Site-Specific Quality Assurance Project Plan Addendum
Brownfields Corrective Action Investigation
Long Falls Paper
161 Wellington Road
Brattleboro, Vermont 05301

February 13, 2020

Prepared for:

Brattleboro Development Credit Corporation
76 Cotton Mill Hill
Brattleboro VT 05301

LE·Environmental

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LEE #18-122

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Section A: Title and Approval Page / Introduction

Long Falls Paper, Brattleboro, Vermont
Brownfields Site Specific Quality Assurance Project Plan Addendum

February 13, 2020

LEE Brownfields Project Manager: Alan Liptak

Signature

LEE Brownfields QA Officer: Angela Emerson

Signature

U.S. EPA Project Manager: Joe Ferrari

Signature

U.S. EPA /QA Officer: Nora Conlon

Signature

Vermont DEC Brownfields Project Manager: Shawn Donovan

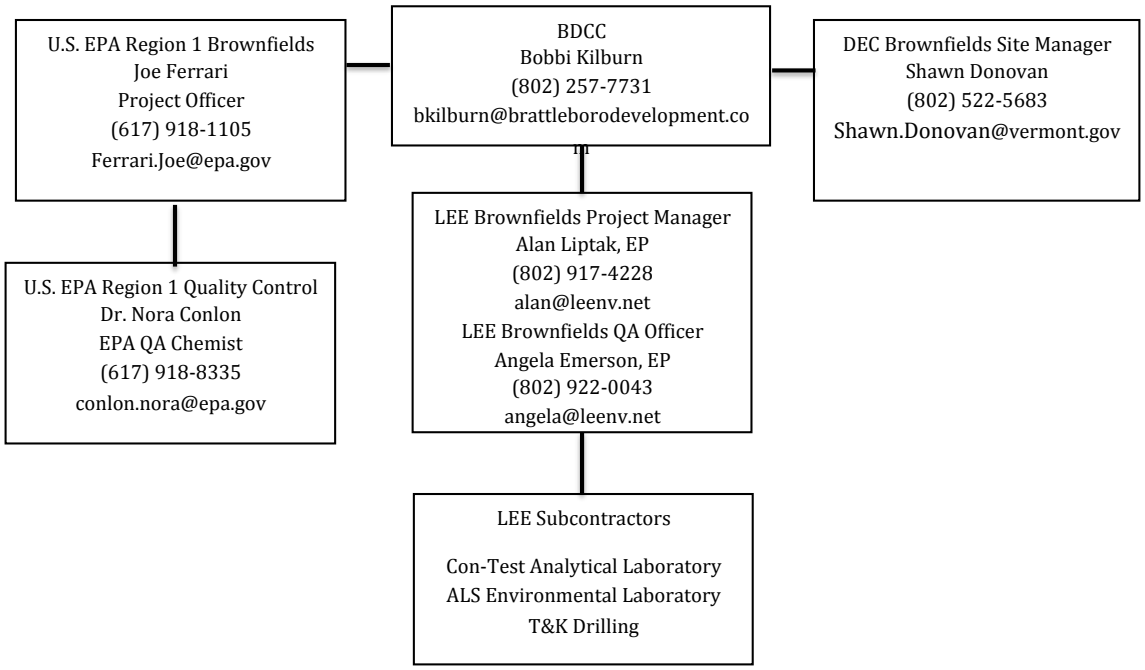
Signature

Introduction

LE Environmental LLC (LEE) of Waterbury, Vermont prepared this Brownfields site-specific quality assurance project plan addendum (SSQAPP addendum) for a Brownfields Corrective Action Investigation at Long Falls Paper, 161 Wellington Road, Brattleboro, Vermont (Site). This SSQAPP was prepared for the Brattleboro Development Credit Corporation (BDCC). BDCC is funding this work via EPA Brownfields Cleanup Grant # BF-BF00A00502. A Site location map is included in Appendix A. This SSQAPP addendum was prepared using rules and guidance provided by USEPA and the Vermont Department of Environmental Conservation (DEC) Investigation and Remediation of Contaminated Properties Rule (I-Rule), July 2019, and the DEC's Hazardous Waste Management Regulations, December 2016.

Section B: Project Organization

Communications during the planning and implementation of the Brownfields Corrective Action Investigation will be performed according to the following organization flow chart.



Section C: Problem Definition / Site Information

Following is the problem definition and relevant Site information as noted in § 35-304 of the Investigation and Remediation of Contaminated Properties Rule (I-Rule).

(1) Table of names

Site Owner and Operator	Mailing Address	Email Address	Phone Number
Brattleboro Development Credit Corporation	76 Cotton Mill Hill Brattleboro, Vermont 05301	bkilburn@brattleborodevelopment.com	(802) 257-7731
Long Falls Paperboard	161 Wellington Road Brattleboro, Vermont 05301	gabriela.constantin@longfallspaperboard.com	(802) 257-0365

(2) Current land uses and activities of the Site

The property consists of a 39.52-acre parcel with a paper manufacturing facility at the north end of Wellington Road in Brattleboro, Vermont (see Appendix A). The property hosts an approximately 200,000 square foot paper manufacturing plant. The plant obtains pulp and recycled paper from outside sources and produces 7-ply hard stock finished product. The property also includes a wastewater treatment plant for process water, a water filtration plant for process water, and an agricultural field that has been leased to area farmers in the past. Historically, the town land records indicate that the property was owned by a succession of individuals through 1958, and then BDCC acquired the property for development as a paper mill. The property was sold by BDCC in 1960, and was owned by a number of corporate entities until late 2018 when BDCC re-acquired the property.

(3) Adjacent Site Uses

Current uses of the adjoining properties were observed as follows:

- North: undeveloped woodland.
- East: Connecticut River.
- South: Green Mountain Power substation, Wellington Road.
- West: (south to north): Suburban Propane; BDCC Business Park (multi-tenant, former Book Press), C&S Wholesale Grocers, Closed Windham Solid Waste Management District (WSWMD) Landfill.

(4) Site Description

The property is at the eastern edge of the Brattleboro Industrial Zone, which encompasses most of the area east of Putney Road and north of I-91 Exit 3 (Appendix A). Development in this zone includes industrial manufacturing, warehouses, retail, and wholesale distribution.

A Phase I ESA[1] and a Phase II ESA[2] were recently performed. Twelve Recognized Environmental Conditions (RECs) were identified during the Phase I ESA. These were evaluated during the Phase II ESA. The outcome of the Phase II ESA was that many of the RECs identified in the Phase I ESA did not have significant subsurface contamination associated with them. The following table summarizes the RECs identified in the Phase I ESA, the results of the Phase II ESA, and recommended next steps.

REC identified in Phase I	Phase II Results	Next Steps
1. Historic #6 Fuel Oil Release	#6 fuel oil remains, but no impact to sensitive receptors	Further evaluation recommended to define limits for institutional control or cleanup.[3]
2. Potential contamination from historic gas and diesel USTs	No evidence of a gasoline release except possibly MTBE in production wells, and no evidence of a diesel fuel release that impacts groundwater.	No further action. Production wells are not used for potable water.
3. On-Site Paper Manufacturing	Historically detected chlorinated solvents in groundwater have dissipated. Per- and polyfluoroalkyl substances (PFAs) are present in some soil and groundwater samples at levels below standards. Vanadium present in soil above standards. Dioxins were present but below standards except in the wastewater holding basin. PCBs were present in the holding basin.	a) Further evaluate contents of wastewater holding basin. b) Vanadium may be naturally occurring; evaluate background concentrations. c) Confirm PFAs concentrations in groundwater.
4. Sumps and Floor Drains	Historically detected solvents have dissipated. No evidence of other releases.	No further action.
5. Equipment yard	Evaluated, no releases noted.	No further action.
6. Abandoned drum	Evaluated, no releases noted.	No further action.
7. Filled area north end of property	Evaluated, no releases noted.	No further action.
8. WSWMD Landfill impact to groundwater	Not investigated due to groundwater reclassification to non-potable.	No further action.
9. Active septic system north of plant	Evaluated, no releases noted.	No further action.
10. Abandoned septic system east of plant	Evaluated, no releases noted.	No further action.
11. Adjoining active railway line	Railway related contamination was below standards.	No further action.
12. Adjoining historic printing press	Evaluated, no releases noted.	No further action.

This SSQAPP Addendum addresses next steps #3a and #3c as noted. The Town of Brattleboro is separately addressing the follow-up to the historic #6 fuel oil release. The background concentration study for vanadium is taking place via a desktop study and does not include additional sampling.

[1] LEE, 2018.
[2] Stone Environmental, 2019.
[3] Further evaluation of #6 fuel oil is being performed separately by the Town of Brattleboro, not included in this document.

(5) Site Characterization Objectives and Strategy

The objectives and strategies of the Corrective Action Investigations are:

1. Further evaluate the contents of the wastewater holding basin; the plant engineer informed LEE that the overflow lagoon is clay-lined and the liner is believed to be 18" thick.[4]
2. Conduct a desktop background study of vanadium concentrations and compare with site-derived concentrations from the Phase II ESA to evaluate whether they represent background.
3. Perform a confirmation round of groundwater monitoring for PFAs and determine whether the results are above or below current standards.

The investigation objectives are further defined in Section D of this SSQAPP.

(6) Identification of Analytical Methods

Analytical methods to be used in this Brownfields Corrective Action Investigation are described in Section F.

(7) List of Standard Operating Procedures

A list of standard operating procedures to be used in this Brownfields Corrective Action Investigation is presented in Section G.

(8) Conceptual Site Model

The property is situated on a flat alluvial terrace overlooking the Connecticut River, and approximately 70 feet higher than the river.[5] The soils beneath the property consist predominantly of sand and gravel according to the subsurface investigations.[6] No natural bodies of water were observed on the property. No exposed bedrock was noted.

Depth to groundwater was approximately 70-75 feet below grade during previous Site investigations. The groundwater flow direction beneath the property was estimated to be northwesterly in 1990 and easterly in 1994 and 2019. The groundwater flow direction may be influenced by the Connecticut River elevation and may be subject to inversion at times.[7]

According to the Agency of Natural Resource (ANR) Atlas, the Site is underlain by schist (primary) and metawacke (secondary) bedrock. The bedrock is described as dark gray to coaly-black, fine-grained plagioclase-muscovite-quartz schist and metawacke, shown southeast of Springfield, in part correlative with staurolite-grade rocks mapped as Littleton

[4] Electronic mail message from Gabriela Constantin, December 4, 2019 and February 4, 2020
[5] USGS, 2018.
[6] Griffin, 1990; Stone Environmental, 2019.
[7] Griffin, 1990 and 1994.

Formation. Bedrock was reported at depths of 137 and 142 feet below ground surface in two bedrock wells drilled to the west and southwest of the Site where ground surface elevations are relatively similar to that of the Site. Overburden groundwater production wells at the Site were drilled to approximately 100 feet below ground surface. Therefore, it is anticipated that bedrock would be encountered between 100 and 150 feet below ground surface at the Site. Depth to water is approximately was measured between 66 and 69 feet below ground surface in the parking area of the site, and 75 feet below ground surface in the area immediately southeast of the lagoons.[8]

During the 2019 Phase II ESA, strata observed were indicative of a meandering river system bisecting through previously deposited lacustrine deltaic sediments. Coarser sediments with angular to sub-angular grains, like those that are prominent between 0 and 20 feet below ground surface Site-wide, suggest that these sediments are close to their source and that the paleo-Connecticut River flowed at a high velocity along the Site. Groundwater at the northeastern portion of the site, northeast of the wastewater treatment system lagoons, has been reclassified as Class IV groundwater due to contaminants from the Windham SWMD landfill located immediately to the northwest of the site.[9]

(9) Investigation Derived Waste:

Soil and groundwater will be generated during the Corrective Action Investigation. Based on the results of the Phase II ESA, soil and lagoon sludge from drilling will be placed back into the boreholes. Purge water from the groundwater wells will be drummed and kept on Site pending the receipt of analytical results. If the analytical results show contamination at levels below the Vermont Groundwater Enforcement Standard for PFAs (groundwater), the drummed water will be disposed of on Site. If concentrations are above standards, then alternate disposal will be evaluated.

(10) Quality Assurance and Quality Control Plan

This document comprises the required Quality Assurance and Quality Control Plan.

(11) Maps

Site maps showing the intended investigation locations are included in Appendix 2.

(12) Latitude/longitude of the Site

The center of property coordinates are 42° 53’ 22.34’’ north latitude and 72° 32’ 34.28’’ west longitude.[10]

[8] Stone Environmental, 2019.
[9] Ibid.
[10] EDR, Page 3.

(13) Estimated Costs

Estimated costs have been presented to BDCC.

(14) Implementation Schedule

The work is forecast to take place according to the following implementation schedule.

- QAPP Review: February 14-March 13, 2020.
- Fieldwork: March 16-April 16, 2020 (four days during this interval).
- Laboratory analysis: March 23-April 23, 2020.
- Reporting: March 23-April 30, 2020.

(15) Signature

Signed in Section A.

Section D: Project Objectives

The project objectives are to provide further information to assist with cleanup planning. The Brownfields Corrective Action Investigation will address this environmental concern under the following assumptions:

- The Site is enrolled in Vermont's Brownfields Reuse and Environmental Liability Limitation Act (BRELLA) program.
- A sludge, soil, and groundwater investigation will be performed on the site to support pending environmental cleanup efforts.

The sampling design set forth in Section E provides sufficient work scope to provide the necessary data to proceed with cleanup planning.

Section E: Sampling Design

The following sampling design will provide necessary data regarding identified REC and other environmental conditions identified in the Phase I ESA and according to the project objectives as outlined in Section D.

Pre-Excavation Activities

Prior to the initiation of subsurface activities, LEE will premark the proposed soil boring locations and obtain a Dig-Safe number. A site specific Health and Safety Plan will be developed and reviewed by field staff prior to exploratory work. The Town of Brattleboro Public Works Department will be contacted to discuss the work scope and any potential utility conflicts. Vermont Underground Utility Locators will screen the drilling locations for possible utility conflicts.

Soil Boring Investigation

LEE will conduct a soil boring investigation to evaluate cleanup needs in the vicinity of the overflow lagoon. Since the lagoon is a lined structure, it is assumed that its contents are classified as waste for regulatory purposes, and not environmental media. One possible cleanup scenario is to remove the waste sludge from the overflow lagoon and dispose of it at a certified waste disposal facility. Characterization samples will be needed for waste facility acceptance.

A hand auger and/or hand operated geoprobe tooling will be used to advance four borings inside the overflow lagoon to collect characterization samples and to verify that the lagoon is lined. A truck mounted geoprobe drill rig will be utilized to advanced three soil borings outside the overflow lagoon to determine if cleanup efforts need to extend beyond the overflow lagoon footprint. Soil borings will be advanced at the locations as shown on the Overflow Lagoon Sampling Locations Map in Appendix B.

Soil Sample Collection and Testing

Continuous soil sampling will be conducted during soil boring advancement. Soil samples will be screened for VOCs using a calibrated photoionization device (PID). One composite sludge sample will be collected from each boring inside the overflow lagoon for laboratory analysis of waste characterization COCs,[11] including the following constituents, and a duplicate will be collected (total of five samples):

- Volatile Organic Compounds (VOCs) via EPA Method 8260c
- Semi-Volatile Organic Compounds (SVOCs) via EPA Method 8270d
- RCRA 8 Metals and vanadium via EPA Method 6010 (total and TCLP Extraction via EPA Method 1311)
- PCBs via EPA Method 8082 with Soxhlet extraction via EPA Method 3540C
- Ignitibility (solids) via Method 1010A
- pH via EPA Method 9045D
- Dioxin/Furan Congeners via EPA Method 8290
- Total Petroleum Hydrocarbons (TPH) via EPA Method 8100
- Reactivity (Cn/S) via SW-846 9014 and 9030A
- PFAs via EPA Method 537 Modified

One grab soil sample will be collected from each boring outside the overflow lagoon, for laboratory analysis of environmental COCs, including the following constituents. The depth of soil sample collection will be at the greatest indication of field contamination if any, or at 0-18" below grade if no significant evidence of contamination is encountered. The soil boring locations outside the overflow lagoon are at lower elevation than the lagoon, therefore a 0-18" sample will be below the clay liner elevation.

[11] Sampling procedure and analytes defined by Casella Waste Systems Special Waste Requirements as of February 2020.

- VOCs via EPA Method 8260c
- Polycyclic Aromatic Hydrocarbons (PAHs) via EPA Method 8270d
- RCRA 8 Metals and vanadium via EPA Method 6020
- PCBs via EPA Method 8082
- Dioxin/Furan Congeners via EPA Method 8290

Samples will be submitted to Con-Test Analytical Laboratory of East Longmeadow, MA (Con-Test) for analysis, except for Dioxin/Furan Congeners, which will be submitted to ALS Environmental of Simi Valley, CA. Samples for PFAs analysis may alternately be submitted to Pace Laboratory of South Carolina.

The sampling locations, media, depths and analytical suites are summarized in the following table.

Boring #	Location and Media	Purpose	Probable Depth	Analytical Suite
LG-1, 2, 3, 4	Overflow lagoon sludge	Waste Disposal Characterization	0-2 feet	VOCs, SVOCs ABN, PCBs, Dioxin, Metals (total and TCLP), TPH, Reactivity, pH, Ignitibility, PFAs, % solids.
LG-5, 6, 7	Outside of Overflow Lagoon	Environmental Characterization for Cleanup Planning	15 feet	VOCs, PAHs, PCBs, Dioxin, Metals.

Groundwater Monitoring

LEE will collect groundwater samples at eight existing groundwater monitoring wells using low-flow sampling techniques. The well locations are shown on the Groundwater Contour Map in Appendix 2. Prior to groundwater sample collection, depth to water and depth to product (if present) will be measured in from the top of casing reference point. These data will be used to calculate the water level elevations and to confirm the groundwater flow direction and horizontal gradient beneath the site. Groundwater samples will be collected from the monitoring wells using a bladder pump. PFA-free polyethylene bladders and tubing will be used during sampling. Purging will take place at 200 milliliters per minute or less until stabilization of pH, conductivity, turbidity, and temperature have taken place, or one hour, whichever comes first. All samples will be analyzed for PFAs via EPA Method 537 Modified. A duplicate sample will be tested for PFAs. Samples will be submitted to Con-Test or Pace South Carolina for analysis.

Data Validation and Reporting

Following receipt of analytical data, LEE's quality assurance officer will validate the data according to the site-specific QAPP and LEE's generic QAPP procedures. A Brownfields Corrective Action Investigation Report will be prepared for review and approval. The reporting format specified for Site Investigations in the July 2019 DEC I-Rule will be

followed including Method 1 data evaluation and Method 2 data evaluation if warranted. A description of the methodologies and results will be included. Comparison with appropriate environmental and materials quality standards will be made. The report will also contain: a site map, sampling locations map, groundwater contour and contamination maps, conceptual site model, laboratory analytical data, recommendations for additional work if necessary, conclusions, and other recommendations, as applicable.

Section F: Sampling and Analytical Method Requirements

Parameter & Matrix	Number of Samples # + QA	Analytical Method (Section G)	Sampling SOP Form F-1	Containers per Sample (number, size and type)	Preservation	Extraction Hold Time (days)	Post Extraction Hold Time (days)
VOCs Sludge & Soil	4+1 (sludge) 3 (soil)	EPA 8260c	A	1-40ml cg 1-p (dry wt)	MeOH	14	n/a
SVOCs Sludge PAHs Soil		EPA M8270c/d/e	A	1-4oz ag	Cool	14	40
PCBs Sludge & Soil		EPA M8082 Soxhlet Extraction EPA M3540c	A	1-8 oz ag	Cool	14	45
RCRA 8 Metals and Vanadium Sludge & Soil		EPA M6020 TCLP Extraction EPA 1311	A	1-4oz cg	Cool	90	90
Dioxin Sludge and Soil		EPA M8290	A	1-8 oz ag	Cool	45	45
Total Petroleum Hydrocarbons Sludge	4+1 (sludge)	EPA M8100	A	1-8 oz ag	Cool	14	40
Reactive CN/S Sludge		SW-846 9014 and 9030A	A	1-8 oz ag	Cool	ASAP	ASAP
pH Sludge		EPA Method 9045D	A	1-8 oz ag	Cool	ASAP	ASAP
Ignitibility Sludge		EPA M1010A	A	1-8 oz cg	Cool	ASAP	ASAP
PFAs Sludge Groundwater	8+1 GW (PFAs only)	EPA M537.1	A	250 ml polypropylene bottle	Cool	14	28
Key to Containers: cg= clear glass; ag=amber glass; p=plastic; ss=stainless steel							

Section G: Methods and SOP Reference Table

Following is a description of LEE and laboratory methods and standard operating procedures to be employed during this work. LEE SOPS are included in LEE's generic QAPP document, Exhibit A. LEE SOP M and laboratory SOPs are included in Appendix 4.

