbopack™ C/B, Tenax (SSV 1000L) or Combination Tubes 1, 2 or 3.

Compound	Suitable sorbents and SSV's where available
1,3,5-Trimethylbenzene	Carbopack™ C/B, Tenax (SSV 1800L), Combination Tubes 1, 2 or 3 or Chromosorb 106 (SSV 2800).
Methylstyrene	Carbopack™ C/B, Tenax (SSV 1200L) or Combination Tubes 1, 2 or 3.
Methyl-2-ethylbenzene	Carbopack™ C/B, Tenax (SSV 1000L) or Combination Tubes 1, 2 or 3.
1,2,4-Trimethylbenzene	Carbopack™ C/B, Tenax (SSV 1800L) or Combination Tubes 1, 2 or 3.
n-Decane	Carbopack™ C/B, Tenax (SSV 2100L), Combination Tubes 1, 2 or 3 or Chromosorb 106 (SSV 37,000L).
1,2,3-Trimethylbenzene	Carbopack™ C/B, Tenax (SSV 1800L) or Combination Tubes 1, 2 or 3.
n-Undecane	Carbopack™ C/B, Tenax (SSV 12,000L) or Combination Tubes 1, 2 or 3.
n-Dodecane	Carbopack™ C, Tenax (SSV 63,000L) or Combination Tubes 1 or 3.

Halogenated Hydrocarbons including PCBs

This procedure is suitable for all aliphatic, aromatic and cyclic halogenated hydrocarbons more volatile than n-C20. Examples include:

Dichloromethane	CS III, C 1000, Spherocarb (SSV 200L) or Combination Tubes 2 or 3.
1,2-Dichloroethane	CS III, C 1000, Spherocarb, Chrom. 106 (SSV 17L), Carbopack™ B, Tenax (SSV 5.4L) or Combination Tubes 1, 2 or 3.
1,1,1-Trichloroethane	Spherocarb (SSV 8,000L), Chrom. 106 (SSV 8L), Carbopack™ B, or Combination Tubes 1, 2 or 3.
Carbontetrachloride	Chrom. 106 (SSV 22L), Carbopack™ B, Tenax (SSV 6.2L) or Combination Tubes 1, 2 or 3.
Trichloroethylene	Chrom. 106, Carbopack™ B, Tenax (SSV 5.6L) or Combination Tubes 1, 2 or 3.
1,1,2-Trichloroethane	Chrom. 106, Carbopack™ B, Tenax (SSV 34L) or Combination Tubes 1, 2 or 3.
Tetrachloroethylene	Chrom. 106, Carbopack™ B, Tenax (SSV 48L) or Combination Tubes 1, 2 or 3.
Chlorobenzene	Chrom. 106, Carbopack™ B, Tenax (SSV 26L) or Combination Tubes 1, 2 or 3.
1,1,1,2-Tetrachloroethane	Chrom. 106, Carbopack™ B, Tenax (SSV 78L) or Combination Tubes 1, 2 or 3.
1,1,2,2-Tetrachloroethane	Chrom. 106, Carbopack™ B, Tenax (SSV 170L) or Combination Tubes 1, 2 or 3.

Compound	Suitable sorbents and SSV's where available
Alcohols	
This procedure is suitable for alcohols more volatile than n-C20 and sufficiently stable to be analyzed by conventional GC techniques. Examples include:	
Methanol	CSIII, C1000, Spherocarb (SSV 130L) or Combination Tubes 2 or 3.
Ethanol	CSIII, C1000, Spherocarb (SSV 3500L) or Combination Tubes 2 or 3.
n-Propanol	Porapak N (SSV 20L), Chrom 106 (SSV 8L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Isopropanol	Chrom 106 (SSV 44L), Carbopack™ B or Combination Tubes 1, 2 or 3.
n-Butanol	Chrom 106 (SSV 50L), Carbopack™ B, Porapak N (SSV 5L), Tenax (SSV 5L) or Combination Tubes 1, 2 or 3.
iso-Butanol	Chrom 106 (SSV 30L), Carbopack™ B, Tenax (SSV 2.8L) or Combination Tubes 1, 2 or 3.
Octanol	Tenax (SSV 1400L), Carbopack™ C or Combination Tubes 1 or 3.
Esters and Gycol Ethers	
This procedure is suitable for all esters and glycol ethers more volatile than n-C20 and sufficiently stable to be analyzed by conventional GC techniques. Examples include:	
Methylacetate	Chromosorb 106 (SSV 2.6L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Ethylacetate	Chromosorb 106 (SSV 20L), Carbopack™ B, Tenax (SSV 3.6L) or Combination Tubes 1, 2 or 3.
Propylacetate	Chromosorb 106 (SSV 150L), Carbopack™ B, Tenax (SSV 18L) or Combination Tubes 1, 2 or 3.
Isopropylacetate	Chromosorb 106 (SSV 75L), Carbopack™ B, Tenax (SSV 6L) or Combination Tubes 1, 2 or 3.
Butylacetate	Chromosorb 106 (SSV 730L), Carbopack™ B, Tenax (SSV 85L) or Combination Tubes 1, 2 or 3.
Isobutylacetate	Chromosorb 106 (SSV 440L), Carbopack™ B, Tenax (SSV 130L) or Combination Tubes 1, 2 or 3.
Methyl-t-butyl ether	Chromosorb 106 (SSV >6L), Carbopack™ B or Combination Tubes 1, 2 or 3.
t-Butylacetate	Chromosorb 106 (SSV 160L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Methylacrylate	Chromosorb 106, Carbopack™ B, Tenax (SSV 6.5L) or Combination Tubes 1, 2 or 3.

Compound	Suitable sorbents and SSV's where available
Ethylacrylate	Chromosorb 106, Carbopack™ B, Tenax (SSV 60L) or Combination Tubes 1, 2 or 3.
Methylmethacrylate	Chromosorb 106, Carbopack™ B, Tenax (SSV 27L) or Combination Tubes 1, 2 or 3.
Methoxyethanol	Chromosorb 106 (SSV 5L), Carbopack™ B, Tenax (SSV 3L) or Combination Tubes 1, 2 or 3.
Ethoxyethanol	Chromosorb 106 (SSV 75L), Carbopack™ B, Tenax (SSV 5L) or Combination Tubes 1, 2 or 3.
Butoxyethanol	Chromosorb 106, Carbopack™ B, Tenax (SSV 35L) or Combination Tubes 1, 2 or 3.
Methoxypropanol	Chromosorb 106, Carbopack™ B, Tenax (SSV 13L) or Combination Tubes 1, 2 or 3.
Methoxyethylacetate	Chromosorb 106 (SSV 860L), Carbopack™ B, Tenax (SSV 8L) or Combination Tubes 1, 2 or 3.
Ethoxyethylacetate	Chromosorb 106 (SSV 4000L), Carbopack™ B, Tenax (SSV 15L) or Combination Tubes 1, 2 or 3.
Butoxyethylacetate	Chromosorb 106, Carbopack™ B, Tenax (SSV 150L) or Combination Tubes 1, 2 or 3.

Aldehydes and Ketones

This procedure is suitable for all aldehydes and ketones more volatile than n-C20 and sufficiently stable to be analyzed using conventional GC techniques. Examples include:

Acetone	CSIII, C1000, Spherocarb, Chrom 106 (SSV 1.5L) or Combination Tubes 2 or 3.
Methylethylketone (2-butanone)	Chromosorb 106 (SSV 10L), Tenax (SSV 3.2L), Porapak N (SSV 50L) Carbopack™ B or Combination Tubes 1, 2 or 3.
n-Butanal	Chromosorb 106, Carbopack™ B, Porapak N (SSV 50L) or Combination Tubes 1, 2 or 3.
Methylisobutylketone	Chromosorb 106 (SSV 250L), Tenax (SSV 26L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Cyclohexanone	Chromosorb 106, Tenax (SSV 170L), Carbopack™ B or Combination Tubes 1, 2 or 3.
3,5,5-Trimethylcyclohex-2-enone	Tenax (SSV 5600L), Carbopack™ B or Combination Tubes 1 or 3.
Furfural	Tenax (SSV 300L), Carbopack™ B or Combination Tubes 1, 2 or 3.

Compound	Suitable sorbents and SSV's where available
Miscellaneous VOCs	
This procedure is suitable for the analysis of most VOCs in air. It is generally compatible with all organics less volatile than ethane, more volatile than n-C20 and sufficiently stable to be analyzed using conventional GC techniques. Examples include:	
Acetonitrile	Porapak N (SSV 3.5L), CSIII, C1000 or Combination Tubes 2 or 3.
Acrylonitrile	Porapak N (SSV 8L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Propionitrile	Porapak N (SSV 11L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Maleic anhydride[a]	Tenax (SSV 88L), Chrom. 106, Carbopack™ B or Combination Tubes 1, 2 or 3.
Pyridine	Tenax (SSV 8L), Porapak N (SSV 200L) Chrom. 106, Carbopack™ B or Combination Tubes 1, 2 or 3.
Aniline	Tenax (SSV 220L), Chrom. 106, Carbopack™ B or Combination Tubes 1, 2 or 3.
Nitrobenzene	Tenax (SSV 14,000L) Carbopack™ C or Combination Tubes 1 or 3.
Acetic acid	Porapak N (SSV 50L), Carbotrap™ B or Combination Tubes 1, 2 or 3.
Phenol	Tenax (SSV 240L) or combination tube 1.

Figure 4. Tube Conditioning Log

Batch ID:

Date:

Tube Type (PAH or Universal)

Conditioning methods:

(1)Universal-TC2 Short Cycle (15minutes ea @ 100,200,300,335)

(2)Univesal-TC2 Long Cycle (1 hour ea @ 100,200,300 and 30 min @335)

(3)Universal-Running as blank On Ultra.

(4)-PAH-Long Cycle 2Hours @330C.

(5)-PAH-Short Cycle 15-30mins @330C.

Serial#	Tube Type	Conditioning Method	Sequence ID	Cycle

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APPENDIX E -
PHILIS SOP L-A-310
Opioids on Soil, Water, and Wipes by Altis UPLC/MS/MS Rev. 5 01/23/2024

STANDARD OPERATING PROCEDURE

FOR

OPIOIDS ON SOIL, WATER AND WIPES BY ALTIS UPLC/MS/MS

PHILIS SOP L-A-310 Rev. 5

Revision Date: 01-23-2024

EPA Contract No. 68HERH21D0002

PREPARED BY

PHILIS

PREPARED FOR

U.S. Environmental Protection Agency
Office of Emergency Management
Washington, DC 20460

Approvals:

PHILIS, Castle Rock Lead Chemist	**January 23, 2024** Date
PHILIS, Edison Lead Chemist	**January 23, 2024** Date
PHILIS, Quality Assurance Manager	**January 23, 2024** Date
PHILIS, Program Manager	**January 23, 2024** Date

Revision History

Revision	Name	Date	Description of Change
0	James Garcia James Travis	05/20/2021	SOP Development
1	James Garcia James Travis	08/27/2021	Revision
2	James Garcia James Travis	09/08/2021	Revision
3	James Garcia James Travis	03/17/2022	Revision
4	James Garcia James Travis	01/31/2023	Revision
5	James Garcia James Travis	01/11/2024	Revision

SOP REVISION FORM

SOP Name:	**Opioids on Soil, Water, and Wipes by Altis UPLC/MS/MS**		
Purpose: *(Review or Revise)*	*SOP #:*	*Rev. #:* *(Being Reviewed or Revised)*	*Origination / Release Date:*
Revision	*SOP No. L-A-310*	4	08/24/2023
Requested by:	James Travis	Date:	01/11/2024

New SOP Revision Date:	**01/23/2024**	**New SOP Revision #:** *(If Applicable)*	**5**

For *Revision* : Summary of Revisions (specify sections)

Tables 8-10	Tables were revised and added for Altis LCMSMS
Figure 2	Revised to present Degradation of Opiate analogues in water
6.9.9	Removed “that were precleaned in methanol”
7.4.4 & 7.4.6	Added “50,000 pg/uL for Methamphetamines”
7.4.4	Added reference for Table 3 and Table 4
9,4	Added “than two times the”
11.2.2.6	Revised
11.2.3.7	Added “the vial with the appropriate cap for your system”
12.2	Added “carfentanil-*d5*, and heroin-*d9*, are”
Table 1	Added cas number for carfentanil-d5

For *Review*: Comments

Standard Operating Procedure
Opioids on Soil, Water and Wipes by
Altis UPLC/MS/MS
L-A- 310 Rev. 5

TABLE OF CONTENTS

TABLES, FIGURES, AND ATTACHMENTS

Standard Operating Procedure
Opioids on Soil, Water and Wipes by
Altis UPLC/MS/MS
L-A- 310 Rev. 5

1.0 Scope and Application

1.1 This SOP is for the analysis of Fentanyl and other opiates. This SOP is executed in accordance with the U.S. Environmental Protection Agency and National Environmental Laboratory Accreditation Program (NELAP) requirements.

1.2 This procedure covers specific requirements for the determination of Opiate analogs in soil, water, and on wipes using ultra performance liquid chromatography (UPLC) and detected with tandem mass spectrometry (MS/MS) using electrospray ionization (ESI). This method prescribes separation using reverse phase chromatography followed by detection using multiple reaction monitoring (MRM) spectrometry. The compounds shown in Table 1 are listed in the order of their retention times and are qualitatively and quantitatively determined by this method.

2.0 Summary of Method

2.1 This sample preparation method was established as a performance-based method to optimize precision, accuracy and operational performance.

2.2 This method is used for the analysis of Opiates in water, soil, and wipes.

2.3 For the analysis of Opiate analogs, samples are shipped to the lab between 0°C and 6°C and analyzed as soon as possible after collection. To prepare for analysis, samples are spiked with surrogate, and then diluted or extracted using the appropriate sample preparation method. The diluted samples or the extracts are filtered using a syringe-driven filter unit and the filtrates are analyzed by LC/MS/MS.

2.4 The UPLC is run using reverse phase chromatography, and the ions are transferred into the gas phase using electrospray (ES). The mass spectrometer is operated in the positive mode (ES+).

2.5 Opiate analogs identified by retention time (within ± 5% of a standard) and by a quantitation Multiple Reaction Monitoring (MRM) transition. MRM is a non-scanning mass spectrometric technique, performed on tandem mass spec instruments in which collision-induced dissociation is used as a means to increase selectivity. The target analytes and surrogate are quantitated using an external calibration procedure.

2.6 The target compounds and the surrogates are identified by retention time and one primary MRM transition. The target analytes and surrogates are quantitated using the MRM transitions utilizing an external calibration.

3.0 Definitions

3.1 Batch‡: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A Preparation Batch is composed of between 1 and 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and the last sample in the batch to be 24hours. An Analytical Batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

All batches require one MB, LCS, and MS/MSD pair or MS and Sample Duplicate when possible.

3.2 Laboratory Control Sample (LCS)‡: (however named, such as laboratory fortified blank, blank spike (BS), or QC check sample). A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

The standard source can be the same as the calibration or a second source. The LCS is analyzed exactly like a sample to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.3 Matrix Spike (spiked sample of fortified sample)‡: A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of the sample for which an independent test results of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

3.4 Matrix Spike Duplicate (spiked sample or fortified sample duplicate)‡: A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

3.5 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. Method Blank analytical results are evaluated to determine the presence of contamination in the analytical method process.

3.6 Method Detection Limit (MDL): The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined by analyzing seven or more replicates of a spiked analyte free matrix and the resulting statistical calculation, in accordance with 40 CFR 136, Appendix B, Revision 2.0.

3.7 Multiple Reaction Monitoring (MRM): Multiple reaction monitoring (also known as Selective Reaction Monitoring or SRM) is a highly specific and sensitive mass spectrometry technique that can selectively quantitate compounds within complex mixtures. The MRM technique is performed on triple quadrupole (MS/MS) instruments by setting the first quadrupole (Q1) at a specific mass to select a precursor (parent) ion, which can be isolated and fragmented to deliver a unique product (daughter) ion. The third quadrupole (Q3) is set at another specific mass to allow the passage of the product (daughter) ion, which can then be quantitated. The specific pairs of m/z values associated to the precursor and product ions selected are referred to as "transitions" and effectively constitute mass spectrometric assays that allow you to identify and quantitate a specific compound. Parallel acquisitions of multiple precursor/product (parent/daughter) ion transitions are completed during a chromatographic run. These transitions are measured within the same analysis on the chromatographic time scale by rapidly toggling between the different precursor/product pairs. Typically, the triple quadrupole instrument cycles through a series of transitions and records the signal of each transition as a function of the elution time. The method allows for additional selectivity by monitoring the chromatographic coelution of multiple transitions for a given analyte.

3.8 Primary Dilution Standard (PDS): A solution of one or several analytes prepared in the laboratory from SSS and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.9 Reporting Limit (RL): The reporting limit, also known as the LOQ is the minimum concentration that can be reported as a quantitated value for a target analyte in a sample. This value can be no lower than the concentration of the lowest calibration standard.

3.10 Required Detection Limit (RDL): Detection limits established by a client or regulatory authority for analytes of concern. The laboratory MDL values must be equal or lower than the RDL. This is also known as the CRQL, the contract-required quantitation limit.

3.11 Second Source Calibration Verification (SCV): A solution prepared from a source that is different from the calibration standards. The SCV is immediately following the ICS, and is used to verify calibration standard accuracy.

3.12 Stock Standard Solution (SSS): A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased as certified from a reputable commercial source.

3.13 Surrogate Standard (SS): Organic compounds which are similar to the target analytes in chemical composition and mimic the behavior of the target analytes throughout the analytical process. Surrogate compounds are not normally found in environmental samples. Each calibration standard, sample, MB, LCS, MS, and MSD is spiked with surrogate standards. Surrogates are used to evaluate analytical efficiency by measuring recovery. See analytical method SOP for a list of specific surrogate compounds that are appropriate for sample-specific analysis.

ǂ EL-V1M2-ISO-2016, 2016 NELAP Standard definition.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in wipes, solvents, reagents, glassware, and other apparatus producing discrete artifacts or elevated baselines. All of these materials are demonstrated to be free from interferences by analyzing method blanks (MB) under the same conditions as samples. Subtraction of blank values from sample results is not performed.

4.2 All glassware and containers should be washed in hot water with detergent followed by distilled water. Glassware must subsequently be cleaned with methanol or acetone.

4.3 Filter papers used for wipes should be washed with distilled water and Acetonitrile prior to use.

4.4 Syringes and syringe filters are rinsed with 1 – 5 mL of methanol followed by 1 – 5 mL of acetonitrile before use.

4.5 All reagents and solvents should be LC/MS or pesticide grade or higher to minimize interference problems.

4.6 Matrix effects are well known phenomena of ESI-MS techniques, especially for co-eluting compounds. Managing the unpredictable suppression and enhancement caused by these effects is recognized as an integral part of the performance and verification of an ESI-MS procedure. The data presented in this procedure were designed to demonstrate that the procedure is capable of functioning with realistic samples. Each analyst is encouraged to observe appropriate precautions and follow the described QC procedures to help minimize the influence of ESI-MS matrix effects on the data reported. Matrix effects include ion suppression/enhancement and high backgrounds.

5.0 Safety

Laboratory personnel are required to be familiar with the general laboratory safety plan including the location and proper use of safety/emergency equipment.

5.1 Employees must abide by the policies and procedures in the Chemical Hygiene Plan and this document. This procedure involves hazardous material, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow the appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are hazardous. Standard laboratory safety procedures should be followed when working with all samples.

5.2 Specific Safety Concerns or Requirements

Eye protection that satisfies ANSI Z87.1, laboratory coat, and disposable nitrile or Silver-Shield gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded. Non-disposable gloves must be cleaned immediately. Latex and Vinyl gloves provide no protection against the organic solvents used in this method.

5.3 Each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Procedures involving primary standards and sample preparation must be performed in a fume hood.

5.4 Extraction solvents such as acetone, hexane and especially methylene chloride have appreciable vapor pressure that requires proper venting if using a separatory funnel. After a few manual shakes, hold the funnel upside down, open the stopcock and position the funnel to be directed in the hood and away from the individual(s) to release buildup of solvent pressure, repeat as necessary.

5.5 Material Safety Data Sheets (MSDS) for each analyte and reagent used in the mobile laboratory are available to all employees. The MSDS and the PHILIS Chemical Hazard Summary Sheet must be read and understood by the analyst prior to initial use of a chemical.

WARNING: Precautions must be used even for the simplest procedures involving these agents. If Fentanyl is suspected, laboratory personnel must be thoroughly trained in appropriate safety procedures prior to using this method.

5.6 The toxicity and/or carcinogenicity of the common reagents and analytes used in this method have been defined; however, each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Procedures involving primary standards and sample preparation should be performed in a fume hood.

5.7 At a minimum, personal protective equipment (PPE) requirements include safety glasses, lab coats, and protective gloves. All work with samples and standards shall be conducted in a fume hood. The availability of emergency response equipment and support personnel should be as indicated in a laboratory Chemical Hygiene Plan.

5.8 Exposure to drug material is possible from contact, and risk is primarily associated with compromise of protective clothing. Respiratory exposure can result from spills or improper use of ventilation controls and PPE.

5.9 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded. Non-disposable gloves must be cleaned immediately. Latex and vinyl gloves provide no protection against the organic solvents used in this method, so nitrile or similar must be used.

5.10 Pure standard materials and stock standards of these compounds should be handled with suitable protection to skin and eyes. Care should be taken not to breathe the vapors or ingest the materials.

5.11 Laboratory personnel are required to be familiar with the general laboratory safety including the location and proper use of safety/emergency equipment.

6.0 Equipment and Supplies

6.1 Sampling and Sample Preparation Equipment for Wipe Samples

6.2 Shaker table, VWR model DMS-2500 High Speed Micro Plate Shaker, catalog number 13500-890, or equivalent.

6.3 Microcentrifuge or centrifuge capable of maintaining a speed of 12,000 rpm

6.4 Vortexer

6.5 Glassware

Graduated cylinders - various sizes

6.6 Syringes

Gas-tight glass syringes - various sizes from 10 µL to 1000 µL.

6.7 Instrumentation

6.7.1 LC/MS/MS Apparatus

6.7.1.1 UPLC System (LC) - A complete LC system is needed to analyze samples. Any system that is capable of performing at the flows, pressures, controlled temperatures, sample volumes, and requirements of the SOP may be used. The system includes HPLC bottles for mobile phases and wash solvents (various sizes, e.g., 500 or 1000 mL), a binary pumping unit and temperature-controlled compartments for the samples and the chromatographic column. PHILIS uses the ThermoFisher Vanquish UPLC system with a 50-µL loop for this method.

6.7.1.2 Analytical Column - Waters Acquity™ HSS T3 C18 column, 2.1 mm x 150 mm, 1.8 µm particle size (part # 186003540) and corresponding guard or pre-column. Any equivalent pair of a guard and analytical column that achieves adequate resolution may be used. The retention time and order of elution may change depending on the type of column used.

6.7.1.3 Tandem Mass Spectrometer (MS/MS) - A MS/MS system capable of MRM analysis. Any system that is capable of performing the requirements. PHILIS uses the ThermoFisher TSQ Altis System.

6.7.1.4 Data System - TraceFinder software (or similar software) interfaced to the LC/MS that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. TraceFinder (or similar software) is used for all quantitation for data generated from the LC/MS unit.

6.8 Other Laboratory Equipment

Analytical balance capable of reading to ±0.0001g with certified reference weights.

6.9 Supplies

6.9.1 Autosampler vials – amber or polypropylene vials for LC autosampler, 1 – 2 mL.

6.9.2 Sample Collection Containers: Precleaned glass bottles, vials or jars with polytetrafluoroethylene-lined caps.

6.9.3 Small glass vials (8mL are used for storage of sample extracts, calibration standards and stock standards).

6.9.4 10 mL vials are used for storage of standards and spiking solutions.

6.9.5 40 mL VOA vials

6.9.6 15 and 25 mL Falcon Tubes

6.9.7 2.1 mL microcentrifuge tubes.

6.9.8 Pasture pipettes

6.9.9 Wipes: Kendall 3" x 3" type VII gauze sponges.

6.9.10 Ottawa Sand, or other clean certified sand matrix

6.9.11 3mm glass beads

7.0 Reagents and Standards

7.1 Reagents

7.1.1 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.

7.1.2 Argon- UHP or greater used for collision gas and should meet or exceed instrument manufacturer's specifications.

7.1.3 Nitrogen- UHP or greater used for desolvation and nebulization and should meet or exceed instrument manufacturer's specifications.

7.1.4 Water- ASTM Type I or equivalent. It must be demonstrated that this water does not contain contaminants at concentrations sufficient to interfere with analysis. LC/MS grade water (Fisher Optima W6-4, or equivalent) may also be used.

7.1.5 Acetonitrile (ACN) (CAS# 75-05-8) LC/MS grade or better.

7.1.6 Methanol (CAS# 67-56-1)- LC/MS grade or better

7.1.7 Isopropyl Alcohol (IPA) (CAS# 67-63-0) Pesticide grade or better

7.1.8 Acetone (CAS# 1567-89-1) Pesticide grade or better

7.1.9 Formic Acid (CAS# 64-18-6) - LC/MS grade or better.

7.1.10 Ammonium formate (CAS#540-69-2) >98%

7.2 Wash Solutions

7.2.1 Needle Washing Solution.

Magic Mix (for high protein contamination), 45% Acetonitrile / 45% Isopropyl Alcohol / 10% Acetone (v/v/v)

Or Non Acetone Magic Mix, 45% Acetonitrile / 45% Isopropyl / 10% Methanol (v/v/v)

7.2.2 Seal wash solution:

75% Isopropyl Alcohol / 25% Water / 0.1% Formic Acid (v/v/v)

7.3 Mobile Phases

Mobile phase A is 0.01% Formic Acid + 2.5 mM Ammonium formate in water.

Mobile phase B is 100% Methanol.

7.3.1 Preparation of Mobile Phase A (aqueous)

Mobile phase A consists of 0.01% of formic acid + 2.5mM ammonium formate in water. To prepare 1000 mL, weigh out 157.65 mg of ammonium formate and add to the 1000 mL volumetric flask. Transfer in about 100 mL of water. Add 100uL of formic acid to a 1000-mL volumetric flask. Dilute to the mark with HPLC grade water. Mix and transfer to a HPLC bottle.

7.4 Standards

Standard solutions may be prepared from certified, commercially available solutions or from neat compounds. Compounds used to prepare solutions must be 96% pure or greater and the weight may be used without correction for purity to calculate the concentration of the stock standard. Solution concentrations listed in this section were used to develop this method and are included as an example. Standards for sample fortification should be prepared in the smallest volume that can be accurately measured to minimize the addition of organic solvent to aqueous samples. Prepare all solutions using Class A volumetric glassware. During storage, protect standards from light and keep in a refrigerator at 0 – 6°C. Stock standards are stable for at least one month but should be replaced when analyzed solution concentrations deviate more than ± 20% from the prepared concentration.

Table 2 lists some suggested stocks that are available from Sigma-Aldrich (St. Louis, MO, USA) as certified solutions at 100 µg/mL.

7.4.1 Surrogate Stock Standard Solution (Surrogate SSS), 1000 – 2000 µg/mL

Standard stock solutions may be prepared from certified commercially available neat compounds, if available. To prepare a stock from neat materials, obtain the isotopically labeled surrogate, fentanyl-*d5*, and accurately weigh about 0.05 g each on an analytical balance. Transfer the surrogates to individual 25-mL volumetric flasks and dilute each to the mark with acetonitrile in order to achieve concentrations of ca. 2000 µg/mL. The surrogate stock standard solutions are stable for at least a month when stored at 0 – 6°C.

If neat materials are not available, certified, commercially available stocks at 100 µg/mL of the surrogate may be obtained from Sigma-Aldrich (St. Louis, MO, USA) or Cerillant.

7.4.2 Surrogate Spike Solution – Prepare a surrogate spike solution at a known concentration in 100% MeOH that will be used for spiking samples and blanks. It is recommended that Heroin-D9 be 10 times more concentrated than the other surrogates.

Recommend concentration for surrogate spiking solution, 1000 pg/uL (10,000 pg/uL Heroin-d9) in 100% MeOH

7.4.3 Analyte Stock Standard Solutions, 500-5000 µg/mL

Standard solutions may be prepared from certified, commercially available neat compounds. If analyte stock solutions are made from neat materials, their recommended concentrations should be 500-5000 µg/mL. For example, a standard stock solution of 2000 µg/mL for each compound can be prepared by diluting 0.05 g of the neat material in a 25-mL volumetric flask with methanol. Analyte stock standard solutions are stable for at least a month when stored at 0 - 6°C.

If neat materials are not available, certified, commercially available stocks at 100 µg/mL of each analyte may be obtained from Sigma-Aldrich (St. Louis, MO, USA) or Cerillant.

7.4.4 Calibration Standard Solutions

Prepare a 1,000 pg/uL (10,000 pg/uL for Heroin and Heroin-d9, 2,000 pg/uL for Remifentanil, 50,000 pg/uL for Methamphetamine) calibration stock standard in 100% Acetonitrile.

Next, all calibration levels are prepared in a 100% MeOH. Remifentanil has been shown to be extremely unstable in water and breaks down at an accelerated rate. The addition of methanol helps to stabilize this compound.

Prepare a 100 pg/uL (A) standard in a total volume of 1 mL of100% MeOH. This can be done with a 1mL syringe into an autoampler via. This will be the base for the serial dilution.

From the base, serially dilute to 50 pg/uL(B) and 25 pg/uL (C) to a final volume of 1 mL in 100% MeOH. with a 1 mL syringe and autosampler vials

Going back to the 100 pg/uL (A) standard serially dilute that to 10, 1.0, 0.1 pg/uL to a final volume of 1mL in 100% MeOH. with a 1 mL syringe and autosampler vials.

Next, using the 50 pg/uL(B) standard, serially dilute to 5.0, 0.5, 0.05 pg/uL to a final volume of 1mL in 100% MeOH. with a 1 mL syringe and autosampler vials.

Finally, using the 25 pg/uL (C) standard, serially dilute to 2.5, 0.25, 0.025 pg/uL to a final volume of 1mL in 100% MeOH. with a 1 mL syringe and autosampler vials.