- LEE SOP A: Soil Sampling (January 24, 2019)
- LEE SOP B: Soil Borings, Groundwater Monitoring Well Installation and Low-flow groundwater sampling (January 24, 2019)
- LEE SOP E: Sample Handling (January 24, 2019)
- LEE SOP F: PID Operation (January 24, 2019)
- LEE SOP G: pH Conductivity and Temperature Meter Operation (January 24, 2019)
- LEE SOP H: Turbidity Meter Operation (January 24, 2019)
- LEE SOP I: Electronic Water Level Measurement Operation (January 24, 2019)
- LEE SOP N: Preparation and Procedures for PFAs Monitoring (February 13, 2020)

Summary of Laboratory Analytical Procedures to be used during this work:

Matrix and Analytes	Laboratory Analytical Procedures
Volatile Organic Compounds in Soil and Groundwater	Standard Operating Procedure Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry, EPA Method 8260C/D, March 27, 2019, Con-Test Analytical Laboratory.
Semi-volatile Organic Compounds in Soil	Standard Operating Procedure Volatile Organic Compounds, EPA Method 8270C/D/E; February 19, 2019, Con-Test Analytical Laboratory.
Metals in Soil and Groundwater	Standard Operating Procedure Inductively Coupled Plasma – Optical Emission Spectrometry, EPA Method 6010C/6010D, August 14, 2019, Con-Test Analytical Laboratory.
PCBs in Soil	Standard Operating Procedure PCB by Gas Chromatography, EPA Method 8082A, November 22, 2019, Con-Test Analytical Laboratory.
Soxhlet Extraction	Standard Operating Procedure Soxhlet Extraction Procedure for Polychlorinated Biphenyls, Method 3540C; January 18, 2018, Con-Test Analytical Laboratory.
TCLP Extraction	Extraction Procedure for Toxicity Characteristic Leaching Procedure, EPA Method 1311, January 23, 2018, Con-Test Analytical Laboratory
Total Petroleum Hydrocarbons	Standard Operating Procedure, Petroleum Hydrocarbons by GC/FID, EPA Method 8100M, September 25, 2019, Con-Test Analytical Laboratory.
Reactive CN & S	Standard Operating Procedure, Reactivity, SW-846 9014 and 9030A, March 12, 2019, Con-Test Analytical Laboratory.
pH	Standard Operating Procedure, pH, March 27, 2019, Con-Test Analytical Laboratory.
Ignitibility	Standard Operating Procedure, Ignitability of Solids, March 12, 2019, Con-Test Analytical Laboratory.
PFAs in Sludge and Groundwater	Standard Operating Procedure, Determination of Selected Perfluorinated Alkyl Acids (PFAs) by Solid Phase Extraction & Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), EPA Method 537.1, November 20, 2019, Con-Test Analytical Laboratory; and December 16, 2019, Pace South Carolina (Shealy Environmental Services Inc.)
Dioxin in Soil	Standard Operating Procedure, Analysis of Polychlorinated Dibenzo-P-Dioxins and Polychlorinated Dibenzofurans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry, February 28, 2018, ALS Environmental

Section H: Field Equipment Calibration and Corrective Action

Data contained in LEE Generic QAPP V1 (RFA 19093), Section H.

Section I: Lab Equipment Calibration and Corrective Action

Data contained in LEE Generic QAPP V1 (RFA 19093), Section I.

Section J: Sample Handling and Custody Requirements

Data contained in LEE Generic QAPP V1 (RFA 19093) Section J.

Section K: Analytical Sensitivity and Project Criteria

The form K tables (Appendix 3) were compiled based on the project's sampling design, analytical requirements, and relevant regulatory criteria. The criteria have been checked to verify that the numbers presented herein are current. The shaded compounds / media / regulatory criteria have one or more applicable regulatory criteria below the laboratory reporting limit. Based on review of these criteria and the project's scope and context, LEE does not believe that the highlighted entries will impede analysis of the data because these compounds are not likely to occur in isolation and are more likely to be associated with other similar compounds.

Section L: Field Quality Control Requirements

Field quality control measures are included in Section F per guidance presented in LEE's Generic QAPP document (RFA 19093), Section L.

Section M: Laboratory Quality Control Requirements

Laboratory quality control requirements are included in laboratory SOPs presented in LEE's Generic QAPP document (RFA 19093), Exhibit 2.

Section N: Data Management and Documentation

Data management and documentation requirements are presented in LEE's Generic QAPP document (RFA 19093), Section N.

Section O: Assessment and Response Actions

Assessment and Response Actions are presented in LEE's Generic QAPP document (RFA 19093), Section O.

Section P: Project Reports

Upon receipt of the laboratory data, a report will be prepared to address data usability and any sampling problems or modifications and will provide a quality assurance and quality control of the field and laboratory data collected and received. The report will include the specific sample locations, field observations, laboratory data summary tables, contaminant distribution maps, and conclusions relating to soil and groundwater. Reports will be submitted to the DEC and the EPA Project Officer for review.

Section Q: Field Data Evaluation

The project manager and QA reviewer will evaluate field data collected during assessment and cleanup activities. The field data will be reviewed for accuracy, completeness, precision and compliance with LEE SOP requirements and site-specific QAPP addendum work scope requirements. The evaluation will be documented in the project quality assurance report, which will be an appendix or attachment to the project report.

Section R: Laboratory Data Evaluation

The laboratory analytical results will be verified by the QA reviewer per LEE Generic QAPP (RFA 19093) Section R.

Section S: Data Usability and Project Evaluation

Assessment of data usability will be performed per LEE Generic QAPP (RFA 19093) Section S.

APPENDIX 1

SITE LOCATION MAP

Neenah Northeast LLC
161 Wellington Road, Brattleboro, Vermont

LE Environmental

2018 USGS Map

LE #: 18-122
Date: December 4, 2018
Source: USGS Store

APPENDIX 2

BROWNFIELDS CORRECTIVE ACTION INVESTIGATION SITE MAPS

Photographic Documentation
Overflow Lagoon Sampling Locations
Long Falls Paper
161 Wellington Road, Brattleboro, VT
LEE #18-122

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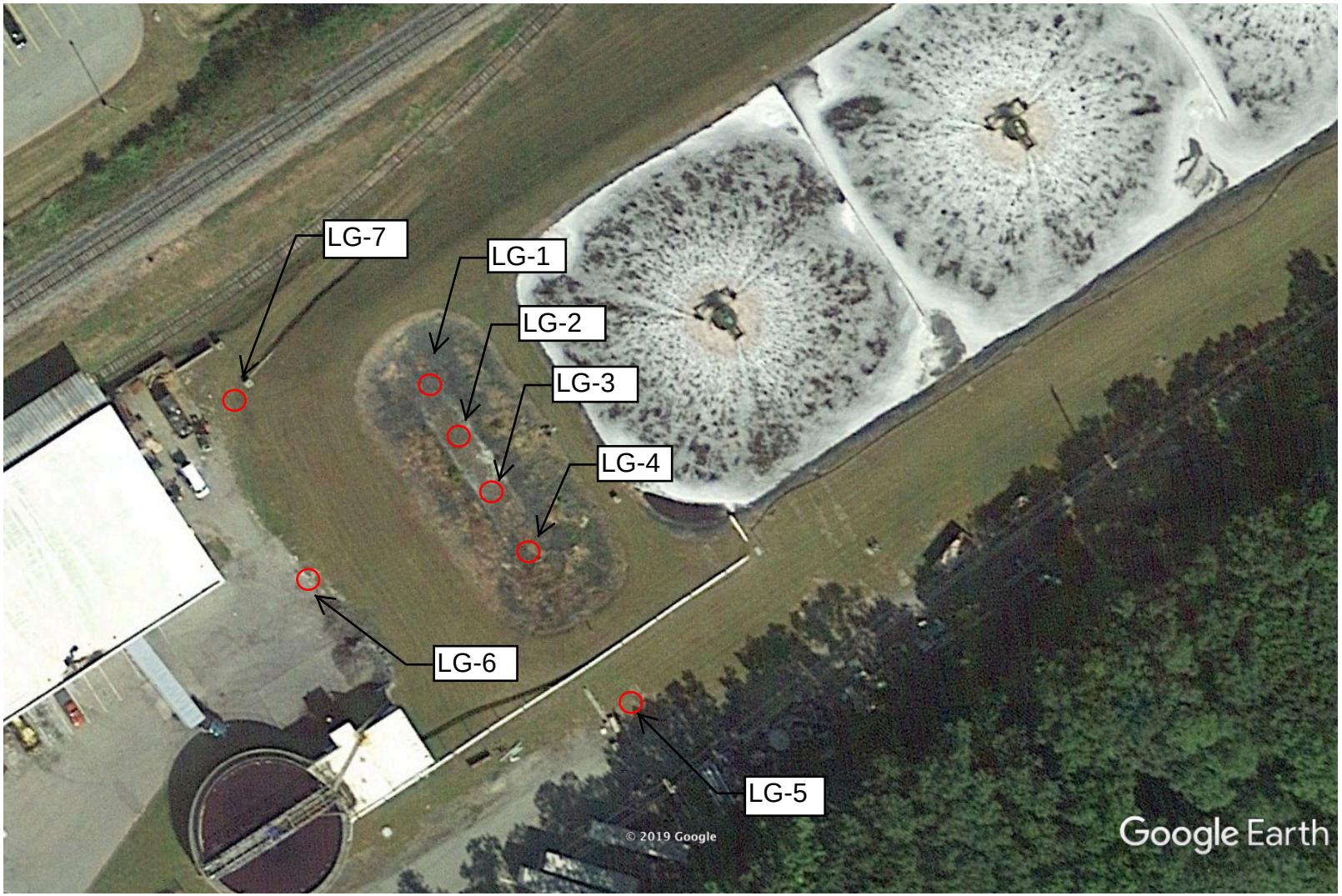

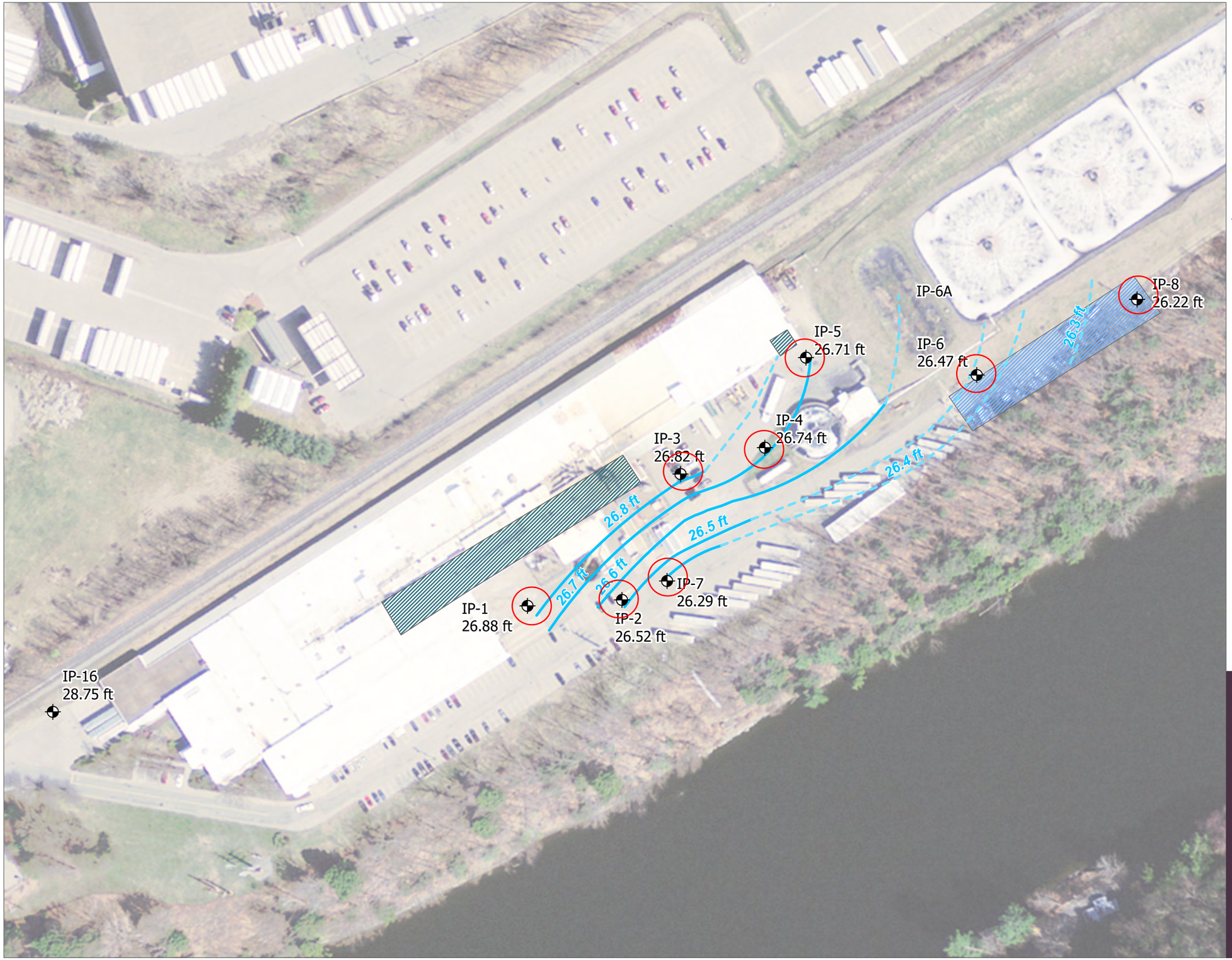

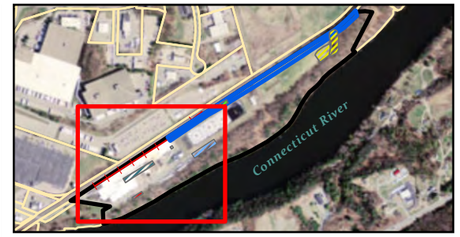

N

0 110 220

Feet

LEGEND

- Groundwater Sample Location
- Groundwater Depth Contour
- Estimated Groundwater Depth Contour

Site Features

- Outdoor Equipment Area
- BasementArea
- Existing well to be sampled for PFAs (annoation by LEE)

Source: Imagery - Esri World Imagery; Sample Locations and Groundwater Depths - Stone Environmental

Path: O:\PROJ-19\EAR\19-015 Long Falls Paper Phase II ESA\GIS\MapDocuments\PresentationsAndReports\19-015 Long Falls Paper Phase II ESA\19-015 Long Falls Paper Phase II ESA.aprx Fig 6 GW Contour Map Exported:

Figure 6 Groundwater Surface Contours

Long Falls Paperboard Phase II Environmental Site Assessment

Prepared For Vermont Department of Environmental Conservation

STONE ENVIRONMENTAL

APPENDIX 3

FORM K TABLES

Brownfields Phase II Environmental Site Assessment
Analytical Sensitivity and Project Criteria (Form K) Tables
Long Falls Paperboard
161 Wellington Road, Brattleboro, Vermont

Soil Analyte Category/Compound	*Reporting Limit*	*EPA Industrial RSL*	*VSS Non-Residential*
VOCs, EPA Method 8260C (mg/kg)			
Dichlorodifluoromethane	0.02	370	-
Chloromethane	0.01	460	-
Vinyl Chloride	0.0	-	0.59
Bromomethane	0.01	30	-
Chloroethane (ethyl chloride)	0.02	57,000	-
Trichlorofluoromethane	0.01	350,000	-
Diethyl Ether	0.02	-	-
Acetone	0.1	-	100,028
1 ,1-Dichloroethene	0.002	1,000	-
Methylene chloride	0.001	1,000	-
Carbon disulfide	0.006	-	662
MTBE	0.004	-	4,464
trans-1,2-Dichloroethene	0.002	-	18,137
1,1-Dichloroethane	0.00	-	13
2,2-Dichloropropane	0.002	-	-
cis-1,2-Dichloroethene	0.002	-	1,814
2-Butanone (MEK)	0.04	-	26,991
Bromochloromethane	0.002	-	597
Tetrahydrofuran(THF)	0.01	-	-
Chloroform	0.004	1.4	-
1,1,1-Trichloroethane	0.002	36,000	-
Carbon tetrachloride	0.002	-	2.2
1 ,1-Dichloropropene	0.002	-	-
Benzene	0.002	-	4.2
1,2-Dichloroethane	0.002	-	1.7
Trichloroethene (TCE)	0.002	-	6.5
1,2-Dichloropropane	0.002	-	9.1
Dibromomethane	0.002	99	-
Bromodichloromethane	0.002	1.3	-
4-Methyl-2-pentanone(MIBK)	0.02	140,000	-
cis-1,3-Dichloropropene	0.001	8.2	-
Toluene	0.002	-	798
trans-1,3-Dichloropropene	0.001	8.2	-
1,1,2-Trichloroethane	0.002	5	-
2-Hexanone	0.02	1,300	-
Tetrachloroethene (PCE)	0.002		14
1,3-Dichloropropane	0.001	23,000	-
Dibromochloromethane	0.001	39	-
1,2-Dibromoethane(EDB)	0.001	-	0.14
Chlorobenzene	0.002	-	726

NOTES:
Vermont Soil Standards (VSS) and Statewide Background Concentrations from July 2019 DEC I-Rule
EPA Regional Screening Levels (RSLs) from April 2019 RSL Summary Table. RSLs not included when a VSS exists.
Blank Cell=no published value (VSS) or published value not applicable (RSL)

Brownfields Phase II Environmental Site Assessment
Analytical Sensitivity and Project Criteria (Form K) Tables
Long Falls Paperboard
161 Wellington Road, Brattleboro, Vermont

Soil Analyte Category/Compound	*Reporting Limit*	*EPA Industrial RSL*	*VSS Non-Residential*
VOCs, EPA Method 8260C (mg/kg) (continued)			
1,1,1,2-Tetrachloroethane	0.001	8.8	-
Ethylbenzene	0.002	-	22
mp-Xylene	0.004	-	257
o-Xylene	0.002	-	
Styrene	0.002	35,000	-
Bromoform	0.002	86	-
IsoPropylbenzene (cumene)	0.002	-	264
Bromobenzene	0.002	1,800	-
1,1,2,2-Tetrachloroethane	0.001	2.7	-
1,2,3-Trichloropropane	0.002	-	0.07
n-Propylbenzene	0.002	-	261
2-Chlorotoluene	0.002	23,000	-
4-Chlorotoluene	0.002	23,000	-
1,3,5-trimethylbenzene	0.002	-	177*
tert-Butylbenzene	0.002	-	102,200
1,2,4-trimethylbenzene	0.002	-	177*
sec-Butylbenzene	0.002	-	102,200
1,3-Dichlorobenzene	0.002	-	-
p-Isopropyltoluene (p-cymene)	0.002	-	-
1,4-Dichlorobenzene	0.002	11	-
1,2-Dichlorobenzene	0.002	9,300	-
n-Butylbenzene	0.002	-	51,100
1,2-Dibromo-3-chloropropane	0.002	0.064	-
1,2,4-Trichlorobenzene	0.002	110	-
Hexachlorobutadiene	0.002	5.3	-
Naphthalene	0.004	-	16
1,2,3-Trichlorobenzene	0.002	930	-

NOTES:
Vermont Soil Standards (VSS) and Statewide Background Concentrations from July 2019 DEC I-Rule
EPA Regional Screening Levels (RSLs) from April 2019 RSL Summary Table. RSLs not included when a VSS exists.
"*" means standard is for sum of TMBs
Dashed Cell=no published value (VSS) or published value not applicable (RSL)

Brownfields Phase II Environmental Site Assessment
Analytical Sensitivity and Project Criteria (Form K) Tables
Long Falls Paperboard
161 Wellington Road, Brattleboro, Vermont