Reference Table 3 for serial dilution matrix.

Reference Table 4 for example calibration level concentrations.

7.4.5 Continuing calibration verification. 10 uL spike of a 1000pg/uL into 990 uL of 100% MeOH. From that, take 100 uL and add to 900 uL of MeOH in another autosampler vial for a final concentration of 1.0 pg/uL.

7.4.6 LCS Spiking Solution

It may be prepared from the primary source (i.e., the stocks used to prepare the calibration standards) or from a secondary source, if available. The preparation and the concentration of the LCS Spiking Solution depend on the specific analyte and the extraction method. The following guidelines are for the preparation of the LCS Spiking Solution for each matrix:

Recommend concentration for LCS spiking standard is 1,000 pg/uL (10,000 pg/uL Heroin, 2,000 pg/uL Remifentanil, 50,000 pg/uL for Methamphetamine.)

8.0 Sample Collection, Preservation, and Storage

8.1 Sample Collection

8.1.1 The exact choice of sampling vessel and procedure is not critical for the analysis and can be adjusted to meet project needs as long as the different materials have been tested and show no presence or interferences of the target analytes.

8.1.2 As an example for wipe samples, the field sampling team collects samples using an appropriate wetted wipe (methanol). The wipe sample is placed in a jar with a sealed cap for shipment to the laboratory, (e.g., VOA vial or glass jar with a Teflon-lined screw cap).

8.1.3 Wipe samples are collected by using precleaned (in MeOH) Kendall 3"x 3" type VII gauze sponges. The required analyte spike solution containing the analytes of interest is added to the surface, allowed to dry, and wiped with each wipe separately. Two wipes are separately wetted with approximately 2.0 mL of methanol. The first wipe is used to wipe the surface in a Z-like pattern horizontally across a defined surface (100 cm^2). The second wipe is used to wipe the same surface in a Z-like pattern vertically across a defined surface (100 cm^2). Wipes are placed in individual 40-mL VOA vials. Field and/or matrix blanks are needed, according to conventional sampling practices.

8.1.4 Sample preservatives are not used in this method.

8.2 Sample Storage and Holding Times

Wipe samples must be analyzed within 72 hours of collection or as soon as possible. The holding times for wipes has not been determined, but should be analyzed as soon as possible, since the target analytes are subject to rapid breakdown. At the laboratory, samples can be stored in a refrigerator at 0 - 6 ºC until requested for analysis. Samples from a particular site should be carefully characterized to ensure that there is no interaction with the wipe or specific surface to cause interferences or degradation of the analytes after 24 hours. After injection in the LC/MS, the vial septa must be replaced and the vials are stored in a refrigerator in case further analysis was needed. Extracts or diluted samples previously analyzed by LC/MS can be stored up to 28 days in the refrigerator at 0 - 6 ºC.

9.0 Quality Control

9.1 Quality control (QC) requirements include the Initial Demonstration of Capability, the determination/verification of the Detection Limit, and subsequent analysis in each analysis batch of a Method Blank (MB), Continuing Calibration Verification Standards (CCV), a Laboratory Control Sample (LCS), a Matrix Spike (MS), and either a Matrix Spike Duplicate (MSD) or a Field Duplicate Sample. This section details the specific requirements for each QC parameter. The QC criteria discussed in the following sections are summarized in Table 5. These criteria are considered the minimum acceptable QC criteria.

9.2 INITIAL DEMONSTRATION OF CAPABILITY (IDC) – Requirements for the Initial Demonstration of Capability include a method blank, precision and accuracy samples, and an mdl determination which are described in the following sections 12.2.1 through 12.2.4.

9.2.1 INITIAL DEMONSTRATION OF LOW SYSTEM BACKGROUND – Before any field samples are analyzed, and any time a new set of reagents is used, it must be demonstrated that a method blank does not contain analytes of interest above the reporting limit and there are no other peaks that will interfere with the determination of the analytes of interest.

9.2.2 INITIAL DEMONSTRATION OF ACCURACY – Prior to the analysis of the IDC samples, verify calibration accuracy with the preparation and analysis of a mid-level CCV as defined in Section 9.6. If the analyte recovery is not within 30% of the true value, the accuracy of the method is unacceptable. The source of the problem must be identified and corrected. After the accuracy of the calibration has been verified, prepare and analyze a minimum of four replicate LCSs fortified at 500ng/L, or near the mid-range of the initial calibration curve, according to the procedure described in Section 10. The average recovery of the replicate values must be within ± 30% of the true value.

9.2.3 INITIAL DEMONSTRATION OF PRECISION – Using the same set of replicate data generated for Section 9.2.2, calculate the standard deviation and percent relative standard deviation of the replicate recoveries. The relative standard deviation (%RSD) of the results of the replicate analyses must be less than 20%.

9.2.4 METHOD MODIFICATIONS – This is a performance based method. The analyst is permitted to optimize LC/MS instrument conditions. The analyst is also allowed to choose an alternate surrogate standard with approval of the Quality Assurance Manager. Each time such method modifications are made, the analyst must document the changes and repeat the procedures of the IDC.

9.3 MDL Procedure

MDLs and RLs are established by analyzing a minimum of seven replicates of a standard at or near the estimated MDL. Tabulation of results and MDL calculations are performed by the method in 40 CFR, Part 136, Method Update Rule Revision 2.

9.3.1 Initial MDLs

9.3.1.1 Initial MDLs are established by analyzing a minimum of seven replicates of the low-level calibration standard and a minimum of seven blanks prepped in three separate batches and analyzed on three separate days. The MDL should be spiked 1 to 5 times the estimated MDL. Extract and analyze the MDL standards and blanks with the same procedure as regular samples.

9.3.1.2 For each compound, calculate the mean and standard deviation of the replicates in micrograms per liter (µg/L). Then calculate the MDL by multiplying the standard deviation by the Student's t value. The one-sided (single-tailed) Student's t values at the 99% confidence levels are used (e.g., t = 3.143 at the 99% confidence level for n = 7). MDL results are stored in Element each time they are calculated. This calculation must be performed separately for the spikes and blanks. The larger of the two values will be used.

9.3.1.3 MDL Blank is determined as follows:

A. If all blanks are non-detect then the MDL blank is not used.

B. If only some of the blanks have detection, then use the highest value for the MDL blank.

C. If all blanks have detection then determine the average value and add the MDL determined from the blank results to the average result.

D. Use the higher of the regular MDL and MDL blank.

9.3.1.4 The Initial MDL should be performed when there is a change of equipment, location of equipment, or a change of procedure.

9.3.2 Ongoing MDL Data Collection

9.3.2.1 Ongoing MDLs are determined by preparing and analyzing two spiked standards at 1-5 times the estimated MDL and two blanks once per quarter for a minimum of seven determinations. The blanks and spikes may be analyzed in the same prep batch, but is not required. If the instruments are being used regularly, the MDL spikes may be added to the routine batches and the regular blanks used. All blanks analyzed during the evaluation period should be used. If client samples are not received on a regular basis, an initial mdl may be performed annually.

9.3.2.2 At least once per year re-evaluate the MDL by, calculating as above in 9.3.1.2. Use the larger of the spiked determinations and blank determinations for the MDL value.

9.3.3 Ongoing MDL Annual Verification

At least once every thirteen months, re-calculate the MDL spike and MDL blank from the collected spiked samples and method blank results.

9.3.4 Include data generated within the last twenty four months, but only data with the same spiking level. Only documented instances of gross failures (instrument malfunctions, mislabeled samples, cracked vials, etc.) may be excluded from the calculations.

9.4 Reporting Level (RL) – The RL is the threshold concentration of an analyte that a laboratory can expect to accurately quantitate in an unknown sample. The RL cannot be established at an analyte concentration that is less than two times the Method Detection Limit or a concentration which would yield a response less than a signal-to-noise (S/N) ratio of three. Depending upon the study's data quality objectives it may be set at a higher concentration. **Although the lowest calibration standard must be at or below the RL, the RL must never be established at a concentration lower than the lowest calibration standard**.

9.5 Data Assessment and Acceptance Criteria--Analytical data generated by the quantitation software is reviewed and evaluated by the analyst as follows:

9.5.1 Instrument calibration, calibration verifications, SS, other QC measures are evaluated and the results documented on separate forms:

9.5.2 For each analyte and surrogate, evaluate the coefficient of determination, R^2, from the initial calibration curve.

9.5.3 Evaluate the % recoveries for all surrogates.

9.5.4 Evaluate the % recoveries for the CCV, SCV, LCS, MS, MSD, and evaluate the RPD for the MS/MSD pair.

9.5.5 Calibration standards must meet the coefficient of determination criteria and other quality control measures must meet the criteria listed in Table 5.

9.5.6 A reported compound that has a retention time outside the established window is considered a false positive response. All false positives are eliminated, and all positively identified target analytes are reported to LIMS.

9.5.7 Manual integration is ONLY applied in cases when the instrument data processing software produces integrated areas that are not valid. Manual adjustments to the chromatographic peak must be performed in a consistent manner for the calibration standards, QC and field samples. Refer to PHILIS SOP L-D-501.

9.5.8 Chromatograms of all field samples are examined to identify additional peaks that are not included in the integration report, which were not identified as target analytes. If such peaks are present, the Lead Chemist should be notified immediately in that case.

9.5.9 Anytime the analyst alters the instrument generated quantitation report, the hard copies of both reports (original and analyst's corrected) must be retained (e.g., manual integration). The analyst should seek to minimize manual integrations by proper instrument maintenance, retention time updates, setting integration parameters, etc.

9.5.10 Discrepancies or anomalies in the analytical run are described in the QA-020B form, discussed with the Lead Chemist, and documented in the case narrative.

9.5.11 Reviewed data are entered into LIMS, hard copies of LIMS report are printed and compared to the original data.

9.5.12 All records (electronic or hardcopy) derived from the analytical process are assembled in the analytical data package that consists of:

9.5.12.1 LIMS work list

9.5.12.2 QA-017 form signed by the Lead Chemist or peer review

9.5.12.3 Quantitation Report for each Sample and QCS

9.5.12.4 Evaluation reports for CCV and LCS

9.5.12.5 Initial calibration curves generated

9.5.12.6 LIMS report of each sample

9.5.13 All electronic data including data packages is stored on a server which is backed up.

9.6 METHOD BLANK (MB) – An MB is required with each analysis batch of samples to determine any background system contamination. If within the retention time window of any analyte, the MB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples. Background contamination must be reduced to an acceptable level before proceeding. Background from method analytes or contaminants that interfere with the measurement of method analytes must be below the MDL. If the target analytes are detected in the MB at concentrations equal to or greater than this level, then all data for the problem analyte(s) must be considered invalid for all samples in the analysis batch. Method blanks for each matrix are prepared as follows:

Wipe MB: Spike a known amount of Surrogate Spiking Solution (Section 10.4.2) on to one clean wipe, keeping in mind a final extraction volume of 15 ml and place in a 40-mL VOA vial.

9.7 CONTINUING CALIBRATION VERIFICATION (CCV) – A CCV is prepared in the same manner as the initial calibration solutions in Table 3 LV5. It is analyzed during an analysis batch at a required frequency to confirm that the instrument meets initial calibration criteria. If an ICAL started the sequence, the beginning CCV may be eliminated. The CCV must be analyzed at the beginning and end of each batch of 20 samples or within 24 hours after the initial calibration curve was generated. The results from the CCV must have a percent deviation of less than 30% from the calculated concentration of the target analytes and surrogates. If the results are not within criteria, the problem must be corrected and either all samples in the batch must be re-analyzed against a new calibration curve or the affected results must qualified as estimated with an indication that they do not fall within the performance criteria of the test method. If the analyst inspects the vial containing the end CCV and notices that the sample evaporation affecting the concentration, a new end CCV may be made and analyzed. If this new end CCV has a percent deviation of less than 30% from the calculated concentration for the target analytes and surrogates, the results may be reported unqualified.

9.8 LABORATORY CONTROL SAMPLE (LCS) – To ensure that the instrument is in control, analyze an LCS that is prepared with the target compounds at a concentration near the mid-point of the calibration curve (Section 10.4.6). The LCS is analyzed with each batch of 20 samples or less. The results from the LCS must fall within the limits in Table 5.

9.9 SURROGATE RECOVERY – The surrogate standard is spiked into all samples, method blanks, LCSs, and MS/MSDs prior to sample analysis. It is also added to the calibration and check standards. The surrogates are a means of assessing method performance. The results obtained for a surrogate recovery must fall within the limits of Table 5. If the limits are not met, the sample must be reanalyzed, and if still outside of limits, then the affected results must be qualified with an indication that they do not fall within the performance criteria of the test method.

9.10 MATRIX SPIKE (MS) – To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch of 20 or fewer samples by spiking the samples with a known concentration of fentanyl and following the analytical method.

9.10.1 If the spiked concentration plus the background concentration exceeds that of the highest calibration standard, the sample must be diluted to a level near the midpoint of the calibration curve. The MS/MSD should be at the same dilution as the original sample.

9.10.2 Calculate the percent recovery of the matrix spike (P) using Eq 1:

$$P = \left[\frac{(A - B)}{C} \right] x\,100$$

Eq. 1

where

A = measured concentration in the fortified sample

B = measured concentration in the unfortified sample, and

C = fortification concentration.

9.10.3 The percent recovery of the matrix spike shall fall within the limits in Table 5. If the percent recovery is not within these limits, a matrix interference may be present in the selected sample. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in a batch must be analyzed by a test method not affected by the matrix interference, or the sample results must be qualified with an indication that they do fall within the performance criteria of the test method.

9.11 MATRIX SPIKE DUPPLICATE (MSD) - To check the precision of sample analyses, analyze a sample in duplicate with each batch of 20 or fewer samples. If the same contains the analyte at a level greater than 5 times the detection limit of the method, the sample and duplicate may be analyzed unspiked; otherwise, an MSD should be used.

9.11.1 Calculate the relative percent difference (RPD) between the duplicate values as shown in Eq. 2. Compare the RPD limit in Table 5.

$$RPD = \left[\frac{|MS - MSD|}{(MS + MSD)/2} \right] 100$$

Eq. 2

where:

RPD = relative percent difference

MS = matrix spike recovery

MSD = matrix spike duplicate recovery

9.11.2 If the result exceeds the precision limit, the batch must be re-analyzed or the result associate with that sample must be qualified with an indication that they do not fall within the performance criteria of the test method.

9.12 Corrective Action for Out of Control

In cases where quality control measures do not meet acceptance criteria, the quality of the analytical data is not acceptable and the analyst does the following:

9.12.1 When the instrument calibration fails to meet acceptance criteria, the analysis does not start. The problem is investigated and the necessary instrument maintenance is performed, followed with tuning and calibration.

9.12.2 If after analysis, any of the criteria for quality control are not met, or the sample is not available for reanalysis, the analyst must notify the Lead Chemist. The Lead Chemist will implement the corrective action plan.

9.12.3 The analyst shall report to the Lead Chemist and indicate on the QA-018 LC/MS/MS Data Review form, any out-of-control event. Such events include:

9.12.3.1 Damage to the sample.

9.12.3.2 Holding time exceeded.

9.12.3.3 Inadequate sample preservation.

9.12.3.4 Sample results exceeds the Agency's action limit.

9.12.3.5 Samples do not reflect historical data.

9.12.3.6 **Upward trending or sample results approaching interval warning limits.**

9.12.3.7 Any non-target analyte peak present on the instrument generated chromatogram.

9.12.4 The Lead Chemist will implement the corrective action plan described in the PHILIS corrective action plan document.

9.12.5 When tuning and instrument calibration fail to meet acceptance criteria, the analysis does not start. The problem is investigated and the necessary instrument maintenance is performed, followed with tuning and calibration.

9.12.6 See Table 5 for a summary of corrective action taken when QC samples or client sample QC does not meet acceptance criteria

9.13 Contingencies for Handling Out of Control or Unacceptable Data

In cases where quality control measures do not meet acceptance criteria, the quality of the analytical data may not be acceptable and the analyst does the following:

9.13.1 When instrument calibration fails to meet acceptance criteria, the analysis does not start with sample analysis. The problem is investigated and the necessary instrument maintenance is performed, followed by another calibration.

9.13.2 If the acceptance criteria for a sample listed in Table 5 of this SOP are not met for MB, CCV, LCS, and the QC samples, then all associated samples must be reanalyzed.

9.13.3 If after analysis, any of the criteria for quality control are not met, or the sample is not available for reanalysis, then the analyst must notify the Lead Chemist. The Lead Chemist will implement the corrective action plan.

9.13.4 The analyst shall report to the Lead Chemist and indicate of the "QC Summary form" any out-of-control event. Such events include:

9.13.5 Damage to the sampling container.

9.13.6 Holding time exceeded.

9.13.7 Samples do not reflect historical data.

9.13.8 Upward trending or sample results approaching interval warning limits.

9.13.9 Any non-target analyte peak present on the instrument generated chromatogram.

10.0 Calibration and Standardization

10.1 The mass spectrometer must be calibrated per manufacturer specifications prior to each analysis batch. In order to obtain accurate analytical values through this test method within the confidence limits, the following procedure must be followed when performing the test method.

10.2 To calibrate the instrument, analyze eight calibration standards containing the target analytes and the surrogate(s) prior to the analysis as shown in Table 3. Prepare the calibration solutions as described in Section 7.4 of this SOP.

10.3 Inject each standard and obtain chromatographic data. An external calibration method is used to monitor the primary MRM transitions of each analyte. For each analyte, the area under its primary MRM transition peak is utilized to conduct quantitation. The mass assignments are given in Table 7 and will vary depending on the instrument tuning conditions and mass axis calibrations.

10.4 The quantitation method is set to an external calibration using the peak areas as a function of concentration in pg/uL. Concentrations may be calculated using the quantitation software to generate linear or quadratic calibration curves. Forcing the calibration curve through zero is prohibited.

10.5 Linear calibration may be used if the coefficient of determination, R^2, is >0.98 for the analyte (Section 12.3). The point of the origin is excluded and a fit weighing of 1/x is used in order to give more emphasis to the lower concentrations. If one of the calibration standards other than the high or the low point causes the R^2<0.98, then this point must be re-injected or a new calibration curve generated. If the low and/or high point is excluded, minimally a five point (six is recommended) curve is acceptable; however, the reporting range must be modified.

10.6 Quadratic calibration may be used if the coefficient of determination, R^2, is >0.98 for the analyte (Section 12.3). The point of the origin is excluded and a fit weighing of 1/x is used in order to give more emphasis to the lower concentrations. If one of the calibration standards other than the high or the low point causes the R^2<0.98, this point must be re-injected or a new calibration curve must be generated. If the low and/or high point is excluded, minimally a six point curve is acceptable, but the reporting range must be modified.

10.7 The retention time window of the peaks of the MRM transitions must be within 5% of the retention time of the analyte in the most recent CCV or the middle point of the associated initial calibration. If the peak is outside of the retention time window then reanalyze the calibration curve to determine if there was a shift in retention time during the analysis, and then the sample needs to be re-injected. If the retention time is still incorrect in the sample, then refer to the analyte as an unknown.

10.8 MRM Ion ratios and acceptance criteria are determined by TraceFinder software for MRM's that have more than one transition.

11.0 Procedure

11.1 Preliminary Sample Preparation

11.1.1 Samples are collected and stored as described in Section 11. Remove samples from storage.

11.1.2 Verify that the samples have been logged into LIMS, and are within holding time. If the sample exceeds holding time, notify the Lead Chemist and follow the corrective action plan.

11.1.3 Batch up to 20 environmental samples for extraction.

11.2 Sample Preparation/Extraction

11.2.1 Wipe Samples

11.2.1.1 Open the jar, and allow the wipe to dry at room temperature. Allow excess MeOH to evaporate off. The wipe can be damp, but not soaking with MeOH. A dry wipe allows for more accurate volume measurements and studies have shown that the analytes interest are relatively stable up to 48 hrs on a completely dry wipe.

11.2.1.2 Place the wipe in a 40 mL VOA vial.

11.2.1.3 Spike the sample with a known concentration (keeping in mind, a final volume of 15 mL) of the Surrogate Spike Solution (Section 10.4.2).

11.2.1.4 Spike each P&A wipe sample with a known concentration (keeping in mind a final volume of 15 mL) of the LCS Spiking Solution for Wipe Samples (Section 10.4.6). For a 1000pg/uL surrogate solution, recommended amount is 30 uL. This will give a final concentration result of 1.0 pg/uL on the instrument

11.2.1.5 Add 15 mL of methanol and vortex on high for 10 - 20 seconds

11.2.1.6 Secure the vial on a shaker table. Extract for 15 minutes at a speed of 1500 - 2000 rpm.

11.2.1.7 After extraction, vortex for 5-10 secs before transferring ~1.0 mL of extract into a microcentrifuge tube.

11.2.1.8 Microcentrifuge at ~15,000 rpm for 5 minutes

11.2.1.9 Carefully transfer supernatant, avoiding solids into an autosampler vial

11.2.1.10 Vortex the AS vial for 2-5 seconds before placing in autosampler.

11.2.1.11 Final calculations based on 15 mL.

11.2.2 Water

11.2.2.1 Transfer 1.0 mL of water using a 1.0 mL syringe into a

A. 2.1 mL microcentrofuge tube.

B. OR into a 15 mL Falcon tube.

11.2.2.2 Spike with a surrogate standard for a final known concentration.

A. Example: 1.0 uL of a 1000pg/uL surrogate for an expected concentration of 1.0 pg/Ul.

11.2.2.3 Vortex the sample for 5 seconds at 3000 rpm to ensure proper mixing.

NOTE: It has been shown that the lack of vortexing has significant adverse effects on recoveries and precision.

11.2.2.4 **Water samples MUST BE extracted and run immediately!** Studies have shown that remifentanil is unstable in water, and a 1.0 pg/uL concentration of remifentanil will completely degrade after 40 hours. (See Figure 2)

11.2.2.5 Centrifuge the sample at 12,000 rpm for 5 minutes.

11.2.2.6 Carefully transfer the supernatant into an AS vial and cap the vial with the appropriate cap for your system.

11.2.2.7 Vortex the AS vial for 5 seconds before placing in autosampler.

11.2.3 Soil

11.2.3.1 Weigh out 5g of soil and add to a 40 mL VOA vial. Add 5-10 glass beads.

11.2.3.2 Spike soil with known concentration of surrogate. (Recommended spiking 15 uL of a 1000pg/uL surrogate solution. This will result in a 1.0 pg/uL concentration on instrument.)

11.2.3.3 Add 15.0 mL of MeOH with a graduated cylinder

11.2.3.4 Vortex on high for 10 sec.

11.2.3.5 Shake for 15 minutes at 1500 rpm.

11.2.3.6 After extraction, vortex for 5-10 secs before transferring ~1.0 mL of extract into a microcentrifuge tube. Centrifuge at 15,000 rpm for 5 minutes

11.2.3.7 Carefully transfer supernatant into an autosampler vial, avoiding any solids and cap the vial with the appropriate cap for your system.

11.2.3.8 Vortex autosampler vial for 2-5 secs at 3000 rpm prior to placing in autosampler.

11.2.3.9 Final calculation based on 15 mL.

11.3 Sample Analysis and Calibration Procedure

11.3.1 Analysis is performed using the LC/MS/MS instrument programmed according to the parameters described in Tables 8, 9 and 10. All samples must be analyzed using the same mass spectrometric conditions.

11.3.2 A typical sequence will start with one or two solvent blanks (MeOH), the ICAL or a CCV standard, an instrument blank, the QC from the batch, the samples, and finally an ending CCV. If the samples being analyzed are suspicious or possibly high in non-target analytes, running solvent blanks at the end of the sequence will help maintain the quality of your instrument.

11.3.3 Once the calibration curve meets acceptance criteria, the analysis of samples may begin. Inject 50 µL of the blank, extracts or QC samples using the sample injection technique as used for the standards. The order of analysis after the calibration is method blank (MB), laboratory control sample (LCS), sample(s), duplicate(s), matrix spike sample(s) followed by a closing continuing calibration verification sample (CCV). For this method, the CCV is equivalent to the Level 5 concentration of the initial calibration. All analysis batches must finish with a closing CCV, and compound recovery in the closing CCV must be less than 30% Recovery. Analysis batches following a successful initial calibration may begin with a CCV provided recoveries for each analyte and surrogate is less than 30% D.

11.3.4 The data system will determine the concentration of each analyte in the extract using calculations in Section 15. Quantitation is based on the curves generated from the initial calibration, not the continuing calibration verification.

11.3.5 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst and reviewed for QC approval. The minimum documentation required is a hard copy of the original data peak integration and a copy showing the manual integration with the analyst initials and date and explanation of the reason for the manual integration.

11.4 Identification of Analytes: See Section 15.1.

11.5 Dilutions

11.5.1 If the response for any analyte exceeds the current calibration range, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range.

11.5.2 If the surrogates are diluted to a level where accurate quantitation is not possible then surrogates should be reported as diluted out.

11.5.3 Reporting Dilutions: The least dilute sample with no target analytes above the calibration range will be reported. Other dilutions will be reported only at the client's request.

12.0 Data Analysis and Calculations

12.1 Identification of Analytes

12.1.1 The analyte is identified by the retention time being within 5% of the retention time of that analyte in the most recent CCV or midpoint of the calibration curve.

12.1.2 For quantitative analysis of fentanyl, and the surrogate, the MRM transitions are identified by comparison of the retention times in the sample to those of the standards. External calibration curves are used to calculate the amounts of the target compounds and surrogates. Calculate the concentration in nanograms (ng) for each analyte. If the concentration of the analyte is determined to be above the calibration range, the sample is diluted with reagent methanol to obtain a concentration near the mid-point of the calibration range and reanalyzed.

12.2 The surrogates, fentanyl-*d5*, carfentanil-*d5*, and heroin-*d9*, are used to monitor the performance of all of the analytes in this method. If the surrogate recovery does not meet the quality control criteria of this method, the data is qualified for the appropriate analyte.

12.3 The concentration of each analyte is calculated using a multipoint linear or quadratic regression curve established in Section 10.0 of this SOP. The curve is generated by plotting Ax as a function of Cx.

where:

A_x is the area of the peak of the quantitation ion selected for MRM transition

C_x is the concentration of the analyte

12.3.1 Calculating the sample concentration based on linear regression:

$$C_x = \frac{A_x - b}{m}$$

where:

C_x is the concentration of the analyte

A_x is the area of the quantitation MRM transition

m is the slope

b is the y-intercept

12.3.2 Calculating the sample concentration based on quadratic regression:

$$C_x = \frac{-b \pm \sqrt{b^2 - 4a(c - A_x)}}{2a}$$

where:

C_x is the concentration of the analyte

A_x is the area of the quantitation MRM transition

a is the coefficient of the quadratic term

b is the coefficient of the linear term

c is the constant term

12.4 Percent deviation calculation for the CCV is performed using the following equation:

$$\%D = \frac{C_{cal} - C_t}{C_t} x100\%$$

where:

C_{cal} is the calculated concentration

C_t is the theoretical spiked concentration

12.5 Percent recovery for MS and LCS are performed using the following equation:

$$\%R = \left[\frac{\left(C_{spk} - C_x\right)}{C_t}\right]100$$

where:

C_{spk} is the concentration of the analyte in the spiked sample

C_x is the concentration of the analyte in the reference (parent) sample; (C_x = 0 for LCS.)

C_t is the theoretical spike concentration.

13.0 Method Performance

Example MDLs, reporting limits and Precision and Accuracy for Fentanyl analogs on wipes, water, and soils are listed in Table 6. Statistical Precision and Accuracy limits will be determined when adequate data is available.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address waste generation. When wastes cannot be feasible reduced at the source, recycling is the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St. N.W., Washington D.C. 20036, http://www.acs.org

15.0 Waste Management

15.1 Laboratory waste should be kept to a minimum. Since these wastes are different than most laboratory wastes, they should be disposed of per the PHILIS Health and Safety Plan, the site disposal waste plan, and in conjunction with the PHILIS Health and Safety Officer.

15.2 The EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society at the address listed in section 17.2.

16.0 References

16.1 Doyle, Rory M. et.al 2018, Quantitative Analysis of 40 Fentanyl, its Precursors, Analogues and Metabolites in Urine, Oral Fluids and Blood using LC-MS/MS for Forensic Use TP189, Thermoscientific Somerset, NJ, USA, (https://assets.thermofisher.com/TFS-Assets/CMD/posters/po-65275-lc-fentanyls-msn-asms2018-po65275-en.pdf)

16.2 Code of Federal Regulations, 40 CFR Part 136, Appendix B. Definition and Procedure for the Determination of the Method Detection Limit – Revision 2.0.