Soil Analyte Category/Compound	*Reporting Limit*	*EPA Industrial RSL*	*VSS Non-Residential*
PAH EPA Method 8270D (mg/kg)			
Naphthalene	0.17	-	16
2-Methylnaphthalene	0.17	3,000	-
1-Methylnaphthalene	0.17	73	-
Acenaphthylene	0.17	-	-
Acenaphthene	0.17	45,000	-
Fluorene	0.17	-	26,371
Phenanthrene	0.17	-	-
Anthracene	0.17	230,000	-
Fluoranthene	0.17	-	26,371
Pyrene	0.17	23,000	-
Benzo(a)anthracene	0.17	21	-
Chrysene	0.17	2,100	-
Benzo(b)fluoranthene	0.17	21	-
Benzo(k)fluoranthene	0.17	210	-
Benzo(a)pyrene	0.17		1.54 (0.58 bkgd)
Indeno(1,2,3-cd)pyrene	0.17	21	-
Dibenz(a,h)anthracene	0.17	2.1	-
Benzo(g,h,i)perylene	0.17	-	-
POLYCHLORINATED DIOXIN (ng/kg, as TEQ)			
Tetrachlorodibenzo-p-dioxin, 2,3,7,8-TCDD)	0.5	-	13.7
TOTAL METALS, EPA Method 6020 (mg/kg, dry)			
Total Arsenic	2.5	-	16
Total Barium	2.5	-	127,382
Total Cadmium	0.25	-	87
Total Chromium	0.5	-	360,223
Total Lead	0.75	-	800
Total Mercury	0.025	-	3.1
Total Selenium	5	5,800	-
Total Silver	5	-	2,483
Total Vanadium	1	-	27
PCBS, EPA Method 8082 (mg/kg, dry)			
Aroclor-1016	0.02	27	-
Aroclor-1221	0.02	0.83	-
Aroclor-1232	0.02	0.72	-
Aroclor-1242	0.02	0.95	
Aroclor-1248	0.02	0.95	-
Aroclor-1254	0.02	0.97	-
Aroclor-1260	0.02	0.99	-
Aroclor-1262	0.02	-	-
Aroclor-1268	0.02	-	-
Total PCBs		-	0.68

NOTES:
Vermont Soil Standards (VSS) and Statewide Background Concentrations from July 2019 DEC I-Rule
EPA Regional Screening Levels (RSLs) from April 2019 RSL Summary Table. RSLs not included when a VSS exists.
Dashed Cell=no published value (VSS) or published value not applicable (RSL)

Brownfields Phase II Environmental Site Assessment
Analytical Sensitivity and Project Criteria (Form K) Tables
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Groundwater Analyte Category/Compound	*Reporting Limit (ug/l)*	*Vermont Groundwater Enforcement Standard (ug/l)*
PFAs, EPA Method 537.1		
Perfluorohexane sulfonic acid (PFHxS)	0.001	0.020
Perfluoroheptanoic acid (PFHpA)	0.001	
Perfluorononanoic acid (PFNA)	0.001	
Perfluorooctanesulfonic acid (PFOS)	0.001	
Perfluorooctanoic acid (PFOA)	0.001	

NOTES:
Groundwater Enforcement Standard from Vermont Groundwater Protection Rule 7/19
VGES applies to the sum of all listed PFAs concentrations
Reporting Limits above standards are shaded

Brownfields Phase II Environmental Site Assessment
Analytical Sensitivity and Project Criteria (Form K) Tables
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Regulated Waste Parameter-TCLP	*Reporting Limit TCLP (mg/l)*	EPA/DEC TCLP Threshold (mg/l)
Arsenic	0.005	5.0
Barium	0.05	100.0
Benzene	0.001	0.5
Cadmium	0.004	1.0
Carbon tetrachloride	0.040	0.5
Chlordane	0.003	0.03
Chlorobenzene	0.040	100.0
Chloroform	0.040	6.0
Chromium	0.01	5.0
o-Cresol (2-methylphenol)	0.010	200.0
m-Cresol (3-methylphenol)	0.010	200.0
p-Cresol (4-methylphenol)	0.010	200.0
Cresol (total)	0.010	200.0
2,4-D	0.2	10.0
1,4-Dichlorobenzene	0.010	7.5
1,2-Dichloroethane	0.040	0.5
1 ,1-Dichloroethene	0.040	0.7
2,4-Dinitrotoluene	0.010	0.13
Endrin	0.0005	0.02
Heptachlor/Heptachlor Epoxide	0.0005	0.008
Hexachlorobenzene	0.010	0.13
Hexachlorobutadiene	0.010	0.5
Hexachloroethane	0.010	3.0
Lead	0.01	5.0
Lindane	0.0005	0.4
Mercury	0.025	0.2
Methoxychlor	0.0005	10.0
2-Butanone(MEK)	0.200	200.0
Nitrobenzene	0.010	2.0
Pentachlorophenol	0.050	100.0
Pyridine	0.010	5.0
Selenium	0.05	1.0
Silver	0.05	5.0
Tetrachloroethene (PCE)	0.040	0.7
Toxaphene	0.005	0.5
Trichloroethene (TCE)	0.040	0.5
2,4,5-Trichlorophenol	0.010	400.0
2,4,6-Trichlorophenol	0.010	2.0
2,4,5-TP Silvex	0.1	1.0
Vinyl Chloride	0.040	0.2

Brownfields Phase II Environmental Site Assessment
Analytical Sensitivity and Project Criteria (Form K) Tables
Long Falls Paperboard
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Regulated Waste Parameter-PCBs	*Reporting Limit (mg/kg)*	EPA/DEC HW Threshold (mg/kg)
Aroclor - 1016	0.02	50 (total)
Aroclor - 1221	0.02	
Aroclor - 1232	0.02	
Aroclor - 1242	0.02	
Aroclor - 1248	0.02	
Aroclor - 1254	0.02	
Aroclor - 1260	0.02	
Aroclor - 1262	0.02	
Aroclor - 1268	0.02	

Regulated Waste Parameter-Other		EPA/DEC HW Threshold (mg/kg)
pH	0.01 SU	$\leq$2 or $\geq$10
Ignitibility/Flashpoint	Pass/Fail	Pass/Fail

NOTES:
TCLP Thresholds from EPA Hazardous Waste Characteristics, October 2009 and Vermont DEC Hazardous Waste Management Regulations, December 31, 2016

APPENDIX 4

STANDARD OPERATING PROCEDURES

Document Title: LEE Standard Operating Procedure N:
Preparation and Procedures for Collection of Samples for Per- and polyfluoroalkyl substances (PFAs) Analysis

Prepared by: _____

Reviewed/Approved by: _____

Date: February 13, 2020

1.0 Scope and Application

This standard operating procedure specifies the purpose, qualifications, equipment, supplies, and procedures to be employed when collecting environmental media or waste samples for Per- and polyfluoroalkyl substances (PFAs). The procedures and other aspects of this standard operating procedure will be the sole means of accomplishing the tasks described herein during work on all LEE projects, unless an alternate methodology is specified in an approved project work plan.

2.0 Purpose

The purpose of this standard operating procedure is to standardize the described procedures to enhance reproducibility, accuracy and precision among multiple users. This standard operating procedure addresses user qualifications, equipment, supplies, and procedures.

3.0 User Qualifications

This standard operating procedure will be implemented only by personnel who have 40-hour OSHA training (29 CFR 1910.120), in addition to in-house training regarding use of the required equipment.

4.0 Procedure

This standard operating procedure will be used in conjunction with LEE SOPs A (soil sampling), B (Soil borings, groundwater monitoring well installation and low flow groundwater sampling) and L (Drinking water sampling). The procedures, supplies, equipment and preparation described in this SOP should be utilized on any Site where PFAs monitoring could take place.

5.0 Supplies

Plain paper clipboards and sharpie markers are acceptable data collection media for PFAs sampling. Avoid waterproof or treated paper or field books, plastic clipboards, non-sharpie markers, post-it notes or other adhesive paper products.

The most inert material (for example, stainless steel, silicone, and HDPE), with respect to known or anticipated contaminants in wells should be used whenever possible. When feasible, use single-use, disposable polyethylene or silicone materials (tubing, bailers, etc.) for monitoring well purging and

sampling equipment. When reuse of materials or sampling equipment across multiple sampling locations is necessary, follow project decontamination protocols with allowed materials (Alconox and liquinox are acceptable), and incorporate collection of equipment rinseate blanks into sampling program, as appropriate. When using positive displacement/submersible pump sampling equipment, familiarize yourself with the sampling pump/accessory equipment specifications to confirm that device components are not made of nor contain Teflon® or PTFE.

Most core and grab sampling devices are constructed of stainless steel. Some core samplers include an HDPE sleeve inserted in the core barrel to retain the sample. Ensure that materials that contact the media to be sampled do not have water-resistant coatings that contain PFAS.

Materials to avoid include:

- Teflon, polytetrafluoroethylene (PTFE)
- waterproof coatings containing PFAS
- food containers
- anything with fluoro in the name
- fluorinated ethylene propylene (FEP)
- ethylene tetrafluoroethylene (ETFE)
- low density polyethylene (LDPE), polyvinylidene fluoride (PVDF)

Many waterproof coatings contain PFAS, such as Gore-tex treated PPE or most waterproof papers, but some products are waterproofed with acceptable materials such as polyurethane, rubber, or PVC. Individual product specifications should be examined closely. In the case of Tyvek PPE, plain Tyvek does not contain PFAS while coated Tyvek does. In addition, materials incidentally transported to sites may contain PFAS. For example, fast food wrappers may contain PFAS. Due to the ubiquitous nature of PFAS, sampling crews must review all materials used to avoid contamination. Collection of quality assurance and quality control (QA/QC) samples is a useful tool to assess field contamination.

6.0 Operation

Wear synthetic or cotton material, previously laundered more than six times without the use of fabric softeners. Avoid clothing or boots made of or with Gore Tex, or other synthetic water resistant and or stain resistant, and Tyvek. Avoid cosmetics, moisturizers, hand cream or other related products. Avoid pre-packaged food, fast food wrappers, or containers.

Using new nitrile gloves collect the sample for PFCs ***first***, prior to collecting samples for any other parameters into any other containers; this avoids contact with any other type of sample container, bottles or package materials. As with all other samples, do not place the sample bottle cap on any surface when collecting the sample, and avoid all contact with the inside of the sample bottle or its cap. When sample is collected and capped, place the sample bottle(s) in an individual sealed plastic bag (e.g. Ziploc®) separate from all other sample parameter bottles, and place in shipping container packed only with ice.

7.0 References

a) Interstate Technology Regulatory Council, Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for per-and Polyfluoroalkyl Substances, March 2018.
b) New Hampshire Department of Environmental Services, PerFluorinated Compound Sample Collection Guidance, November 2016.

VOLATILE ORGANICS BY GC/MS

(Method EPA 8260C/D)

Approved:

Tod Kopyscinski
Laboratory Director

Katherine F. Allen
QA Officer

Revision Number: 13

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Change Record

Revision	Date	Responsible Person	Description of Change
2	04/30/2003	M. Flahive/ S. Kocot	Updates for NELAC format and MCP requirements
3	11/18/03	D. Damboragian	See Section 8.2.4.6 - method for data acquisition when a lower DL is needed
4	09/07/05	DDamboragian /Trillium	Update 2004 AZ audit
5	10/12/2009	J. Morrow/ F. Derose	Updated for annual review and edits; Sec1.0 (compounds removed from list and added.) Sec2.0 (vol. change to water.) Sec5.0 (GC column changed to 20m.) Sec6.0(vol. changes and tables updated.) Sec8.0 (LCS/LCSD added to time 0, "soil only" statements removed, and vol. changes to diluted samples.) Sec10.0 (vol. changes.), Sec13.0(poll. prev. added). Updates for Method 8260B, 8260C, MCP, and RCP protocols.
6	08/25/2010	Tim Reid	Updates from July 2010 NY Audit and new CAM for MCP: Sec 2.0 (deletion of solid samples are placed in the sparger with water"), Sec. 5.0 (equipment update), Sec. 6.4 (reagent change), Sec. 6.7.2.1 (light gases added), Sec. 6.8 (addition of 200ppb Std.), Sec's 8.4.2, 8.4.4, and 10.2.1 (procedural change), Sec. 9.6 (additions), Sec's 10.2.2 and 10.2.3 (changes from new MA MCP), and Sec. 15.0 (ref. addition of new MCP).
7	5/29/12	Tim Reid	Updated stock standard solution table in Section 6.7.2 Updated water calibration levels in table in Section 6.8 Updated stock standard solution table in Section 6.9 Changed Flow rate in Section 8.3.1.1 to 40ml/min Updated High Level Soil calibration concentrations in Section 10.2.2
8	7/25/2013	Fran Derose	Updates from recent Internal Audit: Sec. 6.9 (diff cat #), Sec. 8.3.1 (parameter changes), sec. 8.4.3 (record in 8260 soil prep log) and for frozen samples to warm up to room temp before analysis)), Sec. 8.4.4(record in 8260 soil log), Sec 15.0 (addition of compositing section), Sec. 16.0 (deletion of old MCP ref and addition of 5030C ref.)
9	3/24/2015	Katherine Allen	Updates from annual review: Sec 1.0 (addition of cis1,4-DC-2-B), Sec 5.3 (addition of windows 7), Sec 8.3.3.3 (new temp range), Sec 8.4.4 (surrogate added through auto-sampler),and Sec 10.2.2 (7 pt curve not 10).
10	09/20/16	Katherine Allen	Updates from annual internal audit: Sec 5.0 (addition of Tekmar Teledyne conc/autosampler), Sec 6.7.2 (updated table), addition of Sec 6.10 (Internal standard/surrogate recipes), Sec 8.4 (addition of TEKMAR operating conditions), Sec 8.5.1 and 8.5.2 (1.0uL of IS/Surr added by Arcon and 5.0uL of IS/Surr added by Centurion added) and Sec 16.0 (addition of Tekmar and Centurion manuals).
11	01/18/18	Cathy Rouleau	Update from 2017 NY Audit: Sec 10.2.7 (Matrix match LCS)
12	01/03/19	Cathy Rouleau	Update to include method SW-846 8260D: 8.1.2 Note BFB only before ICAL; 8.2.2 174<200%; 10.2.2 &.3 -Remove 8260B and 8260D.;10.2.7 LCS can be same source as curve or 8260D.; 10.3-80% Library match, and addition of, 8260D reference in Sec 16.17.
13	03/27/19	KFA	Update from annual internal audit: Sec 6.7.2 (deletion of standards not used) and Sec 6.9 (updates to QC standards used).

Distribution/Training List

See Employee Training Record File for signed training statements for trained users.

1.0 SCOPE AND APPLICATION

This method is used to determine volatile organic compounds in a variety of matrices. Method 8260 is applicable to nearly all types of samples including groundwater, soils, sediment, sludges, TCLP extracts, waste solvents, oils and other solid waste matrices.

The following compounds can be determined by this method:

1,1,1,2-TETRACHLOROETHANE	CHLOROFORM
1,1,1-TRICHLOROETHANE	CHLOROMETHANE
1,1,2,2-TETRACHLOROETHANE	CIS-1,2-DICHLOROETHENE
1,1,2-TRICHLOROETHANE	CYCLOHEXANE
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE **"NR"**	CIS-1,3-DICHLOROPROPENE
1,1-DICHLOROETHANE	DIBROMOCHLOROMETHANE
1,1-DICHLOROETHENE	DIBROMOMETHANE
1,1-DICHLOROPROPENE	DICHLORODIFLOUROMETHANE
1,2,3-TRICHLOROBENZENE	DIETHYL ETHER
1,2,3-TRICHLOROPROPANE	DIFLUOROCHLOROMETHANE
1,2,4-TRICHLOROBENZENE	DIISOPROPYL ETHER
1,2,4-TRIMETHYLBENZENE	ETHYL ACETATE
1,2-DIBROMO-3-CHLOROPROPANE	ETHYLBENZENE
1,2-DIBROMOETHANE	ETHYL TERT-BUTYL ETHER
1,2-DICHLOROBENZENE	FLUORODICHLOROMETHANE
1,2-DICHLOROETHANE	HEXACHLOROBUTADIENE
1,2-DICHLOROETHENE (TRANS)	IODOMETHANE
1,2-DICHLOROPROPANE	ISOPROPYLBENZENE
1,3,5-TRICHLOROBENZENE	METHYLCYCLOHEXANE
1,3,5-TRIMETHYLBENZENE	METHYL ACETATE
1,3-DICHLOROBENZENE	M/P-XYLENES
1,3-DICHLOROPROPANE	METHYL TERT-BUTYL ETHER(MTBE)
1,4-DICHLORO-2-BUTENE (trans) **"NR"**	METHYLENE CHLORIDE
1,4-DICHLORO-2-BUTENE (cis) "NR"	
1,4-DICHLOROBENZENE	METHYL ISOBUTYL KETONE (MIBK)
1,4-DIOXANE	NAPHTHALENE
2,2-DICHLORPROPANE	O-XYLENE
2-BUTANONE (METHYL ETHYL KETONE, MEK)	P-ISOPROPYLTOLUENE
2-CHLOROTOLUENE	PROPYLBENZENE
2-HEXANONE	SEC-BUTYLBENZENE
4-CHLOROTOLUENE	STYRENE
ACETONE	TERT-AMYL METHYL ETHER
ACRYLONITRILE **"NR"**	TERT BUTYL ALCOHOL **"NR"**
BENZENE	TERT-BUTYLBENZENE
BROMOBENZENE	TETRAHYDROFURAN
BROMOCHLOROMETHANE	TETRACHLOROETHENE
BROMODICHLOROMETHANE	TOLUENE
BROMOFORM	TRANS-1,3-DICHLOROPROPENE
BROMOMETHANE	TRICHLOROFLUOROMETHANE
BUTYL-BENZENE	TRICHLOROETHENE
CARBON DISULFIDE	VINYL ACETATE
CARBON TETRACHLORIDE	VINYL CHLORIDE
CHLOROBENZENE	
CHLOROETHANE	

"NR" = not required for Massachusetts Contingency Plan (MCP).

2.0 SUMMARY OF METHOD

Helium is bubbled through a 5-ml water sample at ambient temperatures. The volatiles are transferred from the aqueous phase to the vapor phase, and are swept through a sorbent trap where the volatiles are trapped. After purging is completed, the trap is heated and backflushed with helium to desorb the volatiles onto the gas chromatographic column. The gas chromatograph is temperature-programmed to separate the volatiles which are then detected with a mass spectrometer. Solid samples are analyzed via procedures outlined in Methods 5030b/c and 5035(A). Samples can be handled in a closed loop system according to Method 5035 (A).

3.0 INTERFERENCES

- Purge gas contamination
- Sample contamination due to septum diffusion
- Cross contamination
- Column contamination: bake
- Trap contamination: bake
- Purge and trap system contamination: wash purging chamber, bake out spargers, extended dry purges

4.0 SAMPLE PRESERVATION/STORAGE/HOLDING TIME

MATRIX	CONTAINER	PRESERVATION	HOLDING TIME*
Aqueous Samples	(3) 40-mL VOC vials w/Teflon-lined septa screw caps	Add 3-4 drops of 1:1 HCl (to pH<2); cool to 4°C	14 days
Soil/Sediment Samples ***High-Level Analysis*** **(SW-846-5035/5030)**	Vials w/Teflon-lined septa screw caps. (1) 40-mL vial	1 mL purge-and-trap grade methanol for every gram soil/sediment; cool to 4°C; protect from light	14 days
Soil/Sediment Samples ***Low-Level Analysis*** **(SW-846-5035)**	(2) 40-mL glass vials w/Teflon-lined septa screw caps	5grams soil to5 mL sodium bisulfate solution, Teflon-coated magnetic stir bar; cool to 4°C; protect from light; **OR** Freeze sample in vial (containing 5 mLs of purged DI water) within 48 hours of collection.	14 days
*Holding time begins from time of sample collection.			