16.3 PHILIS SOP No. L-D-501, *Manual Integration and Data Integrity.*

17.0 Tables, Figures, and Attachments

Table 1. Analytes Determined

Analyte	CAS#	Formula	Mass (m/z) of Parent Ion	Calibration Range (pg/uL)
Acetyl fentanil	3258-84-2	C21H26N2O2	(M+H)+ at 323	0.05-10
Alfentanil	69049-06-5	C21H32N6O3	(M+H)+ at 417	0.05-10
Carfentanil	61086-44-0	C24H30N2O2	(M+H)+ at 395	0.05-10
Carfentanil-d5	1185158-60-4	C24D5H25N2O2	(M+H)+ at 400	0.05-10
Fentanyl	437-38-7	C22H28N2O	(M+H)+ at 337	0.05-10
Fentanyl-d_5	118357-29-2	C22D5H23N2O	(M+H)+ at 342	0.05-10
Heroin	561-27-3	C21H23NO5	(M+H)+ at 370	0.5-100*
Heroin-d9	1338713-49-7	C21F14D9NO5	(M+H)+ at 379	0.5-100
Remifentanil	132539-07-2	C20H28N2O5	(M+H)+ at 377	0.1-20**
Sulfentanil	60561-17-3	C22H30N2O2S	(M+H)+ at 387	0.05-10
Methamphetamine	537-46-2	C10H15N	(M+H)+ at 151	2.5-500***
Cocaine	50-36-2	C17H21NO4	(M+H)+ at 304	0.05-10

* Heroin is 10 times less sensitive than the other opiates in this list. Recommended calibration range is 0.5-100 pg/uL

** Remifentanil has a slightly lower response in this system. Recommended calibration range is 0.1-20 pg/uL

*** Methamphetamine is 50 times less sensitive than the other compounds in this list. Recommended calibration range is 2.5 – 500 pg/uL

Table 2. Examples of Commercially-Available Neat Standards

Standard Name	Source/Catalog Number	Analyte Type	Listed Purity
Fentanyl	Cerilliant/F-002-1ML (100 µg/mL)	Target	≥ 99%
Fentanyl-d_5	CerilliantF-001-1ML (100 µg/mL)	Surrogate	≥ 99%

Table 3. Serial dilution matrix of calibration standards (Example)

Conc. pg/uL				
100	→	**50**	→	**25**
↓		↓		↓
10		5		2.5
↓		↓		↓
1.0		0.5		0.25
↓		↓		
0.1		0.05		

Table 4. Preparation of Calibration Standards (Example)

Level	Conc. pg/uL	Conc. Heroin/Heroin-d9 pg/uL	Conc. Remifentanil pg/uL	Conc. Methamphetamine pg/uL
LV 1	0.05	0.5	0.1	2.5
LV 2	0.1	1	0.2	5.0
LV 3	0.25	2.5	0.5	12.5
LV 4	0.5	5	1.0	25
LV 5	1	10	2.0	50
LV 6	2.5	25	5.0	125
LV 7	5	50	10	250
LV 8	10	100	20	500

Table 5. L-A-310 Method QC Criteria

Item	Measure	Action
Initial Calibration (ICAL)	Coefficient of determination, R^2.	Evaluate points in the curve for use of linear or quadratic regression (R^2 must be ≥0.98 for linear regression, or R^2 must be > 0.99 for quadratic regressions). Also evaluate upper and lower points for removal. Criteria still not met, recalibrate if compound is an analyte of interest.
ICAL Low Point Eval. for compounds using linear or quadratic regression	Not within ±30% of True Value	Recalibrate if % deviation or drift is not met and compound is an analyte of interest.
Initial Calibration Verification/CCV	Not within ±30% of true value for deviation or drift.	Recalibrate if % deviation is not met and the compound is an analyte of interest.
Method Blank	Analyte(s) at or above reporting limit.	If the associated samples are non-detect, no action is required. If the analyte(s) is/are detected in the sample, flag with a "b" or reanalyze. If the analyte level in the sample is 10 times greater than the blank contamination, the results are not affected. Locate the source of the contamination.
Laboratory Control Spike (LCS)	% recovery. Laboratory acceptance criteria are evaluated every 6 months. Acceptable values are stored in the LIMS system.	If the LCS % recovery is high and the sample is non-detect, no action is required. If the LCS is high and the samples have detects, reanalyze the sample. If the LCS is low, the samples should be reanalyzed.
Laboratory Control Spike Duplicate (LCSD)	Same criteria as the LCS with the addition of RPD. Current Acceptance criteria is 30% and is evaluated every 6 months with the values stored in the LIMS.	% recovery same as the LCS. If the RPD value is above the acceptance criteria in the LIMS, then evaluate the system for possible problems. Reprepare and reanalyze samples as necessary and if possible.
Surrogate(S)	% recovery. Laboratory acceptance criteria are evaluated every 6 months. Acceptable values are stored in LIMS.	If the % recovery is outside laboratory acceptance criteria on a QC sample, evaluate the system. Surrogate recalibration may be necessary.
		If the % recovery is on a client sample, reprep and reanalyze if possible. If the % recovery is within criteria, report the sample within limits. If % recovery is outside criteria and is confirmed, then there is a matrix effect. Flag the results as estimated and report the initial result.

Table 6. Example QC Acceptance Criteria

OPI by UPLCMSMS		OPI on Wipes 03/15/22			
		MDL	RL	RPD	Control Limits
Compound	CAS No.	Wipe (ug/wipe)	Wipe (ug/wipe)	Wipe (%)	Wipe (% Recovery)
Heroin	561-27-3	0.0072	0.0075	30	50 -150
Remifentanil	132539-07-2	0.00079	0.0015	30	50 -150
Acetylfentanyl	3258-84-2	0.00033	0.00075	30	50 -150
Fentanyl	437-38-7	0.00071	0.00075	30	50 -150
Carfentanil	61086-44-0	0.00046	0.00075	30	50 -150
Sulfentanil	60561-17-3	0.00065	0.00075	30	50 -150
Alfentanil	69049-06-5	0.00076	0.0015	30	50 -150
OPI by UPLCMSMS		OPI in Water 03/15/22			
		MDL	RL	RPD	Control Limits
Compound	CAS No.	Water (ug/L)	Water (ug/L)	Water (%)	Water (% Recovery)
Heroin	561-27-3	0.656	1.0	30	50 -150
Remifentanil	132539-07-2	0.158	0.2	30	50 -150
Acetylfentanyl	3258-84-2	0.07	0.1	30	50 -150
Fentanyl	437-38-7	0.047	0.1	30	50 -150
Carfentanil	61086-44-0	0.060	0.1	30	50 -150
Sulfentanil	60561-17-3	0.048	0.1	30	50 -150
Alfentanil	69049-06-5	0.061	0.1	30	50 -150
OPI UPLCMSMS		OPI in Soil 9/3/21			
		MDL	RL	RPD	Control Limits
Compound	CAS No.	Soil (ug/Kg)	SOIL (ug/Kg)	Soil (%)	Soil (% Recovery)
Heroin	561-27-3	2.1	3.0	30	50 -150
Remifentanil	132539-07-2	0.15	0.30	30	50 -150
Acetylfentanyl	3258-84-2	0.068	0.30	30	50 -150
Fentanyl	437-38-7	0.038	0.30	30	50 -150
Carfentanil	61086-44-0	0.12	0.30	30	50 -150
Sulfentanil	60561-17-3	0.059	0.30	30	50 -150
Alfentanil	69049-06-5	0.12	0.30	30	50 -150

* Guidance value only, subject to change based on QC charting.

Table 7A. Retention times and SRM transitions for TSQ-Altis

Compound	Retention time (min)
Methamphetamine	5.41
Heroin-d9	6.45
Heroin	6.49
Cocaine	6.58
Remifentanil	7.14
Acetylfentanil	7.29
Fentanyl-d5	7.95
Fentanyl	7.97
Carfentanil	8.26
Carfentanil-d5	8.28
Sulfentanil	8.71
Alfentanil	8.86

Table 7B. SRM transition data for TSQ-Altis

Compound	Start Time (min)	End Time (min)	Precursor (m/z)	Product (m/z)	Collision Energy (V)	Min Dwell Time (ms)	RF Lens (V)	Use Quan Ion
Methamphetamine	5.0	6.5	150.88	91.125	20.12	23.591	31	True
Methamphetamine	5.0	6.5	150.88	119.125	11.36	23.591	31	False
Cocaine	5.0	9.5	304.175	150.0	24.21	23.591	71	False
Cocaine	5.0	9.5	304.175	182.083	18.81	23.591	71	True
Acetylfentanyl	5.0	9.5	323.175	105.125	36.13	23.591	71	False
Acetylfentanyl	5.0	9.5	323.175	188.137	22.73	23.591	71	True
Acetylfentanyl	5.0	9.5	323.175	202.137	22.48	23.591	71	False
Fentanyl	5.0	9.5	337.25	105.196	37.48	23.591	72	False
Fentanyl	5.0	9.5	337.25	188.208	22.94	23.591	72	True
Fentanyl-D5	5.0	9.5	342.27	105.125	36.17	23.591	70	False
Fentanyl-D5	5.0	9.5	342.27	188.208	22.82	23.591	70	True
Heroin	5.0	9.5	370.088	211.125	31.12	23.591	79	False
Heroin	5.0	9.5	370.088	268.054	28.88	23.591	79	True
Heroin	5.0	9.5	370.088	328.155	26.4	23.591	79	False
Remifentanil	5.0	9.5	377.138	285.125	19.28	23.591	62	False
Remifentanil	5.0	9.5	377.138	317.137	15.95	23.591	62	True
Remifentanil	5.0	9.5	377.138	345.125	12.54	23.591	62	False
Heroin-d9	5.0	9.5	379.175	212.125	31.58	23.591	89	False
Heroin-d9	5.0	9.5	379.175	272.226	29.47	23.591	89	True
Heroin-d9	5.0	9.5	379.175	335.208	27.49	23.591	89	False
Sulfentanil	5.0	9.5	387.175	111.125	36.97	23.591	72	False
Sulfentanil	5.0	9.5	387.175	238.125	18.9	23.591	72	True
Sulfentanil	5.0	9.5	387.175	355.208	19.2	23.591	72	False
Carfentanil	5.0	9.5	395.3	246.155	21.47	23.591	71	False
Carfentanil	5.0	9.5	395.3	335.238	18.44	23.591	71	True
Carfentanil	5.0	9.5	395.3	363.208	13.26	23.591	71	False
Carfentanil-d5	5.0	9.5	400.25	246.155	21.72	23.591	72	False
Carfentanil-d5	5.0	9.5	400.25	340.22	19.03	23.591	72	True
Carfentanil-d5	5.0	9.5	400.25	368.167	13.51	23.591	72	False
Alfentanil	5.0	9.5	417.212	197.208	25.3	23.591	75	False
Alfentanil	5.0	9.5	417.212	268.155	17.76	23.591	75	True
Alfentanil	5.0	9.5	417.212	385.238	18.23	23.591	75	False

Table 8. Vanquish UPLC Settings

Vanquish UPLC Settings		
Sample Manager		Column Compartment
Injection volume (uL)*	1.0	Column: Waters Acquity™ HSS T3, 2.1 mm x 150 mm, 1.8 µm particle size (part # 186003540) Guard Column: Waters VanGuard™ HSS T3 2.1 mm x 5 mm, 1.8 µm particle size (part # 186003967) Column temp: 50 ºC Forced Air. Fan, 5 Preheater Left: 50 ºC IF FLOW PATH THROUGH UV-VIS post column cooler: 40 ºC, ELSE OFF.
Draw speed (uL/s)	5.0	
Dispense speed (uL/s)	5.0	
Wash mode	Both	
Wash time (s)	8.0	
Wash speed (uL/s)	50	
Puncture offset (um)	100	
Temperature control (C)	20	
System		
15 min		

LC Gradient			
Line No.	Time (min)	Flow Rate (mL/min)	%B
1	0	Run	
2	0	0.25	10
3	0.5	0.25	10
4	6	0.25	60
5	8	0.25	98
6	12	0.25	98
7**	12	0.25	10
8	New Row		
9	15	STOP RUN	

*Note, Injection volume is defined under the Master Method in TraceFinder software.
**Note, Line 7 is correct. The double 12 mins allow for a vertical drop in the gradient.

Table 9. Vanquish UV-VIS Settings

Vanquish UV-VIS
Not used for this analysis. NOTE: due to the temperature of the column compartment exceeding 40C, if the flow path of the UPLC passes through the UV-VIS, the post column cooler MUST be turned ON and set to 40C or the light pipe can shatter.

Table 10. TSQ-Altis MS/MS Settings

TSQ Altis Parameters			
Global Parameters		Scan Parameters	
Ion Source Properties		SRM Properties	
Method duration (min)	15	Polarity	Positive
Ion source type	H-ESI	Use cycle time	Yes
Spray voltage	Static	Cycle Time (sec)	0.8
Positive ion (V)	500	Use calibrated RF lens	No
Negative ion (V)	2500	Q1 resolution (FWHM)	0.7
Sheath gas (arb)	50	Q3 resolution (FWHM)	0.7
Aux gas (arb)	10	CID gas (mTorr)	1.5
Sweep gas (arb)	1.0	Source fragmentation	0
Ion transfer tube (C)	325	Chromatographic peak width (s)	6
Vaporizer (C)	350	Use chromatographic filter	Yes
		Use Retention time reference	No

TSQ Altis Divert Valve Parameters	
Based on user preferences and analyte retention times.	
1-2: From UPLC system to TSQ 1-6: From UPLC to waste	
Time (min)	Position
0	1-6
4.9	1-2
9.5	1-6

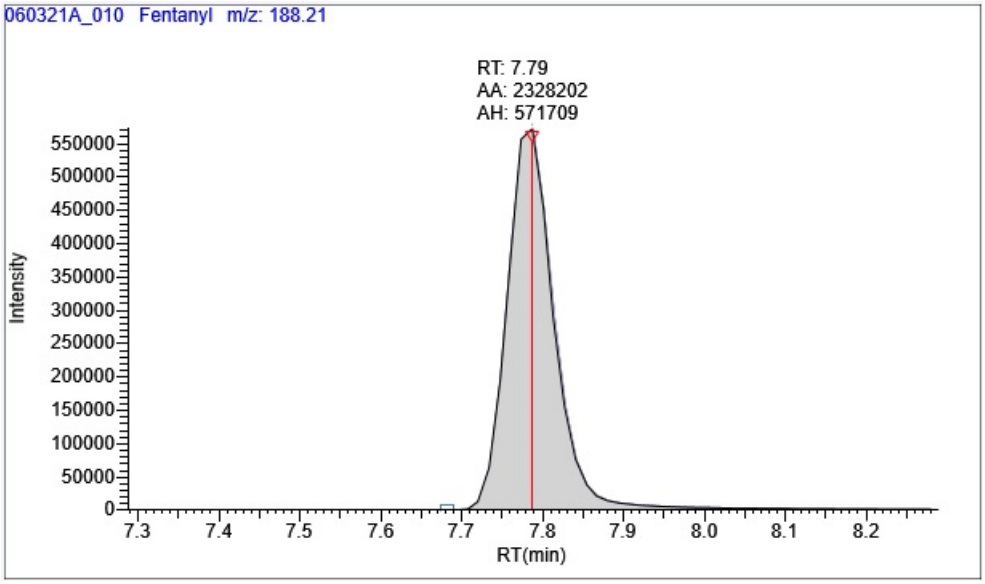
Table 11. Wipe Recoveries for Common Surfaces

Wipe % Recovery of Opioid Analogs on Various Surfaces												
	Linoleum		Concrete Smooth		Concrete Porous, rough		Concrete Painted		Metal counter		Desktop	
	%Rec	%RSD	%Rec	%RSD	%Rec	%RSD	%Rec	%RSD	%Rec	%RSD	%Rec	%RSD
Heroin-d9	92.6	46.3	82.3	21.8	73.4	17.9	95.6	28.5	70.5	6.5	73.3	22.0
Fentanyl-d5	86.5	20.4	26.0	5.4	37.5	1.9	83.0	15.3	88.0	9.6	54.5	11.7
Carfentanil-d5	86.0	13.2	54.5	1.3	62.0	0.0	91.5	7.0	97.0	2.9	76.5	10.2
Heroin	77.2	18.7	50.0	4.7	11.8	13.2	88.7	24.5	64.1	12.6	60.7	18.9
Remifentanil	72.3	3.4	46.5	9.1	10.8	36.2	73.8	0.5	72.0	5.9	57.8	12.9
Acetylfentanyl	64.0	4.4	11.5	6.1	3.5	60.6	42.0	0.0	52.5	1.3	28.0	20.2
Fentanyl	74.0	5.7	16.5	12.9	5.0	56.6	52.5	9.4	68.0	4.2	37.5	17.0
Carfentanil	64.0	11.0	32.0	8.8	7.5	47.1	59.0	12.0	69.0	10.2	49.0	11.5
Sulfentanil	77.5	6.4	63.0	2.2	8.5	58.2	82.5	6.0	78.0	7.3	66.0	10.7
Alfentanil	76.0	3.7	70.5	3.0	10.5	47.1	82.5	9.4	81.0	8.7	71.5	8.9

Note: n=3 study, 1 ng/wipe spike

Figure 1. Examples of MRM Chromatograms

Fentanyl and Fentanyl-d5



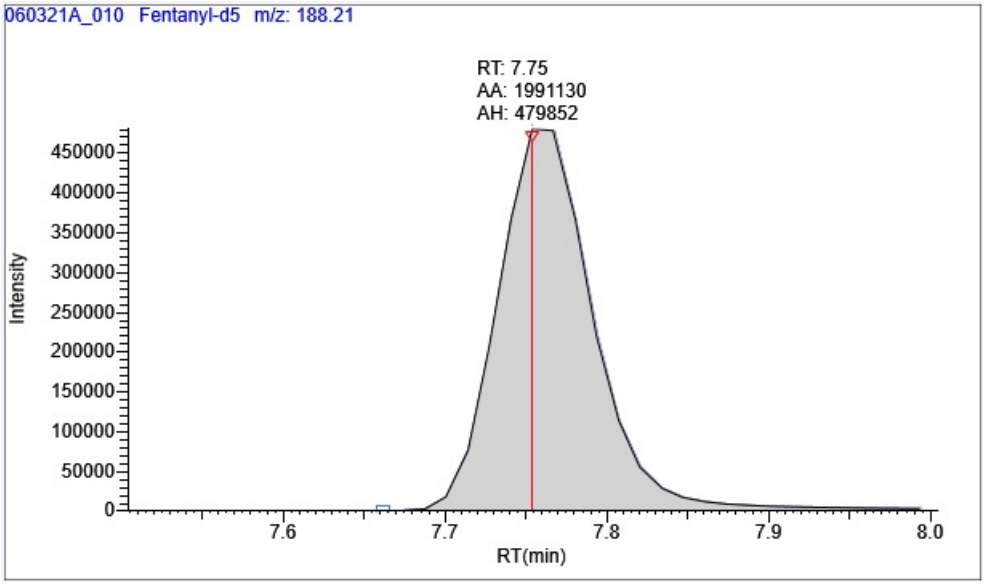
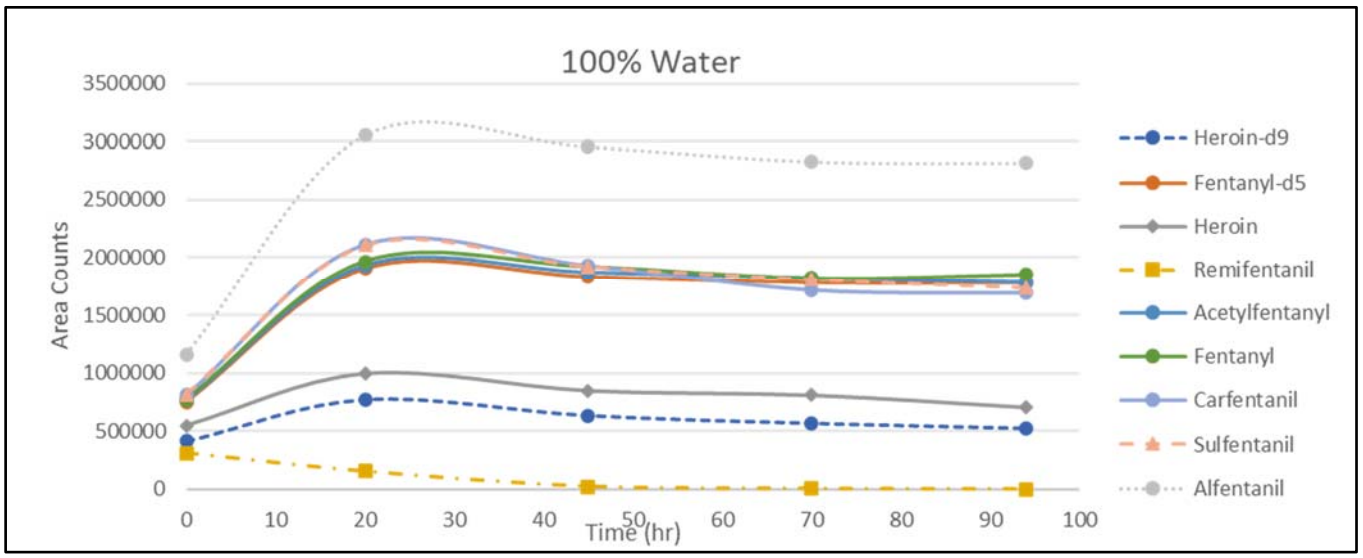


Figure 2. Degradation of opiate analogues in water



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APPENDIX F -
PHILIS SOP L-A-100
Moisture Determination Rev. 1 08/24/2023

STANDARD OPERATING PROCEDURE

FOR

MOISTURE DETERMINATION

PHILIS SOP L-A-100 Rev. 1

Revision Date: 08-24-2023

EPA Contract No. 68HERH21D0002

PREPARED BY

PHILIS

PREPARED FOR

U.S. Environmental Protection Agency
Office of Emergency Management
Washington, DC 20460

Approvals:

PHILIS, Castle Rock Lead Chemist	**August 24, 2023** **Date**
PHILIS, Edison Lead Chemist	**August 24, 2023** **Date**
PHILIS, Quality Assurance Manager	**August 24, 2023** **Date**
PHILIS, Program Manager	**August 24, 2023** **Date**

Revision History

Revision	Name	Date	Description of Change
A	James Travis	04/01/2021	Transitional Issue
0	James Travis	09/15/2022	Program Issue
1	James Travis Sang Chung Tom Fowler	08/11/2023	Annual Review

SOP REVISION FORM

SOP Name:	**Moisture Determination**		
Purpose: *(Review or Revise)*	*Document #:*	*Rev. #:* *(Being Reviewed or Revised)*	*Origination / Release Date:*
Program Issue	*SOP No. L-A-100*	0	09/22/2022
Requested by:	James Travis	Date:	08/11/2023

New SOP Revision Date:	**08/24/2023**	**New SOP Revision #:** *(If Applicable)*	**1**

For *Revision* : Summary of Revisions (specify sections)

Title Page	Changed Project Manager to Program Manager
Document	Updated section headings to current format

For *Review*: Comments

Standard Operating Procedure
Moisture Determination
L-A-100 Rev. 1

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TABLES, FIGURES, AND ATTACHMENTS

Standard Operating Procedure
Moisture Determination
L-A-100 Rev. 1

1.0 Scope and Application

1.1 This SOP is applicable for the determination of moisture from solid samples. PHILIS will report all solid samples on a dry weight basis unless directed by a specific QAPP or written client instructions.

1.2 Dry weight is calculated from the % Moisture and this value is used to convert results from as received to dry weight basis.

1.3 This standard operating procedure (SOP) documents CSS's application of the moisture analysis section of EPA SW846 Method 3545A for moisture determination of samples for instrumental analysis. CSS's policy is to report analytical results on a dry weight basis, unless a Quality Assurance Project Plan (QAPP) or client instructions indicate to report on an as received basis.

1.4 This SOP is executed in accordance with the U.S. Environmental Protection Agency and National Environmental Laboratory Accreditation Program (NELAP).

1.5 This is a gravimetric method and is applicable to soil, sediment samples and other solid matrices.

1.6 A detection limit is not applicable for this test.

2.0 Summary of Method

2.1 An aliquot of a representative sample is added to a weighed aluminum dish and re-weighed. The sample is placed in a drying oven at 105 °C overnight. The sample is allowed to come to room temperature in a desiccator and is weighed again. Percent moisture is calculated as a percentage of the total weight lost.

2.2 A moisture analyzer may also be used when there are relatively few samples. An aliquot of a well-mixed sample is weighed and placed on the moisture analyzer. The instrument is started and when the sample comes to a constant weight, the analysis is complete. Results are transferred to the Laboratory Information Management System (LIMS).

3.0 Definitions

3.1 Batch‡: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A Preparation Batch is composed of between 1 and 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and the last sample in the batch to be 24hours. Each Preparation Batch requires; one MB, LCS, and MS/MSD pair. An Analytical Batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

An 8260 volatiles analytical batch will consist of no more than twenty (20) environmental samples in addition to the SOP Quality Control requirements.

All batches require one MB, LCS, and MS/MSD pair or MS and Sample Duplicate when possible.

3.2 Laboratory Duplicate (LD): Two sample aliquots taken in the laboratory and analyzed separately with identical procedures. Analyses of the aliquots indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.3 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. Method Blank analytical results are evaluated to determine the presence of contamination in the analytical method process.

‡ EL-V1M2-ISO-2016, 2016 NELAP standard definition.

4.0 Interferences

Samples that contain a high quantity of volatile compounds may yield a result that is biased high for % moisture.

5.0 Safety

Laboratory personal are required to be familiar with the general laboratory safety plan including the location and proper use of safety/emergency equipment

5.1 Employees must abide by the policies and procedures in the Chemical Hygiene Plan and this document. This procedure involves hazardous material, operations, and equipment. This SOP does not purport to address all the safety problems associated with its use. It is the responsibility of the user of the method to follow the appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are hazardous. Standard laboratory safety procedures should be followed when working with all samples.

5.2 Specific Safety Concerns or Requirements

Eye protection that satisfies American National Standards Institute (ANSI) Z87.1, a laboratory coat, and disposable nitrile or Silver-Shield gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded. Non-disposable gloves must be cleaned immediately.

Wear heat protective gloves to protect hands while holding hot samples being removed from the oven, which heats samples to 105 ºC.

5.3 Each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Procedures involving primary standards and sample preparation must be performed in a fume hood.

5.4 The drying oven should be located in a fume hood, be vented, or in a well ventilated area.

6.0 Equipment and Supplies

6.1 Oven capable of maintaining 105 °C.

6.2 Aluminum weighing dishes

6.3 Balance, top loading, accurate to 0.01 g

6.4 Weights, calibrated and certified

6.5 Spatulas, disposable

7.0 Reagents and Standards

Not Applicable.

8.0 Sample Collection, Preservation, and Storage

8.1 Samples should be representative and taken in a 4 oz jar with a tight fitting lid.

8.2 Samples should be shipped and stored at 0 – 6 °C

9.0 Quality Control

9.1 Method Blank: One blank should be analyzed for each batch of 20 or fewer samples. The weight of the blank should not vary enough to give a reportable value for % solids.

9.2 Laboratory Duplicate: Analyzed one per batch with a precision of 30% Relative Percent Difference (RPD) or less.

9.3 Certified weights are used to verify balance or moisture analyzer calibration daily and the temperature of the oven is recorded daily when in use. The calibration of the balances, weights, moisture analyzers, and thermometers is verified annually by an independent source.

9.4 Data Assessment and Acceptance Criteria for Quality Control Measures

Analytical data generated is reviewed and evaluated by the analyst as follows:

9.4.1 The data is assumed valid if the balance calibration was checked, the oven temperature was within range, and the method blank and laboratory duplicate were all in control.

9.4.2 Reviewed data is entered into LIMS, hard copies of the LIMS report is printed and compared to the original data. The review may also be completed electronically.

9.4.3 All records derived from the analytical process are assembled in the analytical data packages.

9.5 Corrective Action for Our of Control

9.5.1 In cases where quality control measures do not meet acceptance criteria, the quality of the analytical data is not acceptable and the analyst does the following:

9.5.2 If the acceptance criteria listed in Section 12 of this SOP are not met for the method blank and laboratory duplicate, the affected quality control samples and associated samples should be reanalyzed or treated as per laboratory or QAPP protocols.

9.5.3 If after analysis, any of the criteria for quality control are not met, or the sample is not available for reanalysis, the analyst must notify the Lead Chemist. The Lead Chemist will implement the corrective action plan.

9.5.4 Contingencies for Handling Out of Control or Unacceptable Data

See the QAPP that the samples were analyzed under for guidance.

10.0 Calibration and Standardization

The balance or moisture analyzer calibration must be verified each day prior to use. The weights used must bracket the amounts being weighed.

11.0 Procedure

11.1 % Moisture using a drying oven:

11.1.1 Verify the balance calibration by checking weights above and below the expected weights being measured.

11.1.2 Label a weighing dish for a method blank, a laboratory duplicate, and each sample.

11.1.3 Weigh the dish and record the weight on the balance sheet.

11.1.4 Mix the sample well prior to taking the sample aliquot.

11.1.5 Weigh approximately 10 grams sample and record the weight of the sample and dish on the balance sheet (Attachment A).

11.1.6 Place the samples in the drying oven overnight or until the samples are at a constant weight.

11.1.7 Desiccate the samples for approximately 30 minutes or until cool.

11.1.8 Weigh the dry sample and dish and record on the balance sheet.

11.1.9 Calculate the % Moisture (see Section 15) and enter the data into LIMS.

11.1.10 If the samples are not kept in the drying oven overnight, then leave the sample in the oven for two hours, desiccate for approximately thirty minutes, weigh, return to the oven for 30 additional minutes, desiccate again, and reweigh. If the dry weight is not constant, continue the process until it is constant before entering the data into LIMS.

11.2 % Moisture using an Ohaus Moisture Analyzer:

11.2.1 Verify that the instrument is level; adjust the feet as necessary. It is recommended that the instrument be placed in a fume hood due to off gassing of the samples.

11.2.2 Check the calibration of the balance at 1.0 g and 20.0 g and document in the balance logbook. The weight checks must bracket the mass placed on the sample pan. The balance is recalibrated annually by an independent vendor.

11.2.3 Place a new sample pan in the instrument and tare the system.

11.2.4 Add 5 to 10 grams of well mixed sample to the sample pan and record the amount in the logbook. A method blank and a laboratory duplicate must be analyzed with every preparation batch (20 field samples or less).

11.2.5 Press “Start” on the moisture analyzer. The run will be completed once the sample has reached a constant weight. The instrument will automatically calculate the % Moisture and % Solids. Document both values in the logbook.

11.2.6 In LIMS, create a bench sheet for Dry Weight. In Data Entry, open up the Dry Weight batch and under instrument data, record the % Solids from the logbook. The person performing the peer review will verify that no transcription errors have happened in the transfer of the data.

12.0 Data Analysis and Calculations

12.1 % Moisture = M Wet – M Dry / M Wet x 100

M Wet – Mass of Wet Soil Sample (wet weight – tare weight) (grams)

M Dry – Mass of Dry Soil Sample (dry weight – tare weight) (grams)

12.2 % Dry Weight = 100 - % Moisture

13.0 Method Performance

13.1 Lab Precision will be set at 30% RPD until sufficient lab data is available to calculate lab specific acceptance criteria.

13.2 Other specific Quality Assurance Objectives (QAO) may be found in the appropriate statement-of-work or QAPP for specific projects.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. The EPA places pollution prevention as the management option of first choice with regard to laboratory waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 The Environmental Protection Agency requires that laboratory waste management practices be compliant with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult the PHILIS Chemical Hygiene Plan.