5.0 EQUIPMENT & SUPPLIES

5.1 Purge and trap systems:
- 5.1.1 EST Encon concentrator and EST Archon Autosampler (4)
- 5.1.2 EST Encon Evolution concentration and EST Centurion WS Autosampler (1)

5.2 GC/MS systems
- 5.2.1 HP 6890/HP5973 and
- 5.2.2 HP7890/HP5975

5.3 GC/MS data system: Windows NT or 2000 and Windows 7

5.4 GC column
- 5.4.1 Restek DB- 624 capillary 20 m, 0.18 mm ID, 1um thickness
- 5.4.2 Restek DB-VRX capillary 20m, 0.18mm ID, 1um thickness

5.5 Analytical Trap: VOCARB3000 or equivalent.

5.6 40-ml vials/cap and teflon silicone septum

5.7 Micro syringes

5.8 Volumetric glassware

5.9 Analytical balance; capable of accurately weighing 0.0001g

5.10 2-ml vials/caps and Teflon silicone septum

5.11 50mL Gastight Syringe

5.12 5mL Gastight Syringe

5.13 Teledyne Tekmar Atomx Autosampler/concentrator

6.0 REAGENTS & STANDARDS

6.1 Organic free water: distilled and purged with ultra high purity nitrogen for 30min.

6.2 Methanol: purge and trap grade

6.3 Ultra high purity helium: carrier and purge gas

6.4 Internal Standard/Surrogate Stock: Purchased as certified solutions from Agilent. IS solutions have a 6 month expiration date and should be refrigerated when not in use.

6.4.1 The internal standard stock solution (cat # STM-341N) contains pentafluorobenzene, d4-dichlorobenzene, chlorobenzene-d5, and 1.4-difluorobenzene-d4: all are at a concentration of 2000 ug/mL in methanol.

6.4.2 The surrogate stock solution (cat #STM-260) contains 4-bromofluorobenzene, 1, 2-dichloroethane-d4, and toluene-d8: all are at a concentration of 2500 ug/mL in methanol.

6.4.3 All client samples, blanks, and quality control samples contain the internal standard compounds at a concentration of 30ug/L and the surrogate standards at 25ug/L.

Note: 1.0 uL of the working internal standard/surrogate solution is added by the Archon Autosampler directly to all client samples, blanks, and quality control samples before purging is initiated.

Note: 5.0 uL of the working internal standard/surrogate solution is added by the Centurion WS Autosampler directly to all client samples, blanks, and quality control samples before purging is initiated.

Note: IS solutions have a 6-month expiration date and should be refrigerated when not in use.

6.7 GC/MS Volatile Organic Standards

6.7.2 The GC/MS VOA (8260) Working Stock is prepared from the following stocks:

Stock	Vendor	Stock Conc. (mg/mL)	uL Stock Added into 10 mLs MeOH	Working Stock Conc. (ug/mL)
M-8260-ADD-10X	AccuStandard	2.0	500	100
M-502	AccuStandard	2.0	50	10
M-8015B/5031-03	AccuStandard	10	100	100
S-17412-R2	AccuStandard	2/20	50	10/100
70174	Absolute	1	1000	100

6.7.2.1 Methanol solutions prepared from liquid analytes are stable for at least 4 weeks when stored at 4°C. Methanol solutions prepared from gaseous analytes are not stable for more than one week.

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 usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. The light gases including Dichlorodifluoromethane, Chloroethane, chloromethane, bromomethane and vinyl chloride 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 need to be replaced after six months 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.

6.7.2.2 All three xylene isomers will be included at a concentration of 0.5 ppb each in the low concentration initial calibration standard. The RL for each of the xylene isomers will be considered to be 0.5 ppb or the lowest standard in the initial calibration.
Note: m+p xylenes reported together (co-elute) (1.0 ppb RL) o-xylene reported separately (0.5 ppb R.L)

6.8 Calibration Standards: standard concentrations are prepped daily from the working solution.

For 8260 Water (Stock = 10ug/mL); 5mL of std. is purged on the autosampler:

Working Stock (uLs)	Final Volume D.I. water (mLs)	Final Conc. (ppb)
4uL	100mL	0.4ppb
5uL	100mL	0.5ppb
10uL	100mL	1.0ppb
20ul	100mL	2.0ppb
50uL	100mL	5.0ppb
100uL	100mL	10ppb
200uL	100mL	20ppb
100uL (50ug/mL)	100mL	50ppb
200uL (50ug/mL)	100mL	100ppb
400uL (50ug/mL)	100mL	200ppb

For 8260 Soil (Stock = 50ug/mL); 5mL of water is added to 5mL of std. before purge by the autosampler:

Working Stock (uLs)	Final Volume D.I. water (mLs)	Final Conc. (ppb)
4uL (10ug/mL)	100mL	0.2ppb
2uL (50ug/mL)	100mL	0.5ppb
4uL (50ug/mL)	100mL	1.0ppb
20uL (50ug/mL)	100mL	5.0ppb
40uL (50ug/mL)	100mL	10ppb
80uL (50ug/mL)	100mL	20ppb
10uL (50ug/mL)	5mL	50ppb
16uL (50ug/mL)	5mL	80ppb

Note: After the calibration standards are prepared in 100 mL volumetric flasks, they are transferred to 40-mL vials and placed into the Autosampler.

6.9 QC Check/LCS & Matrix Spike Stock

Stock	Vendor*	Cat # *	Stock Conc. ug/mL	uL Stock Added Into 10 mLs MeOH	Final Working Conc. (ug/mL)
VOC Mixture with MTBE	Agilent	DWM-596-1	2000	100	20
Custom Gas Mix	Ultra	CUS-28408	Various concentrations	100	20/200
Vinyl Acetate	RESTEK	30216	2000	1ml	200
Ethanol	RESTEK	30288	2000	1mL	200
Custom Mix	Agilent	CUS-28609	2000/20000	100	20/200

* Or equivalent.

6.10 Internal Standards/Surrogates

624/8260 H2O IS/SURR mix VOA 3,5+6

Stock	Vendor	Stock Conc. (mg/mL)	µL Stock added into 50mLs	Working Stock Conc. (µg/mL)
STM-341N(IS)	Ultra Scientific	2.0	750	30
STM-262(SURR)	Ultra Scientific	2.5	500	25

624/8260 H2O IS/SURR mix VOA 2

Stock	Vendor	Stock Conc. (mg/mL)	µL Stock added into 10mLs	Working Stock Conc. (µg/mL)
STM-341N(IS)	Ultra Scientific	2.0	750	150
STM-262(SURR)	Ultra Scientific	2.5	500	125

8260 Soil IS/SURR mix VOA 1

Stock	Vendor	Stock Conc. (mg/mL)	µL Stock added into 5mLs	Working Stock Conc. (µg/mL)
STM-341N(IS)	Ultra Scientific	2.0	750	300
STM-262(SURR)	Ultra Scientific	2.5	500	250

8260 Soil IS/SURR mix VOA 4

Stock	Vendor	Stock Conc. (mg/mL)	µL Stock added into 25mLs	Working Stock Conc. (µg/mL)
STM-341N(IS)	Ultra Scientific	2.0	750	60
STM-262(SURR)	Ultra Scientific	2.5	500	50

7.0 SAFETY

See Material Safety Data Sheets (MSDS's) and Con-Test Chemical Hygiene Plan.

8.0 PROCEDURE

8.1 Analysis Sequence

8.1.1 The order of analysis for each 12-hour analysis shift is as follows:

Time 0:	BFB Instrument Performance Check
	Calibration Verification Standard
	LCS/LCSD
	Method Blank
Last Reported Sample Runs at 12Hrs:	Samples

8.1.2 The last sample in the sequence must be injected within 12 hours of the time that the BFB instrument performance check was injected at the start of the sequence.

Note: For 8260D BFB is only required to pass before ICAL, not every 12 hours.

8.1.3 If more than 20 samples are run during any 12-hour shift, then additional batch QC samples must be analyzed to achieve an overall frequency of 5 percent (1 set of QCs and blank for every 20 samples) during each analysis shift.

8.1.4 The analysis sequence is documented on an analysis run log maintained by the analyst.

8.2 MS Calibration and Tuning

8.2.1 Auto tune with PFTBA with column temperature at 45 °C

8.2.2 Tune with 50ng of BFB with column temperature at 125 °C and meet the following criteria:

Mass	m/z abundance criteria
50	15 to 40% of Mass 95
75	30 to 60% of Mass 95
95	Base Peak, 100% relative abundance
96	5 to 9% of Mass 95
173	<2% of Mass 174
174	>50% but <200% of Mass 95
175	5 to 9% of Mass 174
176	>95% but <101% of Mass 174
177	5 to 9% of Mass 176

8.2.3 The mass spectrum of BFB that is evaluated against the acceptance criteria is obtained in the following manner: three scans (the peak apex and the scans immediately preceding and following the apex) are averaged, and a single scan no more than 20 scans prior to the BFB peak is subtracted. No part of the BFB peak itself may be background-subtracted.

8.2.4 The BFB relative abundance criteria must be met before any standards, site samples, or quality control samples are analyzed.

8.3 Default Archon/Centurion and Encon Instrument Conditions (VOA Instruments #1, 2, and 5)

8.3.1 Encon concentrator:

8.3.1.1 Flow rate: 40.0 ml/min.
8.3.1.2 Purge ready temp.: 35 °C
8.3.1.3 Purge time: 11min.
8.3.1.4 Desorb time: 1.0 min.
8.3.1.5 Desorb temp: 250 °C
8.3.1.6 Bake time: 8 min.
8.3.1.7 Bake temp: 260 °C
8.3.1.8 Dry Purge: 2 min.
8.3.1.9 Water Management: Ready – 40°C
Bake – 260°C

8.3.2 Archon Autosampler

8.3.2.1 Sample volume: 5 mL
8.3.2.2 Rinse volume: 5 ml (waters only).
8.3.2.3 # Rinses: 2 (waters only).
8.3.2.4 Syringe flushes: 1
8.3.2.5 Preheat temp: 40 (soils only).
8.3.2.6 Preheat time: 0.5 min (soils only).
8.3.2.7 Purge time: 11 min.
8.3.2.8 Desorb time: 0.5-1.0 min.

8.3.3 Gas Chromatogram

8.3.3.1 Injector temp.: 200 °C
8.3.3.2 Detector temp.: 230 °C
8.3.3.3 Interface temp: 180-230 °C (instrument dependent)
8.3.3.4 Oven equilibration time: 0.5min.
8.3.3.5 Column program: 45 °C for 3 min.,
Ramp at 15-28 °C/min.,
final temp. 210-220 °C for 1-2 min.
8.3.3.6 Run time: 12-15 min.
8.3.3.7 Splitless valve time: 0.0
8.3.3.8 Split flow: 50-90ml/min
8.3.3.9 Split ratio: 50-60:1

8.3.4 Mass Spec

8.3.4.1 Mass range: 35 to 300
8.3.4.2 Number of A/D samples: 16
8.3.4.3 Peak threshold: 10000
8.3.4.4 Threshold: 20 counts
8.3.4.5 Scan start time: 0.5-1.4 min.
8.3.4.6 The use of selected ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full EI spectra. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound, and compounds quantitated by SIM must be noted in the final report.

8.4 Default Tekmar Instrument Conditions (VOA Instruments #3 and 6)

8.4.1 Purge

8.4.1.1 Valve Oven Temp: 140°C
8.4.1.2 Transfer Line Temp: 140°C
8.4.1.3 Sample Mount temp: 90°C
8.4.1.4 Water Heater Temp: 90°C
8.4.1.5 Sample Vial Temp: 20°C
8.4.1.6 Sample Equilibrate Time: 0.00 min
8.4.1.7 Soil Valve Temp: 50°C
8.4.1.8 Standby Flow: 10mL/min

8.4.1.9 Purge Ready Temp: 40°C
8.4.1.10 Condensate Ready Temp: 45°C
8.4.1.11 Presweep Time: 0.25 min
8.4.1.12 Prime Sample Fill Volume: 3.0mL
8.4.1.13 Sample Volume: 5.0mL
8.4.1.14 Sweep Sample Time: 0.25 min
8.4.1.15 Sweep Sample Flow: 100mL/min
8.4.1.16 Sparge Vessel Heater: Off
8.4.1.17 Sparge Vessel Temp: 20°C
8.4.1.18 Prepurge Time: 0.00 min
8.4.1.19 Prepurge Flow: 0mL/min
8.4.1.20 Purge Time: 11.00 min
8.4.1.21 Purge Flow: 40mL/min
8.4.1.22 Purge Temp: 20°C
8.4.1.23 Condensate Purge Temp: 20°C
8.4.1.24 Dry Purge Time: 0.50 min
8.4.1.25 Dry Purge Flow: 100mL/min
8.4.1.26 Dry Purge Temp: 20°C

8.4.2 Desorb

8.4.2.1 Methanol Needle Rinse: Off
8.4.2.2 Methanol Needle Rinse Volume: 3.0mL
8.4.2.3 Water Needle Rinse Volume: 7.0mL
8.4.2.4 Sweep Needle Time: 0.25 min
8.4.2.5 Desorb Preheat Temp: 245°C
8.4.2.6 GC Start Signal: Start of Desorb
8.4.2.7 Desorb Time: 1.00 min
8.4.2.8 Drain Flow: 250mL/min
8.4.2.9 Desorb Temp: 250°C

8.4.3 Bake

8.4.3.1 Methanol Glass Rinse: Off
8.4.3.2 Number of Methanol Glass Rinses: 1
8.4.3.3 Methanol Glass Rinse Volume: 3.0mL
8.4.3.4 Number of Water Bake Rinses: 1
8.4.3.5 Water Bake Rinse Volume: 7.0mL
8.4.3.6 Bake Rinse Sweep Time: 0.25 min
8.4.3.7 Bake Rinse Sweep Flow: 100mL/min
8.4.3.8 Bake Rinse Drain Time: 0.40min
8.4.3.9 Bake Time: 8.00 min
8.4.3.10 Bake Flow: 200mL/min
8.4.3.11 Bake Temp: 280°C
8.4.3.12 Condensate Bake Temp: 200°C

8.5 Sample Preparation and Analysis

8.5.1 Low level water samples

Low level water samples need no preparation. 5 mL of the sample is transferred from the 40mL vial and transferred to the concentrator. Internal standards and surrogates are added by the autosampler. 1.0uL of IS/Surr standard is added by the Archon AS or 5.0uL of IS/Surr standard is added by the Centurion AS.

8.5.2 High level water samples

High level water samples are diluted in a volumetric flask by analyst. The diluted sample is then transferred to a 40 ml VOA vial. 5 mL of the sample is transferred from the 40mL vial and to the concentrator for analysis. Internal standards and surrogates are added by the autosampler. 1.0uL of IS/Surr standard is added by the Archon AS or 5.0uL of IS/Surr standard is added by the Centurion AS.

8.5.3 Low level soils

If low level soil samples are not preserved then lab analyst will weigh samples to nearest 0.1 gram using approximately 5 grams and record in the 8260 soil prep log.

OR

Method 5035A: Low concentration soil method (generally applicable to soils and other solid samples with VOC concentrations in the range of 0.5 to 200 ug/kg).

Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample, weighed in the field at the time of collection, and placing it in a pre-weighed vial with a septum-sealed screw-cap that already contains sodium bisulfate preservative solution. The vial is sealed and shipped to a laboratory or appropriate analysis site. The entire vial is then placed, unopened, into the instrument carousel. Immediately before analysis, organic-free reagent water, surrogates, and internal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40 degrees C and the volatiles purged into an appropriate trap using an inert gas. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

Method 5035A Low concentration soil method for frozen soil samples.

Samples are taken in the field with DI vials provided by the lab and then vials are frozen within 48 hours. These vials are sampled with approximately 5 grams; same procedure as the above 5035. Frozen samples are to be allowed to warm up to room temperature for ~ 30 minutes prior to analysis.

8.5.4 High level soils/wastes/oils

High level samples are extracted with methanol in a 40 mL vial. Samples are weighed, between 0.1g and 10g, recorded in the 8260 soil prep log, (to the nearest 0.1g) in a 40 mL vial and 15mls of purge&trap methanol are added. 1mL of surrogate solution is added through the septum, using a 1mL syringe, when requested by client, otherwise surrogate is added through the auto-sampler. The sample is shaken for two minutes and allowed to settle. After settling a portion of the methanol extract, between 5uL and 500 uL is added to a final volume of 100mL. (Varied amounts depending on sample

matrix) and Transfer 40mL to VOA vial. 5 mL of the sample is transferred from the 40mL vial and transferred to the concentrator. Internal standards and surrogates are added by the autosampler. *Note: the amount of sample used and the amount of extract analyzed may vary depending on the expected concentration of the sample.*

OR

Method 5035A: High concentration soil method (generally applicable to soils and other solid samples with VOC concentrations greater than 200 ug/kg).

Samples are preserved in preweighed vials containing methanol in the field. Analysis proceeds as above.

The low level sample introduction technique listed above is not applicable to all samples, particularly those containing high concentrations (generally greater than 200 ug/kg) of VOCs which may overload either the volatile trapping material or exceed the working range of the determinative instrument system. In such instances, this method describes two collection options and the corresponding sample purging procedures.

1. The first option is to collect a bulk sample in a vial or other suitable container without the use of preservative solution. A portion of that sample is removed from the container in the laboratory and is dispersed in a water-miscible solvent to dissolve the volatile organic constituents. An aliquot of the solution is added to 5 mL of reagent water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using Method 5030, and analyzed by an appropriate determinative method. Because the procedure involves opening the vial and removing a portion of the soil, some volatile constituents may be lost during handling.

2. The second option is to collect an approximately 15-g sample in a pre-weighed vial with a septum-sealed screw-cap that contains 15 mL methanol. At the time of analysis, an aliquot of the solvent is removed from the vial, diluted w/ H20, and purged using Method 5030 and analyzed by an appropriate determinative method.

High concentration oily waste method (generally applicable to oily samples with VOC concentrations greater than 200 ug/kg that can be diluted in a water-miscible solvent).

Samples that are comprised of oils or samples that contain significant amounts of oil present additional analytical challenges. This procedure is generally appropriate for such samples when they are soluble in a water-miscible solvent.

8.5.5 TCLP extracts

The TCLP extract is diluted 10x with zero headspace in a 40 ml VOA vial. 5 mL of the sample is transferred from the 40mL vial and transferred to the concentrator. Internal standards and surrogates are added by the autosampler.

9.0 CALCULATIONS

9.1 Water Samples

Sample concentration, ppb = (direct reading from instrument) X (dilution factor, if any dilutions were required).

9.2 Soil Samples

$$\frac{\text{(ug/L from instrument) X (0.010 L sparger volume)}}{\text{(g/mL, from sample prep) X (mL of sample used)}} = \text{ug/gram} = \text{mg/Kg (ppm)}$$

9.3 Internal Standard Calculation from Response Factor 8260 Method:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:

A_s = Peak area (or height) of the analyte or surrogate.

A_{is} = Peak area (or height) of the internal standard.

C_s = Concentration of the analyte or surrogate.

C_{is} = Concentration of the internal standard.

9.4 When performing manual integration of any peak in a calibration standard, client sample, or quality control sample, the integration must be performed in conformance with the procedures outlined in the Manual Integration SOP. In summary:

9.4.1 The most appropriate instrument parameters should be used during method development to allow for automatic integration by the data system in most cases.

9.4.2 All data must be integrated consistently for all standards, samples and QC samples.

9.4.3 In those instances when the automated software does not integrate a peak correctly, manual integration may be used to correct the improper integration performed by the data system. Manual integration should always be performed to create the analyst's best estimate of the actual peak area discerned from the chromatogram.

9.4.4 All manual integrations must be documented by printing before and after, initialing and dating the manual integrations as well as by recording the reasons for the manual integrations.

9.5 A minimum signal-to-noise ratio of 3:1 (based on peak height) must be achieved for any peak used in a calibration standard, client sample, or quality control sample.

9.6 To prevent overwriting manual integrations, the analyst should not re-quantitate calibration standard files, unless dictated by certain regulations to validate the calibration.

9.7 When preparing to establish a new initial calibration, to prevent carry-over of numbers from previous calibrations, the analyst should "clear all response factors" (which is a function in the software) from old calibration curves prior to processing the new curve.

10.0 QUALITY CONTROL

10.1 Definitions

For definitions and explanations of quality control measures, refer to section 4.0 of the Con-Test Analytical Quality Control Manual.

10.2 Quality Control Measures & Acceptance Criteria

An analytical batch is defined as up to 20 client samples of a similar matrix for the same analysis. All quality control samples are assigned to and associated with a particular analytical batch, which is designated at the time samples are logged-in or at the time of sample preparation. All quality control samples must be traceable to the associated analytical batch for review and evaluation purposes.

10.2.1 Laboratory Reagent Blank

Analyze on each working day to demonstrate that no contamination is present. The LRB is analyzed with each batch prior to sample analysis. Any background contamination should be <MDL. The LRB consists of 5ml DI water and follows the same analytical procedure as client samples of similar matrix.

10.2.2 Calibration Curve

Initial calibration is performed before any samples are analyzed. Initial calibration must also be performed whenever the following corrective action or maintenance procedures are performed: changing the trap in a purge and trap, changing the electron multiplier or ion source chamber, and column replacement, or if the calibration verification criteria can not be met.

Calibration Criteria for samples run by Method 8260 C and MA MCP protocols:

A minimum (5)-point calibration curve is used to calibrate the system for all target analytes and surrogates. The low concentration initial calibration standard must be less than or equal to the reporting limit (RL). Target analytes detected in a sample at concentrations below the concentration of the low initial calibration standard should not be reported as quantitative results. If reported, they must be qualified as estimates.

The %RSD for all target analytes compounds over the working range must be ≤20% for the average RRF to be used for subsequent calculations.

A minimum response factor for compounds in TABLE 1.0, must be demonstrated for each individual calibration level. Meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. Compounds not meeting criteria should be considered estimated.

If %RSD is >20% for any target analyte, then a linear regression must be established using the calibration data for that compound (see EPA Method 8000C, Section 11.5.2). For the linear regression to be acceptable for quantitative purposes, the correlation coefficient must be greater than or equal to 0.99. If this criterion is met, the linear regression analysis must be incorporated into the curve used to calculate results. When calculating the calibration curves using linear regression, a minimum quantitation check should be performed by re-fitting the response from the low concentration calibration standard back into the curve (SEE Method 8000C). The recalculated concentration of the low calibration point should be within ± 30% of the standards true calculation. Analytes which do not meet the minimum quantitation calibration criteria should be considered " Out of control" and corrective action such as redefining the lower limit and/or reporting "Out of control" analytes as estimated.

Calibration Criteria for samples run by CT RCP protocols:

A minimum (5)-point calibration curve is used to calibrate the system for all target analytes and surrogates. The low concentration initial calibration standard must be less than or equal to the reporting limit (RL). Target analytes detected in a sample at concentrations below the concentration of the low initial calibration standard should not be reported as quantitative results. If reported, they must be qualified as estimated.

The SPCC (system performance check compounds) minimum response factors must be 0.30 for chlorobenzene and 1,1,2,2-tetrachloroethane, and 0.10 for chloromethane, 1,1-dichloroethane, and bromoform. If these minimum average RRF criteria are not met, corrective action, up to and including repeating the initial calibration analyses, must be taken before sample analyses are performed. Any compound with a minimum RRF < 0.05 must be narrated and qualified.

The percent relative standard deviations (%RSDs) for the six calibration check compounds (CCCs) (1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride) must be less than or equal to 30%. If the %RSD for any CCC is greater than 30%, or if >20% of analytes have % RSD >30%, then corrective action (e.g., to eliminate a system leak and/or column reactive sites) must be performed before re-attempting initial calibration.

The %RSD for all target analytes except ccc compounds over the working range must be ≤15% for the average RRF to be used for subsequent calculations.

If %RSD is >15% for any target analyte, then a linear regression must be established using the calibration data for that compound (see EPA Method 8000C, Section 11.5.2). For the linear regression to be acceptable for quantitative purposes, the correlation coefficient must be greater than or equal to 0.99 and must not be forced through the origin. If this criterion is met, the linear regression analysis must be incorporated into the curve used to calculate results

Calibration Criteria for samples run by Method 8260 D protocols:

A minimum (5)-point calibration curve is used to calibrate the system for all target analytes and surrogates. The low concentration initial calibration standard must be less than or equal to the reporting limit (RL). Target analytes detected in a sample at concentrations below the concentration of the low initial calibration standard should not be reported as quantitative results. If reported, they must be qualified as estimates.

The %RSD for all target analytes compounds over the working range must be ≤20% for the average RRF to be used for subsequent calculations.

A minimum response factor for compounds in TABLE 4.0, is for guidance, it is neither expected nor required that these minimum RFs be meet. However, is recommended that if RF is <0.01, that the concentration of said analyte be increase.

If %RSD is >20% for any target analyte, then a linear regression must be established using the calibration data for that compound (see EPA Method 8000C, Section 11.5.2). For the linear regression to be acceptable for quantitative purposes, the correlation coefficient must be greater than or equal to 0.99. If this criterion is met, the linear regression analysis must be incorporated into the curve used to calculate results. When calculating the calibration curves using linear regression, a minimum quantitation check should be performed by re-fitting the response from the low concentration calibration standard back into the curve (SEE Method 8000C). The recalculated concentration of the low calibration point should be within ± 50% of the standards true calculation if its is the lowest point and ± 30% for all others(i.e above the low standard). Analytes which do not meet the minimum quantitation calibration criteria should be considered " Out of control" and corrective action such as redefining the lower limit and/or reporting "Out of control" analytes as estimated.

For all 8260 methods:

If any initial calibration standard analysis is determined to be unusable (e.g., a bad injection), the standard may be re-analyzed before any samples are run. The re-analysis results may be incorporated into the initial calibration in their entirety, in place of the original analysis. If the initial calibration still does not meet acceptance criteria, even with the replacement standard, then the entire initial calibration should be performed again.

If the initial calibration still does not meet acceptance criteria for a particular analyte, the analyst may consider dropping the lowest or highest point for that analyte and recalculating the average RRF and %RSD or linear regression. Note that ONLY the lowest or highest data point may be dropped – a data point from the middle of the calibration range may NOT

be dropped. Note also that if the low standard is dropped, the RL for that analyte must be adjusted so that the lowest standard used for the calibration is less than or equal to the RL.

When the instrument data system is updated to reflect the new initial calibration, the analyst verifies that it has been properly set up to calculate each target analyte according to the actual model used to establish the initial calibration (i.e., average RRF or linear regression) and to reflect any abbreviated ranges established for individual analytes.

High level soil surrogate calibration for MeOH preservation samples is run on a 7pt curve: 1ppb, 2ppb, 5ppb, 10ppb, 25ppb, 50ppb, and 100ppb. The criteria are the same as initial calibration curve for method 8260.

The initial calibration curve is verified immediately, using a second source standard. The acceptable limits are 70-130%. Analytes outside of criteria should be considered estimated.

10.2.3 Continuing Calibration Check (Calibration Check Standard)

Continuing Calibration Criteria for samples run by Method 8260 C and MA MCP protocols:

At the start of each 12-hour analysis sequence, before any samples are analyzed, a 10ppb calibration check standard is analyzed to check the calibration curve. The percent difference or percent drift must be $\leq$20%. Exceedances are noted in a case narrative.

A minimum response factor for compounds in TABLE 1.0, must be demonstrated for the calibration level. Compounds not meeting criteria should be considered estimated.

Continuing Calibration Criteria for samples run by CT RCP protocols:

At the start of each 12-hour analysis sequence, before any samples are analyzed, a 10ppb calibration check standard is analyzed to check the calibration curve. The percent difference or percent drift must be $\leq$30% for all target analytes, except CCCs; the SPCC (system performance check compounds) minimum response factors must be 0.30 for chlorobenzene and 1, 1, 2, 2-tetrachloroethane, and 0.10 for chloromethane, 1, 1-dichloroethane, and bromoform.

The percent deviations (%D) for the six calibration check compounds (CCCs) (1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride) must be less than or equal to 20. If the %D for any CCC is greater than 20%, then corrective action (e.g., to eliminate a system leak and/or column reactive sites) must be performed before re-attempting continuing calibration.

Continuing Calibration Criteria for samples run by Method 8260 D protocols:

At the start of each 12-hour analysis sequence, before any samples are analyzed, a 10ppb calibration check standard is analyzed to check the calibration curve. The percent difference or percent drift must be $\leq$20%. Exceedances are noted in a case narrative.

For all 8260 methods:
If the minimum RRF or percent difference/drift criteria are not met for any target analyte based on the data quality objectives for the samples, then the analytical system should be evaluated for problems and corrective action taken as appropriate (change septa, compressed gas cylinders, syringes, column fittings, etc.; clean the MS source, changing an injector port or filament, cleaning the inlet, etc.). If corrective action that may affect instrument response is taken, then the calibration verification standard must be rerun before samples are analyzed. If the corrective actions do not resolve the problem(s) with the calibration verification standard, then a new initial calibration must be performed.

Any non-conformance associated with initial or continuing calibration that affects the usability of the data or otherwise as specified in an associated QAPP or the data quality objectives must be narrated and the data qualified.

Internal Standard (IS) retention times must be evaluated in the calibration check standard. The IS retention times should be within ± 30 seconds of the retention times from the midpoint standard of the initial calibration. If the retention times shift more than 30 seconds, the system is inspected for malfunctions and corrections made as required. When corrections are made, a new calibration check standard is run.

IS areas must be evaluated in the calibration check standard. If the IS areas change by more than a factor of two (-50% to +100%) from the areas in the midpoint standard of the most recently analyzed initial calibration, then the system is inspected for malfunctions and corrections made as required. When corrections are made, a new calibration check standard is run.

If corrective action requires that the column or trap on a purge-and-trap be replaced, or that the electron multiplier or ion source chamber be replaced, then performing a new initial calibration is automatically required.

If two calibration check standards are run in succession, one immediately following the other, and neither is deemed to have been a bad injection, then the one closest in injection time to the associated sample analyses, or both standards, must be evaluated for and pass method performance criteria for sample analyses to continue. In addition, the two calibration check standards are documented by the analyst for evaluation of reproducibility.

10.2.4 Surrogates

Surrogates are added to all blanks, standards, client samples, and quality control samples. The surrogates are checked and documented. Percent recoveries must be 70-130%R for individual surrogate compounds. If the %R is outside of control limits, the sample must be reanalyzed unless interference is noted. One high surrogate standard recovery associated with a sample that has all target compounds "non-detected" is permissable.

10.2.5 Internal Standards

Internal standards are monitored in each client sample, blank, quality control sample analysis. Acceptable criteria for the internal standards response is 50-200% of the response in the associated continuing calibration standard. Retention times of internal standards must be within $\pm$30 seconds of retention times in the associated continuing calibration standard.

The internal standard selected for calculation of the RRF for the concentration of each target analyte should be the internal standard with a retention time closest to the analyte being measured.

10.2.6 Method Blank

A matrix-specific method blank must be analyzed 1 per batch of 20 samples or less, prior to running samples and after calibration standards. Target analytes must be <RL except for common laboratory contaminants (such as acetone, chloroform, methylene chloride, toluene, and MEK which must be <5x the RL). Flag any contamination to qualify the sample results.

If the method blank does not meet these criteria, appropriate corrective action is taken (bake the trap or column, flush the transfer lines, etc.). An acceptable method blank must be analyzed prior to sample analyses.

10.2.7 Laboratory Control Sample

A matrix-specific LCS and duplicate is analyzed 1 per batch of 20 samples or less, or for each new window. The LCS is prepared from a different stock than that of the calibration curve, and is matrix matched to the samples of that batch. The concentration should be between the low and mid-level standard, and must contain all analytes. The percent recoveries must be 70-130%R for most compounds (document exceedances for "difficult compounds"). Difficult compounds are evaluated regularly. Reduction in the number of difficult compounds is a laboratory goal through corrective action and technical improvements. No greater than 10% of the total targets can be outside of control limits for analysis to proceed.

8260D allowed Matrix spikes and Laboratory Control Samples to be the same source as the ICAL (Section 7.12 of 8260D Method). However, when done this way is required to pass same criteria as CCV.

10.2.8 Matrix Spikes

Analyzed at a frequency equivalent to 1 per batch of 20 samples or less. The MS working stock is prepared at a concentration of 20 ug/mL (from a source different than that of the calibration curve). Must contain all of the target analytes.

Water prep: 20 uL working stock into 40 mL sample (when enough sample is collected)
True value = 10 ppb

Soil prep: 5 UL working stock into sample vial with either DI or Bisulfate. The Archon adds another 5mL purge&trap water; final volume = 10 mL.
True value = 10 ppb

The %R must be 70-130. If percent recoveries exceed these limits, check the LCS: if recoveries are acceptable in the LCS, narrate nonconformance.

10.2.9 Matrix Spike Duplicates

Analyze MS in duplicate at a frequency of 1 per batch of 20 samples or less when additional VOA vial is available. RPDs must be $\leq$30% for all matrices.

10.2.10 TCLP Method Blank

A TCLP method blank must be analyzed with each set of TCLP extracts. The TCLP method blank is diluted 10x with zero headspace in a 40 ml volumetric VOA vial, 1.0uL of the I.S./Surr. Std. is added (via Archon AS) and the sample is purged.

10.2.11 TCLP Matrix Spike

A representative TCLP matrix spike must be analyzed with each set of TCLP samples. The TCLP matrix spike is diluted 10x with zero headspace in a 40 ml VOA vial, 40 uL of the matrix spike solution and 1.0 uL of the I.S. /Surr. Std. is added (via Archon AS) and the sample is purged.

10.3 Guidance for Evaluation of Tentatively Identified compounds (TICs)

Initially include all the non-target compounds that have a peak area count of $\geq$ 10% of the nearest internal standard.

Use the following guidelines for making tentative identification:

1. The spectral library match must be ≥85% for a tentative identification to be made.
   For 8260D match must be ≥80%
2. The relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
3. The relative intensities of the major ions should agree within ± 20%.
4. Molecular ions present in the reference spectrum should be present in the sample spectrum.

5. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
6. 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 co-eluting peaks.

Quantitative analysis:
1. The nearest internal standard shall be the one that is used to calculate concentration, and the RF for the compound should be assumed to be 1.
2. The resulting concentration should be reported indicating that the value is an estimate.

11.0 DATA PROCESSING

11.1 GC/MS VOA files

11.1.1 Data files numbered sequentially starting with instrument, date, and file number.

11.2 Reporting Package

The reporting package that is delivered to clients will consist of the sample results, the surrogate recovery results and any matrix spikes, blanks, duplicates and lab fortified blanks that pertain to the clients' samples.

MCP Data Enhancement and Connecticut RCP projects will include required deliverables plus a case narrative and certification form.

11.3 Data Filing

11.3.1 Data to be filed in File Boxes

11.3.1.1 All raw data for client sample files, standards, blanks, and QC.

11.3.2 Data to be saved on CD or DVD.

11.3.3.1 All data batch files from instruments.

12.0 CORRECTIVE ACTIONS/CONTINGENCIES OF HANDLING OUT-OF-CONTROL DATA

12.1 Corrective action is performed any time acceptance criteria are not met, as described throughout this document. All corrective actions are fully documented by the analyst on a Corrective Action Form, as described in the Corrective Action SOP. Corrective Action Forms are a part of the QA record and copies are included with the data for the analyses.

12.2 Refer to Con-Test Quality Assurance Manual.

13.0 POLLUTION PREVENTION

Pollution prevention encompasses any technique that reduces or eliminates the quantity and or eliminates the quantity and or toxicity of waste at the point of generation. Many opportunities of pollution prevention exist in laboratory operation. Whenever feasible, laboratory personal should use pollution prevention techniques to address waste generation. When it is not feasible to reduce wastes at the source, recycling is recommended as the next best option. Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

14.0 WASTE MANAGEMENT

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing the waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.

15.0 GUIDANCE FOR COMPOSITING AQUEOUS SAMPLES PRIOR TO ANALYSIS

Syringe Compositing: In the syringe compositing procedure, equal volumes of individual grab samples are aspirated into a 50mL syringe while maintaining zero headspace in the syringe. (50mL Gastight Model 1050 Sample lock syringe).

This procedure uses multiple 5mL syringes that are filled with the individual grab samples and then injected sequentially into the 50mL syringe. If less than 10 samples are used for compositing, a proportionately greater amount should be used. The composited 50mL syringe is then aspirated into a 40mLVoa Vial, with a Teflon Lined cap, to ensure zero headspace. Sample is then ready to be analyzed.

16.0 REFERENCES

16.1 EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW-846, Rev.2, December 1996, Method 8260B.

16.2 Con-Test Analytical Chemical Hygiene Plan.

16.3 Con-Test Analytical Quality Assurance Manual.

16.4 HP 5890 Gas Chromatograph Operating Manual, Edition 5, October 1991.

16.5 HP 5970 Gas Chromatograph Operating Manual, 1991

16.6 Encon Purge & Trap Operating Manual, EST Analytical, 2002

16.7 Archon Purge & Trap Autosampler System Operating Manual, Varian, 2000, p/n 03-914642

16.8 CT DEP. Recommended Reasonable Confidence Protocol. Quality Assurance and Quality Control Requirements. VOC Method 8260, SW-846, Ver. 3.0, July 2006.

16.9 EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW-846, Rev.3, August 2006, Method 8260C.

16.10 EPA, Test Methods 8000C, Determinative Chromatographic Separations, Rev. 3, March 2003.

16.11 EPA, Test Methods 8000B, Determinative Chromatographic Separations, Rev. 2 December 1996.

16.12 MA DEP, MCP Data Enhancement Program, “Quality Control Requirements and Performance Standards for the Analysis of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) in support of Response Actions under the Massachusetts contingency Plan (MCP)”, Rev.1, July 1, 2010.

16.13 EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW-846, Rev 1, July 2002, Method 5035A.

`16.14 EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW-846, Rev. 3 May 2003, Method 5030C.

16.15 Teledyne Tekmar Atomx Auto sampler/concentrator Operator Manual.

16.16 Centurion Auto Sampler System Operating Manual.

16.17 EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW-846, Rev.4, June 2018, Method 8260D.

TABLE 1.0 Recommended minimum relative response factor criteria for Initial and Continuing Calibration Verification. – Method 8260C

Volatile Compounds	Minimum RRF
Dichlorodifluoromethane	0.100
Chloromethane	0.100
Vinyl Chloride	0.100
Bromomethane	0.100
Chloroethane	0.100
Trichlorofluoromethane	0.100
1, 1-Dichloroethene	0.100
1, 1, 2-Trichloro-1, 2,2-Trifluoroethane	0.100
Acetone	0.100
Carbon disulfide	0.100
Methyl Acetate	0.100
Methylene Chloride	0.100
Trans-1, 2-Dichloroethene	0.100
Cis-1, 2-Dichloroethene	0.100
Methyl tert-Butyl Ether	0.100
1, 1-Dichloroethane	0.200
2-Butanone	0.100
Chloroform	0.200
1, 1, 1-Trichloroethane	0.100
Cyclohexane	0.100
Carbon tetrachloride	0.100
Benzene	0.500
1, 2-Dichloroethane	0.100
Trichloroethene	0.200
Methylcyclohexane	0.100
1, 2-Dichloropropane	0.100
Bromodichloromethane	0.200
Cis-1, 3-Dichloropropene	0.200
Trans-1, 3-Dichloropropene	0.100
4-Methyl-2-pentanone	0.100
Toluene	0.400
1, 1, 2-Trichloroethane	0.100
Tetrachloroethene	0.200
2-Hexanone	0.100
Dibromochloromethane	0.100
Chlorobenzene	0.500
1, 2-Dibromoethane	0.100
Ethylbenzene	0.100
Meta/para-Xylene	0.100
Ortho-Xylene	0.300
Styrene	0.300
Bromoform	0.100
Isopropylbenzene	0.100
1, 1, 2, 2-Tetrachloroethane	0.300
1, 3-Dichlorobenzene	0.600
1, 4-Dichlorobenzene	0.500
1, 2-Dichlorobenzene	0.400
1, 2-Dibromo-3-chloropropane	0.050
1, 2, 4-Trichlorobenzene	0.200

SEMI-VOLATILE ORGANICS

(Method EPA 8270C/D/E)

Approved:

Tod Kopyscinski
Laboratory Director

Katherine Allen
QA Officer

Revision Number: 15

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Change Record

Revision	Date	Responsible Person	Description of Change
2	04/03/02	A.Kelller	NELAC format
3	09/07/05	D.Damboragian	Updates for AZ audit
4	03/23/06	S.Slesinski	Tune sec (9.4):peaktailing CCAL sec(9.6) I S criteria
5	01/06/09	B.Lagueux	Reformat Extractions sec (7.0) Update spikes sec (8.0) Maintenance sec (10.3.5)
6	08/25/09	F. Derose	Reformat – Updates for methods 8270C, 8270D, MCP and RCP protocols.
7	10/06/09	F. Derose	Updates
8	09/29/2011	F. Derose	Updates to the following: Sec 7.3 prep of samples taken out. Sec. 7.1.4 and 7.1.5 switched, Sec. 11.0 (when using linear check with a low std.), Sec. 21.12 (addition of new MA MCP CAM), and Sec. 15.0 (addition of SIM analysis). General editing done on entire SOP.
9	12/06/2012	F. Derose	Updates to include LL SIM analysis: Section 15.0 (Inclusion of instrument conditions and calibration for the SIM analysis).
10	7/29/2014	K. Allen	Updates from annual SOP review: Sec 8.4 (new table and combined soil and water prep), Sec 10.1 (addition to table with extras), Sec 10.2 (Cal table changed), and Sec 10.2.2 (addition of method D criteria).
11	3/23/2015	K. Allen	Updates from annual Internal Audit: Sec 1.0 (addition of App II), Sec's 5.0, 7.0, and 21.0 (addition of BUCHI), Sec 5.0 (addition of amber vials), and Sec 10.0 (addition of new point to curve), Sec 10.1 (addition of App II prep), Sec 13.1 (new parameters), addition of 15.1 and 15.2
12	11/15/2017	K. Allen	Update from annual internal audit: Sec 5.14(deletion of Turbo Vap), Sec 15.1(change of parameters), and Sec 15.2 (label cal charts for each instrument and not added #3 is backup only)
13	01/18/2018	K. Allen	Update from NY 2017 audit: Sec 11.0 (note added for analytes not meeting ICAL or ICV criteria, they are reported as "estimated".
14	01/03/2019	C. Merchant	Update to Sec 10.2.2 to include 8270E requirements (8270E Tune requirements added) and Sec 21.14 (addition of 8270E method reference).
15	02/19/2019	Charles Balicki	Updates from Annual SOP Review: Section 10.2.1 Added additional internal standard prep information. Added Appendix A on Coelution to end of document.