14.3 Waste from the field samples is disposed in the Hazardous Waste container.

14.4 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036.

15.0 Waste Management

Waste management procedures are specified in the Hazardous Waste Management Plan.

16.0 References

16.1 Environmental Protection Agency, "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods - EPA Publication No. SW-846," Method 3545A, Office of Solid Waste and Emergency Response, Washington, D.C. (February, 2007)

17.0 Tables, Figures, and Attachments

Attachment A – Example Moisture Determination Log

PHILIS Program

CSS

MOISTURE DETERMINATION LOG

ANALYST:	DATE:

Top Loading Balance Serial No.: ☐ CO: 14636752 ☐ CO: 7130230150 ☐ NJ: 07252016155 ☐ NJ: 07252016156 ☐ NJ: 11232019178

Instructions: Input values in the green fields. Results will automatically propagate in the orange field

Dish No.	Sample No.	Dish Wt. (g)	Wet Sample + Dish Wt. (g)	Dry Sample + Dish Wt. (g)	% Moisture	% Dry Weight
1	Method Blank					
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						

A Method Blank and a Sample Duplicate should be determined per batch of twenty samples or less.

PHILIS2 Form ID#: QA-029 / Release Date: 04/11/2022

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APPENDIX G -
PHILIS SOP L-P-101
Sep Funnel Extraction for SVOA in Water Rev. 2 06/21/2024

STANDARD OPERATING PROCEDURE

FOR

SEP FUNNEL EXTRACTIONS FOR SVOAs, PESTICIDES & PCBs

PHILIS SOP L-P-101 Rev. 2

Revision Date: 06-21-2024

EPA Contract No. 68HERH21D0002

PREPARED BY

PHILIS

PREPARED FOR

U.S. Environmental Protection Agency
Office of Emergency Management
Washington, DC 20460

Approvals:

	June 21, 2024
PHILIS, Castle Rock Lead Chemist	**Date**
	June 21, 2024
PHILIS, Edison Lead Chemist	**Date**
	June 21, 2024
PHILIS, Quality Assurance Manager	**Date**
Julia Capri	**June 21, 2024**
PHILIS, Program Manager	**Date**

Revision History

Revision	Name	Date	Description of Change
A	James Travis	04/01/2021	Transitional Issue
0	James Travis Sang Chung	05/17/2021	Program Issue Development
1	James Travis Tom Fowler	11/03/2022	Revision
2	Thomas Antony	04/30/2024	Revision

SOP REVISION FORM

SOP Name:	**SEP Funnel Extractions for SVOAs, Pesticides & PCBs**		
Purpose: *(Review or Revise)*	*SOP #:*	*Rev. #:* *(Being Reviewed or Revised)*	*Origination / Release Date:*
Revision	*SOP No. L-P-101*	1	11/18/2022
Requested by:	Thomas Antony	Date:	04/30/2024

New SOP Revision Date:	**6/21/2024**	**New SOP Revision #:** *(If Applicable)*	**2**

For *Revision*: Summary of Revisions (specify sections)

11.12	Section was removed. No longer using Dry Vap.
11.12.2	Added “or filter paper” and “Approximately 5 to 10g”
11.14	Removed “Starting at section 14.9”
11.15.1	Corrected to reflect that extraction steps end at 11.14.2, rather than 11.15.2
11.17.10	Removed “Cap extract and set aside.” Not necessary.
11.17.11	Removed “Once at samples have been concentrated.” Not necessary.

For *Review*: Comments

Standard Operating Procedure
SEP Funnel Extractions for
SVOAs, Pesticides & PCBs
L-P-101 Rev. 2

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TABLES, FIGURES, AND ATTACHMENTS

Standard Operating Procedure
SEP Funnel Extractions for
SVOAs, Pesticides & PCBs
L-P-101 Rev. 2

1.0 Scope and Application

1.1 This standard operating procedure (SOP) documents the PHILIS Program application of EPA Method 3510C. This SOP describes the procedure for isolation and concentration of organic compounds from aqueous samples. This procedure is applicable for analysis of water-insoluble and slightly water-soluble organic compounds of interest in preparation for a variety of chromatographic procedures.

1.2 This SOP is executed in accordance with the U.S. Environmental Protection Agency and National Environmental Laboratory Accreditation Program (NELAP).

1.3 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use of separatory funnels, TurboVaps concentrators, and general laboratory equipment. Each analyst must demonstrate the ability to generate acceptable results with this method before extracting field samples.

1.4 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods described in the procedure (see Table 1).

1.5 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

1.6 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of Method

2.1 This method is applicable to aqueous samples. CSS utilizes this method for the determination of semivolatile analytes, pesticides, diesel range organics, and PCB's in aqueous samples, including groundwater, surface water, and waste water.

2.2 A measured volume of sample, usually 100mL (other volumes may be used based on RL requirements), at a specified pH (see Table 1), is serially extracted with methylene chloride using a separatory funnel.

2.3 The extract is dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method to be used (see Table 1). Pesticide and PCB sample extracts are exchanged into hexane.

3.0 Definitions

3.1 Batch‡: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A Preparation Batch is composed of between 1 and 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and the last sample in the batch to be 24hours. An Analytical Batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

All batches require one MB, LCS, and MS/MSD pair or MS and Sample Duplicate when possible.

3.2 Holding Time: The maximum amount of time permitted between sampling and sample preparation and/or sample preparation and sample analysis. Also the period of time a sample may be stored prior to analysis when there is no preparation step. See the specific method or SW846 8000B table 4.1.

3.3 Internal Standards (IS)‡: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method

3.4 Laboratory Control Sample (LCS)‡: (however named, such as laboratory fortified blank, blank spike (BS), or QC check sample). A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

The standard source can be the same as the calibration or a second source. The LCS is analyzed exactly like a sample to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.5 Matrix Spike (spiked sample of fortified sample)ǂ: A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of the sample for which an independent test results of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

3.6 Matrix Spike Duplicate (spiked sample or fortified sample duplicate)ǂ: A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

3.7 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. Method Blank analytical results are evaluated to determine the presence of contamination in the analytical method process.

3.8 Method Detection Limit (MDL): The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined by analyzing seven or more replicates of a spiked analyte free matrix and the resulting statistical calculation, in accordance with 40 CFR 136, Appendix B, Revision 2.

3.9 Reporting Limit (RL): The reporting limit, also known as the LOQ is the minimum concentration that can be reported as a quantitated value for a target analyte in a sample. This value can be no lower than the concentration of the lowest calibration standard.

3.10 Required Detection Limit (RDL): Detection limits established by a client or regulatory authority for analytes of concern. The laboratory MDL values must be equal or lower than the RDL. This is also known as the CRQL, the contract-required quantitation limit.

3.11 Surrogate Standard (SS): Organic compounds which are similar to the target analytes in chemical composition and mimic the behavior of the target analytes throughout the analytical process. Surrogate compounds are not normally found in environmental samples. Each calibration standard, sample, MB, LCS, MS, and MSD is spiked with surrogate standards. Surrogates are used to evaluate analytical efficiency by measuring recovery. See analytical method SOP for a list of specific surrogate compounds that are appropriate for sample-specific analysis.

ǂ EL-V1M2-ISO-2016, 2016 NELAP Standard definition.

4.0 Interferences

4.1 Matrix interferences may be caused by contaminants that are extracted from the sample during the extraction process. The amount of matrix interference varies from sample to sample. Cleanup procedures may help eliminate some of the interferences.

4.2 Contaminants in the solvents, reagents, glassware, and other extraction components may lead to matrix interferences. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running MBs with every batch. If interferences are detected, it is necessary to determine if the source of interference is in the preparation and then take corrective action to eliminate the interference.

4.3 Use of high purity reagents, solvents, and gases minimizes interference problems.

4.4 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510. Contaminants in the solvents, reagents, glassware, and other extraction components may lead to matrix interferences. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running MB's with every batch. The data from all GC/MS data for every MB, LCS, MS, MSD, and sample must be evaluated for determining the presence of interferences. If interferences are detected, it is necessary to determine if the source of interference is in the preparation and then take corrective action to eliminate the interference.

4.5 Aldol condensates can occur when ketones are present in the extraction process.

4.6 Phthalate contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of the contamination problem in the sample preparation step of the analysis.

5.0 Safety

Laboratory personal are required to be familiar with the general laboratory safety plan including the location and proper use of safety/emergency equipment

5.1 Employees must abide by the policies and procedures in the Chemical Hygiene Plan and this document. This procedure involves hazardous material, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow the appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are hazardous. Standard laboratory safety procedures should be followed when working with all samples.

5.2 Specific Safety Concerns or Requirements

Eye protection that satisfies ANSI Z87.1, laboratory coat, and disposable nitrile or Silver-Shield gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded. Non-disposable gloves must be cleaned immediately. Latex and vinyl gloves provide no protection against the organic solvents used in this method.

5.3 Each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Procedures involving primary standards and sample preparation must be performed in a fume hood.

5.4 Extraction solvents such as acetone, hexane and especially methylene chloride have appreciable vapor pressure that requires proper venting if using a separatory funnel. After a few manual shakes, hold the funnel upside down, open the stopcock and position the funnel to be directed in the hood and away from the individual(s) to release buildup of solvent pressure, repeat as necessary.

5.5 Safety Data Sheets (SDS) for each analyte and reagent used in the mobile laboratory are available to all employees. The SDS and the PHILIS Chemical Hazard Summary Sheet must be read and understood by the analyst prior to initial use of a chemical.

6.0 Equipment and Supplies

6.1 Equipment

6.1.1 TurboVap with trays to hold 40 mL vials and 15 mL concentrator tubes, which can be regulated at a temperature of 35°C. A DryVap (Horizon Technology, Salem, NH, USA) or equivalent may also be used.

6.1.2 Horizon Reclaimer™ Solvent Recovery System.

6.1.3 Centrifuge capable of holding 40mL vials.

6.1.4 Re-pipettor capable of dispensing 6mL of solvent.

6.2 Supplies

6.2.1 Separatory funnel – 125 mL, with polytetrafluoroethylene (PTFE) stopcock and topper. (Other sizes may be used based on RL requirements)

6.2.2 Glass funnels.

6.2.3 40mL clear vials.

6.2.4 Glass wool.

6.2.5 Vials – 2 mL, glass with PTFE-lined screw-caps or crimp tops.

6.2.6 pH indicator paper - pH range including the desired extraction pH.

6.2.7 Syringe – 1 mL.

6.2.8 Graduated cylinder – 100 mL.

6.2.9 Separatory funnel racks.

6.2.10 15 mL concentrator tubes with toppers.

6.2.11 Aluminum foil.

6.2.12 Timer that can be set to 3 and 5 minutes, decreasing time.

7.0 Reagents and Standards

7.1 Original containers of reagents shall be labeled with date of receipt. All containers with prepared reagents must bear a name of preparer, preparation date, and must be linked to the preparation records in Element.

7.2 Reagent grade chemicals will be used for all sample preparation procedures. 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. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.3 Organic Free Reagent Water: Water that does not contain analytes of interest or interferences that would prevent detection of analytes of interest at the reporting limit. DI water or bottled water may be used provided it meets the above requirements.

7.4 Sodium hydroxide solution (10 N), NaOH. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL. Other concentrations of hydroxide solutions may be used to adjust sample pH, provided the volume added does not appreciably change (e.g., <1%) the total sample volume. The making of this solution generates an excessive amount of heat. Precaution must be taken to dissipate the excess heat and protection must be used for eyes and skin.

7.5 Sodium sulfate (granular, anhydrous), Na2SO4. Purify by heating to 400°C for 4 hours in a shallow tray, or by pre-cleaning the sodium sulfate with methylene chloride. If the sodium sulfate is pre-cleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

7.6 Sulfuric acid solution (1:1), H2SO4. Slowly add 50 mL of H2SO4 (sp. gr. 1.84) to 50mL of organic-free reagent water. Other concentrations of acid solutions may be used to adjust sample pH, provided that the volume added does not appreciably change (e.g., <1%) the total sample volume.

7.7 Extraction/exchange solvents - All solvents must be pesticide quality (nano grade) or equivalent.

7.8 Methylene chloride, MeCl2, boiling point 39°C. GC, GC/MS or pesticide grade.

7.9 Hexane, boiling point 68.7°C. GC, GC/MS or pesticide grade.

7.10 Acetone, (CH3)2CO, boiling point 56.5 °C. GC, GC/MS or pesticide grade.

7.11 For the extraction of Aroclors from waters followed by GC/ECD analyses (SOP L-A-401), the following spike standards are used:

7.11.1 Surrogate Spike Solution at 2 µg/mL - Dilute 50 µL of a stock at 200 µg/mL (Restek 322457, or equivalent) to 5.0 mL with acetone to produce a solution contain 20 µg/mL each of 2,4,5,6-tetrachloro-m-xylene (TCMX) and decachlorobiphenyl.

7.11.2 Aroclor Spiking Solution for LCS, MS, or MSD – Prepare a solution at 10 µg/mL in acetone by diluting 50 µL each of Aroclor 1016 and Aroclor 1260 stocks at 1000 µg/mL (AccuStandard C-216S-H-10X and C-260S-H-10X, or equivalent) to 5.00 mL.

7.11.3 To each 100-mL water sample to be analyzed by the procedures in SOP L-A-401, add 50 µL of the surrogate spike solution at 2 µg/mL (10.11.1).

7.11.4 To each 100-mL aqueous LCS, MS or MSD to be analyzed by the procedures in SOP L-A-401, add 50 µL of the Aroclor spike solution at 10 µg/mL (10.11.2).

8.0 Sample Collection, Preservation, and Storage

Samples are collected by field crews in amber bottles or amber jars based on extraction volume needed to meet reporting limits and are put on ice to maintain a temperature of 0°C to 6°C and shipped to the laboratory. Typical bottle size is 125mL amber with Teflon lined lid based on 100mL extraction. See the PHILIS SOP's (L-P-001, L-P-002, and L-P-003) for sample login procedures and sample acceptance criteria.

8.1 Samples received on the collection day shall be considered acceptable if there is evidence that the chilling process has begun such as arrival on ice. In such cases, sample temperatures that are in excess of 6°C upon receipt are acceptable.

8.2 Samples are maintained within the temperature range from 0°C to 6°C.

8.3 Sample extraction holding time is 7 days for analysis of extractable organic compounds in aqueous samples. Refer to the analytical method or SW846 Chapter 4 Table 4 for method holding times.

9.0 Quality Control

9.1 Initial Demonstration of Capability (IDOC) - must be successfully performed by the prep extraction chemist prior to extracting any field samples and any time major modifications are made to the extraction process.

An initial Demonstration of capability is performed by extracting 4 replicate LCSs fortified at a known concentration near the midpoint of the calibration curve. Precision and accuracy are calculated. Acceptance criteria for RSD precision is ≤ 30%. Accuracy as a mean percent recovery must be within the limits generated by laboratory historical analytical data.

9.2 Ongoing QC is applied with every batch when performing this extraction method. Every prep batch must contain at least one MB, LCS, MS, and MSD. Surrogates should be included with every batch sample per the applicable SOP. If there is not enough volume for an MS/MSD pair, then an LCSD must be performed for precision data. Where applicable, surrogates are added prior to extraction and internal standards added to each sample after extraction but prior to analysis.

9.3 QC Control Limits

9.3.1 Control limits are determined for surrogates, laboratory control samples, and matrix spike samples. These QC samples should be determined every 6 months. The recovery limits are the mean recovery +/-3 standard deviations for surrogates, MS, and LCS. Precision limits for the MS/MSD pair results are the absolute value of the mean relative percent difference (RPD) +/-3 standard deviations.

9.3.2 These limits do not apply to dilutions, but the surrogate and matrix spike recoveries will be reported unless the dilution is 4x or more.

9.3.3 All surrogates, LCS, and MS recoveries (except for dilutions) must be entered into Element so that historical control limits can be generated. For multiple dilutions reported from the same extract, surrogates will be reported for all dilutions of less than 4x.

9.4 Method Blank (MB)

9.4.1 For aqueous samples the method blank is reagent water. The method blank is free of the analytes of interest and is spiked with surrogates. At least one method blank must be analyzed with every prep batch.

9.4.2 Acceptance Criteria: The result for the method blank must be less than ½ the RL or less than 10% of the analyte concentration found in the associated samples, whichever is higher.

9.4.3 Corrective Action: If a compound fails to meet these criteria, the batch will need to be re-extracted. However, if the analyte in the method blank was not detected in any of the associated samples, the data can still be reported, but flagged accordingly.

9.5 Laboratory Control Sample (LCS)

9.5.1 The LCS is prepared using reagent water. An LCS is prepared and analyzed with every batch of samples. It is spiked with the compounds listed in PHILIS SOP L-A-201 Semivolatile Organics by Method 8270E, Table 1, the compounds listed in SOP L-A-401, Polychlorinated Biphenyls by Method 8082A, Pesticides listed in SOP L-A-403 or Diesel Range Organics listed in SOP L-A-205.The compounds should be spiked at a level near the midpoint of the calibration curve.

9.5.2 Acceptance Criteria: All analytes must be with laboratory acceptance criteria to report definitive data.

9.5.3 Corrective Action: If any analyte in the LCS is outside the established control limits, a corrective action must be performed.

9.5.4 If the batch is not re-extracted or re-analyzed, the reasons for accepting the batch must be clearly presented in the report. An example of acceptable reasons for this might be the MS/MSD are acceptable and sample surrogate recoveries are within control limits, showing that the problem was just on the LCS. Also, if the analyte that failed is not a target analyte for the project or the analyte recovered above the control limit, but was not detected in the associated samples.

If re-extraction and re-analysis of the batch are not possible due to limited sample volume, the LCS is reported, all associated samples are flagged accordingly, and the appropriate comments are made in the report narrative.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1 The matrix spike is a second aliquot of one of the samples in the batch, and the matrix spike duplicate is a third aliquot of the same sample. The MS/MSD are spiked with the same analytes as the LCS and at the same level. An MS/MSD is prepared with every batch. If there is inadequate sample to prepare and MS/MSD, then prepare an MS with a sample duplicate. If there is inadequate sample to prepare the above, the prepare an LCS duplicate.

9.6.2 Acceptance Criteria: The percent recovery must be within the control limits. The RPD for the pair must be less than or equal to the laboratory established control limits.

9.6.3 Corrective Action: If the recovery of an analyte is out of control, or if an RPD fails, then a corrective action must be performed. Typically, if the recoveries of the MS/MSD are similar but not within control limits and the recoveries of the LCS are within control limits, then the analysis can continue. This is documented as matrix interference.

9.6.4 If there are recoveries failures in the MS/MSD and the LCS, then the batch must be re-extracted or,

9.6.5 Re-analyzed. If re-extraction is not possible due to limited sample volume, then a duplicate LCS(LCSD) must be run with the re-extraction batch. The RPD of the LCS/LCSD must be less than or equal to the laboratory established acceptance criteria.

9.7 Surrogates

9.7.1 Each sample, MB, and QC sample is spiked with the surrogate standards at a concentration within the working range of the ICAL. The SVOA target compound surrogates are listed in the PHILIS SOP L-A-201 Semivolatile Organics by Method 8270E, Table 4. After analysis, if any of the surrogates fail to meet criteria, the sample must be re-extracted or re-analyzed. If the re-extraction fails in the same manner, it can be documented in the report that the failure is due to matrix interference.

9.7.2 If a sample has a surrogate failure and it has an MS/MSD associated with it, and the surrogate recoveries in the pair also fail, then the sample and the MS/MSD do not require re-extraction. This indicates matrix interference.

9.7.3 If the sample is re-extracted and the surrogates in the re-analysis are acceptable, the re-analysis should be reported. This indicates the failure was within the control of the analyst. However, if the sample is re-extracted outside of the hold time, both sets of results should be reported.

9.7.4 If the re-extraction confirms the surrogate failure, the original results should be reported and the matrix interference should be documented in the report.

9.8 This method is used with EPA 8270E, 8015D, 8081B, and 8082A (PHILIS SOPs L-A-201, L-A-205, L-A-401 or L-A-403) to determine method detection limits. This method may also be used for other methods requiring extraction.

9.9 Method detection limits are determined using the procedure outlined in 40 CFR Part 136, Appendix B, Revision 2.

9.10 Data assessment and acceptance criteria, corrective actions for out of control, and contingencies for handling out of control are listed in their analytical SOPs listed above. The Lead Chemist is responsible for client contact regarding issues.

10.0 Calibration and Standardization

See Section 10 of the analytical method SOP will have calibration requirements.

11.0 Procedure

11.1 Open each sample bottle and test the pH of the samples, using a wide-range pH strip.

11.2 Document the initial pH of each sample in LIMS on the sample preparation data page.

11.3 Using a 100 mL graduated cylinder, measure 100 mL (nominal) of sample. Other volumes may be used based on QAPP requirements.

11.3.1 Alternatively, if the entire contents of the sample bottle are to be extracted, mark the level of sample on the outside of the bottle. If high analyte concentrations are anticipated, a smaller sample volume may be taken and diluted to 100mL with organic-free reagent water, or samples may be collected in smaller sample bottles and the whole sample used.

11.3.2 For QC samples, such as method blanks and laboratory control samples use reagent water, measured at 100 mL using a graduated cylinder.

11.4 Pour contents of the graduated cylinder into a separatory funnel that has been rinsed twice with acetone and twice with methylene chloride prior to use. This rinse solvent must be disposed of in the proper satellite waste container.

11.5 For SVOA samples to be analyzed by GC/MS, pipette 100 µL of the surrogate solution into each sample. For Pesticide or Aroclor samples to be analyzed by GC/ECD, add 50 µL of the surrogate solution in Section 10.11.1 into each sample.

11.6 For SVOA samples to be analyzed by GC/MS, add 250 µL of the spiking solution to the sample in each batch selected for use as the MS/MSD. For Aroclor MS or MSD samples to be analyzed by GC/ECD, add 50 µL of the Aroclor spike solution in Section 10.11.2 into each sample.

11.7 For SVOA samples to be analyzed by GC/MS, add 250 µL of spiking solution to the LCS (and LCSD if applicable). For Aroclor LCS or LCSD samples to be analyzed by GC/ECD, add 50 µL of the Aroclor spike solution in Section 10.11.2 into each sample.

11.8 If performing an extraction that requires pH adjustment, adjust the pH at this time. For extracts used for 8270E analysis, adjust the pH to <2 using the sulfuric acid solution. Document the pH change in LIMS on the bench sheet.

11.9 Add 6 mL of methylene chloride to each sample.

11.10 Seal and shake the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure.

WARNING: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken for a few seconds. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors.

11.11 Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

11.12 Rinse a glass funnel with methylene chloride.

11.12.1 Add a small layer of glass wool (or Whatman 40 filter paper) to cover the hole in the funnel.

11.12.2 Cover the glass wool or filter paper with sodium sulfate Approximately 5 to 10g.

11.12.3 Rinse the sodium sulfate with methylene chloride. Make sure to rinse to the point of saturation.

11.12.4 Discard rinse solvent in the appropriate waste container.

11.13 Pour the methylene chloride from the sample through the funnel, into the vial.

Rinse the sodium sulfate with clean methylene chloride.

11.14 Repeat the extraction two more times using fresh portions of solvent.

11.14.1 After the third extraction, let the sample sit for 10 minutes, instead of 5 minutes.

11.14.2 Combine the three solvent extracts into one vial.

11.15 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH. Record the pH change in LIMS on the bench sheet.

11.15.1 For 8270E, Using the sodium hydroxide solution adjust the pH to >12 and repeat the extraction steps 11.9 through 11.14.2.

11.15.2 Transfer the basic phase of each sample in a different vial from the acidic phase vial.

11.16 If performing GC/MS analysis (Method 8270E), the acid/neutral and base extracts may be combined after drying with sodium sulfate and prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid/neutral or base compounds at low concentrations must be determined, separate extract analyses may be warranted).

11.17 Concentration using the TurboVap. Equivalent concentrators may be used.

11.17.1 Turn on the TurboVap, the vacuum pump, the Horizon solvent-recovery system, if available, and the Nitrogen.

11.17.2 Adjust the temperature of the bath to 35°C and the nitrogen pressure to 5-10 psi.

11.17.3 Verify that there is a sufficient amount of water in the bath. Add more water if necessary.

11.17.4 Insert the appropriate rack for the vials used during extraction.

11.17.5 Combine the different phases into one vial, by analytically transferring and rinsing one vial into the other twice using methylene chloride. Add these rinses to the vial that will be used for concentration.

11.17.6 Once the bath is up to temperature, insert the vials into the rack and set the timer to begin concentration. Close the lid.

CAUTION: Verify the samples are not splashing out of the vials into the TurboVap. This could lead to loss of compounds and/or contamination of other samples.

11.17.7 For SVOAs, combine the extracts and concentrate the samples down to approximately 8-10 mL, transfer them to 15 mL concentrator tubes rinse the vial twice with Methylene Chloride and add these rinses to the concentrator tube.

11.17.8 Prior to use, rinse the concentrator tubes twice with Acetone and twice with Methylene Chloride. Dispose of the rinseate in the appropriate waste container.

11.17.9 Continue concentration, rinsing the walls of the concentrator tube occasionally with methylene chloride.

11.17.10 Remove the extract from the bath once the volume is between 0.7 and 0.9mL.

11.17.11 Transfer the extracts into amber 2 mL autosampler vials at the volume of 1.0 mL. Samples requiring PCB analysis are extracted as above and then exchanged into hexane prior to analysis on the GC. Addition of the Hexane should occur when the sample volume is at 5-10 mLs.

CAUTION: When the volume of solvent is reduced below 1 mL, semi volatile analytes may be lost.

11.18 Transferring sample extracts once concentrated

11.18.1 Label 2 mL amber vials with sample ID, batch, and test performed.

11.19 Take a 1.0 mL syringe or pipette to measure the extract volume and rinse three times with methylene chloride. Make sure to rinse the syringe between every sample.

11.19.1 Pull all of the extract into the syringe and remove the air-bubble. Do this by inverting the syringe, pulling in some air, and then pushing the air out.

11.19.2 Rinse the walls of the concentrator tube with a small amount of methylene chloride or hexane, based on the solvent.

11.19.3 Pull this rinse into the syringe.

11.19.4 Repeat previous section until there is 1.0 mL in the syringe.

11.19.5 Transfer the contents of the syringe into the appropriately labeled vial.

11.19.6 Add the appropriate amount of IS to the sample.

11.19.7 PAHSIM, 10 µL of IS will be added for a 1.0 mL extract.

11.19.8 Cap the sample and store in an appropriately identified tray until analysis.

11.19.9 The extract may now be analyzed for the target analytes using the appropriate determinative technique.

11.19.10 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters.

11.19.11 Any variation in procedure shall be completely documented by the analyst and included in the final report.

12.0 Data Analysis and Calculations

12.1 Percent recovery for LCS and MS are performed using the following equation:

$$\%R = \left[\frac{(C_{spk} - C_x)}{C_t}\right] 100$$

where :
C_{spk} = the concentration of the analyte in the spiked sample.
C_x = the concentration of the analyte in the reference (parent) sample; (Cx = 0 for LCS).
C_t = the theoretical spike concentration.

12.2 Relative percent difference for duplicate is calculated using the following equation:

$$RPD = \left[\frac{|C_1 - C_2|}{(C_1 - C_2)/_2}\right]$$

where :
C_1 = concentration of the first sample
C_2 = concentration of the second sample

13.0 Method Performance

13.1 Demonstration of laboratory accuracy and precision are presented in PHILIS SOP L-A-201 Semivolatile Organics by Method 8270E, Table 2, and MDL data is presented in Table 3. Precision, accuracy, and MDL data for Arolcors are given in SOP L-A-401. Precision, accuracy, and MDL data for pesticides are given in SOP L-A-403. Precision, accuracy, and MDL data for diesel range organics are given in SOP L-A-205.

13.2 Other specific Quality Assurance Objectives (QAO) may be found in the appropriate statement-of-work or Quality Assurance Project Plan (QAPP) for specific projects.

14.0 Pollution Prevention

14.1 The waste produced from EPA Method 3510C consists of waste collected from the extraction equipment, excess sample, Standards, methylene chloride, and acetone.

14.2 Excess reagents are disposed following the SDS and hazardous waste management plan instructions.

14.3 Refer to EPA Method 3510C for additional guidance.

14.4 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.4.1 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

14.4.2 The Environmental Protection Agency requires that laboratory waste management practices conducted are consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society.

15.0 Waste Management

15.1 The waste produced from EPA Method 8270E, EPA Method 8081B and EPA Method 8082A consists of waste collected from the extraction equipment, excess sample, standards, methylene chloride, acetone, hexane, and methanol.

15.2 Excess reagents are disposed following the SDS and hazardous waste management plan instructions.

15.3 Glass pipettes are disposed in the glassware waste container.

15.4 Refer to EPA Method 8270E, EPA Method 8081B, EPA Method 8082A and EPA Method 8015D for additional guidance.

16.0 References

16.1 EPA Method 8082A, Polychlorinated Biphenyls by Gas Chromatography, Revision 1, February 2007; U.S. EPA Office of Solid Waste.

16.2 EPA Method 8270E, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Revision 3, August 2006; U.S. EPA Office of Solid Waste.

16.3 EPA Method 8015D Non-Halogenated Organics Using GC/FID, Revision 4, June 2003

16.4 EPA Method 8081B Organochlorine Pesticides by Gas Chromatography Revision 2 February 2007.

16.5 EPA Method 3510C, Separatory Funnel Liquid-Liquid Extraction, Revision 3, May 2003; U.S. EPA Office of Solid Waste.

16.6 EPA Method 3500C, Organic Extraction and Sample Preparation, Revision 3, May 2003; U.S. EPA Office of Solid Waste.

16.7 NELAC Manuals, 2003, 2009, and 2016.

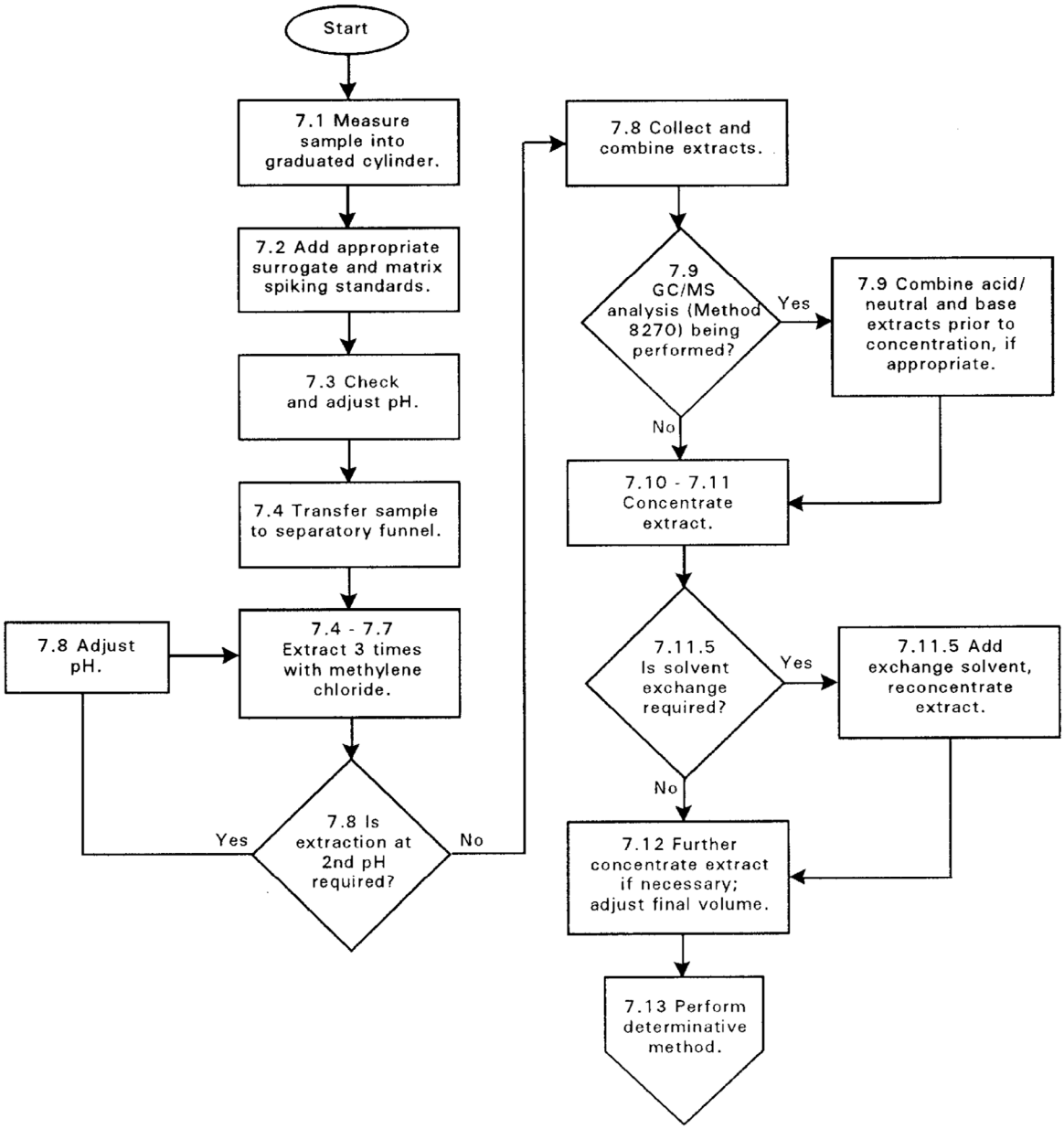
17.0 Tables, Figures, and Attachments

Table 1. Specific Extraction Conditions for Various Determinative Methods

Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)[a]
8041	≤2	none	2-propanol	hexane	1.0	1.0, 0.5[b]
8061	5-7	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8081	5-9	none	hexane	hexane	10.0	10.0
8082	5-9	none	hexane	hexane	10.0	10.0
8091	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8111	as received	none	hexane	hexane	2.0	10.0
8121	as received	none	hexane	hexane	2.0	1.0
8141	as received	none	hexane	hexane	10.0	10.0
8270[c,d]	<2	>11	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0
8321	as received	none	methanol	-	-	1.0
8325	7.0	none	methanol	-	-	1.0
8410	as received	none	methylene chloride	methylene chloride	10.0	0.0 (dry)

[a] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.
[b] Phenols may be analyzed, by Method 8041, using a 1.0 mL 2-propanol extract by GC/FID. Method 8041 also contains an optional derivatization procedure for phenols which results in a 0.5 mL hexane extract to be analyzed by GC/ECD.
[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.
[d] Extraction pH sequence may be reversed to better separate acid and neutral waste components. Excessive pH adjustments may result in the loss of some analytes (see Sec. 3.2).

Figure 1. Method 3510C - Separatory Funnel Liquid-Liquid Extraction



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APPENDIX H -
PHILIS SOP L-P-203
Microwave Extraction Rev. 0 05/09/2024

STANDARD OPERATING PROCEDURE

FOR

MICROWAVE EXTRACTION

PHILIS SOP L-P-203 Rev. 0

Revision Date: 05-09-2024

EPA Contract No. 68HERH21D0002

PREPARED BY

PHILIS

PREPARED FOR

U.S. Environmental Protection Agency
Office of Emergency Management
Washington, DC 20460

Approvals:

PHILIS, Castle Rock Lead Chemist	**May 9, 2024** **Date**
PHILIS, Edison Lead Chemist	**May 9, 2024** **Date**
PHILIS, Quality Assurance Manager	**May 9, 2024** **Date**
PHILIS, Program Manager	**May 9, 2024** **Date**

Revision History

Revision	Name	Date	Description of Change
0	James Travis Thomas Antony	12/07/2023	Program Issue

SOP REVISION FORM

SOP Name:	**Microwave Extraction**		
Purpose: *(Review or Revise)*	*SOP #:*	*Rev. #:* *(Being Reviewed or Revised)*	*Origination / Release Date:*
Program Issue	*SOP No. L-P-203*	N/A	N/A
Requested by:	Thomas Antony	Date:	12/07/2023

New SOP Revision Date:	**05/09/2024**	**New SOP Revision #:** *(If Applicable)*	**0**

For *Revision*: Summary of Revisions (specify sections)

For *Review*: Comments

Standard Operating Procedure
Microwave Extraction
L-P-203 Rev. 0

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Standard Operating Procedure
Microwave Extraction
L-P-203 Rev. 0

1.0 Scope and Application

1.1 This standard operating procedure (SOP) documents the PHILIS Program application of EPA Method SW846 3546 – Microwave extraction that will be used in the PHILIS Mobile Labs.

1.2 This SOP is executed in accordance with the U.S. Environmental Protection Agency and National Environmental Laboratory Accreditation Program (NELAP).

1.3 This method is a procedure for extracting water insoluble or slightly water soluble organic compounds from soils, clays, sediments, sludges, and solid wastes. This method was developed and validated on commercially-available solvent extraction systems. Its procedure uses microwave energy to produce elevated temperature and pressure conditions (i.e., 100 - 115 EC and 50 - 175 psi) in a closed vessel containing the sample and organic solvent(s) to achieve analyte recoveries equivalent to those from Soxhlet extraction (Method 3540), using less solvent and taking significantly less time than the Soxhlet procedure. Other systems and other types of vessels may be used, provided that the analyst demonstrates appropriate performance for the specific application.

1.4 This method is applicable to the extraction of semivolatile organic compounds, organophosphorus pesticides, organochlorine pesticides, chlorinated herbicides, phenoxyacid herbicides, substituted phenols, PCBs, and PCDDs/PCDFs, which may then be analyzed by a variety of chromatographic procedures. This method may also be applicable for the extraction of additional target analytes, provided that the analyst demonstrates adequate performance for the intended application (see Method 3500)

1.5 This method has been validated for solid matrices containing from 50 to 10,000 µg/kg of semivolatile organic compounds, 250 to 2,500 µg/kg of organophosphorus pesticides, 10 to 5,000 µg/kg of organochlorine pesticides and chlorinated herbicides, 50 to 2,500 µg/kg of substituted phenols, 100 to 5,000 µg/kg of phenoxyacid herbicides, 1 to 5,000 µg/kg of PCBs, and 10 to 6000 ng/kg of PCDDs/PCDFs.

1.6 This method may be applicable to samples containing these analytes at higher concentrations and may be employed after adequate performance is demonstrated for the concentrations of interest (see Method 3500). It may also be applicable to classes of analytes, to fuel types, and to petroleum fractions other than those listed in Sec 1.2. However, to use this method for additional analytes, fuel types, petroleum fractions, or different concentrations, the analyst must demonstrate that the extraction conditions are appropriate for the analytes of interest. The analyst must also perform the initial

demonstration of proficiency described in Sec. 9.2 and Methods 3500 and 8000. When expanding this method to other fuel types or petroleum hydrocarbons, the boiling point range or carbon number range of the material should be carefully defined and the quantitation approach be modified to match such 3546-2 Revision 0 February 2007 ranges. Analysts are advised to consult authoritative sources, such as the American Petroleum Institute (API), for appropriate definitions of other fuel types or petroleum fractions.

1.7 This method is only applicable to solid samples with small particle sizes. If worker safety or the loss of analytes during drying is a concern, soil/sediment samples may be mixed with anhydrous sodium sulfate or pelletized diatomaceous earth. (Drying samples containing PCDDs/PCDFs is not recommended, due to safety concerns.) The total mass of material to be prepared depends on the specifications of the determinative method and the sensitivity needed for the analysis, but an amount of 2 - 30 g of material is usually necessary and can be accommodated by this extraction procedure.

1.8 This method has been validated using a solvent mixture of hexane/acetone or methylene chloride/acetone (1:1) from matrices such as soil, glass-fibers and sand. This solvent system or other solvent systems may be employed, provided that adequate performance is demonstrated for the analytes of interest (see. Sec. 7.4).

1.9 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern. In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.10 Use of this method is restricted to use by, or under supervision of, appropriately experienced and trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of Method

2.1 Sample is weighed into Teflon vessel, spiked with surrogate, and extraction solvent is added.

2.2 Vessel is sealed, placed in microwave carousel, and heated according to pre-programed method.

2.3 Mixture is allowed to cool. The vessel is filtered through sodium sulfate and concentrated to the appropriate volume.

3.0 Definitions

3.1 Batch‡: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A Preparation Batch is composed of between 1 and 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and the last sample in the batch to be 24 hours. Each Preparation Batch requires; one MB, LCS, and MS/MSD pair. An Analytical Batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

All batches require one MB, LCS, and MS/MSD pair or MS and Sample Duplicate when possible.

3.2 Holding Time: The maximum amount of time permitted between sampling and sample preparation and/or sample preparation and sample analysis. Also the period of time a sample may be stored prior to analysis when there is no preparation step. See the specific method or SW846 8000B table 4.1.

3.3 Internal Standards (IS)‡: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

3.4 Laboratory Control Sample (LCS)‡: (however named, such as laboratory fortified blank, blank spike (BS), or QC check sample). A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

The standard source can be the same as the calibration or a second source. The LCS is analyzed exactly like a sample to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.5 Matrix Spike (spiked sample of fortified sample)ǂ: A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of the sample for which an independent test results of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

3.6 Matrix Spike Duplicate (spiked sample or fortified sample duplicate)ǂ: A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

3.7 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. Method Blank analytical results are evaluated to determine the presence of contamination in the analytical method process.

3.8 Method Detection Limit (MDL): The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined by analyzing seven or more replicates of a spiked analyte free matrix and the resulting statistical calculation, in accordance with 40 CFR 136, Appendix B, Revision 2.

3.9 Reporting Limit (RL): The reporting limit, also known as the LOQ is the minimum concentration that can be reported as a quantitated value for a target analyte in a sample. This value can be no lower than the concentration of the lowest calibration standard.

3.10 Required Detection Limit (RDL): Detection limits established by a client or regulatory authority for analytes of concern. The laboratory MDL values must be equal or lower than the RDL. This is also known as the CRQL, the contract-required quantitation limit.

3.11 Surrogate Standard (SS): Organic compounds which are similar to the target analytes in chemical composition and mimic the behavior of the target analytes throughout the analytical process. Surrogate compounds are not normally found in environmental samples. Each calibration standard, sample, MB, LCS, MS, and MSD is spiked with surrogate standards. Surrogates are used to evaluate analytical efficiency by measuring recovery. See analytical method SOP for a list of specific surrogate compounds that are appropriate for sample-specific analysis.

ǂ EL-V1M2-ISO-2016, 2016 NELAP Standard definition.

4.0 Interferences

4.1 Contaminants in the solvents, reagents, glassware, and other extraction components may lead to matrix interferences. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis through preparation and analysis of MBs with every batch. The data from all GC/MS data for every MB, LCS, MS, MSD, and sample must be evaluated for interferences. If interferences are detected, it is necessary to determine if the source of interference is in the preparation and then take corrective action to eliminate the interference.

4.2 Refer to Method 3500 for information regarding interferences.

4.3 If necessary, Florisil and/or sulfur cleanup procedures may be employed. In such cases, proceed with the method – in SOP L-P-110 and/or L-P-109. Refer to SOP L-P-108 for acid cleanup of PCB extracts.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Chemical Hygiene Plan and this document. This procedure involves hazardous material, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow the appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are hazardous. Standard laboratory safety procedures should be followed when working with unknown samples. Gloves should be worn while handling any chemicals, standards, or samples. Other required personal protective equipment (PPE) are safety glasses, lab coats, and closed-toe, non-absorbent shoes.

5.2 Specific Safety Concerns or Requirements

Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded. Non-disposable gloves must be cleaned immediately. Latex and Vinyl gloves provide no protection against the organic solvents used in this method, so nitrile or similar must be used.

5.3 The toxicity and/or carcinogenicity of the reagents and analytes used in this method have been precisely defined; therefore, each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Procedures involving primary standards and sample preparation must be performed in a fume hood.

5.4 Safety Data Sheets (SDS) for each analyte and reagent used in the mobile laboratory are available to all employees. The SDS must be consulted prior to initial use of a chemical by an analyst.

5.5 Laboratory personal are required to be familiar with the general laboratory safety plan including the location and proper use of safety/emergency equipment.

5.6 The use of organic solvents, elevated temperatures, and high pressures in this method present potential safety concerns in the laboratory. Common sense laboratory practices can be employed to minimize these concerns. The sections to follow describe additional steps that should be taken.

5.7 Extraction cells in the heating block are hot enough to burn unprotected skin. Allow the cells to cool for 10-15 min before removing them from the oven or use appropriate protective equipment (e.g., Gripper; insulated gloves or tongs), as recommended by the manufacturer.

5.8 During the gas purge step, some solvent vapors may exit through a vent port in the instrument. Follow the manufacturer's directions regarding connecting this port to a fume hood to prevent release of solvent vapors to the laboratory atmosphere.

5.9 The instrument may contain flammable vapor sensors and should be operated with all covers in place and doors closed to ensure proper operation of the sensors. Follow the manufacturer's directions regarding replacement of extraction cell seals to ensure against vapor leaks.

6.0 Equipment and Supplies

6.1 Equipment

6.1.1 MARS 6 Microwave Extractor or equivalent

6.1.2 Teflon Extraction Vessels

6.1.3 **Optional**: Disposable Glass Vessel Linear Inserts (Required for CWA extractions)

6.1.4 Glass Wool or Filter Paper

6.1.5 Top Loading Balance – capable of weighing to 0.01g

6.1.6 Glass Filter Funnels

6.1.7 Various sized Hamilton syringes or equivalent

6.1.8 50 mL Glass Beakers

7.0 Reagents and Standards

7.1 Reagent grade Methylene Chloride, Acetone, and Hexanes

7.2 Granular anhydrous Sodium Sulfate

7.3 Spiking and surrogate solutions appropriate for target analytes

7.4 TCL (Target Compound List)-free sand. All references to sand in this method refer to TCL-free sand.

8.0 Sample Collection, Preservation, and Storage

8.1 Samples are normally collected in 6 oz amber jars but may come in different sizes and volumes.

8.2 Samples are delivered to the PHILIS or held at 0°C - 6°C before shipment to the lab for analysis within holding time.

8.3 The samples received in the PHILIS laboratories must be transported in coolers with ice packs. Sample temperatures are measured upon receipt. Any samples that exceed acceptable temperatures require client notification. See SOP L-P-001. Samples are maintained at the temperature range from 0°C to 6°C range.

8.4 Sample extraction holding time is 14 days for soil samples.

8.5 Samples should NOT be preserved upon receipt.

9.0 Quality Control

9.1 Any reagent blanks, laboratory control samples, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

9.2 See PHILIS SOP L-A-201, Semivolatile Organics by Method 8270E, PHILIS SOP L-A-401, Polychlorinated Biphenyls by Method 8082A, SOP L-A-403, Pesticides by Method 8081B or Method 8015D Diesel Range Organics for specific quality control information.

9.3 Initial Demonstration of Capability: This method must be successfully performed by the prep extraction chemist prior to preparing any project samples, and at any time major modifications are made.

9.4 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. For this method, this can be accomplished through the analysis of a solid matrix method blank (e.g. clean sand). As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination.

9.5 Standard quality assurance practices should be used with this method as included in appropriate systematic planning documents and laboratory SOPs. All instrument operating conditions should be and are stored on the instrument.

9.6 Also refer to Method 3500 for extraction and sample preparation QC procedures and the determinative methods to be used for determinative QC procedures.

9.7 When listed in the appropriate determinative method, surrogate standards should be added to all samples prior to extraction. See Methods 3500 and 8000D, and the appropriate determinative methods for more information.

9.8 As noted earlier, use of any extraction technique, including pressurized fluid extraction, should be supported by data that demonstrate the performance of the specific solvent system and operating conditions for the analytes of interest, at the levels of interest, and in the sample matrix.

9.9 Corrective Actions for Out of Control The analyst shall report to the Lead Chemist any out control event. Such events include: Damage to the sample, Holding time exceeded, Inadequate sample preservation.

9.10 The Lead Chemist will implement the corrective action plan described in the PHILIS corrective action plan document

9.11 Detection Limits

9.11.1 This method is used with SW846 Method 8081B, SW846 Method 8082A, SW846 Method 8270E, and SW846 Method 8015D to determine method detection limits. Other methods may be used that require soil extraction methods.

9.11.2 Method detection limits are determined using the procedure outlined in 40 CFR Part 136, Appendix B, Revision 2.

9.11.3 The detection limit is estimated to be 0.33 µg/kg for EPA Method 8081B, 10 µg/kg for EPA Method 8082A, and 83 µg/kg for EPA Method 8270E. The detection limit for Method 8015D DRO is 0.90 mg/Kg

10.0 Calibration and Standardization

See PHILIS SOP L-A-201 Semivolatile Organics by Method 8270E, SOP L-A-401, Polychlorinated Biphenyls by GC, SOP L-A-403 Pesticides by Method 8081B or SOP L-A-205 Diesel Range Organics Section 10 for instrument calibration.

11.0 Procedure

11.1 Obtain clean Teflon sample Vessels

11.2 Weigh out approximately 30g of soil into Teflon sample vessel. Be sure to avoid large rocks and other detritus (Sticks, leaves, etc). Sample should be dry and free flowing like sand.

11.3 Add appropriate surrogates and spiking solutions according to method and sample type. Spike reagents into vessels directly onto soil matrix.

11.4 Add approximately 30 mL of extraction solvent to the vessel making sure all soil is covered.

11.5 Seal vessel with plug and cap. Use torque wrench to tighten cap until wrench clicks twice. NOTE: Do not over tighten with hands.

11.6 Place vessel in carousel and place carousel in microwave.

11.7 Choose appropriate microwave extraction method. In most cases it will be EPA 3546 100C and start microwave.

11.8 Once method is complete remove carousel from microwave and then remove vessels from carousel.

Caution: If vessels are hot to touch allow them to cool before opening. Opening a hot vessel can result in rapid volatilization of solvent causing injury.

11.9 Prepare a sodium sulfate filter using a glass funnel plugged with glass wool or filter paper topped with approximately 5 to 10 g of sodium sulfate depending on the moisture content of the samples.

11.10 Filter contents of sample vessels through sodium sulfate into conical concentration tube.

11.11 Rinse with extra solvent three times or until filter is thoroughly rinsed

11.12 Place in turbovap at 35 C and concrete sample to 1 mL.

11.13 Transfer sample to sample vial.

11.14 Sample is ready for instrument analysis.

12.0 Data Analysis and Calculations

See PHILIS SOP L-A-201, Semivolatile Organic Compounds by EPA Method 8270E, Section 15, PHILIS SOP L-A-401, Polychlorinated Biphenyls by EPA Method 8082A, Section 15, or PHILIS SOP L-A-403 Pesticides by EPA Method 8081B, Section 15.

13.0 Method Performance

See PHILIS SOP L-A-201, Semivolatile Organic Compounds by EPA Method 8270E, Section 16, PHILIS SOP L-A-401, Polychlorinated Biphenyls by EPA Method 8082A, Section 16, or PHILIS SOP L-A-403, Pesticides by EPA Method 8081B Section 16.

14.0 Pollution Prevention

14.1 The waste produced from EPA Method 3546 consists of waste collected from the extraction equipment, excess sample, standards, methylene chloride, and acetone.

14.2 Excess reagents are disposed following the SDS and Hazardous Waste Management Plan instructions.

14.3 Refer to EPA Method 3546 for additional guidance.

14.4 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.5 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

14.6 The Environmental Protection Agency requires that laboratory waste management practices conducted are consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society.

15.0 Waste Management

15.1 The waste produced from EPA Methods 8015A, 8081B, 8082A and 8270E consists of waste collected from the extraction equipment, excess sample, standards, methylene chloride, acetone, and methanol.

15.2 Excess reagents are disposed following the SDS and hazardous waste plan instructions.

15.3 Refer to PHILIS SOP L-A-101 Semivolatile Organics by EPA Method 8270E, Section 15, PHILIS SOP L-A-401 Polychlorinated Biphenyls by EPA Method 8082A, Section 15 PHILIS SOP L-A-403, Pesticides by EPA Method 8081B, or PHILIS SOP 205 Diesel Range Organics Section 15 for additional guidance.

16.0 References

16.1 Method 3546: Microwave Extraction, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Revision 1, February 2007; U.S. EPA Office of Solid Waste.

16.2 Standard Operating Procedure for Pressurized Solvent Extractions (PSE) PHILIS SOP L-P-200, Rev. 0, November 2022; PHILIS.

17.0 Tables, Figures, and Attachments

Not applicable for this method.

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APPENDIX I -
PHILIS SOP L-A-704
Analysis of Opioids by GCMS QUAD LVI Rev. 0 07/08/2024

STANDARD OPERATING PROCEDURE

FOR

ANALYSIS OF OPIOIDS BY GC-MS LVI QUAD

PHILIS SOP L-A-704 Rev. 0

Revision Date: 07-08-2024

EPA Contract No. 68HERH21D0002

PREPARED BY

PHILIS

PREPARED FOR

U.S. Environmental Protection Agency
Office of Emergency Management
Washington, DC 20460

Approvals:

PHILIS, Castle Rock Lead Chemist	**July 8, 2024** **Date**
PHILIS, Edison Lead Chemist	**July 8, 2024** **Date**
PHILIS, Quality Assurance Manager	**July 8, 2024** **Date**
PHILIS, Program Manager	**July 8, 2024** **Date**

Revision History

Revision	Name	Date	Description of Change
0	Tom Antony	06/25/2024	SOP Developed

SOP REVISION FORM

SOP Name	**Analysis of Opioids by GC-MS LVI Quad**		
Purpose: *(Review or Revise)*	*SOP #:*	*Rev. #:* *(Being Reviewed or Revised)*	*Origination / Release Date:*
Program Issue	*SOP No. L-A-704*	N/A	N/A
Requested by:	Tom Antony	Date:	06/25/2024

New SOP Revision Date:	**07/08/2024**	**New SOP Revision #:** *(If Applicable)*	**0**

For *Revision*: Summary of Revisions (*specify sections*)

Throughout	Removed the words "TOF" and "Time of flight"
Throughout	Changed 1.0 uL injection to 10.0 uL injection
2.0	Changed "TOF" to "LVI Quad"
6.3.3	Updated Mass ranged to 50 to 550 amu and scan rate to 2.9 scan per second
6.3.4	Updated autosampler to Agilent 7693
6.3.6	Changed "Chromatof" to "ChemStation"
6.3.7	Changed Gerstel to Agilent
6.3.9	Added Quadrupole
7.1.4	Changed nitrogen to Liquid N2 – industrial grade
7.3	Changed the word Ampouled to Ampuled
9.3	Changed to 200pg to 500pg
10.1.1.1	Updated the GC parameters to fit current acquisition method
10.1.2	Change Mass Spec parameters to match parameters on the quadrupole
11.2.1	Changed "Chromatof" to "ChemStation"
12.2.6	Changed equation numbering for eq. "5 through 11" to "4 through 9" to reflect the missing equations number 4 and 6; updated the references to these equations throughout the document
Table 1	Update tune criteria for a GCMS Quad

For *Review*: Comments

Standard Operating Procedure
Analysis of Opioids by GC-MS LVI Quad
L-A-704 Rev. 0

TABLE OF CONTENTS

TABLES, FIGURES, AND ATTACHMENTS

Standard Operating Procedure
Analysis of Opioids by GC-MS LVI Quad
L-A-704 Rev. 0

1.0 Scope and Application

This standard operating procedure (SOP) is a gas chromatography/mass spectrometry technique for analysis of fentanyl at the low part per billion (ug/L or ug/Kg) level in waters and soils and nanogram levels (ng/wipe) in environmental samples. This procedure follows the general guidelines of EPA method 8270E for full scan GC/MS analysis.

1.1 This protocol is for the determination and measurement of the opioids listed below. It is based on USEPA (i.e., SW-846) Methods 8270E, 3510C, 3511, 3545A, and 3570 for the analysis and preparation of solid, wipe, and water samples.

Contaminant	CAS Number
Fentanyl	437-38-7
Acetylfentanil	3258-84-2
Alfentanil	69049-06-5
Carfentanil	61086-44-0
Heroin	561-27-3
Remifentanil	132539-07-2
Sulfentanil	69049-06-5

1.2 Procedures in this protocol have been tested for the target analytes listed in Section 1.2 in reference matrices (i.e., reagent water, Ottawa sand, dried soils, and wipes) and have not all been evaluated in field samples.

2.0 Summary of Method

2.1 This procedure involves solvent extraction of the sample followed by gas chromatography/ mass spectrometry (GC/MS LVI QUAD) analysis to determine drug concentration in environmental samples.

2.2 Prior to analysis, samples must be prepared using sample preparation techniques appropriate for each analyte and matrix type. Aqueous, solid, and wipe samples may be extracted by microscale extraction based on the required detection limits. Extracts may require a concentration step using nitrogen evaporation to achieve appropriate levels of quantitation.

2.3 Development of the method follows the same protocol as is used in the SW846 Method 8270E.

3.0 Definitions

3.1 Batch‡: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A Preparation Batch is composed of between 1 and 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and the last sample in the batch to be 24hours. Each Preparation Batch requires; one MB, LCS, and MS/MSD pair. An Analytical Batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

3.2 Holding Time: The maximum amount of time permitted between sampling and sample preparation and/or sample preparation and sample analysis. Also the period of time a sample may be stored prior to analysis when there is no preparation step. See the specific method or SW846 8000D Table 4.1.

3.3 Internal Standards (IS)‡: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

3.4 Laboratory Control Sample (LCS)‡: (however named, such as laboratory fortified blank, blank spike (BS), or QC check sample). A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

The standard source can be the same as the calibration or a second source. The LCS is analyzed exactly like a sample to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.5 Matrix Spike (spiked sample of fortified sample)‡: A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of the sample for which an independent test results of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

3.6 Matrix Spike Duplicate (spiked sample or fortified sample duplicate)‡: A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

3.7 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. Method Blank analytical results are evaluated to determine the presence of contamination in the analytical method process.

3.8 Reporting Limit (RL): The reporting limit, also known as the LOQ is the minimum concentration that can be reported as a quantitated value for a target analyte in a sample. This value can be no lower than the concentration of the lowest calibration standard.

3.9 Surrogate Standard (SS): Organic compounds which are similar to the target analytes in chemical composition and mimic the behavior of the target analytes throughout the analytical process. Surrogate compounds are not normally found in environmental samples. Each calibration standard, sample, MB, LCS, MS, and MSD is spiked with surrogate standards. Surrogates are used to evaluate analytical efficiency by measuring recovery. See analytical method SOP for a list of specific surrogate compounds that are appropriate for sample-specific analysis.

ǂ EL-V1M2-ISO-2016, 2016 NELAP Standard definition.

4.0 Interferences

4.1 Matrix interferences can be caused by contaminants that are extracted from the sample during the extraction process. The amount of matrix interference varies from sample to sample. Cleanup procedures may help eliminate some of the interferences.

4.2 Contaminants in the solvents, reagents, glassware, and other extraction components may lead to matrix interferences. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running MBs with every batch. The data for all MB, LCS, MS, MSD, and samples must be evaluated for interferences. If interferences are detected, it is necessary to determine if the source of interference is in the preparation and then take corrective action to eliminate the interference. Using high purity reagents, solvents, and gases helps minimize interference problems.

4.3 Carryover contamination may occur when a sample containing low levels of analytes is injected immediately following a sample containing high levels of analytes or background. If this situation occurs during analysis, the sample containing the low concentration SVOCs may require reanalysis. A solvent blank should be run after the high level sample to ensure that the system is free of contamination. To reduce carryover, the injection syringe must be rinsed with solvent between samples.

4.4 Phthalate contamination is commonly observed, and its occurrence should be carefully evaluated as an indicator of the contamination problem in the sample preparation step of the analysis.

5.0 Safety

WARNING: The toxicity of the opioids analyzed by this method presents hazards unfamiliar to most experienced laboratory personnel. Special techniques and precautions must be used even for the simplest procedures involving these agents. If opioids are suspected target analytes, laboratory personnel must be thoroughly trained in appropriate safety procedures prior to using this method.

5.1 There are specific requirements for operations with opioids. Analysts must have read the PHILIS Chemical Hygiene Plan relating to opioids and receive all required training prior to conducting the analytical procedures described in this protocol.