Distribution/Training List

See Employee Training Record File for signed training statements for users

1.0 SUMMARY OF METHOD

This method is used to analyze for certain base/neutral and acid compounds in waters, solids, and sludges. For water samples, approximately one liter of sample is extracted with methylene chloride at a pH greater than 11 and then again at a pH of less than 2 using a separatory funnel. For solids samples, approximately 30 grams of sample is extracted with 1:1 methylene chloride and acetone. The methylene chloride is dried and concentrated to a volume of 1.0mL and analyzed be GC/MS. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of three characteristic masses (m/z). Quantitation is accomplished by using the response of a major ion relative to an internal standard and a response factor generated from at least a minimum of a five-point calibration curve. Quantification by selective ion monitoring (SIM) is also described in this Standard Operation Procedure (SOP). The following compounds can be determined by this method:

Method 8270 Base/Neutral Extractables:

Acenaphthene	Acenaphthylene
Acetophenone	Aniline
Anthracene	Benzo(b)fluoranthene
Benzo(k)fluoranthene	Benzo(a)pyrene
Benzo(g,h,i)perylene	Benzidine
Benzoic Acid	Bis(2-chloroethyl)ether
Benzyl buty phthalate	Bis(2-chloroisopropyl)ether
Bis(2-chloroethoxy)methane	Benzo(a)anthracene
Bis(2-ethylhexyl)phthalate	4-Bromophenyl phenyl ether
Carbazole	2-Chloronaphthalene
4-Chlorophenyl phenyl ether	Chrysene
4-Chloroaniline	Dibenzofuran
Dibenz(a,h)anthracene	Di-n-butylphthalate
1,3-Dichlorobenzene	1,2-Dichlorobenzene
1,4-Dichlorobenzene	3,3-Dichlorobenzidine
Diethyl phthalate	Dimethyl phthalate
2,4-Dinitrotoluene	2,6-Dinitrotoluene
Di-n-octylphthalate	Fluoranthene
Fluorene	Hexachlorobenzene
1,2-Diphenyl-hydrazine	Hexachlorocyclopentadiene
Hexachlorobutadiene	Hexachloroethane
Indeno(1,2,3-cd)pyrene	Isophorone
Naphthalene	Nitrobenzene
2-Methylnaphthalene	1-Methylnaphthalene
2-Nitroaniline	3-Nitroaniline
4-Nitroaniline	N-Nitrosodiphenylamine
N-Nitrosodi-n-propylamine	N-Nitrosodimethylamine
Pentachloronitrobenzene	Phenanthrene
Pyrene	Pyridine
1,2,4,5-Tetrachlorobenzene	1,2,4-Trichlorobenzene

Method 8270 Acid Extractables:

4-Chloro-3-methylphenol	2-Chlorophenol
2,4-Dichlorophenol	2,4-Dinitrophenol
2-Methylphenol	3,4-Methylphenol
2-Methyl-4,6-dinitrophenol	2-Nitrophenol
4-Nitrophenol	Pentachlorophenol
Phenol	2,4,6-Trichlorophenol
2,4,5-Trichlorophenol	2,4-Dimethylphenol

Method 8270 Appendix II Extractables

3-Methylcholanthrene
1,3,5-Trinitrobenzene
Disulfoton
Diphenylamine
Dimethoate
Diallate
Chlorobenzilate
Caprolactam
Biphenyl
Benzyl alcohol
Benzaldehyde
Atrizine
7,12-Dimethylbenz(a)anthracene
Famphur
4-Aminobiphenyl
Hexachloropropene
3'3'-Dimethylbenzidine
2-Naphthylamine
2-Acetylaminofluorene
2,6-Dichlorophenol
2,3,4,6-Tetrachlorophenol
1-Naphthylamine
1,4-Naphthoquinone
1,3-Dinitrobenzene
5-Nitro-o-toluidine
Safrole
Pronamide
Phorate
Phenacetin
Pentachlorobenzene
Parathion
p-Phenylenediamine
p-Dimethylaminoazobenzene
o-Toluidine
Ethyl methanesulfonate
Thionazin
N-Nitrosopyrrolidine
N-Nitrosopiperidine
N-Nitrosomorpholine
N-Nitrosomethylethylamine
N-Nitrosodiethylamine
N-Nitrosidibuytlamine
Methyl parathion
Methyl methanesulfonate
Methapyrilene
Kepone
Isosafrole
Isodrin
O,O,O-Triethyl phosphorothioate

2.0 INTERFERENCES

2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and or cause elevated baselines in the total ion current profiles.

2.2 Interferences by phthalate esters can pose a problem, this is usually the result of contamination during extraction. Avoiding the use of plastics in the laboratory, and during field sample collection, can best minimize these interferences.

2.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample.

3.0 SAMPLE PRESERVATION, STORAGE, AND HOLDING TIME

3.1 All water samples are to be collected in glass amber bottles with Teflon lined caps. Soil samples do not need to be collected in amber glass containers. If residual chlorine is suspected, 80mg of sodium thiosulfate per 1-Liter of sample must be added, and mixed well.

3.2 All samples must be iced or refrigerated at 4°C from time of collection until extraction.

3.3 Sample holding time is seven (7) days from date of collection for extraction of waters, fourteen (14) days from date of collection for soils. Extracts must be analyzed within 40 days of extraction.

3.4 All sample extracts must be stored so as to be protected from the light.

4.0 REAGENTS AND STANDARDS

4.1 Reagent Water: interferent free

4.2 Methylene Chloride: Pesticide quality or equivalent

4.3 Methanol, Acetone: Pesticide quality or equivalent

4.4 Sodium Sulfate: (ACS), granular, anhydrous

4.5 Glass wool: Pesticide quality or equivalent

4.6 Sodium thiosulfate: (ACS) Granular

4.7 Sodium hydroxide solution (10N): Dissolve 40g of NaOH (ACS) to 50mL of reagent water

4.8 Sulfuric acid: (1:1) – slowly add 100mL of H_2SO_4 to 100mL of reagent water

4.9 Nitrogen: Ultra high purity

4.10 Helium: Ultra high purity

4.11 Stock Standard Solutions: Purchased as certified solutions

4.12 Surrogate, Internal Standard, and DFTPP Solutions: Purchased as certified solutions.

5.0 EQUIPMENT AND SUPPLIES

5.1 GC/MS with splitless injector, auto-injector

5.2 Enviroquant data system (HP ChemStation)

5.3 Capillary column-See section 13

5.4 Gas-tight syringes

5.5 Vials: 2mL snap cap and crimp top, and 4mL screw cap vials

5.6 Amber Vials: 2mL snap cap auto-sampler vials

5.7 Sample containers: 1-Liter Amber glass container with a Teflon lined screw cap.

5.8 Separatory Funnel: 2-Liter-Teflon with Teflon stopcock

5.9 pH paper

5.10 Pipettes: disposable 9in, and 1mL volumetric, Class A

5.11 500 mL Amber Bottles

5.12 Glass funnels

5.13 Filter paper: Whatman, or equivalent, Grade 413, 11cm

5.14 N-Evap concentrator system

5.15 25mL and 10mL N-Evap concentration glassware:

5.16 Buchi Syncore Concentrator

5.17 Buchi Syncore Concentrator Tubes

5.18 Graduated cylinder: 1Liter, 100mL

5.19 Balance: Analytical, capable of accurately weighing 0.0001 g

6.0 GLASSWARE CLEANING

6.1 Refer to Glassware Cleaning SOP

6.2.1 Alternative cleaning: Soap and warm water, reagent water rinse, acetone rinse, and methylene chloride rinse (x2).

7.0 EXTRACTION PROCEDURE

7.1 **EXTRACTION OF WATERS- Method 3510C**

7.1.1 To measure the sample volume, draw a line on the sample container at the meniscus. Transfer the entire sample to a separatory funnel. At a later time, place water in the sample container so the meniscus is up to the line drawn. Measure this volume in a graduated cylinder and record. If one liter of sample is not available, record the amount of sample used and bring up to one liter with reagent water.

7.1.2 Add 1.0mL of working surrogate standard to all samples, spikes, and blanks.

7.1.3 Add 1.0mL of matrix spike standard to all laboratory fortified blanks, and matrix spikes.

7.1.4 Check the pH of all samples with pH paper by dipping a disposable pipette into the sample and blotting the pH paper. Use a new pipette for each sample. Adjust the pH of the sample to <2 with 1:1 Sulfuric Acid (H_2SO_4).

7.1.5 Add 60 mL of methylene chloride to the sample container, seal and rinse the inner container. Transfer the solvent to the separatory funnel. Cap funnel and shake vigorously for 2 minutes with periodic venting to release excess pressure. Alternatively, the separatory funnel may be put on the rotator and be rotated for 5 minutes. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If an emulsion exists between the layers, the analyst must employ mechanical techniques to complete phase separation. (Mechanical Methods: Use a Teflon stir rod to break up emulsion or centrifuge). Pass the solvent layer through a glass funnel lined with a filter paper containing pre-rinsed anhydrous sodium sulfate (baked for 4 hours at 400° C before use), into a 500 mL amber bottle. Repeat extraction two more times, using a fresh portion of solvent added directly to the separatory funnel and combine each portion.

7.1.6 Check with pH paper. Adjust the pH to >11 with 10N NaOH. Check pH again to make sure pH is in proper range, if needed add more 10N NaOH. Mix sample thoroughly. Repeat step 7.1.5 adding the 60 mL directly to the separatory funnel.

7.1.7 Transfer the extract to a glass Buchi concentrator tube and place in the Buchi Syncore concentrator.

7.1.8 Prior to concentrating samples, allow the cooling plate to stabilize to its appropriate temperature.

7.1.9 Turn the chiller and vacuum pump on via the green toggle switch on each device. Next press the start button on the vacuum pump. Allow the temperature to reach 9°C.

7.1.10 Add at least ¼ inch of de-ionized water to each cell in the concentration platform. Avoid filling a cell so much that excess DI spill out.

7.1.11 Each day fill the cold-water bath that chills the solvent collection vessel. Run coolant line through the cold-water bath and add ice when necessary. Note this is not required when operating the Syncore concentrator designation for waters.

7.1.12 Before starting, check that the secondary contaminant solvent vessels are empty! **It is extremely important that this be checked throughout the day!!**

7.1.13 Transfer the extracted samples from the BOD bottles into the rinsed Turbo Vap cells. After adding the sample to the cell, rinse the BOD bottle with methylene chloride and add that rinseate to the sample.

7.2 Sample Concentration (Waters)

Note: All glassware should be similar in length to ensure a proper seal when under vacuum

7.2.1 Rinse all concentration glassware with Acetone 2 times and Methylene Chloride 2 times. (Enough to coat glassware to ensure sufficient rinsing)

7.2.2 Transfer sample extract from the BOD bottle to Buchi concentration glassware. Rinse the BOD bottle 2 times with Methylene Chloride and add rinsate to sample.

7.2.3 Place samples in the Syncore, cover with the top cooling plate and hand tighten.

7.2.4 Turn the Syncore concentration platform on via the green toggle switch. Press the start button and adjust the rotation dial to 0.

7.2.5 Check that **"Gradient"** is shown in the upper left corner of the display on the vacuum unit. If it is not selected, push the menu button and adjust the black dial until **"Gradient"** is selected, hit OK.

7.2.6 Check that the **"Water Met Final 1 mL" program** is selected and hit start.

7.2.7 Adjust the concentration platform to "250" using the black Dial.

7.2.8 For samples that require a solvent exchange: (3546 and 3510c soils and waters)

7.2.8.1 Run the **"Waters Met Final 1 mL" program** (1 hr. 22 min.). Add 50 mL of hexanes to each sample and aspirate. Select **"Hex Exchange Final" program** (22 min.) and hit start. When the program has finished, bring samples to their appropriate final volume and vial.

7.2.9 After the program finishes, adjust the concentration platform so that 0 is displayed and it is no longer moving. Check that the vacuum is steady at ambient pressure and remove the top plate. Bring samples to their appropriate final volume and vial.

7.3 EXTRACTION OF SOILS- Method 3546

Microwave sample preparation imposes a unique set of safety considerations. **Never heat liquids in a sealed vessel or container that is not equipped with a pressure relief valve.** Microwave heating of alkaline or salt solutions in a closed vessel will concentrate the solution, causing precipitation of salts and formation of crystal deposits on the vessel wall. These crystal deposits will absorb microwave energy, causing localized heating, which may char and damage vessel components.

Because samples are extracted at high temperatures and pressures, exercise extreme caution when removing a vessel. **Never open a hot vessel, wait until vessel has cooled (approx.10min)** Protective gear should always be worn.

7.3.1 **Vessel Preparation**: All cells / vessels are washed with warm soap and water, rinsed with reagent water, and then solvent rinsed. i.e. – Rinsed with acetone, methylene chloride and then hexane.

7.3.2 **Procedure**: Weigh out desired amount of sample (30 g) into a weigh boat. Add sodium sulfate, mix well, adding more sulfate if needed, making sure sample is free flowing.

7.3.2.1 Load pre-weighed and dried, soil sample into cleaned microwave vessel.

7.3.2.2 Add appropriate surrogate (100ppm base neutrals / 200ppm acids) to all samples, blanks, laboratory control samples, and matrix spike samples. (1.0 mL)

7.3.2.3 Add appropriate matrix spike (8270 Matrix Spike at 50ppm) (1.0 mL) to all Laboratory control samples and Matrix spike / Matrix spike duplicate samples.

7.3.2.4 Add 25 mLs of the appropriate solvent system or until the sample is covered with solvent. (1:1 methylene chloride: acetone)

7.3.2.5 The vessel is then capped, first adding the Teflon insert, then adding the screw cap. The vessel is then tightened using the CEM Capping Station.

7.3.2.6 Invert vessel, making sure sample and solvent are mixed well.

7.3.2.7 The vessel is put into the appropriate numbered slot in the carrousel, and the position number is entered in the 8270 Log Book.

7.3.2.8 The carrousel is then put into the oven. Method 3546 – is loaded and the method is started (Press Green Button)

Microwave Parameters:	Method 3546
Ramp to Temperature:	115 C
Time at Temperature:	10 minutes
Pressure:	50 – 150 psi
Cooling:	10 minutes cooling down process

After cooling, the vessel is opened and the contents is filtered through a solvent rinsed, glass funnel lined with filter paper containing sodium sulfate into a 60 ml vial.

7.3.2.9 Transfer the extract to a glass Buchi concentrator tube and place in the Buchi Syncore concentrator.

7.3.2.10 Prior to concentrating samples, allow the cooling plate to stabilize to its appropriate temperature.

7.3.2.11 Turn the chiller and vacuum pump on via the green toggle switch on each device. Next press the start button on the vacuum pump. Allow the temperature to reach 9°C.

7.3.2.12 Add at least ¼ inch of de-ionized water to each cell in the concentration platform. Avoid filling a cell so much that excess DI spill out.

7.3.2.13 Each day fill the cold-water bath that chills the solvent collection vessel. Run coolant line through the cold-water bath and add ice when necessary. Note this is not required when operating the Syncore concentrator designation for waters.

7.4 **Sample Concentration (Soils)**

7.4.1 Refer to sections 7.1.9 thru 7.1.12 for prepping the Syncore concentrator before working on samples.

7.4.2 Target sample volume after drying through sodium sulfate should be ~50 mL to avoid the sample going above the level of the cooling plate.

7.4.3 Pour the dried sample into a Buchi Concentration tube. Start the Syncore Concentrator using the following programs where applicable:

7.4.3.1 For **ETPH/8100 and 8270**, use program **"Soil Met in Use."** (43 min.)

7.4.3.2 For **8081/8082** use program **"Soil Pest/PCB 2 ml." (**32 min.)

7.4.3.3 For **EPH** first use program **"Soil Met in Use."** After the program finishes, perform a solvent exchange run the Syncore using program **"Hex exchange 2 ml final."** (22 min.)

7.4.4 When the program has finished, bring samples to their appropriate final volume and vial.

8.0 PREPARATION OF SURROGATE AND SPIKING STANDARDS

Note: All Standards must be stored in amber vials, for protection from light.

Note: All Standards have an expiration date of 6 months from when prepared or manufacturer's documented expiration date, whichever comes first.

Note: After opening Stock Standards, transfer the stock standard into vials with PTFE lined caps. Store protected from light at –10 C or less. Stock standard solutions should be checked frequently for signs of degradation or evaporation.

8.1 B/N STOCK SURROGATE PREPARATION

Compound	Vendor	Weight/Volume	Final Volume (mL)	Final Concentration (mg/mL)
2-Fluorobiphenyl	Aldrich	0.50 g	200 mL	2.5
o-Terphenyl-d14	Aldrich	0.50 g	200 mL	2.5
Nitrobenzene-d5	Aldrich	400 uL	200 mL	2.5

Weigh out 0.5 g o-Terphenyl-d14 and 0.50 g of 2-Fluorobiphenyl.

Add 5.0 mL of toluene, 10 mL of methanol, and 10.0 mL of methylene chloride.

Add 50.0 mL of acetone then 400 uL of Nitrobenzene-d5.

Bring up to final volume with methylene chloride. All solutions are combined in one 200ml final volume.

8.2 ACID STOCK SURROGATE PREPARATION

Compound	Vendor	Weight/Volume	Final Volume (mL)	Final Concentration (mg/mL)
2-Fluorophenol	Aldrich	800.0 uL	100 mL	10
Phenol-d6	Aldrich	1.0 g	100 mL	10
2,4,6-Tribromophenol	Aldrich	1.0 g	100 mL	10

-Weigh out 1.0 g phenol-d6 and 1.0 g 2,4,6-Tribromophenol.

-Add 5.0 ml of acetone.

-Add 800 ul of 2-Fluorophenol.

-Bring to volume with acetone in a 100ml volumetric flask.

All solutions are combined in one volume.

8.3 WORKING SURROGATE STANDARD PREPARATION

Compound	Volume (mL)	Final Volume (mL)	Final Concentration (µg/mL)
BN Stock Standard	10.0	250.0	100
Acid Stock Standard	5.0	250.0	200

To prepare the working solution add 10.0 mL of BN STOCK STANDARD and 5.0 mL of ACID STOCK STANDARD, to a final volume of 250.0 ml. Bring to volume in acetone. (See Table 19.1 For Surrogate Control Limits)

Surrogate Standard Check – When new surrogate spiking solution is prepared, a sample should be prepped with internal standard and injected to confirm appropriate concentrations of surrogates.