5.2 At a minimum, personal protective equipment (PPE) requirements include safety glasses, lab coats, and protective gloves. All work with samples and standards shall be conducted in a fume hood. The availability of emergency response equipment and support personnel should be as indicated in a laboratory Chemical Hygiene Plan.

5.3 Exposure to drug material is possible from contact, and risk is primarily associated with compromise of protective clothing. Respiratory exposure can result from spills or improper use of ventilation controls and PPE.

5.4 Employees must abide by the policies and procedures in the Chemical Hygiene Plan and this document. This procedure involves hazardous material, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow the appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are hazardous. Standard laboratory safety procedures should be followed when working with unknown samples.

5.5 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded. Non-disposable gloves must be cleaned immediately. Latex and vinyl gloves provide no protection against the organic solvents used in this method, so nitrile or similar must be used.

5.6 The toxicity and/or carcinogenicity of the reagents and analytes used in this method have not been precisely defined; therefore, each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. This entire extraction procedure must be performed in a fume hood.

6.0 Equipment and Supplies

6.1 Glassware

6.1.1 Autosampler vials with Teflon lined crimp tops used for analysis and storage of sample extracts. The vials may be clear or amber.

6.1.2 Mini inserts with plastic springs may be used with autosampler vials to allow for smaller extract aliquots.

6.1.3 10-mL/40-mL/60-mL vials used for storage of standards and spiking solutions

6.2 Syringes

Gas-tight micro syringes- various sizes for transferring the concentrated extracts, adding internal standards to extracts, and aliquoting the calibration standards Instrumentation.

6.3 Equipment and Supplies

6.3.1 Gas chromatograph/Mass spectrometer –: an analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source, and the instrument must be operated in splitless injection mode.

6.3.2 Gas Chromatography Column – Recommended length 30 m x 0.25 mm ID (or 0.32 mm) bonded phase silicon coated fused silica capillary column DB-5 (J&W Scientific); RTX-5, RTX-5Sil MS (Restek); Zebron ZB-5(Phenomenex); SPB-5 (Supelco); AT-5 (Alltech); HP-5 (Agilent); CP-Sil 8 CB (Chrompack); 007-2 (Quadrex); BP-5 (SGE); or equivalent. Although a film thickness of 1.0 micron is recommended because of its larger capacity, a film thickness of 0.25 micron may be used. A capillary column is considered equivalent if:

6.3.2.1 The column does not introduce contaminants that interfere with the identification and quantification of the compounds listed in Table 3.

6.3.2.2 The analytical results generated using the column meet the initial and continuing calibration verification technical acceptance criteria listed in the protocol and the quantitation levels determined as described in Section 12.8.

6.3.2.3 The column provides equal or better resolution of the compounds listed in Table 3, when compared to columns listed in Section 6.3.2.

6.3.3 Mass Spectrometer – Must be capable of detecting masses from 50 – 550 atomic mass unit (amu) at 2.9 scans/ second, using 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum that meets the tuning acceptance criteria when 50 ng or less of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet. The instrument must be vented to the outside of the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.3.4 Autosampler: Agilent 7693.

6.3.5 GC/MS interface: Any GC/MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.3.6 Data System The data system is equipped with the ChemStation software for data acquisition, data processing and Gerstel's Maestro for the autosampler. Any equivalent system would work.

6.3.7 Syringe: 10-µL Agilent syringe, or equivalent.

6.3.8 Carrier gas: ultra-high purity, equivalent or better helium.

6.3.9 Quadrupole mass spectrometer

7.0 Reagents and Standards

7.1 Reagents

Original containers of reagents shall be labeled with expiration date when applicable. All containers of prepared reagents must bear a name, preparation date, and must be linked to the preparation records.

7.1.1 Organic-free Reagent Water – Defined as water in which an interferant is not observed at or above the RL for each analyte of interest. Reagent water may be generated by passing tap water through a filter bed containing activated carbon or may be purchased.

7.1.2 Reagent soil – TCL-free sand is used for QC samples.

7.1.3 Helium carrier gas- 99.999% (UHP) or better such as Research Grade, 99.9999%.

7.1.4 Liquid N2 – industrial grade

7.2 Solvents

7.2.1 Methylene Chloride–nano grade or equivalent.

7.2.2 Methanol—HPLC grade or equivalent.

7.3 Standards

The laboratory must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the laboratory and presented upon request. Standard solutions purchased from a chemical supply house as extracts in sealed, glass ampules may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the ampuled standard solutions, if unopened, may be retained and used for two years from the preparation date. The expiration date of the ampuled standards, upon the breaking of the glass seal, is six months (or sooner, if the standard has degraded or evaporated). Note: For many

of the target compounds, neat standards may be unavailable; therefore, the laboratory may need to purchase diluted standards.

7.3.1 Prepare standards for a calibration curve with a minimum of five points. Five points are valid for average response factor or linear regression curve fitting. Six calibration points are required for quadratic (second order) curve fits. The low point of the calibration curve must be at or below the reporting limit. The high standard defines the range of the calibration.

7.3.2 An internal standard (IS) solution is prepared by dissolving the compounds in MeOH or by purchasing a mixture from a commercial source. See Table 2 for a list of the internal standards used. The final concentration in the extract should be 500pg/µL.

7.3.3 Surrogate Standard Spiking Solution: Prepare as instructed in the extraction SOP (PHILIS SOP L-P-114) will result in a concentration of 500ng/mL. Other concentrations may be used provided the resulting amount in the samples and standards doesn't change. Surrogate compounds are listed in Table 2.

7.3.4 DFTPP GC/MS Tuning Standard: A solution in methylene chloride containing 50 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared.

7.3.5 Laboratory Control Spiking Solution: Prepared as instructed in the extraction SOPs. This solution must contain all target analytes.

7.3.6 Matrix Spike Solution: This is the same as the Laboratory Control Spiking Solution.

7.3.7 The standards must be stored away from any light source at 0 - 6 °C in Teflon lined screw cap amber bottles. The standard solutions expire six months after preparation date or at the earliest expiration date assigned by the vendor to any parent standard, whichever is earlier. Continuing calibration standards and other dilute standards should be checked weekly for degradation or when the standards fail to meet criteria, whichever is first.

7.3.8 Protect all standards from light. Samples, sample extracts, and standards must be stored separately.

7.3.9 The laboratory is responsible for maintaining the integrity of standard solutions and verifying the solution prior to use. The standards must be brought to room temperature prior to use, checked for losses, and checked to ensure that all components have remained in solution. Guidance on standard verification procedures can be found in EPA's Superfund Analytical Services / Contract Laboratory Program, Multi-Media, Multi-Concentration Organics Analysis, SOM01.2, Exhibit E, Section 7, May 2005. (http://www.epa.gov/superfund/programs/clp/download/som/som11e-h.pdf)

8.0 Sample Collection, Preservation, and Storage

8.1 Sample Preservation

Samples must be iced or refrigerated at 0 - 6°C from the time of collection until extraction.

8.2 Sample Storage

8.2.1 Samples must be protected from light and refrigerated at 0 - 6°C from the time of receipt until 60 days after delivery of results to the reference agency. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 Samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3 Sample Extract Storage

8.3.1 Sample extracts must be protected from light and stored at 0 - 6°C until one year after delivery of results to the reference agency.

8.3.2 Samples, sample extracts, and standards must be stored separately.

8.4 Technical Holding Times

8.4.1 Certain analytes will start to degrade immediately after sample collection; therefore, it is recommended that samples be extracted immediately upon receipt in the laboratory.

8.4.2 Extracts must be analyzed within 14 days following extraction.

9.0 Quality Control

9.1 Initial Demonstration of Capability (IDC)

An initial demonstration of capability (IDC) shall be performed prior to the analysis of any samples and with each significant change in instrument type (e.g., different detection technique), personnel or method. An IDC consists of the following:

9.1.1 An initial demonstration of precision and recovery (IPR) determination (Section 9.2).

9.1.2 A method detection limit (MDL) study (Section 9.7).

9.1.3 A quantitation limit (QL) determination (Section 12.8) on a clean matrix (reagent water, Ottawa sand, pre-cleaned wipes).

The IDC consists of four replicate samples of a clean matrix spiked with opioids around the midpoint of the calibration curve and carried through the entire analytical process. Prior to performing the IDC it is required that, a valid initial calibration (Section 10.3) be established.

9.2 Initial Precision and Recovery (IPR)

9.2.1 For preparation of IDC samples, see PHILIS SOP L-P-114.

9.2.2 Calculations for IDC.

Calculate the percent recovery of each compound in the IDC sample using Equations 4-6 (Section 12.2.6). Calculate an average percent recovery for each compound.

Calculate a percent relative standard deviation (%RSD) for each compound in the IPR samples.

9.2.3 Technical Acceptance Criteria for IDC

The average percent recovery of each compound in the IDC should be within the analyte acceptance limits in Table 4 and the surrogate acceptance limits in Table 5.

9.2.4 Corrective Action for IDC

If the technical acceptance criteria in Table 4 and Table 5 are not met, inspect the system for problems and take corrective actions to achieve the acceptance criteria.

9.3 Method Blanks

A method blank is a volume of a clean reference matrix (e.g., reagent water for water samples, clean inert sand along with purified sodium sulfate or Hydromatrix drying agent for solid samples, or clean wipes for wipe samples) spiked with a sufficient amount of surrogate standard spiking solution such that the same amount of surrogate is added as for the associated samples and carried through the entire analytical procedure. Internal standard solution is added just prior to analysis by GC/MS to give a concentration 500 pg/uL for each internal standard. The volume or weight of the reference matrix must be approximately equal to the volume or weight of the samples associated with the blank.

9.3.1 Frequency of Method Blanks

A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples [excluding MS/MSDs and Performance Evaluation (PE) samples]. In addition, a method blank shall:

9.3.1.1 Be extracted by the same procedure used to extract samples.

9.3.1.2 Be analyzed on each GC/MS system used to analyze associated samples and conditions (i.e., GC/MS settings).

9.3.1.3 Under no circumstances should method blanks be analyzed at a dilution.

9.3.2 Technical Acceptance Criteria for Method Blank Analysis

9.3.2.1 All blanks must be analyzed at the frequency described in Section 10.3.1 on a GC/MS system meeting the DFTPP tuning criteria in Section 13.2.4 and Table 1, initial calibration in Section 10.3, and continuing calibration verification (CCV) technical acceptance criteria in Section 10.4.5.

9.3.2.2 The Percent Recovery (%Recovery) of each of the surrogates in the blank must be within the acceptance limits listed in Table 5.

9.3.2.3 The blank must meet the sample acceptance criteria listed in Section 9.3.

9.3.2.4 A method blank for solid, water, and wipe samples must contain less than the RL of target compounds. Note: In cases where a blank has detects above the RL, but associated samples have detects greater than 10 times the blank, consult the agency to determine if re-extraction is required.

9.3.3 Corrective Action for Method Blanks

9.3.3.1 If a method blank does not meet the technical acceptance criteria for method blank analysis, the laboratory shall consider the analytical system to be out of control.

9.3.3.2 If contamination is the problem, then the source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. It is the laboratory's responsibility to ensure that interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in the GC/MS be eliminated. If possible, an aliquot of any sample associated with the contaminated blank must be re-extracted and reanalyzed or the data flagged.

9.3.3.3 If surrogate recoveries in the method blank do not meet the acceptance criteria listed in Table 5, first reanalyze the method blank. If the surrogate recoveries do not meet the acceptance criteria after reanalysis, the method blank and an aliquot of any sample associated with that method blank must be re-extracted, if possible, and reanalyzed or documented in the case narrative.

9.3.3.4 If the method blank does not meet internal standard response requirements listed in Section 9.3, follow the corrective action procedure outlined in Section 9.4. The laboratory shall resolve and document the resolution of the problem before proceeding with sample analysis.

9.3.3.5 If the method blank does not meet the retention time (RT) requirements for internal standards, check the instrument for malfunction and recalibrate. Reanalyze the method blank. Sample analyses cannot proceed until the method blank meets these requirements.

9.4 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

To evaluate the effects of the sample matrix on the methods used for analyses, a mixture of target compounds must be spiked into two aliquots of a water or solid sample and analyzed in accordance with the appropriate method. Mixtures should be spiked at levels at a concentration near the midpoint of the calibration range.

An MS/MSD pair shall be analyzed with each sample batch of each matrix type where possible.

As part of EPA's quality assurance/quality control (QA/QC) program, water rinseate samples and/or field blanks (field QC) or PE samples may accompany solid, water, air, and/or wipe samples that are delivered to the laboratory for analysis. The laboratory must not perform MS/MSD analysis on any of the field QC or PE samples.

If the reference agency designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample remaining to perform an MS/MSD, then the laboratory shall choose another sample on which to perform an MS/MSD analysis. At the time the selection is made, the laboratory shall notify the reference agency that insufficient sample was received and identify the reference agency sample selected for the MS/MSD analysis.

If there is insufficient sample remaining in any of the samples in a batch to perform the required MS/MSD, the laboratory will report this in the data narrative.

9.4.1 Dilution of MS/MSD

Before any MS/MSD analysis, analyze the original sample, then analyze the MS/MSD at the same concentration as the most concentrated extract for which the original sample results will be reported.

9.4.2 Calculations for MS/MSD

Calculate the percent recovery of each matrix spike compound in the MS/MSD sample (see EQ. 9 in Section 12.2.9).

Calculate the Relative Percent Difference (RPD) of the concentrations of each compound in the MS/MSD using EQ. 1.

Concentrations of the matrix spike compounds are calculated using the same equations as used for target compounds (Equation 4 for water samples and Equation 5 for solid samples in Section 12.2.6).

EQ. 1 Relative Percent Difference Calculation

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

Where:
C_1 = Measured concentration of the first sample aliquot
C_2 = Measured concentration of the second sample aliquot

9.4.3 Technical Acceptance Criteria for MS/MSD

All MS/MSDs must be analyzed on a GC/MS system meeting DFTPP, initial and continuing calibration verification technical acceptance criteria, and the method blank technical acceptance criteria.

The MS/MSD must be extracted and analyzed within the technical holding time (Section 8.4).

The retention time (RT) shift for each of the internal standards must be within ± 0.50 minutes (30 seconds) between the MS/MSD sample and the most recent CCV standard analysis.

The limits for matrix spike compound recovery and RPD are given in Tables 5 & 6.

9.4.4 Corrective Action for MS/MSD

If recovery or RPD limits are not met and the LCS, CCV and method blank are within acceptable limits, this may be an indication of matrix interferences.

If MS/MSD recovery limits cannot be met, flag the results of the associated sample.

9.5 Laboratory Control Sample (LCS)

An LCS consists of an aliquot of clean reference matrix, of the same weight or volume as the corresponding field samples, and spiked with the same compounds at the same concentrations used to spike the MS/MSD. When the results of the MS/MSD analysis indicate matrix interference may be present, the LCS results are used to verify that the interferences are due to the sample matrix and not from artifacts introduced in the laboratory.

9.5.1 Frequency of LCS Analyses

One LCS must be prepared, extracted, analyzed, and reported for every 20 field samples or fewer extracted in a batch of a similar matrix. The LCS must be extracted and analyzed concurrently with the samples, using the same extraction procedure, cleanup procedure (if required), and instrumentation.

9.5.2 Calculations for LCS

Calculate the recovery of each compound in the LCS using Equation 10 (Section 12.2.9).

9.5.3 Technical Acceptance Criteria for LCS Analysis

All laboratory control samples must be extracted and analyzed at the frequency described in Section 9.5.1 on a GC/MS system meeting the tuning, initial and continuing calibration verification, and the method blank technical acceptance criteria.

The limits for LCS compound recovery can be found in Table 4 and Table 5.

9.5.4 Corrective Action for LCS

If LCS recovery limits are not met, inspect the system for problems and take corrective actions to achieve the acceptance criteria including reanalysis.

If LCS recovery limits cannot be met, flag all associated sample and blank data accordingly.

9.6 Instrument Detection Limit (IDL) Determination

Before any field samples are analyzed, laboratories may determine an IDL for each target compound on each instrument used for analysis. While determining IDLs are not required, IDL results can be helpful in determining an appropriate spike level for use in determining the MDL (Section 9.7). It is recommended that IDLs be verified annually thereafter, or after major instrument maintenance. Major instrument maintenance includes, but is not limited to: cleaning or replacement of the mass spectrometer source, mass filters, electron multiplier, and installing a different GC column type. An IDL is instrument-specific and independent of sample matrices.

9.6.1 An IDL is determined for each compound as the concentration that produces an average signal-to-noise ratio of between 3:1 and 5:1 for at least three replicate injections.

9.6.2 All documentation for the IDL determination shall be maintained at the laboratory and provided to the reference agency or the data user upon request.

9.7 Method Detection Limit (MDL) Determination

Before any field samples are analyzed, laboratory MDLs must be determined for each target analyte in appropriate reference matrices (i.e., reagent water, Ottawa sand, or clean wipes), using the sample preparation and analytical procedures described in this protocol for each specific matrix, and following the instructions and requirements described at 40 CFR Part 136, Appendix B.

9.7.1 The laboratory must use full method procedures to prepare and analyze at least seven replicates.

9.7.2 Spike each replicate sample at concentrations of 1 – 5 times the IDL concentration for each analyte and analyze the samples following protocol procedures.

9.7.3 To determine analyte MDLs, the following equation is applied to the analytical results (Student's t-factor is dependent on the number of replicates used; 3.14 assumes seven replicates):

MDL = 3.14 x sd

Where:
sd = the standard deviation for the analytical results, and
3.14 = the Student's t-value for seven replicate samples

9.7.4 The MDL results calculated using the equation in Section 9.7.3 must meet the following requirements as well as all other requirements specified in 40 CFR Part 136, Appendix B:

9.7.5 MDL result must not be greater than the spiking level used for the MDL determination.

9.7.6 MDL results must not be less than one tenth the spiking level used for the MDL determination.

9.7.7 If either requirement is not met, the laboratory must adjust their spiking level appropriately and repeat the MDL determination.

9.7.8 See Table 7 for MDLs.

9.8 Reporting Limit (RL) Determination

Laboratory RLs can be determined by multiplying the standard deviation of the results used to determine the MDL by 10. This approach uses the variability of the results used to determine the MDL, to estimate the concentration that would yield a 10% relative standard deviation (RSD) under ideal conditions. The resulting RL should be evaluated against the criteria listed below. These criteria are provided as guidance. If any of the criteria are not met, the laboratory should consult project managers to determine if the RL is sufficient to address project needs:

9.8.1 Results from spikes at the RL should be above the MDL.

9.8.2 The RL should be at or above the lowest calibration level.

9.8.3 The RL should be at least two times the MDL.

9.8.4 The relative standard deviation of results from spikes at the RL should be less than 20%.

9.8.5 The mean recovery of spikes at the RL must be within 50 – 150%.

9.8.6 See Table 7 for RLs.

10.0 Calibration and Standardization

10.1 Instrument Operating Conditions

10.1.1 Gas Chromatograph (GC)

10.1.1.1 The following GC analytical conditions are provided for guidance (pulsed splitless injection) and may be modified if needed to optimize analytical results. Other conditions may be used, provided that all technical acceptance criteria in Sections 10.2.4, 10.3.4, 10.4.5, and 12.3 are met. Initial column temperature: 110°C for 1.5 minutes

Column temperature program: 40°C/minute for 2 min; 40C/min to 320C; hold for 4 min.

Injector prgm: Init. 25C for 0.08 min; 720C/min to 280C hold for 7 min.

Vent pressure: 0 psi until 0.34 min;

Vent flow: 100 ml/min

Purge flow to split vent: 100 ml/min at 2 min.

Injector liner: 4mm Single Gooseneck

Injection mode: Solvent vent

10.1.1.2 Sample injection volume: 10.0 µL

10.1.1.3 GC column: Agilent HP-5MS, (5%-phenyl)- methylpolysiloxane (see Section 6.4.2 for equivalent columns)

10.1.1.4 Column dimensions: 30 m x 0.25 mm x 0.25 µm

10.1.1.5 Carrier gas: Helium at 32 cm/second

Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, blanks, and MS/MSDs.

10.1.2 Mass Spectrometer (MS)

The following GCMS-analytical conditions are provided in this section to optimize analytical results. Other settings may be used provided they are equivalent or better. Examples of alternate conditions using MS are provided in Appendix A.

10.1.2.1 MS transfer line temperature: 280°C

10.1.2.2 Source temperature: 230°C or according to manufacturer's specifications

10.1.2.3 Electron energy: 70 eV (nominal)

10.1.2.4 Mass range: 50 to 550 m/z

10.1.2.5 Ionization mode: Electron Ionization (EI), positive

10.1.2.6 Scans per second: -~2.9

10.2 Library searching: NIST 05 Mass Spectral Database MS Mass Calibration (Tuning) and Ion Abundance

10.2.1 Summary of MS Instrument Performance Check

The MS system must be tuned to meet the manufacturer’s specifications, using a suitable calibration compound such as perfluoro-tri-n-butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration and resolution of the MS system are verified by the analysis of the instrument performance check solution (Section 10.3.4). Prior to the analysis of any samples, including MS/MSDs, blanks, or calibration standards, the laboratory must establish that the MS system meets the mass spectral ion abundance criteria for the instrument performance check solution (Table 1) containing DFTPP.

10.2.2 Frequency of GC/MS Instrument Performance Check – The instrument performance check solution must be analyzed prior to each initial calibration.

10.2.3 GC/MS Instrument Performance Check

The analysis of the instrument performance check solution may be performed as an injection of 50 ng or less of DFTPP into the MS or by adding a sufficient amount of DFTPP to the calibration standards to result in an on-column amount of 50 ng or less of DFTPP (Section 10.3.4) and analyzing the calibration standard.

10.2.4 Technical Acceptance Criteria for GC/MS Instrument Performance Check

The instrument performance check solution must be analyzed at the frequency described in Section 10.2.2.

Abundance criteria are listed in Table 1 for guidance. The mass spectrum of DFTPP must be acquired in the following manner: three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.

Note: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical GC/MS instrument run conditions.

10.2.5 Corrective Action for GC/MS Instrument Performance Check

If the GC/MS instrument performance check technical acceptance criteria are not met, re-tune the GC/MS system. It may be necessary to perform maintenance to achieve the technical acceptance criteria.

The instrument performance check technical acceptance criteria in Section 10.2.4 must be met before any standards, samples, including MS/MSDs, or required blanks are analyzed.

10.3 Initial Calibration

Prior to sample analysis, and after instrument performance check technical acceptance criteria have been met, each GC/MS system must be calibrated at a minimum of five concentrations (Section 10.2.2 and Table 6) to determine instrument sensitivity and the linearity of GC/MS response for the target and surrogate compounds. If the RSD criteria cannot be met, a linear or quadratic curve may be used. Each initial calibration standard contains all the target compounds, surrogates, and internal standards.

10.3.1 Frequency of Initial Calibration

Each GC/MS must be calibrated whenever the laboratory takes corrective action that may change or affect the initial calibration criteria, or if the CCV technical acceptance criteria are not met.

If time remains in the 12-hour period after meeting initial calibration acceptance criteria, samples may be analyzed. It is not necessary to analyze a continuing calibration standard within this period.

10.3.2 Procedure for Initial Calibration

Prepare at least five calibration standards containing all the detected target compounds and associated surrogates at the concentrations described in Table 6.

Add a sufficient amount of internal standard solution (Section 7.3.2) to aliquots of calibration standards to result in 500pg/µL of each internal standard. Standards specified in Section 7.3.1 should permit most of the target compounds to have relative retention times (RRTs) of approximately 0.60 to 1.70, using the assignments of internal standards to target compounds given in Table 2.

Analyze each calibration standard by injecting 10.0 µL of standard.

10.3.3 Calculations for Initial Calibration

Calculate the relative response factor (RRF) for each analyte and surrogate using Equation 2 and the primary characteristic ions found in Table 3. Assign target compounds and surrogates to internal standards according to Table 2. For internal standards, use the primary ion listed in Table 3 unless interferences are present. Note: Unless otherwise stated, the area response of the primary characteristic ion is the quantitation ion.

EQ. 2 Relative Response Factor Calculation

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where:
A_x = Area of the characteristic ion for the compound to be measured (Table 3)
A_{is} = Area of the characteristic ion for specific internal standard (Table 2)
C_{is} = Amount of the internal standard injected (ng)
C_x = Amount of the target compound or surrogate injected (ng)

The Mean Relative Response Factor ($\overline{RRF}$) for the Initial Calibration RRFs and mean RRFs must be calculated for all compounds. Calculate the percent relative standard deviation (%RSD) of the RRF values for the initial calibration. If linear regression or quadratic curve fitting is needed, consult SW-846 Method 8000D for guidance on the appropriate calculations.

10.3.4 Technical Acceptance Criteria for Initial Calibration

An initial calibration should be performed at the frequency described in Section 10.3.1 on a GC/MS system meeting the instrument performance check technical acceptance criteria (Section 10.2.4).

The RRF for each target compound and surrogate should be greater than or equal to 0.01.

10.3.5 The %RSD of the RRFs over the initial calibration range for each target compound and surrogate should be less than or equal to 20.00. If %RSD for a target analyte or surrogate cannot meet the acceptance criteria, curve fitting by linear or quadratic regression may be used provided the R^2 value is greater than or equal to 0.99.

10.3.6 Corrective Action for Initial Calibration

If technical acceptance criteria using at least one of the three optional approaches to initial calibration (%RSD of the RRFs, linear regression, or quadratic regression) are not met, inspect the system for problems, take corrective actions, and re-calibrate the system. If criteria are not met with re-calibration, the laboratory will flag all data associated with the calibration.

Initial calibration technical acceptance criteria must be met before any samples, including MS/MSDs or required blanks are analyzed and reported without data qualification.

10.4 Continuing Calibration Verification

10.4.1 Summary of Continuing Calibration Verification

Prior to the analysis of samples, each GC/MS system must be routinely checked by analyzing a CCV standard or calibration with tune to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements. The CCV standard contains all the target compounds, surrogates, and internal standards. The same injection volume must be used for all standards, samples, and blanks.

10.4.2 Frequency of Continuing Calibration Verification – Each GC/MS used for analysis must be checked once every 12-hour time period of operation. The 12-hour time period begins with the injection of DFTPP prior to calibration analysis or the injection of the opening CCV on other sequences without a calibration.

10.4.3 Procedure for Continuing Calibration Verification

Add a sufficient amount of internal standard solution (Section 7.3.4.) to an aliquot of CCV standard to result in a concentration of 500pg/µL

Analyze the CCV standard by injecting 10.0 µL of standard.

10.4.4 Calculations for CCV

Calculate an RRF for each target compound and surrogate using Equation 2 and the primary characteristic ions found in Table 3.

Calculate the Percent Difference (%Difference) between the $\overline{RRF}$ from the most recent initial calibration and the continuing calibration verification RRF for each target compound and surrogate using Equation 3.

EQ. 3 Relative Response Factor Percent Difference Calculation

$$\%\text{Difference}_{RRF} = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

Where:
RRF_i = Mean Relative Response Factor from the most recent initial calibration meeting technical acceptance criteria.
RRF_c = Relative Response Factor from CCV standard.

10.4.5 Technical Acceptance Criteria for CCV

The CCV standard must be analyzed at or near the mid-point concentration level, at the frequency described in Section 13.4.2, on a GC/MS system meeting the instrument performance check and the initial calibration technical acceptance criteria.

The RRF for each target compound and surrogate should be ≥ 0.01.

The RRF percent difference for each target compound in all CCVs should be within the range of ±50 %. (Note: This range may be updated following additional laboratory testing of the method.) If regression techniques are used for the initial calibration, the CCV must be evaluated in terms of percent drift using concentrations (See Equation 3a).

EQ. 3a Percent Drift (PD) Calculation for CCV

$$PD = \frac{\text{CalculatedConcentration} - \text{Theoretical Concentration}}{\text{Theoretical Concentration}} \text{x} 100\%$$

The percent drift (PD) for each target compound should be within the range of ±50.

Excluding those ions in the solvent front, no quantitation ion may saturate the detector.

10.4.6 Corrective Action for CCV

If the CCV technical acceptance criteria in Section 10.4.5 are not met, recalibrate the GC/MS instrument according to Section 10.3.

CCV technical acceptance criteria should be met before any samples MS/MSDs, or required blanks, are analyzed. If CCV criteria are not met, flag associated samples and blanks accordingly.

10.5 Instrument Blank

10.5.1 Summary of Instrument Blank

An instrument blank is comprised of DCM spiked with internal standards at the same concentration used for associated samples. The purpose of the instrument blank is to minimize the impact of carryover.

10.5.2 Frequency of Instrument Blank

An instrument blank is recommended for analysis following suspected carry-over or during analysis of samples containing suspected high concentrations.

10.5.3 Procedure for Instrument Blank Analysis

Add sufficient amount of internal standard solution (Section 7.3.4) to an aliquot of clean solvent to result in a concentration of 500pg/µL. Analyze each instrument blank by injecting 10.0 µL of standard.

10.5.4 Calculations for Instrument Blank

Calculate the concentrations of any observed target analyte using Equation 4, setting V_t, V_o, and DF all equal to 1.

10.5.5 Technical Acceptance Criteria for Instrument Blank

If an instrument blank is analyzed, the concentration of all target analytes in the instrument blank should be less than the concentration of the target analytes in the low calibration standard. The area response of the internal standards should be within 50 – 150% of the associated CCV or mid-level concentration of the initial calibration.

10.5.6 Corrective Action for Instrument Blank

If an instrument blank is analyzed and the instrument blank technical acceptance criteria are not met, analyze an additional instrument blank. If the problem persists, inspect the system for problems and take corrective actions to achieve the acceptance criteria. Instrument blank technical acceptance criteria should be met before samples are analyzed. Samples that are analyzed with corresponding instrument blanks that do not meet the instrument blank criteria should be reanalyzed, or the corresponding data should be flagged.

11.0 Procedure

11.1 Sample Analysis

11.1.1 Analysis is performed using an automated injection GC/MS instrument.

11.1.2 In ChemStation or equivalent instrument software, load the sequence from the previous run and enter in the sequence information for the day. A typical sequence will have one or two rinses, the CCV, an instrument blank, the QC from the batch, then extracts of the samples.