8.4 SEMIVOLATILE WATER AND SOIL SPIKING SOLUTION PREPARATION

Compound	Vendor	Conc. (ug/mL)	Volume (mL)	Final Volume (mL)	Final Conc. (µg/mL)
OP Pesticide mix	Restek	2000	2.5	100.0 mL in acetone	50
8270 Mega Mix	Restek	500-1000	5.0		
Benzoic Acid	Restek	2000	2.5		
Benzidines Mix	Restek	2000	2.5		
Appendix 9 mix #1	Restek	2000	2.5		
Appendix 9 mix #2	Restek	1000	5.0		

To prepare Spiking solution add 2.5 mL of Appendix 9 mix #1 Standard, 5.0 mL of 8270 Mega Mix Standard, 2.5 mL of Benzoic Acid Standard and 2.5 mL of Benzidines Mix Standard, 5.0 mL of Appendix 9 mix #2 Standard, and 2.5 mL of OP Pesticide mix Standard, to a 100 mL volumetric flask.

Bring to volume with acetone.

9 SAFETY

See Material Safety Data Sheet (MSDS) and Con-Test Chemical Hygiene Plan

10 CALIBRATION AND ANALYSIS

Stock standards are purchased as certified solutions from Absolute Standards Inc. They are used to prepare calibration standards, which are used to create the calibration curve.

10.1 WORKING STANDARD PREPARATION – SEMI-BNA

Compound	Conc. (µg/mL)	Amount (µL)	Final Volume (mL)	Final Concentration (µg/mL)
Toxic #1 Mix #4	2000	400	5.0 mL in MeCl2	160
Toxic #2 Mix #5	2000	400		
Benzidine Mix #6	2000	400		
BN Mix #1	2000	400		
BN Mix #2	2000	400		
Phenols Mix #8	2000	400		
PAH Mix #7	2000	400		
625 Adds Mix #9	2000	400		
625 Adds Mix #11	2000	400		
BN Surrogate Stock	2500	320		
Acid Surrogate Stock	10000	160		
SVOA Extra	2000	400		

Bring up to Final Volume of 5mL with methylene chloride.

Final Concentration = 160 µg/mL

10.1.1 WORKING STANDARD PREP – APPENDIX II COMPOUNDS

Compound	Conc. (µg/mL)	Amount (µL)	Final Volume (mL)	Final Concentration (µg/mL)
Apex 2 Custom	1000	800	5.0 mL in MeCl2	160
B/N Surrogate	2500	320		160
Acid Surrogate	10000	160		320

10.2 CALIBRATION CURVE – PREPARATION

Cal. Std. Level	Stock Conc. (ppm)	Amount (µL)	Volume MeCl2 (µL)	Final Volume (µL)	Final Conc. (µg/mL, ppm)
1	160	25	1975	2000	2
2	160	62.5	1937.5	2000	5
3	160	62.5	937.5	1000	10
4	160	125	875	1000	20
5	160	312.5	687.5	1000	50
6	160	500	500	1000	80
7	160	625	375	1000	100
8	160	750	250	1000	120
9	160	1000	0	1000	160

The curve is then prepped with internal standard, 200 µL final volume with 2.0 µL internal standard (4.0 mg/mL) to the vial insert. (Note: the 2 +5 ppm is double the volume).

10.2.1 INTERNAL STANDARD PREPARATION

Internal Standard Criteria for samples run by Methods: 8270E, 8270D, 8270C, MA MCP and CT protocols:

An internal standard mix is purchased from Ultra Scientific, and contains the following compounds all at a concentration of 4000 µg/mL :
Acenaphthene-d10, Chrysene-d12, 1,4-Dichlorobenzene-d4, Naphthalene-d8, Perylene-d12, and Phenanthrene-d10.

Dilute 2.5x in $MeCl_2$, 1.0 mL internal standard @4000 µg/mL to 1.5mL $MeCl_2$, 2.5mL final volume, 1600 µg/mL concentration.

Add 25 µL of stock internal standard at 1600 µg/mL to 1.0 mL of room temperature sample extract.

The Internal Standard must be added to each sample extract and mixed thoroughly immediately before being analyzed by GC/MS

10.2.2 DFTPP TUNING

At the start of each working day, DFTPP Tuning solution must be injected.
The DFTPP Tuning Solution consists of four compounds: DFTPP (*Decafluorotriphenylphosphine)*, Benzidine, Pentachlorophenol, and DDT, and is purchased from Ultra Scientific. The tuning solution is prepared as follows:

Compound	Conc. (µg/mL)	Amount (µL)	Final Volume (mL)	Final Conc. (µg/mL, ppm)
Tuning Standard	1000	250	5.0 mL in $MeCl_2$	50.0

The mass spectrum of DFTPP must meet the performance criteria established by the method (listed below). If it does not, analyst must retune the mass spectrometer and repeat the test until all criteria are achieved.

The mass spectrum of DFTPP that is evaluated against the acceptance criteria is obtained in the following manner: Three scans (the peak apex and the scans immediately preceding and following the apex) are averaged, and a single scan no more than 20 scans prior to the DFTPP peak is subtracted. No part of the DFTPP peak itself may be background-subtracted.

8270C DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-60% of m/z 198
68	<2% of m/z 69
70	<2% of m/z 69
127	40-60% of m/z 198
197	<1% of m/z 198
198	Base Peak, 100% Relative Abundance
199	5-9% of m/z 198
275	10-30% of m/z 198
365	>1% of m/z 198
441	Present, but <m/z 443
442	>40% of m/z 198
443	17-23% of m/z 442

8270D DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	10-80% of Base peak
68	<2% of m/z 69
70	<2% of m/z 69
127	10-80% of Base peak
197	<2% of m/z 198
198	Base Peak, or >50% of m/z 442
199	5-9% of m/z 198
275	10-60% of Base peak
365	>1% of m/z 198
441	Present, but <24% of m/z 442
442	Base peak, or >50% of m/z 198
443	15-24% of m/z 442

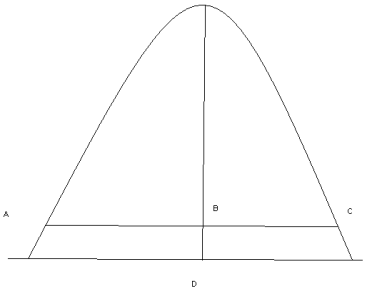
8270E DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

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

The tailing factor for benzidine and pentachlorophenol must be evaluated to see if acceptable performance criteria are achieved.

Peak tailing exceedances are an indication that maintenance is needed. Peak tailing must be evaluated before samples are analyzed; exceedances must be reported in the report case narrative, and column maintenance performed before the next DFTPP window is initiated.

Tailing factor can either be manually calculated (see calculation below) or by electronic methods using Agilent Technologies – Environmental ChemStation.



Peak Tailing Calculation:

TAILING FACTOR = $^{BC}/_{AB}$

RF= $\frac{(A_s)\,(C_{is})}{(A_{is})\,(C_s)}$

Example calculation:
Peak Height=DE
10% Peak Height=BD
Peak width at 10% peak height = AC

The GC/MS tuning standard solution must also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%.

Failing tailing and degradation factors should be documented as non-conformence. Before the next 12-hour window, maintenance must be done to meet compliance.

DFTPP Criteria for samples run by Methods: 8270C and CT RCP protocols

Benzidine peak tailing factor must be < 3. Pentachlorophenol peak tailing factor must be < 5.

DFTPP Criteria for samples run by Method: 8270D and MA MCP protocols

Benzidine peak tailing factor must be <2. Pentachlorophenol peak tailing factor must be < 2.

DFTPP Criteria for samples run by Method: 8270D and MA MCP protocols

Tailing factor checks are not required, but monitoring responses and tailing factors remain a good indicator or system reactivity and the need for maintenance.

i. DAILY MAINTENANCE

Daily maintenance is done to prevent these tailing and degradation issues.
Daily maintenance includes replacement of the following:

Injection liner, inlet base seal and clipping of dirty column.

11.0 INITIAL CALIBRATION

Initial calibration is performed before any samples are analyzed. A new initial calibration must be performed whenever the following corrective action or maintenance procedures are performed: Changing the electron multiplier or ion source chamber, column replacement, or if the calibration check standard criteria cannot be met.

The initial calibration requires a minimum of five different concentrations of all target analytes and surrogates. The calibration standards routinely used in this method are listed in Section 9.1.2. The low concentration initial calibration standard must be less than or equal to the reporting limit (RL). Target analytes detected in a sample at concentrations below the concentration of the lowest initial calibration standard should not be reported as quantitative results. If reported, they must be qualified as estimates or "J" flags. If linear regression is used, then the lowest point in the calibration curve must be analyzed with 70-130% recovery. If not, point must be dropped from curve and the next highest point evaluated until 70-130% recovery is achieved.

NOTE: Analytes that do not meet ICAL or ICV criteria must be reported as "estimated"

Initial Calibration requirements for samples run by Method 8270 C protocols:

The % RSD for all target analytes over the working calibration range must be less than or equal to 15% for the average RRF or "r" $\geq$ 0.99 if a linear regression curve fit is used for subsequent quantitations. If any of the target compounds exceed the 15% RSD limit or when the compound is calibrated by linear regression where the correlation coefficient < 0.99 alternative, can not be achieved, the system is considered too reactive and the calibration must be repeated.

When the %RSD exceeds the criteria, then a linear regression must be established using the calibration data for that compound (SEE EPA METHOD 8000C). For linear regression to be acceptable for quantitative purposes, the correlation coefficient must be incorporated into the curve used to calculate results.

Additional quality control measures for samples run by CT RCP protocols:

The minimum average relative response factor (RRF) for the semivolatile system performance check compounds (SPCC's) is 0.05. (SEE TABLE 22.4) If the minimum RRF for any SPCC are not met, the system is evaluated, corrective action, up to and including repeating the initial calibration analyses, is taken as necessary before sample analyses are performed. If any other analytes fall below minimum of 0.05 RRF, report with qualifier. Possible Problems: Standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or the chromatographic system.

The %RSD for all target analytes except CCCs over the working calibration range must be less than or equal to 15% for the average RRF or "r" $\geq$ 0.99. CCCs must be $\leq$ 30% RSD or "r" $\geq$0.99 to be used for subsequent quantitations. If any of the CCCs compounds exceed the 30% RSD limit or when the compound is calibrated by linear regression where the correlation coefficient < 0.99 alternative, cannot be achieved, the system is considered too reactive and the calibration must be repeated. If regression analysis is used, the curve must not be forced through the origin.

(CCC Compounds: 1,4-dichlorobenzene,N-nitrosodiphenylamine,acenaphthene,fluoranthene, hexachlorobutadiene,di-n-octylphthalate, benzo(a)pyrene, phenol, 2-nitrophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, pentachlorophenol, and 2,4,6-trichlorophenol)

Initial Calibration requirements for samples run by MA MCP or Method 8270 D protocols:

The % RSD for all target analytes over the working calibration range must be less than or equal to 20% for the average RRF or "r" $\geq$ 0.99 to be used for subsequent quantitations. If any of the target compounds exceed the 20% RSD limit or when the compound is calibrated by linear regression where the correlation coefficient < 0.99 alternative (SEE EPA METHOD 8000D), can not be achieved, the system is considered too reactive and the calibration must be repeated.

The minimum average relative response factor (RRF) for compounds in TABLE 22.3 (8270D requirements) - SEE TABLE 22.3 – RECOMMENDED MINIMUM RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION.

In some cases, the detector response may not be linear because of the broad range of the standards. Data points for individual target analytes at either extreme end of the calibration range may be discarded and the %RSD recalculated. Discarding an individual point in the middle of the calibration range is not permitted. If the low concentration standard is discarded, the reporting limits must be adjusted so that the lowest standard used for the calibration is less than or equal to the reporting limit.

Note: No points may be dropped from the initial calibration curve for any surrogate compound.

If any initial calibration standard is determined to be unusable (e.g., bad injection), the standard in question may be rerun within eight (8) hours of the last initial calibration standard analyzed and before any samples are run. The rerun standard may be incorporated into the initial calibration in its entirety, replacing the original standard. If the initial calibration still does not meet acceptance criteria, even with the replacement standard, then the entire initial calibration should be performed again.

All changes made to the calibration curve are documented with the reason given for the change.

When the instrument data system is updated to reflect the new initial calibration, the analyst verifies that it has been properly set up to calculate each target analyte according to the actual model used to establish the initial calibration (i.e., average RRF or Linear Regression) and to reflect any abbreviated ranges established for individual analytes.

The initial calibration is verified by analyzing a secondary source (ICV)-(Same solution as the LCS source). Criteria is 70-130 % recovery.

According to the MA MCP program if $\leq$10% of compounds exceed criteria, recalibration is not required as long as %RSD <40, r >0.98, or r^2 >0.98.

12.0 CONTINUING CALIBRATION CHECK (CALIBRATION CHECK STANDARD)

The calibration relationship established during the Initial Calibration is verified at the beginning of analytical sequence.

The analyst sequence is documented on an analysis run log maintained by the analyst.

At the start of each 12-hour analysis sequence, before any samples are analyzed, a mid point calibration standard is analyzed to check the calibration curve.

Continuing Calibration requirements for samples run by Method 8270 C protocols:

Each SPCC in the calibration check standard must meet the minimum RRF of 0.05 before sample analyses begins.

The %difference or %drift for each continuing calibration check compound (*CCC: 1,4-dichlorobenzene,N-nitrosodiphenylamine,acenaphthene,fluoranthene, hexachlorobutadiene,di-n-octylphthalate, benzo(a)pyrene, phenol, 2-nitrophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, pentachlorophenol, and 2,4,6-trichlorophenol)* in the continuing calibration must be ≤ 20%. If any CCC has a %D greater than 20%, then corrective action (e.g., to eliminate a system leak or reactive sites) must be performed before re-attempting continuing calibration.

All remaining compounds % difference or % drift must be ≤ 30% RSD.

If any of the CCCs compounds or greater then 10% of the remaining analytes is >30% RSD, then corrective action must be must be performed before re-attempting continuing calibration.

If the percent difference criteria is not met for any target analyte, then the analytical system should be evaluated for problems and corrective action taken as appropriate (change septa, check compressed gas cylinders, syringes, column fittings, etc., clean MS source, change the injector port or check filament, clean the inlet.)

If corrective action that may affect instrument response is taken, then the calibration check standard must be rerun before samples are analyzed. If the corrective actions do not resolve the problem(s) with the calibration check standard, then a new initial calibration must be performed.

Continuing Calibration requirements for samples run by CT RCP protocols:

The percent difference or percent drift must be less than or equal to 30% for all target compounds.

Each SPCC in the calibration check standard must meet the minimum RRF of 0.05 before sample analyses begins.

The %difference or %drift for each continuing calibration check compound (*CCC: 1,4-dichlorobenzene,N-nitrosodiphenylamine,acenaphthene,fluoranthene, hexachlorobutadiene,di-n-octylphthalate, benzo(a)pyrene, phenol, 2-nitrophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, pentachlorophenol, and 2,4,6-trichlorophenol)* in the continuing calibration must be ≤ 20%. If any CCC has a %D greater than 20%, then corrective action (e.g., to eliminate a system leak or reactive sites) must be performed before re-attempting continuing calibration.

All remaining compounds % difference or % drift must be ≤ 30% RSD.

If any of the CCCs compounds or greater then 10% of the remaining analytes is >30% RSD, then corrective action must be must be performed before re-attempting continuing calibration.

If the percent difference criteria is not met for any target analyte, then the analytical system should be evaluated for problems and corrective action taken as appropriate (change septa, check compressed gas cylinders, syringes, column fittings, etc., clean MS source, change the injector port or check filament, clean the inlet.)

If corrective action that may affect instrument response is taken, then the calibration check standard must be rerun before samples are analyzed. If the corrective actions do not resolve the problem(s) with the calibration check standard, then a new initial calibration must be performed

Continuing Calibration requirements for samples run by MA MCP and Method 8270 D protocols:

The percent difference or percent drift must be less than or equal to 20% for all target compounds

Due to the large number of compounds being analyzed, no more than 20% of the total compounds or >15% of analytes from a particular class can fail (Greater than 20% difference or drift), then corrective action must be taken. Additionally, if any compound is >40% D analysis must be repeated.

Each of the compounds in TABLE 22.3 should be evaluated to meet the minimum response factors as noted in the table. If the RRF is not met, the system should be evaluated, and corrective action should be taken before sample analysis begins.

If the percent difference criteria is not met for any target analyte, then the analytical system should be evaluated for problems and corrective action taken as appropriate (change septa, check compressed gas cylinders, syringes, column fittings, etc., clean MS source, change the injector port or check filament, clean the inlet.)

If corrective action that may affect instrument response is taken, then the calibration check standard must be rerun before samples are analyzed. If the corrective actions do not resolve the problem(s) with the calibration check standard, then a new initial calibration must be performed.

Note: Quantitation Check

When calculating the calibration curve using linear regression, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration standard back into the curve (SEE METHOD 8000 C). The recalculated concentration of the low calibration point should be within $\pm$ 30% of the standards true concentration. Analytes which do not meet the minimum quantitation calibration re-fitting criteria should be considered “out of control” and corrective action such as redefining the lower limit of quantitation and/or reporting those “out of control” target analytes as estimated.

Internal Standard (IS) retention times must be evaluated in the calibration check standard. The IS retention times should be within $\pm$ 30 seconds of the retention times from the midpoint standard of the initial calibration. If the retention times shift more than 30 seconds, the system is inspected for malfunctions and corrections made as required. When corrections are made, a new calibration check standard is to be run.

IS areas must be evaluated in the calibration check standard. If the IS areas change by more than a factor of two (50-200%) from the areas in the midpoint standard of the most recently analyzed initial calibration, proceed as follows:

a. If I.S. is failing high, run the CCAL a 2nd time; (re-prep CCV) if results confirm, then the system needs to be inspected for malfunctions and corrections made as required. A new ICAL would need to be run.
b. If I.S. is failing low, adjust the tune and begin a new window with CCAL and blank; if maintenance and tune do not correct the failure, make corrective actions and re-calibrate.

If corrective action requires that the column be replaced, or that the electron multiplier or ion source be replaced, then performing a new initial calibration is automatically required.

If two calibration check standards are run in succession, one immediately following the other, and neither is deemed to have a bad injection, then both standards must be evaluated for and pass method performance criteria for sample analyses to continue.

13.0 ANALYSIS

13.1 Instrument set up

AGILENT TECHNOLOGIES – GCMS/SV #2 5973 S/N:US00008893
- GCMS/SV #4 5973 S/N:US80818740
-GCMS/SV #3 5973 S/N: CN10511066

Column: DB-5ms, 0.25 I.D. X 0.25 micron X 30 meter, or equivalent

Injection Temperature: 250 C

Detector Temperature: 290 C

Injection Volume: 1.0 uL split (split ratio 10:1)

Pulse split Injection: Pulse 25psi for 0.4 min.

Liner: 4mm Gooseneck single taper with glass wool plug.

Temperature Program:

40 C Hold for 0.5 min.
Ramp at 40 C/min to 260 C
Ramp at 6 C/min to 295 C
Ramp at 25 C/min to 320 C Final Temperature
Hold for 2 Minutes

Mode: Constant Flow, Flow: 1.4 mL/min, split flow 13.5 mL/min

Scan Range: 35 to 45 amu sampling = 1

13.2 MANUAL INTEGRATIONS

When performing manual integration of any peak in a calibration standard, client sample, or quality control sample, the integration must be performed in conformance with the procedures outlined in the SOP for Chromatographic integration procedures. In Summary:

13.2.1 The most appropriate instrument parameters should be used during method development to allow for automatic integration by the data system in most cases.

13.2.2 All data must be integrated consistently for all standards, samples, and QC samples.

13.2.3 In those instances when the automated software does not integrate a peak correctly, manual integration may be used to correct the improper integration performed by the data system. Manual integration should always be performed to create the analyst's best estimate of the actual peak area discerned from the chromatogram.

13.2.4 All manual integrations must be documented by printing, initialing and dating the before and after reports with manual integrations as well as by recording the reasons for the manual integrations.