11.1.3 Calibrate the instrument as described in Section 10.3.2. All instrument tuning and calibration criteria must be met prior to the analysis of samples.

11.1.4 All samples must be analyzed using the same instrument conditions as the preceding ICAL, and CCV standards.

11.1.5 Add internal standard to the sample extract to result in a 500pg/µL concentration of internal standard. Mix thoroughly before injection into the instrument.

11.1.6 If samples are to be diluted, add the internal standard after the dilution is made.

11.1.7 Inject the sample aliquot into the GC/MS using the sample injection technique as used for the standards. Injection amount is 10 µL.

11.1.8 The data system will determine the concentration of each analyte in the extract using calculations based on the initial calibration, not the continuing calibration verification.

11.1.9 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst. The minimum documentation required is a hard copy of the original data peak integration and a copy showing the manual integration with the analyst initials and date and explanation of why the manual integration was performed.

11.1.10 The internal standard response in the sample must be within 50- 200% of the response in the CCV or midpoint of the calibration curve.

11.2 Dilutions

11.2.1 If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for an analysis at a lesser dilution, the sample must be re-analyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.2.2 Add the internal standard to the diluted extract for a resulting concentration of 500pg/µL of each internal standard, and analyze the diluted extract.

11.2.3 Reporting Dilutions

The most concentrated dilution with no target analytes above the calibration range will be reported. Other dilutions will be reported only at the client's request.

12.0 Data Analysis and Calculations

12.1 Qualitative Identification of Target Compounds

12.1.1 The compounds listed in Table 3 must be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of the standard of the suspected compound. Two criteria must be satisfied to verify the identifications:

12.1.1.1 Elution of the sample analyte within the GC RRT unit window established from the 12-hour calibration standard.

12.1.1.2 Correspondence of the sample analyte and calibration standard component mass spectra.

12.1.2 For establishing correspondence of the GC RRT, the sample component must compare within ±0.06 RRT units of the standard component. For samples analyzed during the same 12 hour time period as the initial calibration standards, compare the analyte RTs to

those from the midpoint initial calibration standard. Otherwise, use the corresponding CCV standard. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using EICPs for ions unique to the component of interest.

12.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained from a calibration standard on a GC/MS meeting the daily instrument performance requirements for DFTPP are required. Once obtained, these standard spectra may be used for identification purposes only if the GC/MS meets the DFTPP instrument performance requirements.

12.1.4 All ions present in the standard mass spectrum at a relative intensity greater than 10% (the most abundant ion in the spectrum equaling 100%) must be present in the sample spectrum. The relative intensities of ions specified in Table 3 must agree within ± 20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 – 70%). Ions greater than 10% in the sample spectrum, but not present in the standard spectrum, must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. When target compounds are below LOQs, but the spectrum meets the identification criteria, report the concentration with a "J". For example, if the LOQ is 5.0 g/L and concentration of 3.0 g/L is calculated, report as "3.0 J". Reporting below the LOQ is performed at client request.

12.1.5 If a compound cannot be verified by all of the spectral identification criteria in Sections 12.1.1 – 12.1.4, but in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the laboratory must report the identification and proceed with quantitation.

12.2 Data Analysis and Calculations of Target Compounds

12.2.1 Target compounds identified shall be quantitated by the internal standard method. The internal standard used shall be the one assigned to that analyte for quantitation (Table 2). The EICP area of primary characteristic ions of analytes listed in Table 3 are used for quantitation.

12.2.2 It is expected that situations will arise when the automated quantitation procedures in the GC/MS software provide an inappropriate result. This normally occurs when there is compound coelution, baseline noise, or matrix interferences. In these circumstances, the laboratory must perform a manual quantitation. Manual integrations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific target compound. The area integrated must not include baseline background noise. The area integrated must not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is

not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system.

12.2.3 In all instances where the data system report has been edited or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report and shall include the integration scan range. The GC/MS operator must also mark each integrated area on the quantitation report. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data.

12.2.4 The requirements listed in Sections 12.2.1 – 12.2.3 apply to all standards, samples, and blanks.

12.2.5 The $\overline{RRF}$ from the initial calibration is used to calculate the concentration in the sample. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. If linear regression is used, a regression curve must be used to calculate the concentration in samples. Refer to Section 12.2.7 for calculating sample concentration using linear regression techniques.

12.2.6 Calculate the concentration in the sample using the $\overline{RRF}$ and Equations 4-6.

EQ. 4 Concentration of Water Sample

$$\text{Concentration (ug/L)} = \frac{(A_x)(I_s)(V_t)(DF)}{(A_{is})(\overline{RRF})(V_o)(V_i)}$$

Where:
A_x = Area of the characteristic ion for the target compound
A_{is} = Area of the characteristic ion for the internal standard
I_s = Amount of internal standard injected in ng
V_o = Volume of water extracted in mL
V_i = Volume of extract injected in µL
V_t = Volume of the extract in µL
(Note: Extraction of water samples does not include concentration, and V_t is equal to the sum of the volumes added for extraction and addition of surrogates, internal standards, and any spiked target compounds.)
$\overline{RRF}$ = Mean Relative Response Factor determined from the initial calibration standard
DF = Dilution Factor. If no dilution is performed, DF = 1.0. The DF for analysis of water samples is defined as:

$$DF = \frac{\text{µL most conc. extract used to make dilution + µL clean solvent}}{\text{µL most conc. extract used to make dilution}}$$

EQ. 5 Concentration of Solid Sample

Note: Equation 5 includes a %moisture (D) factor for those cases when data is to be reported on the basis of dry sample weight. In cases where results are reported in terms of sample weight, this factor is deleted from the equation.]

$$\text{Concentration } \mu g/Kg \text{ (Dry weight basis)} = \frac{(A_x)(I_s)(V_t)(DF)}{(A_{is})(V_i)(\overline{RRF})(W_s)(D)}$$

Where:
A_x, I_s, A_{is}, V_i are as given for water, above.
V_t = Volume of concentrated extract in µL

$$D = \frac{100 - \%\text{Moisture}}{100}$$

W_s = Weight of sample extracted in g
$\overline{RRF}$ = Mean Relative Response Factor determined from the initial calibration standard
DF = Dilution Factor

EQ. 6 Concentration of Wipe Sample

$$\text{Concentration } \mu g/\text{std } cm^2 = \frac{(A_x)(I_s)(V_t)(DF)}{(A_{is})(V_o)(V_i)(\overline{RRF})}$$

Where:
A_x = area response for the compound to be measured, counts
A_{is} = area response for the internal standard, counts
I_s = amount of internal standard, µg
$\overline{RRF}$ = the mean RRF from the most recent initial calibration, dimensionless
Area = area of surface wiped, cm^2
V_t = volume of concentrated extract, µL
V_i = volume of extract injected, µL
DF = dilution factor for the extract. If there was no dilution, DF equals 1. If the sample was diluted, DF is greater than 1.

12.2.7 Calculate the concentration in the sample using linear regression.

Set y = (Peak Area of Target/Peak Area of Internal Standard) and x = (Theoretical Concentration of Target/Theoretical Concentration of Internal Standard).

Plot (Peak Area of Target/Peak Area of Internal Standard [Y-axis]) vs. (Theoretical Concentration of Target/Theoretical Concentration of Internal Standard).

Determine the slope of the line (m) and the y-intercept (b).

Rearrange the line equation to solve for x: x = (y-b)/m.

Multiply x by the concentration of the internal standard to get the concentration of target in extract.

Multiply the concentration of target analyte in the extract by the extract volume and divide by the sample volume to get concentration of target analyte in sample.

12.2.8 Adjusted LOQ Calculations

EQ. 7 Aqueous Adjusted LOQ

$$\text{Adjusted LOQ} = \text{Method LOQ} \times \frac{(V_x)(V_t)(DF)}{(V_o)(V_c)}$$

Where:
V_t, DF, and V_o are as given in Equation 4.
V_x = Method sample volume
V_c = Method concentrated extract volume

EQ. 8 Solid Adjusted LOQ

$$\text{Adjusted LOQ} = \text{Method LOQ} \times \frac{(W_x)(V_t)(DF)}{(W_s)(V_c)(D)}$$

Where:
V_t and DF are as given in Equation 4.
W_s and D are as given in Equation 5.
W_x = Method sample weight
V_c = Method concentrated extract volume

12.2.9 Surrogate Recoveries

Calculate surrogate recoveries for all samples, blanks, and MS/MSDs. Determine if recovery is within limits (Table 4).

Calculate the concentrations of the surrogates using the same equations as used for the target compounds. Calculate the recovery of each surrogate using EQ.9.

EQ. 9 Percent Recovery

$$\text{Recovery} = \%R = \frac{C_s}{C_n} \times 100$$

Where:
C_s = Measured concentration of the spiked sample aliquot.
C_n = Nominal (theoretical) concentration increase that results from spiking the sample, or the nominal concentration of the spiked aliquot (for LCS).

12.3 Technical Acceptance Criteria for Sample Analysis

12.3.1 The samples must be analyzed on a GC/MS system meeting the instrument performance check, initial calibration, CCV, and blank technical acceptance criteria.

12.3.2 The sample must be extracted and analyzed within the technical holding times.

12.3.3 The sample must have an associated method blank meeting the blank technical acceptance criterion.

12.3.4 The percent recoveries of the surrogates in a sample should be within the recovery limits listed in Table 4. These limits are based on a workgroup consensus and will be updated following method validation. Note: The surrogate recovery requirements do not apply to samples that have been diluted.

12.3.5 The instrumental response (EICP area) for each of the internal standards in the sample must be within the range of 50.0 – 200% of the response of the internal standard in the most recent CCV standard analysis.

12.3.6 The RT shift for each internal standard must be within ± 0.50 minute (30 seconds) between the sample and the most recent CCV standard analysis.

12.3.7 Excluding those ions in the solvent front, no ion may saturate the detector. If a target compound concentration exceeds the upper limit of the initial calibration range, a more dilute aliquot of the sample extract must also be analyzed.

12.4 Corrective Action for Sample Analysis

12.4.1 The sample technical acceptance criteria must be met before data are reported. If the corrective actions described in this section did not solve the problem, all associated sample and blank data must be flagged accordingly.

12.4.2 Corrective action for failure to meet instrument performance checks and initial and continuing calibration verification must be completed before the analysis of samples. If the corrective actions described in Sections 10.2.5 (instrument performance check), 10.3.5 (initial calibration), or 10.4.6 (CCV) did not solve the problem, all associated sample and blank data must be flagged accordingly.

12.4.3 Corrective action for surrogate recoveries in a sample fail to meet the acceptance criteria specified in Section 12.3.4, check calculations, sample preparation logs, surrogate standard spiking solutions, and the instrument operation.

12.4.3.1 If the calculations were incorrect, correct them and verify that the surrogate recoveries meet their acceptance criteria.

12.4.3.2 If the sample preparation logs indicate that the incorrect amount of surrogate standard spiking solution was added to the sample, then re-extract (if possible) and reanalyze the sample after adding the correct amount of surrogate standard spiking solution.

12.4.3.3 If the surrogate standard spiking solution was improperly prepared, concentrated, or degraded, re-prepare the solution, re-extract (if possible), and reanalyze the samples.

12.4.3.4 If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. Verify that the surrogate recoveries meet their acceptance criteria.

12.4.3.5 If the instrument malfunction affected the calibrations, recalibrate the instrument before reanalyzing the sample extract.

12.4.3.6 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

12.4.3.7 Re-extract (if possible) and reanalyze the sample. EXCEPTION: If surrogate recoveries in a sample used for a matrix spike/matrix spike duplicate (MS/MSD) were considered unacceptable, then it should be re-extracted/reanalyzed only if surrogate recoveries met the acceptance criteria in both the MS/MSD analyses.

12.4.3.8 If the surrogate recoveries meet acceptance criteria in the re-extracted/reanalyzed sample, then the problem was within the laboratory's control.

12.4.3.9 Submit data from both analyses. Distinguish between the initial analysis and the extraction/reanalysis on all deliverables.

12.4.4 Corrective action for internal standards in a sample that fail to meet their acceptance criteria, check calculations, internal standard solutions, and instrument operation.

12.4.4.1 If the calculations were incorrect, correct them, and verify that the internal standard responses meet their acceptance criteria.

12.4.4.2 If the internal standard solution was improperly prepared, concentrated, or degraded, re-prepare solutions and reanalyze another aliquot of the sample extract (if possible) after adding the correct amount of the freshly prepared internal standard solution.

12.4.4.3 If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract.

12.4.4.4 If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

12.4.4.5 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

12.4.4.6 Reanalyze the sample extract.

EXCEPTION: If internal standard responses in a sample used for an MS and/or MSD were outside the acceptance windows, then the sample should be reanalyzed only if internal standard compound recoveries met the internal standard acceptance criteria in both the MS/MSD analysis.

12.4.4.7 If the internal standard responses meet acceptance criteria in the reanalyzed sample extract, then the problem was within the laboratory's control.

12.4.4.8 Submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables.

12.5 Data Assessment and Acceptance Criteria for Quality Control Measures

12.5.1 Analytical data generated by the instrument software are reviewed and evaluated by the analyst as follows:

12.5.2 DFTPP, instrument calibration, calibration verifications, IS/SS, QC measures are evaluated and the results documented on the separate forms:

12.5.2.1 For each 12-hour sequence, a tune evaluation report of DFTPP is generated. A tune is only required if a calibration is performed in that sequence.

12.5.2.2 For each ICAL, an instrument calibration report showing relative and average response factors and percent relative standard deviations is generated.

12.5.2.3 For each CCV, a report showing response factors and percent deviations compared to the associated ICAL is generated.

12.5.2.4 Generate a QA-QC check report for internal standard area counts and percent recoveries for the surrogates.

12.5.2.5 Calculate analyte percent recoveries CCV, LCS, ICV, MS, and RPD for MSD.

12.5.3 All false positives are Q-Deleted, and all positively identified target analytes are reported to LIMS. Include the spectra in the data package for positive results.

12.5.4 Manual integration is applied in cases when the instrument data processing software produces integrated areas that are not valid. The manual adjustments to the chromatographic peak must be performed in a consistent manner for the calibration standards, QC and field samples.

12.5.5 Anytime the analyst alters the instrument generated quantitation report, the hard copies of both reports (original and corrected) must be retained (e.g., manual integration). This may also be documented on pdfs and attached to the final report.

12.5.6 Discrepancies in the analytical run are described in the “QC Summary form” and discussed with the Lead Chemist.

12.5.7 Reviewed data is entered into LIMS, hard copies of LIMS reports are printed and compared to the original data.

12.5.8 All records derived from the analytical process are assembled in the analytical data packages that consist of:

12.5.8.1 LIMS work-order list.

12.5.8.2 Analytical run sheet.

12.5.8.3 "QC Summary Form" signed by the Lead Chemist.

12.5.8.4 DFTPP tune evaluation report.

12.5.8.5 QA-QC check report.

12.5.8.6 Quantitation Report for each Sample and QCS.

12.5.8.7 Evaluation reports for CCV, ICV, LCS, MS, and MSD.

12.5.8.8 Initial calibration form.

12.5.8.9 LIMS report of each sample.

12.5.9 Data packages are placed in files and stored in the PHILIS document storage area.

12.6 Corrective Actions for Out of Control

See the QAPP for the data affected and follow the instructions.

12.7 Contingencies for Handling Out of Control or Unacceptable Data

In cases where quality control measures do not meet acceptance criteria, the quality of the analytical data is not acceptable and the analyst does the following:

12.7.1 When tuning and/or instrument calibration fail to meet acceptance criteria, the analysis does not start. The problem is investigated and the necessary instrument maintenance is performed, followed with reanalysis of DFTPP and/or calibration.

12.7.2 If after analysis, any of the criteria for quality control are not met, or the sample is not available for reanalysis, the analyst must notify the Lead Chemist. The Lead Chemist will implement the corrective action plan.

12.7.3 The analyst shall report to the Lead Chemist and indicate any out control event listed on the "QC Summary form". Such events include:

12.7.3.1 Damage to the sample.

12.7.3.2 Holding time exceeded.

12.7.3.3 Inadequate sample preservation.

12.7.3.4 Sample results exceeds agencies Action Limit

12.7.3.5 Samples do not reflect historical data.

12.7.3.6 Upward trending or sample results approaching internal warning limits.

12.7.3.7 Any non-target analyte peak present on the instrument generated chromatogram.

12.7.3.8 The Lead Chemist will implement the corrective action plan described in the PHILIS corrective action plan document.

13.0 Method Performance

13.1 Laboratory accuracy and precision will be those listed in the single and multiple lab studies from the CWA protocol in the 2013 draft.

13.2 Other specific Quality Assurance Objectives (QAO) may be found in the appropriate statement-of-work or Quality Assurance Project Plan (QAPP) for specific projects.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477.

15.0 Waste Management

15.1 The waste produced from this procedure consists of waste collected from the extraction equipment, excess sample, Standards, Methylene Chloride, Acetone, and Methanol.

15.2 Excess reagents are disposed following the SDS instructions.

15.3 Glass pipettes are disposed in the lab scraps waste.

15.4 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

15.5 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.6 The Environmental Protection Agency requires that laboratory waste management practices conducted are consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society.

16.0 References

16.1 U.S. Environmental Protection Agency. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). SW-846 Method 8270E. Revision 6. June, 2018.

16.2 U.S. Environmental Protection Agency. Organic Compounds in Water by Micro extraction. SW-846 Method 3511. Revision 0. November 2002.

16.3 U.S. Environmental Protection Agency. Microscale Solvent Extraction. SW-846 Method 3570. Revision 0. November 2002.

16.4 US Environmental Protection Agency. Cleanup. SW-846 Method 3600C. Revision 3. December 1996.

16.5 U.S. Environmental Protection Agency. Silica Gel Cleanup. SW-846 Method 3630C. Revision 3. December 1996.

16.6 U.S. Environmental Protection Agency. Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS). Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Compendium Method TO-13A. January 1999.

16.7 U.S. Environmental Protection Agency, *Standard Analytical Methods for Environmental Restoration Following Homeland Security Events* (SAM) document and information are posted at: http://www.epa.gov/sam/

17.0 Tables, Figures, and Attachments

Table 1. Decafluorotriphenylphosphine (DFTPP) Key Ions and Ion Abundance Recommendations

These recommendations are from "Draft Analytical Protocol for Chemical Warfare Agents using GCMS"

Mass	Ion Abundance Criteria
	Time of Flight (TOF)
68	Less than 2.0% of mass 69
69	0 – 200% of mass 198
70	Less than 2.0% of mass 69
197	Less than 2.0% of mass 198
198	Present
199	5.0 – 9.0% of mass 198
365	1.0 – 100% of mass 198
441	Less than 150% of mass 443
442	0 – 200% of mass 198
443	15.0 –24% of mass 442

Note: All ion abundances MUST be normalized to m/z 198.

Table 2. Internal Standards and Surrogates

CWA	Surrogate Compounds	Internal Standards
Fentanyl	Fentanyl-d_5	Chrysene-d_{12}
Acetylfentanil	Fentanyl-d_5	Chrysene-d_{12}
Alfentanil	Fentanyl-d_5	Chrysene-d_{12}
Carfentanil	Fentanyl-d_5	Carfentanil-d5
Heroin	Fentanyl-d_5	Chrysene-d_{12}
Remifentanil	Fentanyl-d_5	Chrysene-d_{12}
Sulfentanil	Fentanyl-d_5	Chrysene-d_{12}

Table 3. Example Retention Times, Relative Retention Times and Characteristic Ions for Target Compounds, Surrogate Compounds, and Internal Standards

Contaminant	Retention Time (sec)	Relative Retention Time	Full Scan	
			Primary Quantitation Ion	Secondary Quantitation Ions
Fentanyl	589.464	49.14	245	189,57,105
Acetylfentanil	453.9	32.557	231	
Alfentanil	496.1	74.782	289	
Carfentanil	482.2	60.855	303	
Heroin	448.0	26.668	369	
Remifentanil	443.1	11.7778	168	
Sulfentanil	472.5	51.114	289	
Carfentanil-d5	481.6	60.255	308	
Fentanyl-d5 (S)	588.882	48.56	151	194,250
Chrysene-d_{12} (IS)	540.319		240	236, 120

Notes:
(S) = Surrogate
(IS) = Internal Standard

Table 4. Example Precision (RPD) and Recovery (%Rec) Limits

Contaminant	%Rec	RPD
Water		
Fentanyl	+/-50%	≤20
Acetylfentanil	+/-50%	≤20
Alfentanil	+/-50%	≤20
Carfentanil	+/-50%	≤20
Heroin	+/-50%	≤20
Remifentanil	+/-50%	≤20
Sulfentanil	+/-50%	≤20
Soil		
Fentanyl	+/-50%	≤20
Acetylfentanil	+/-50%	≤20
Alfentanil	+/-50%	≤20
Carfentanil	+/-50%	≤20
Heroin	+/-50%	≤20
Remifentanil	+/-50%	≤20
Sulfentanil	+/-50%	≤20
Wipes		
Fentanyl	+/-50%	≤20
Acetylfentanil	+/-50%	≤20
Alfentanil	+/-50%	≤20
Carfentanil	+/-50%	≤20
Heroin	+/-50%	≤20
Remifentanil	+/-50%	≤20
Sulfentanil	+/-50%	≤20

Table 5. Example Surrogate Recoveries

Surrogate	%Rec
Water	
Fentanyl-d_5	+/-50%
Soil	
Fentanyl-d_5	+/-50%
Wipes	
Fentanyl-d_5	+/-50%

Table 6. Example Calibration Standard Concentrations (pg on column) used during Laboratory Method Development

GC/MS – Selective Ion Monitoring								
Analyte	**CAS RN**	**Cal 1**	**Cal 2**	**Cal 3**	**Cal 4**	**Cal 5**	**Cal 6**	**Cal 7**
Fentanyl	437-38-7	20	50	100	5000	1000	2500	5000
Acetylfentanil	3258-84-2	20	50	100	5000	1000	2500	5000
Alfentanil	69049-06-5	20	50	100	500	1000	2500	5000
Carfentanil	59708-52-0	20	50	100	500	1000	2500	5000
Heroin	561-27-3	20	50	100	500	1000	2500	5000
Remifentanil	132539-07-2	20	50	100	500	1000	2500	5000
Sulfentanil	60561-17-3	20	50	100	500	1000	2500	5000
Carfentanil-d5	1185158-60-4	20	50	100	500	1000	2500	5000
Fentanyl-d_5	118357-29-2	20	50	100	500	1000	2500	5000
Chrysens-d_{12}	1719-03-5	20	50	100	500	1000	2500	5000

Notes:
* These surrogates or internal standards are not required for the compounds being addressed by this protocol, but may be used if they are already included in solutions that will be used by the laboratory.
** Programmable injector/ solvent vent only. Data not available for pulsed splitless injection.

Table 7. Example Analyte Method Detection Limits (MDLs) and Reporting Limits (RL)

Method List		**MDL**	**RL**	**MDL**	**RL**	**MDL**	**RL**
Compound	**CAS No.**	**100 mL Water Sep Funnels ug/L**	**Water ug/L**	**Soil ug/Kg**	**Soil ug/Kg**	**Wipes ug/Wipe**	**Wipes ug/Wipe**
Fentanyl	437-38-7	0.277	1.0	0.73	2.0	0.0118	0.030
Acetylfentanil	3258-84-2	0.36	1.0	0.6	2.0	0.0106	0.030
Alfentanil	69049-06-5	0.35	1.0	0.567	2.0	0.0109	0.030
Carfentanil	59708-52-0	0.289	1.0	0.55	2.0	0.011	0.030
Heroin	561-27-3	0.802	2.0	0.726	2.0	0.0153	0.050
Remifentanil	132539-07-2	0.333	1.0	0.657	2.0	0.0125	0.030
Sulfentanil	60561-17-3	0.327	1.0	0.64	2.0	0.0103	0.030

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APPENDIX J -
PHILIS SOP L-P-200
Pressurized Solvent Extraction (PSE) Rev. 1 06/27/2024

STANDARD OPERATING PROCEDURE

FOR

PRESSURIZED SOLVENT EXTRACTIONS (PSE)

PHILIS SOP L-P-200 Rev. 1

Revision Date: 06-27-2024

EPA Contract No. 68HERH21D0002

PREPARED BY

PHILIS

PREPARED FOR

U.S. Environmental Protection Agency
Office of Emergency Management
Washington, DC 20460

Approvals:

	June 27, 2024
PHILIS, Castle Rock Lead Chemist	**Date**
	June 27, 2024
PHILIS, Edison Lead Chemist	**Date**
	June 27, 2024
PHILIS, Quality Assurance Manager	**Date**
Julia Capri	**June 27, 2024**
PHILIS, Program Manager	**Date**

Revision History

Revision	Name	Date	Description of Change
A	James Travis	04/01/2021	Transitional Issue
0	James Travis Crystal Chu	06/09/2022	Program Issue
1	Thomas Antony	06/26/2024	Annual Review

SOP REVISION FORM

SOP Name:	**Pressurized Solvent Extractions (PSE)**		
Purpose: *(Review or Revise)*	*SOP #:*	*Rev. #:* *(Being Reviewed or Revised)*	*Origination / Release Date:*
Annual Review	*SOP No. L-P-200*	0	11/29/2022
Requested by:	Thomas Antony	Date:	06/26/2024

New SOP Revision Date:	**06/27/2024**	**New SOP Revision #:** *(If Applicable)*	**1**

For *Revision*: Summary of Revisions (specify sections)

9.1	Changed “exactly the same” to “the same”

For *Review*: Comments

Standard Operating Procedure
Pressurized Solvent Extractions (PSE)
L-P-200 Rev. 1

TABLE OF CONTENTS

Standard Operating Procedure
Pressurized Solvent Extractions (PSE)
L-P-200 Rev. 1

1.0 Scope and Application

1.1 This standard operating procedure (SOP) documents the PHILIS Program application of EPA Method SW846 3545A – Pressurized Fluid Extraction (PSE) that will be used in the PHILIS Mobile Labs.

1.2 This SOP is executed in accordance with the U.S. Environmental Protection Agency and National Environmental Laboratory Accreditation Program (NELAP).

1.3 This method is a procedure for extracting insoluble or slightly water soluble organic compounds from soils, clays, sediments, sludges, and solids. This method uses elevated temperature (100-180°C) and pressure (100 bar) to achieve analyte recoveries equivalent to those from Soxhlet extraction, using less solvent and taking significantly less time than the Soxhlet procedure. This procedure was developed and validated on a commercially available, automated extraction system.

1.4 This method is applicable to the extraction of semi volatile organic compounds, organo-phosphorus pesticides, organo-chlorine pesticides, chlorinated herbicides, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs), and diesel range organics (DRO), which may then be analyzed by a variety of chromatographic procedures. The quantitative analysis of DRO is operationally defined on the basis of the retention times of characteristic components. This definition can be found in Method 8015. This method may also be applicable for the extraction of additional target analytes, provided that the analyst demonstrates adequate performance for the intended application (see EPA Method 3500).

1.5 This method has been validated for solid matrices containing from 0.33 µg/kg and up for pesticides by 8081B, 10 µg/kg and up for PCB's by EPA Method 8082A, and 83 µg/kg and up for EPA Method 8270E semivolatile organic compounds. This method may be applicable to samples containing these analytes at higher concentrations and may be employed after adequate performance has been demonstrated for the concentrations of interest (see EPA Method 3500). It may also be applicable to classes of analytes, to fuel types, and to petroleum fractions other than those listed in Sec 1.2. However, in order to be used for additional analytes, fuel types, petroleum fractions, or different concentrations, the analyst must demonstrate that the extraction conditions are appropriate for the analytes of interest. The analyst must also perform the initial demonstration of proficiency described in Sec. 9.3. If this method is expanded to address

other fuel types or petroleum hydrocarbons, the boiling point range or carbon number range of the material also needs to be carefully defined and the quantitation approach be modified to match such ranges. Analysts are advised to consult authoritative sources, such as the American Petroleum Institute (API), for appropriate definitions of other fuel types or petroleum fractions.

NOTE: Mention of the analyses of other fuel types and petroleum fractions does not imply a regulatory requirement for such analyses, using this or any other method.

1.6 This method is only applicable to solid samples, and is most effective on dry materials with small particle sizes. Therefore, waste samples must undergo phase separation and only the solid-phase material is to be extracted by this procedure. If possible, soil/sediment samples may be air-dried and ground to a fine powder prior to extraction. Alternatively, if worker safety or the loss of analytes during drying is a concern, soil/sediment samples may be mixed with pelletized diatomaceous earth. (Drying and grinding samples containing PCDDs/PCDFs is not recommended, due to safety concerns.) The total mass of material to be prepared depends on the specifications of the determinative method and the sensitivity necessary for the analysis, but an amount of 10-30 g of material is usually necessary and can be accommodated by this extraction procedure.

1.7 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000D) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.8 Use of this method is restricted to use by, or under the supervision of, appropriately experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of Method

2.1 This procedure is applicable for all solid matrices, such as: soils, clays, sediments, sludges, wipes, and waste solids.

2.2 Pressurized solvent extraction is a technique that reduces solvent consumption and sample preparation time. Solvent is pumped into an extraction vessel containing the sample and is heated and pressurized. The pressurized solvent at high temperature accelerates the extraction process by increasing the solubility of the analyte in the solvent and also increasing the kinetic rate of desorption of the analyte from the sample matrix.

2.3 The Speed Extractor E-916 is an automated system that can process up to six samples simultaneously. The parallel processing technology of the SpeedExtractor E-916 dramatically increases sample throughput compared to Soxhlet or pressurized solvent extraction systems that employ serial processing. In addition to rapid extraction times, significant reduction in solvent consumption is achieved. Pressurized solvent extraction can be used to replace Soxhlet and sonication techniques and is approved for use as EPA Method 3545A.

2.4 This method is a procedure for extracting water insoluble or slightly water soluble, semi-volatile organic compounds from soils, clays, sediments, sludges, wipes and waste solids using pressurized solvent extraction. The EPA Method 3545A is applicable to the extraction of semi-volatile organic compounds, organo-phosphorous pesticides, organo-chlorine pesticides, chlorinated herbicides, diesel range organics (DRO) and PCBs.

2.5 Samples are prepared for extraction either by air drying and grinding, or by mixing the samples with pelletized diatomaceous earth. The sample is then loaded into the extraction cell.

WARNING: The drying and grinding of samples containing PCDDs/PCDFs is not recommended, due to safety concerns. Grinding may also be a concern for other more volatile analytes (see Sec. 14.1.1).

2.6 The extraction cell containing the sample is heated to the extraction temperature (see Sec. 11.7.1), pressurized with the appropriate solvent system, and extracted for 5-10 minutes (or as recommended by the instrument manufacturer). Multiple extractions are recommended for some groups of analytes. The solvent systems used for this procedure vary with the analytes of interest and are described in Sec. 7.4.

2.7 The solvent is collected away from the heated extraction vessel and allowed to cool. Since the extraction cells contain frits, no filtration of the extracts is needed. However, for the extraction of very wet samples (e.g., >30% moisture), it may be necessary that the extract be dried with - anhydrous sodium sulfate (see note in Sec.11.4).

2.8 The extract may be concentrated, if necessary, and, as needed, exchanged into a solvent compatible with the cleanup or determinative step being employed.

3.0 Definitions

3.1 Batch‡: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A Preparation Batch is composed of between 1 and 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and the last sample in the batch to be 24 hours. Each Preparation Batch requires; one MB, LCS, and MS/MSD pair. An Analytical Batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

All batches require one MB, LCS, and MS/MSD pair or MS and Sample Duplicate when possible.

3.2 Holding Time: The maximum amount of time permitted between sampling and sample preparation and/or sample preparation and sample analysis. Also the period of time a sample may be stored prior to analysis when there is no preparation step. See the specific method or SW846 8000B table 4.1.

3.3 Internal Standards (IS)‡: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

3.4 Laboratory Control Sample (LCS)‡: (however named, such as laboratory fortified blank, blank spike (BS), or QC check sample). A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

The standard source can be the same as the calibration or a second source. The LCS is analyzed exactly like a sample to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.5 Matrix Spike (spiked sample of fortified sample)‡: A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of the sample for which an independent test results of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

3.6 Matrix Spike Duplicate (spiked sample or fortified sample duplicate)ǂ: A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

3.7 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. Method Blank analytical results are evaluated to determine the presence of contamination in the analytical method process.

3.8 Method Detection Limit (MDL): The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined by analyzing seven or more replicates of a spiked analyte free matrix and the resulting statistical calculation, in accordance with 40 CFR 136, Appendix B, Revision 2.

3.9 Reporting Limit (RL): The reporting limit, also known as the LOQ is the minimum concentration that can be reported as a quantitated value for a target analyte in a sample. This value can be no lower than the concentration of the lowest calibration standard.

3.10 Required Detection Limit (RDL): Detection limits established by a client or regulatory authority for analytes of concern. The laboratory MDL values must be equal or lower than the RDL. This is also known as the CRQL, the contract-required quantitation limit.

3.11 Surrogate Standard (SS): Organic compounds which are similar to the target analytes in chemical composition and mimic the behavior of the target analytes throughout the analytical process. Surrogate compounds are not normally found in environmental samples. Each calibration standard, sample, MB, LCS, MS, and MSD is spiked with surrogate standards. Surrogates are used to evaluate analytical efficiency by measuring recovery. See analytical method SOP for a list of specific surrogate compounds that are appropriate for sample-specific analysis.

ǂ EL-V1M2-ISO-2016, 2016 NELAP Standard definition.

4.0 Interferences

4.1 Contaminants in the solvents, reagents, glassware, and other extraction components may lead to matrix interferences. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis through preparation and analysis of MBs with every batch. The data from all GC/MS data for every MB, LCS, MS, MSD, and sample must be evaluated for interferences. If interferences are detected, it is necessary to determine if the source of interference is in the preparation and then take corrective action to eliminate the interference.

4.2 Refer to Method 3500 for information regarding interferences.

4.3 If necessary, Florisil and/or sulfur cleanup procedures may be employed. In such cases, proceed with the method – in SOP L-P-110 and/or L-P-109. Refer to SOP L-P-108 for acid cleanup of PCB extracts.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Chemical Hygiene Plan and this document. This procedure involves hazardous material, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow the appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are hazardous. Standard laboratory safety procedures should be followed when working with unknown samples. Gloves should be worn while handling any chemicals, standards, or samples. Other required personal protective equipment (PPE) are safety glasses, lab coats, and closed-toe, non-absorbent shoes.

5.2 Specific Safety Concerns or Requirements

Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded. Non-disposable gloves must be cleaned immediately. Latex and Vinyl gloves provide no protection against the organic solvents used in this method, so nitrile or similar must be used.

5.3 The toxicity and/or carcinogenicity of the reagents and analytes used in this method have been precisely defined; therefore, each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Procedures involving primary standards and sample preparation must be performed in a fume hood.

5.4 Safety Data Sheets (SDS) for each analyte and reagent used in the mobile laboratory are available to all employees. The SDS must be consulted prior to initial use of a chemical by an analyst.

5.5 Laboratory personal are required to be familiar with the general laboratory safety plan including the location and proper use of safety/emergency equipment.

5.6 The use of organic solvents, elevated temperatures, and high pressures in this method present potential safety concerns in the laboratory. Common sense laboratory practices can be employed to minimize these concerns. The sections to follow describe additional steps that should be taken.

5.7 Extraction cells in the heating block are hot enough to burn unprotected skin. Allow the cells to cool for 10-15 min before removing them from the oven or use appropriate protective equipment (e.g., Gripper; insulated gloves or tongs), as recommended by the manufacturer.

5.8 During the gas purge step, some solvent vapors may exit through a vent port in the instrument. Follow the manufacturer's directions regarding connecting this port to a fume hood to prevent release of solvent vapors to the laboratory atmosphere.

5.9 The instrument may contain flammable vapor sensors and should be operated with all covers in place and doors closed to ensure proper operation of the sensors. Follow the manufacturer's directions regarding replacement of extraction cell seals to ensure against vapor leaks.

6.0 Equipment and Supplies

6.1 Equipment

6.1.1 Pressurized solvent extraction device

SpeedExtractor E-916 unit (Buchi, New Castle, DE, USA) with appropriately-sized extraction cells. Currently, cells are available that will accommodate 1-g, 5-g, 10-g, 20-g and 30-g samples. Cells should be made of stainless steel or other material capable of withstanding the pressure levels (2000+ psi) necessary for this procedure.

Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

6.1.2 Apparatus for determining percent dry weight

6.1.2.1 Drying oven or moisture analyzer.

6.1.2.2 Desiccators.

6.1.2.3 Disposable aluminum weighing pans.

6.1.3 Top loading balance, capable of weighing to 0.01 g.

6.1.4 TurboVap with trays that hold 40-mL vials, 60-mL vials, and 15-mL concentrator tubes, which can be regulated at 35 °C. A DryVap (Horizon Technology, Salem, NH, USA) or equivalent may also be used.

6.1.5 Solvent vapor recovery system (Horizon or equivalent).

6.1.6 Water bath - Heated, with cover, capable of temperature control (±5°C). The bath should be used in a hood.

6.2 Supplies

6.2.1 Vials for collection of extracts -- 40-mL or 60-mL, pre-cleaned, open-top screw-cap with polytetrafluoroethylene (PTFE)-lined silicone septum.

6.2.2 Filter disk -- 1.983-cm, cellulose or glass fiber.

6.2.3 Cell cap sealing disk.

6.2.4 Stir rods.

6.2.5 1-mL syringe.

6.2.6 Metal spoons.

6.2.7 Wooden spatulas.

6.2.8 Funnels.

6.2.9 50-mL concentrator tubes or smaller.

6.2.10 Vials - 2-mL, glass with PTFE-lined screw-caps or crimp tops.

7.0 Reagents and Standards

7.1 Reagent-grade chemicals must be used in all phases of sample preparation and analysis. Unless otherwise indicated, it is intended that all reagents 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. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 TCL (Target Compound List)-free sand. All references to sand in this method refer to TCL-free sand.

7.3 Drying agents

7.3.1 Sodium sulfate (granular anhydrous), Na_2SO_4.

7.3.2 Pelletized diatomaceous earth (speed / hydromatrix).

7.3.3 Drying agents should be purified by heating at 150°C for one hour in a shallow tray, or by pre-cleaning the sodium sulfate with methylene chloride. If the sodium sulfate is pre-cleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

7.4 Extraction solvents

7.4.1 Samples should be extracted using a solvent system that gives optimum, reproducible recovery of the analytes of interest from the sample matrix, at the concentrations of interest. The choice of extraction solvent will depend on the analytes of interest and no single solvent is universally applicable to all analyte groups. Whatever solvent system is employed, including those specifically listed in this method, the analyst must demonstrate adequate performance for the analytes of interest, at the levels of interest. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Method 8000D describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results. Many of the solvent systems described below include the combination of a water-miscible solvent, such as acetone, and a water-immiscible solvent, such as methylene chloride or hexane. The purpose of the water-miscible solvent is to facilitate the extraction of wet solids by allowing the mixed solvent to penetrate the layer of water on the surface of the solid particles. The water-immiscible solvent extracts organic compounds with similar polarities. Thus, a non-polar solvent such as hexane is often used for non-polar analytes such as PCBs, while a polar solvent such as methylene chloride may be used for polar analytes. The polarity of acetone may also help extract polar analytes in mixed solvent systems.

CAUTION: When extracting very wet samples (e.g., >30% moisture), large amounts of water may be collected along with the extracts if a mixed solvent containing acetone is used. All solvents should be pesticide quality or equivalent. Solvents may be degassed prior to use.

7.4.2 Semivolatile organics may be extracted with acetone/methylene chloride (1:1, v/v), or acetone/hexane (1:1, v/v).

7.4.3 PCBs may be extracted with acetone/hexane (1:1, v/v) or acetone/methylene chloride (1:1, v/v). For the extraction of Aroclors for GC/ECD analyses (SOP L-A-401), the extraction solvent is acetone/methylene chloride (1:1, v/v).

7.4.4 Other solvent systems may be employed, provided that the analyst can demonstrate adequate performance for the analytes of interest in the sample matrix.

7.5 High-purity gases such as UHP nitrogen, are used to purge and/or pressurize the extraction cell. Follow the instrument manufacturer's recommendation for the choice of gases.

7.6 For the extraction of Aroclors from soil or solid matrices followed by GC/ECD analyses (SOP L-A-401), the following spiking standards can be used:

7.6.1 Surrogate spike solution at 20 µg/mL - Dilute 500 µL of a stock at 200 µg/mL (Restek 322457, or equivalent) to 5.0 mL with acetone to produce a solution contain 20 µg/mL each of 2,4,5,6-tetrachloro-*m*-xylene (TCMX) and decachlorobiphenyl (DCB).

7.6.2 Aroclor spiking solution for LCS, MS, or MSD – Prepare a solution at 100 µg/mL in acetone by diluting 500 µL each of Aroclor 1016 and Aroclor 1260 stocks at 1000 µg/mL (AccuStandard C-216S-H-10X and C-260S-H-10X, or equivalent) to 5.00 mL.

7.6.3 To each soil sample to be analyzed by the procedures in SOP L-A-401, add 50 µL of the surrogate spike solution at 20 µg/mL (10.6.1).

7.6.4 To each soil LCS, MS or MSD to be analyzed by the procedures in SOP L-A-401, add 50 µL of the Aroclor spike solution at 100 µg/mL (10.6.2).

7.7 For the extraction of Pesticides and toxaphene from soil or solid matrices followed by GC/ECD analyses (SOP L-A-403), the following spike standards can be used:

7.7.1 Surrogate spike solution at 2 µg/mL – Same as above (10.6.1)

7.7.2 Pesticide spiking solution for LCS, MS, or MSD – Prepare a solution at 2 µg/mL by diluting 50 uL of the pesticides AB 200 ug/mL to a final volume of 5 mL with hexane.

7.7.3 Toxaphene spiking solution for LCS, MS, or MSD – Prepare a solution of 10 µg/mL by diluting 50 uL of toxaphene standard at 1000 ug/mL to a final volume of 5 mL with hexane.

7.8 For the extraction of semivolatiles from soil or solid matrices followed by GC-MSD analyses (SOP L-A-201), the following spike standards can be used:

7.8.1 Surrogate BNA mix - Dilute 1 mL of the Acid surrogate mix 10,000 ug/mL and 2 mL of the 5,000 ug/L BN mix to a final volume of 10 mL with methylene chloride. The final concentration will be 1000 ug/mL for all the surrogates.

7.8.2 To each soil add 50 uL of the BNA surrogate mix (10.8.1)

7.8.3 For the LCS, MS or MSD – add 50 uL of the stock solution SV Mega mix at 1000 ug/mL (Restek 31850) and 50 uL of 2,4-Dinitrophenol 1000 ug/mL (Restek 31291).

7.9 For the extraction of Diesel Range Organics from soil or solid matrices followed by GC-FID analyses (SOP L-A-205), the following spike standards can be used:

7.9.1 Surrogate spike. Add 5 uL of the surrogate stock solution O-terphenyl (Restek 31097)

7.9.2 For the LCS, MS or MSD – add 25 uL of the stock solution DRO at 20,000 ug/L (SPEX S-DF2-20K)

7.10 The standards used in 10.6 through 10.9 are examples and other concentrations may be used as long as method quality control can be met. Also samples for other analytical methods may be prepared for analysis using this SOP whether they are listed here or not.

8.0 Sample Collection, Preservation, and Storage

8.1 Samples are normally collected in 6 oz amber jars, but may come in different sizes and volumes.

8.2 Samples are delivered to the PHILIS or held at 0°C - 6°C before shipment to the lab for analysis within holding time.

8.3 The samples received in the PHILIS laboratories must be transported in coolers with ice packs. Sample temperatures are measured upon receipt. Any samples that exceed acceptable temperatures require client notification. See SOP L-P-001. Samples are maintained at the temperature range from 0°C to 6°C range.

8.4 Sample extraction holding time is 14 days for soil samples.

8.5 Samples should NOT be preserved upon receipt.

9.0 Quality Control

9.1 Any reagent blanks, laboratory control samples, matrix spikes, or replicate samples should be subjected to the same analytical procedures as those used on actual samples.

9.2 See PHILIS SOP L-A-201, *Semivolatile Organics by Method 8270E*, PHILIS SOP L-A-401, *Polychlorinated Biphenyls by Method 8082A,* SOP L-A-403, Pesticides by Method 8081B or Method 8015D Diesel Range Organics for specific quality control information.

9.3 Initial Demonstration of Capability: This method must be successfully performed by the prep extraction chemist prior to preparing any project samples, and at any time major modifications are made.

9.3.1 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. For this method, this can be accomplished through the analysis of a solid matrix method blank (e.g. clean sand). As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination.

9.3.2 Standard quality assurance practices should be used with this method as included in appropriate systematic planning documents and laboratory SOPs. All instrument operating conditions should be and are stored on the instrument.

9.3.3 Also refer to Method 3500 for extraction and sample preparation QC procedures and the determinative methods to be used for determinative QC procedures.

9.3.4 When listed in the appropriate determinative method, surrogate standards should be added to all samples prior to extraction. See Methods 3500 and 8000D, and the appropriate determinative methods for more information.

9.3.5 As noted earlier, use of any extraction technique, including pressurized fluid extraction, should be supported by data that demonstrate the performance of the specific solvent system and operating conditions for the analytes of interest, at the levels of interest, and in the sample matrix.

9.4 Corrective Actions for Out of Control

The analyst shall report to the Lead Chemist any out of control event. Such events include:

9.4.1 Damage to the sample.

9.4.2 Holding time exceeded.

9.4.3 Inadequate sample preservation.

9.5 The Lead Chemist will implement the corrective action plan described in the PHILIS corrective action plan document

9.6 Detection Limits

9.6.1 This method is used with SW846 Method 8081B, SW846 Method 8082A, SW846 Method 8270E, and SW846 Method 8015D to determine method detection limits. Other methods may be used that require soil extraction methods.

9.6.2 Method detection limits are determined using the procedure outlined in 40 CFR Part 136, Appendix B, Revision 2.

9.6.3 The detection limit is estimated to be 0.33 µg/kg for EPA Method 8081B, 10 µg/kg for EPA Method 8082A, and 83 µg/kg for EPA Method 8270E. The detection limit for Method 8015D DRO is 0.90 mg/Kg.

10.0 Calibration and Standardization

See PHILIS SOP L-A-201 Semivolatile Organics by Method 8270E, SOP L-A-401, Polychlorinated Biphenyls by GC, SOP L-A-403 Pesticides by Method 8081B or SOP L-A-205 Diesel Range Organics Section 10 for instrument calibration.

11.0 Procedure

11.1 Prepare the extraction vessels for analysis by placing a cellulose filter disk in the bottom opening followed by a 10µm stainless steel frit, and secure them in place with a retaining nut.

11.2 Sample preparation

11.2.1 As is the case for many other extraction procedures, pressurized fluid extraction performs best on dry, finely-ground solids. However, the processes of sample drying and grinding involve the potential for a loss of analytes, the introduction of other contaminants into the sample, the contamination of the laboratory environment, and exposure of the analyst to environmental contaminants. Therefore, the analyst must determine the most appropriate approach to be used for each combination of sample matrix and analytes of interest, balancing analytical accuracy, practicality, and worker safety. No single approach should be expected to work for all matrices or analytes. The following sections describe the general procedures that may be applied to different matrices, types of solid samples, and/or samples for specific classes of analytes.

11.2.2 Sediment/wet soil samples: Decant and discard any water layer on a sediment sample. Discard any foreign objects such as sticks, leaves, and rocks. Mix the sample thoroughly, especially composite samples. When practical, air-dry the sample at room temperature for 48 hrs in a glass tray or on hexane-rinsed aluminum foil.

CAUTION: Drying should always be performed in a hood, to avoid contamination of the laboratory.

11.2.3 Waste samples: Multiphase waste samples must be prepared by the phase separation method before extraction. This extraction procedure is applicable for solids only.

11.2.4 Visually inspect the samples to determine approximate particle size. For many samples, pre-treatment prior to loading into the extraction cells is not necessary, other than mixing with diatomaceous earth.

11.2.5 Gummy, fibrous, or oily materials not amenable to grinding: cut, shred, or otherwise reduce in size the samples to allow mixing and maximum exposure of the sample surfaces for the extraction. If necessary, mix drying agents in the samples to make them more amenable to grinding.

NOTE: The weight of a specific sample that a cell will contain depends on the bulk density of the sample and the amount of drying agent that must be added to the sample in order to make it suitable for extraction. Generally, an 11-mL cell will hold about 10 g of material, a 22-mL cell will hold about 20 g of material, and a 33-mL cell will hold about 30 g of material. The analyst should ensure that the sample aliquot extracted is large enough to provide the necessary sensitivity and choose the extraction cell size accordingly. If the sample is weighed in the extraction cell, then prepare the cell by placing a disposable cellulose or glass funnel in the cell outlet before adding the sample. Tare the balance and add the sample to the cell.

11.3 Determination of percent dry weight

When sample results are to be calculated on a dry weight basis, a separate portion of sample for this determination should be weighed at the same time as the portion used for analytical determination.

CAUTION: The drying oven must be contained in a hood or vented to eliminate the potential for fumes to enter the laboratory environment. Significant laboratory contamination may result from drying a heavily contaminated sample. Immediately after weighing the sample for extraction, weigh an additional 5- to 10-g aliquot of the sample into a tared weighing pan. Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\%\ dry\ weight = \frac{g\ of\ dry\ sample}{g\ of\ sample}\ x\ 100$$

This oven-dried aliquot is not used for the extraction and should be appropriately disposed of once the dry weight is determined.

11.4 Surrogates

Add 1.0mL surrogate solution listed in the determinative method to each sample in its extraction cell. Consult Method 3500 and the determinative method for information on appropriate surrogates and internal standards. Add 1.0mL spiking solution listed in the determinative method to the laboratory control sample, matrix spike, matrix spike duplicate, and laboratory control sample duplicate.

11.5 Before spiking the surrogates or other compounds, if needed, add sufficient drying agent to the sample in order to make it suitable for extraction (see the note below). Some samples may not need any drying agent. Very wet samples may need twice the weight of the sample in drying agent. Carefully mix the sample and the drying agent in the cell, using a clean spatula or other suitable tool. If the sample will be mixed in a container other than the extraction cell, then add a weighed amount of the sample to the container, followed by a sufficient amount of the drying agent.

NOTE: The use of sodium sulfate as a drying agent with very wet samples (e.g., >30% moisture) can lead to clogging of the frits in the cell with re-crystallized sodium sulfate, particularly if a mixed solvent containing acetone is used. In these cases, palletized diatomaceous earth and not sodium sulfate should be used as a drying agent. (Alternatively, pelletized diatomaceous earth may be used as a drying agent in the cell in place of sodium sulfate for all levels of moisture.) For very wet samples, regardless of the drying agent used, it will be necessary to add sodium sulfate to the vials after collection and to pass the extracts through a drying column or drying cartridge to dry the extract completely. Due to the high temperatures used, more water will be co-extracted than with other extraction procedures. The analyst must make sure that adequate attention is given to rinsing the sodium sulfate in the vial and the cleanup column to ensure good analyte recovery. If no drying agent is needed, then TCL-free sand may be used to fill any void volume in the extraction cells. If desired, fill TCL-free sand to within 0.5-1 cm in height between the sample bed and the upper filter to prevent clogging and uniform flow directed in the SpeedExtractor E-916 Operation Manual.

NOTE: Since sand is not intended to dry the sample, it need not be mixed with the sample, but can be placed at one end of the cell.

11.6 Seal the extraction cell according to the manufacturer's instructions. Use disposable cellulose or glass fiber filters in the cell outlets. Place the extraction cell into the instrument as described by the instrument manufacturer.

11.7 Place a pre-cleaned collection vessel in the instrument for each sample, as described by the instrument manufacturer. The total volume of the collected extract will depend on the specific instrumentation and the extraction procedure recommended by the manufacturer and may range from 0.5 to 1.4 times the volume of the extraction cell. Ensure that the collection vessel is sufficiently large to hold the extract.

NOTE: The volume of solvent used for each extraction is a function of the size of the extraction cell, not the weight of the sample. Consult the manufacturer's instructions for the appropriate volume of solvent to employ for a given cell size and the necessary collection vessel volume.

11.8 Recommended extraction conditions for semi volatiles and PCBs

11.8.1 PSE Method 2

Heating Block temperature: 100 °C
Pressure: 100 bar
Vial: 60-mL
Cell: 40-mL
Solvent: acetone/methylene chloride (1:1, v/v)
# of cycles: 1
Cycle:
Heat up: 1 min
Hold (Static time): 6 min
Discharge: 1 min

Flush with solvent:1 min (2 min for high concentrated samples)
Flush with Nitrogen: 1 min (2 min for high concentrated samples)

11.8.2 Optimize the conditions, as needed, according to the manufacturer's instructions. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction cell is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the sample. The pressure in the cell should range from 1500-2000 psi (~100 bar).

11.8.3 Once established, the same pressure should be used for all samples extracted for the same type of analysis.

11.9 Collect each extract in a clean vial (see Sec. 6.2.1). Generally, the extracts are near room temperature upon collection.

11.10 Next, the extract is ready for concentration, cleanup, or analysis, depending on the extent of interferants and the determinative method to be employed. Refer to Method 3600 for guidance on selecting appropriate cleanup methods. Excess water present in extracts may be removed by filtering the extract through a bed of anhydrous sodium sulfate. Certain cleanup and/or determinative methods may need a solvent exchange prior to cleanup and/or sample analysis.

When extracting very wet samples (e.g., >30% moisture) with acetone containing solvents, it is often necessary to add sodium sulfate to the collection vials after extraction to remove excess water. Amounts of 1 to 10 g may need to be added depending on the amount of water in the sample. It is important that the vial and sodium sulfate is thoroughly rinsed to ensure complete analyte recovery.

11.11 Perform the concentration using the TurboVap (Biotage). Other concentrators that are equivalent, such as the DryVap (Horizon Technology) may be used. If DryVap concentration procedures (SOP L-P-103) are used, skip to Section 11.9.12.

11.11.1 Turn on the TurboVap, the pump, the solvent-recovery system, and the nitrogen.

11.11.2 Adjust the temperature of the bath to 35°C.

11.11.3 Verify that there is a sufficient amount of water in the bath. Add more water if more is required.

11.11.4 Insert the appropriate rack for the vials used during extraction.

11.11.5 Combine the different phases into one vial, rinsing the vial that will not be used during concentration twice with methylene chloride. Add these rinses to the vial that will be used for concentration.

11.11.6 Once the bath is up to temperature, insert the vials into the rack and set the timer to begin concentration. Close the lid.

11.11.7 Verify that the samples are not splashing out of the vials into the TurboVap. This could lead to loss of compounds and/or contamination of other samples.

11.11.8 Concentrate the samples down to approximately 8-10 mL and then transfer them to a 15 or 50 mL concentrator tubes. Rinse the vial twice with methylene chloride and add these rinses to the concentrator tube. Samples requiring pesticide or PCB analysis require hexane exchange--add approximately 25mLs to concentrator tubes.

11.11.9 Prior to use, rinse the concentrator tubes with Acetone twice and methylene chloride twice. Dispose of the rinses in the appropriate waste container.

11.11.10 Continue concentration, rinsing the walls of the concentrator tube occasionally with methylene chloride or hexane.

11.11.11 Remove the extract from the bath once the volume is between 0.7 and 0.9 mL. Cap the extract and set aside.

11.11.12 Once all sample extracts have been concentrated, transfer the extracts into amber 2 mL vials at the volume of 1.0 mL.

CAUTION: When the volume of solvent is reduced below 1 mL, semi volatile analytes may be lost.

11.12 Transferring sample extracts once concentrated

11.12.1 Label 2mL amber vials with sample ID, batch, and test performed.

11.12.2 Take a 1.0 mL syringe and rinse three times with methylene chloride or hexane.

11.12.3 Make sure to rinse the syringe between every sample.

11.12.4 Pull all of the extract into the syringe and remove the air-bubble.

11.12.5 Do this by flipping the syringe upside-down, pulling in some air, and then pushing the air out.

11.12.6 Rinse the walls of the concentrator tube with a small amount of methylene chloride. Pull this rinse into the syringe.

11.12.7 Repeat 11.10.6 until there is 1.0 mL in the syringe.

11.12.8 Transfer the contents of the syringe into the appropriately labeled vial.

11.12.9 For GC/MS samples, add the appropriate amount of IS to the 1.0 mL extract. Samples requiring PCB analysis are extracted as above and then exchanged into hexane prior to analysis on the GC. Addition of the Hexane should occur when the sample volume is at 5-10 mLs.

11.12.10 Cap the sample and store in an appropriately identified tray until it is ready to be analyzed.

11.12.11 The extract may now be analyzed for the target analytes using the appropriate determinative technique.

12.0 Data Analysis and Calculations

See PHILIS SOP L-A-201, *Semivolatile Organic Compounds by EPA Method 8270E,* Section 15, PHILIS SOP L-A-401, *Polychlorinated Biphenyls by EPA Method 8082A,* Section 15, or PHILIS SOP L-A-403 Pesticides by EPA Method 8081B, Section 15.

13.0 Method Performance

See PHILIS SOP L-A-201, *Semivolatile Organic Compounds by EPA Method 8270E*, Section 16, PHILIS SOP L-A-401, *Polychlorinated Biphenyls by EPA Method 8082A,* Section 16, or PHILIS SOP L-A-403, Pesticides by EPA Method 8081B Section 16.

14.0 Pollution Prevention

14.1 The waste produced from EPA Method 3545A consists of waste collected from the extraction equipment, excess sample, standards, methylene chloride, and acetone.

14.2 Excess reagents are disposed following the SDS and Hazardous Waste Management Plan instructions

14.3 Refer to EPA Method 3545A for additional guidance.

14.4 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.5 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

14.6 The Environmental Protection Agency requires that laboratory waste management practices conducted are consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society.

15.0 Waste Management

15.1 The waste produced from EPA Methods 8015A, 8081B, 8082A and 8270E consists of waste collected from the extraction equipment, excess sample, standards, methylene chloride, acetone, and methanol.

15.2 Excess reagents are disposed following the SDS and hazardous waste plan instructions.

15.3 Glass pipettes are disposed in the glassware waste container.

15.4 Refer to PHILIS SOP L-A-101 *Semivolatile Organics by EPA Method 8270E*, Section 15, PHILIS SOP L-A-401 *Polychlorinated Biphenyls by EPA Method 8082A*, Section 15 PHILIS SOP L-A-403, *Pesticides by EPA Method 8081B*, or PHILIS SOP 205 Diesel Range Organics Section 15 for additional guidance.

16.0 References

16.1 EPA Method 3545A Pressurized Fluid Extraction (PFE), Revision 1, February 2007; U.S. EPA Office of Solid Waste.

17.0 Tables, Figures, and Attachments

Not applicable for this method.

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APPENDIX K -
CHAIN OF CUSTODY

CHAIN OF CUSTODY RECORD

Project Name:		**Project Manager:**		**Analysis Turnaround Time**	**Date:**
Project Number:		**Address:**			**COC No:**
Sample Team Leader:		**Phone No:**			**Lab ID:**
Phone No:		**Carrier/Waybill No.:**			**SDG ID:**

Sample ID	Sample Description	Collected		CWA / Toxic Sample Field Screening Result (mg/m3)	Analysis Requested	Grab/ Comp.	No. of Cont.	Quantity	Preservative
		Date	Time						

Description of Packaging, Containers, Custody Seal and Observations:

Possible Hazard Identification:

☐ *Non-Hazard* ☐ *Flammable* ☐ *Skin Irritant* ☐ *TIC*

☐ *CWA* ☐ *Other:* _____

Special Instructions / QC Requirements & Comments:

Relinquished By:	Date/Time:	Received By:	Date/Time:
Relinquished By:	Date/Time:	Received By:	Date/Time:
Relinquished By:	Date/Time:	Received By:	Date/Time:
Received at Lab By:	Date/Time:		