13.2.5 To prevent overwriting manual integrations, the analyst should not re-quantitate calibration standard files.

13.2.6 A minimum signal to noise ratio of 3:1 (based on peak height) must be achieved for any peak used in a calibration standard, client sample, or quality control sample.

13.2.7 When preparing to establish a new initial calibration, to prevent carry-over of numbers from previous calibrations, the analyst should “Clear all response factors “(which is a function in the software) from old calibration curves prior to running the new curve.

13.3 IDENTIFICATION OF ANALYTES

Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within three standard deviations of the mean retention time of the compound in the calibration mixture.

13.3.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10-50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

13.3.2 Identification requires expert judgment when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component. (i.e. broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes co elute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the co eluting compound.

13.3.3 Because target organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes.

13.3.4 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs.

13.3.5 All raw data must be properly identified with initials of the proper analyst and date analyzed.

14.0 Tentatively Identified Compounds (TICs)

Initially include all of the non-target compounds that have a peak area count of ≥ 10% of the nearest internal standard.

The spectra library match must be ≥ 85% for a tentative identification to be made.

The major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

The relative intensities of the major ions should agree within 20%.

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

Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or for the presence of co-eluting compounds.

Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different chromatographic retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks.

15.0 SIM – Selective Ion Monitoring Mode

A GC/MS system is operated in the SIM mode to increase sensitivity. In the SIM mode, the mass spectrometer repeatedly scans a smaller number of pre-selected masses rather than the typical mass range (35 to 500 amu) utilized in the full scan mode. In the GC/MS SIM acquisition mode, the masses to be monitored are selected based on the mass spectra of compounds to be analyzed. At this time, only PAH compounds are monitored under SIM Mode.

GC/MS SIM improves detection limits without compromising positive identification of analytes. Sample preparation, chromatographic conditions, analyte identification, analyte quantification are the same whether the GC/MS system is operated in the full scan or SIM Mode.

SIM Parameters:

SIM Group	Ions (m/z) / Dwell in Group
#1	150.0, 152.0
#2	68.0, 82.0, 117, 127, 128, 129, 136, 201, 223, 225
#3	115, 141, 142, 171, 172
#4	139, 151, 152, 153, 154, 162,164,168
#5	139, 142, 166, 167, 264, 266,284
#6	94,166,167,176,178,179,188,229,230
#7	200,202,203,244,245
#8	149,167,226,228,229,236,240
#9	125,252,253,260,264
#10	138,139,276,277,278,279

15.1 Instrument Conditions for GCMSSV5 (SIM) S/N: CN10939098

Oven Program: 40 C for 3 min, 25 C/min to 245 C for 0.0 min, 6.0 C/min for 0.2 min. Total Run = 24 min
Syringe Size: 10 uL
Injection Volume: 1 uL
Injector Temp: -10.0 C for 0.1 min., 400 C/min to 320 C for 0.0 min. (Mode: PTV Solvent Vent)
Gas Saver: On 20 mL/min after 4.0 min

Purge Flow to Split Vent: 100 mL/min at 3.0 min
Vent Flow: 50 mL/min
Vent Pressure: 0.0 psi until 0.05 min
Transfer Line Temp: 290 C
Column: 1.4 mL/min, constant flow
Acquisition Mode: SIM Mode

15.2 Instrument Conditions for GCMSSV3 (SIM) S/N: CN10511066 **(Backup Instrument only)**

Oven Program: 40 C for2 min, 12 C/min to 100 C, 25C/min to 250 C, 15C/min to 290 C for 7 min.
Column: DB-5ms, 0.25 i.d. x 0.25micron x 30m, or equivalent
Injection Volume: 1 uL (syringe size 10uL)
Injector Temp: 280C
Detector Temp: 290C
Purge Flow: 30 mL/min purge time 0.5 m
Mode: Pulse splitless, pulse 18psi for 0.4min.
Column: 1.1 mL/min, constant flow
Acquisition Mode: SIM Mode

Calibration Stock:

Stock standard is purchased as certified solution from Absolute Standards. They are used to prepare 7 Calibration standards, which are used to create the calibration curve.

PAH Standard (CUSTOM); 100 ug/mL in dichloromethane/benzene 1:1 – Absolute Standards Cat#96981)

Cal Table for GCMSSV5:

Working Level	Calibration Stock Amount (ul)	Final Volume (mL)	Final Conc (ug/mL)
1	1.25	5.0	0.025
2	2.5	5.0	0.05
3	12.5	5.0	0.25
4	50	5.0	1.0
5	125	5.0	2.5
6	250	5.0	5.0
7	500	5.0	10.0

Working Standaerd Prep – SIM 8270D

Compound	Conc (ug/mL)	Amount (uL)	Final Vol. (mL)	Final Conc. (ug/mL)
SVOA Extd 1	100	500	5mL	10
B/N Surrogate	2500	200	in MeCl2	100
Acid Surrogate	10000	100		200
o-Terphenyl Stock	5000	100		100

Calibration Curve Table for GCMSSV3:

Working **Level**	**Stock Conc. (ug/mL))**	**CAL Amount (uL)**	**Volume MeCl2 (uL)**	**Final Volume (mL)**	**Final Conc. (ug/mL)**
1	0.5	100	900	1	0.05
2	0.5	200	800	1	0.10
3	0.5	400	600	1	0.20
4	10	100	1900	2	0.50
5	10	200	1800	2	1.0
6	10	200	800	1	2.0
7	10	500	500	1	5.0
8	10	1000	0	1	10.0

The curve is then prepped with the internal standard, 200uL final volume with 2uL internal standard (4mg/mL) to the vial insert.

16.0 QUALITY CONTROL

16.1 DEFINITIONS

For definitions and explanations of quality control measures (Method Blanks, LCS/LFB, MS/MSD, Surrogates, Internal Standards, Etc.) Refer to the Con-Test Analytical Laboratory Quality Assurance Manual.

16.2 QC Measures and Acceptance Criteria

An analytical batch is defined as up to 20 client samples of a similar matrix for the same analysis. All quality control samples (Method Blanks, LCS/LFB, MS/MSD) are assigned to and associated with a particular analytical batch, which is designated at the time client samples are logged-in or at the time of sample preparation. All quality control samples must be traceable to the associated batch for review and evaluation purposes

17.0 CALCULATIONS

17.1Calculation #1:

$$\frac{\text{FINAL EXTRACT VOLUME}}{\text{SAMPLE VOLUME EXTRACTED (ML)}} \text{ X DILUTION FACTOR X INSTRUMENT VALUE (UG/ML) = UG/L}$$

17.2 Calculation #2:

All calculations are based on the internal standard technique.

$$Cx = \frac{AxCis}{AisRRF}$$

Cx = Compound concentration = instrument value
Ax = Area of the characteristic ion for the compound to be measured, counts
Ais = Area of the characteristic ion for the specific internal standard, counts
Cis = Concentration of the internal standard spiking mixture, ppm

RRF = Relative Response Factor is the average Response factor for the compound from the initial calibration

Relative Retention Times (RRT) Calculate the RRTs for each target compound over the initial calibration range using the following equation:

$$RRT = \frac{RTc}{RTis}$$

Where: RTc = Retention time of the target compound, seconds
Rtis = Retention time of the internal standard, seconds

Mean of the Relative Retention Times (RRT) Calculate the mean of the relative retention times (RRT) for each analyze target compound over the initial calibration range using the following equation:

$$\overline{RRT} = \sum_{i=1}^{n} \frac{RRT}{n}$$

Where: $\overline{RRT}$ = Mean Relative Retention time for the target compound for each initial calibration standard
RRT = Relative Retention time for the target compound at each calibration level.

Mean Retention Times (RT) Calculate the mean of the retention times (RT) for each internal standard over the initial calibration range using the following equation:

$$\overline{RT} = \sum_{i=1}^{n} \frac{RTi}{n}$$

Where: $\overline{RT}$ = Mean retention time, seconds
RT = Retention time for the internal standard for each initial calibration standard, seconds

18.0 CORRECTIVE ACTIONS / CONTINGENCIES OF HANDLING OUT OF CONTROL DATA

18.1 Corrective Action is performed any time acceptance criteria are not met, as described throughout this document. All corrective actions are fully documented by the analyst on a Corrective Action Form, as described in the SOP for Corrective Actions. Corrective Action Forms are a part of the QA record and copies are included with the data for the analyses.

18.2 Refer to Con-Test Quality Assurance Manual.

18.3 Refer to Con-Test Corrective Action SOP.

19.0 POLLUTION PREVENTION

Pollution Prevention encompasses any technique that reduces or eliminates the quantity and or eliminates the quantity and or toxicity of waste at the point of generation. Many 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 waste generation. When it is not feasible to reduce wastes at the source, the Agency recommends recycling as the next best option.

20.0 WASTE MANAGEMENT

It is the Laboratory's responsibility to comply with all federal, state, and local regulations governing the waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.

21.0 REFERENCES

21.2 SW-846 Method 8270D, Test Methods for Evaluating Solid Waste, "Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry", February 2007, Revision 4.

21.2 Instrument Manuals, HP GCMS 5970 and 5973.

21.3 Con-Test Analytical Laboratory Chemical Hygiene Plan.

21.4 Con-Test Analytical Laboratory Quality Assurance Manual.

21.5 Con-Test Analytical Laboratory SOP for Chromatographic Integration Procedures.

21.6 Con-Test Analytical Laboratory "Procedure of Maintaining Controlled Documents" SOP

21.7 Con-Test Analytical Laboratory on Procedures for Implementing Corrective Actions

21.8 Massachusetts DEP, Quality Assurance and Quality Control Requirements for SW-846 8270C, SemiVolatile Organic Compounds by GC/MS for the MCP, Revision 5, August 2004.

21.9 Connecticut DEP, RCP, Quality Assurance and Quality Control Requirements, Semi-Volatile Organic Compounds by method 8270, SW-846, Version 2, July 2006.

21.10 USEPA – "Determinative Chromatographic Separations", SW846, 3rd edition, March 2003, Method 8000C.

21.11 SW-846 Method 8270C, Test Methods for Evaluating Solid Waste, "Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry", December 1996, Revision 3.

21.12 Massachusetts DEP, "Quality Control Requirements and Performance Standards for the Analysis of Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) in Support of Response Actions under the Massachusetts Contingency Plan (MCP)", Revision 1, July 1 2010.

21.13 Syncore Application Guide for Buchi Turbo Vap Concentrator, Version A, January 2012.

21.14 SW-846 Method 8270E, Test Methods for Evaluating Solid Waste, "Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry", June 2018, Revision 6.

22.0 TABLES

22.1 **Surrogate Control Limits**

Surrogate Compound	Ret. Time (min)	Primary QIon	Spike Amount (ppm)	Acceptable Recovery Range
2-Fluorophenol	3.795	112	200	**Acid Fraction 15%-110%**
Phenol-d6	4.609	99	200	
2,4,6-Tribromophenol	9.744	330	200	
Nitrobenzene-d5	5.351	82	100	**Base/Neutral Fraction 30%-130%**
2-Fluorobiphenyl	7.378	172	100	
Terphenyl-d14	14.191	244	100	

22.2 LCS/Matrix spike Control Limits

Spike Compounds	Water	Soil
Base Neutrals	40-140	40-140
Acids	30-130	30-130

Note:

Wider limits may apply to certain compounds which routinely fall out of these default limits. The laboratory maintains documentation for these "Problem analytes" and routinely evaluates their performance.

22.3 Recommended Minimum Response Factor Criteria for Initial and Continuing Calibration Verification. – from SW-846 8270D

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

Table 22.4

Minimum average response factor (RRF) System Performance Check Compounds (SPCC)

Compound	Minimum Response Factor
4- Nitrophenol	0.05
2,4-Dinitrophenol	0.05
N-Nitroso-di-n-propylamine	0.05
Hexachlorocychlopentadiene	0.05

Appendix A

8270 Chromatography Issues

8/30/18 - Aniline (93, 66, 65) and Bis(2-chloroethyl)ether (93, 63, 95) are showing serious co-elution issues with instruments B and C. Once the chromatographic column starts to get old, and maintenance shortens the column, this co-elution gets worse. In order to maintain acceptable chromatography, I would like to try a change to the data collected. Specifically, we may have the ability to choose alternate quant ions for these two compounds to minimize unacceptable area contribution during quantitation of the co-elution pair. Our current response factor is strong for all ions used for quantitation and it's feasible to swap the quant ion for a qualifier in one of these two compounds to minimize interference.

Current ions

63 Secondary ion for Bis(2-chloroethyl)ether. Very low abundance in Aniline.
65 Tertiary ion for Aniline. Similar abundance in Bis(2-chloroethyl)ether.
66 Secondary ion for Aniline. Does not appear in Bis(2-chloroethyl)ether.
93 Quant ion for both Aniline and Bis(2-chloroethyl)ether.
95 Tertiary ion for Bis(2-chloroethyl)ether. Does not appear in Aniline.

The following changes will be implemented on GCMSSV3:

1. Change quant ion for Aniline from 93 to 66.
2. Change qualifiers for Aniline from 66 and 65 to 93 and 65.
3. Change quant ion for Bis(2-chloroethyl)ether from 93 to 63.
4. Change qualifiers for Bis(2-chloroethyl)ether from 63 and 95 to 93 and 95.

Please note that co-elution of qualifier ion 93 will still occur when the chromatographic system deteriorates, however normal quantitation problems should be minimized.

We will follow up about the changes made and how the chromatography and calibration hold over time.

09/12/18 **FINAL UPDATE** - Brian has implemented changes to GCMSSV2 and GCMSSV3 successfully. Chromatography looks great. These same integration parameters will be used for all future calibrations for all systems.

02/07/19 I checked with Brian and he says the change has been implemented on all systems and chromatography looks better, so changes that were made have proved beneficial.

ICP

Inductively Coupled Plasma Optical Emission Spectroscopy

6010C/6010D

Non-potables and Solids

Approved:

Tod Kopyscinski	Katherine F. Allen
Laboratory Director	QA Officer

Revision Number: 18

NON-CONTROLLED COPY

Change Record

Revision	Date	Responsible Person	Description of Change
2	12/17/2002	Peter Mathisen	Updates for NELAC format, and Massachusetts Data Enhancement Program
3	10/21/2003	Peter Mathisen	SOP Modification/updates
4	01/06/2004	Peter Mathisen	Change/Updates, per AZ audit: sections 5.11.1, 7.1.11, 8.2c, 8.2h, 8.2j, and 8.2l
5	01/09/2006	Katherine Delisle	Equip. updates and Updates for "Controlled Document Status"; sections 4.0 and 7.2 (removal of Jarrel Ash 61E), 9.0 (corrective action SOP), and 11.0 (ref. addition).
6	11/17/2006	Katherine Delisle	Updates due to internal audit. Sections 1.0 (wording), 3.0 (storage of samples), 7.1.6 (omit bullet test), 8.2e1 (soil recovery), 8.2h (omit AZ ref.), and 11.0 (CT RCP ref.) ICP Limits listed in new appendix.
7	09/07/2007	Katherine Delisle	Update due to internal audit. Section 5.0 (addition of argon gas).
8	12/01/2008	Katherine Delisle	Update due to internal audit. Addition of Sec. 8.2m (Identifying false hits), and Sec. 8.2n (Monitoring internal standards).
9	10/01/2009	Andrea Palpini	Update to incorporate SW846-6010C, adjusted low level check concentrations.
10	10/19/10	Andrea Palpini	Update due to internal audit findings. Removal of Appendix 12. Removed meinhart and burgener nebulizers from sec 4.1. Added RLV. Added microwave reference. Updates for new MCP CAM. (RL adj.)
11	12/01/2010	Katherine F. Allen	Updates to include special precautions for Boron in Sec's 3.6 and 5.11.1.
12	09/04/2013	Charles W. Balicki	Updates from AIHA Audit for prep of spiked media: Sections 8.2e, 8.2f, 8.2q.
13	010/12/2015	Katherine Allen	Update to include SW-846 6010D and from Sept 2015 AIHA audit: Sec 8.2C (ICV for lead to be at regulatory conc.), Sec 11.0 (6010D ref added).
14	06/30/2016	Andrea Palpini/KFA	Updated for 6010D. Changed Sec. 8.2o IDLs – now 10 replicates and calculation changed. Changed wording for Sec 5.1. Inserted reference to HCl Sec 5.2 (all subsequent reagents shifted down by 0.1). Added Spectral Interference Check (SIC) as an alternative name for Interference Checks to Sec. 5.15, 5.16, 5.17, 5.18, 8.2J, 8.2k. Elements to run for an IEC study added to Sec. 8.2k. Added 6010D post spike recovery range to Sec 8.2p.1. Changed concentration requirement for serial dilution to 50 times above the RL, added 6010D criteria of +/- 20% and that the dilution test is not required for RCP data in Sec 8.2p.2.
15	03/23/2017	Andrea Palpini	Updated summary and scope, added no digestion required for dissolved GW samples. Removed references to 6010B. Sec 2.1.3 – added information about IEC equations. Sec 2.1.4 – specified frequency of analysis. Sec 5.0 – added/removed standards and updated acid concentrations. Sec 7.0 – revised procedure for multi-point calibration. Sec 8.2 - added note about subjectivity to change in spike amounts, standards, and concentrations. Sec 8.2.1 – added multipoint calibration criteria. Sec 8.2.4 added extra criteria for RCP. Sec 8.2.5 – added mid-level readback for 6010D and action for CCV failure. Sec 8.2.7 – added information about dissolved method blank. Sec 8.2.9 - changed weights for paint from 0.5 g to 0.05g and 0.25g. Sec 8.2.10 – added note that MSDs may be done in lieu of sample duplicate and run a 5x on matrices that cannot be prepared with a duplicate (or run twice). Sec 8.2.11 - added criteria for <30% re-digestion, added MCP criteria of reporting both sets of data. Sec 8.2.12 – added criteria for MS DUP. Added Sec 11.0 – updated RCP reference to most recent revision, added Dissolved metals prep SOP reference. Added table 1 for ICP reporting limits and table 2 for QA/QC requirements.
16	12/08/2017	Deborah Dalton	Updated 2.1.2 to be +/- 2x RL for spectral interference, 5.0 Allows for use of alternative custom mixes and different QC concentrations 5.20, 5.22 Removed all references to ICSAB 8.23 ICB < ½ RL 8.24 LLCV +/- 20% for 6010C/D 8.2.6 ICSA frequency only after calibration (exception need closing ICSA for air samples), non-spiked analytes +/- RL, 8.2.17 Samples reported up to high calibration standard, but can be extended by running a daily LDR standard that recovers within 90-110% 2.1.3/2.4/4.1/7.1 Added 8300 & Syngistix software where 4300 & Winlab were referenced.
17	04/03/2019	Jackie Clement	Sec 3.3 Removed wait time and turbidity check on dissolved samples. Sec. 5 changed all acid matrix to 2%HNO3/1%HCl. Sec. 5.10 changed 1000ppm to varying conc. of stds. Added 5.15 new sources for calibration std and renumbered. Sec. 5.17 updated cal std prep using new sources. Sec. 5.18 updated conc. & list of elements in std. Added Sec. 5.19. Sec. 5.20 updated procedure and sources. Added 5.21 and 5.22. Sec. 5.24 added reference to SIC/IEC B. Sec. 5.25 and 5.26 updated source vol. to reduce waste. Sec 7.1.8.1 and 7.1.8.2 increased acceptance window per PE service tech. Added Section 7.2 – Sample Preparation, changed reference to MSDS to SDS (Section 6.0), Sec. 8.2 changed AIHA ICV for soil from 5ppm to 4ppm. Section 8.2.16 – changed frequency of IDL study to annually and removed reference to three non-

			consecutive days. Section 8.2.6 – added reference to SIC/IEC B and criteria for non-fortified elements to be +/- 2x the RL, Section 8.2.3 – reworded criteria for ICB and CCB, Section 11 – added references to Metals in Air and Determination of Metals in Suspended Particulate Matter.
18	08/14/2019	Jackie Clement	Sec 8.2.2 New Lead Wipe Regulation changed from 40ug/ft^2 to 10ug/ft^2; Changed wording to run an ICV "at or below the regulatory level" from "at or near the regulatory level"; corrected the off-instrument concentrations for Paint to 1.2 ppm from 1ppm; removed "4ppm is acceptable" for soil.

Distribution/Training List

See Employee Training Record File for signed training statements for trained users.

1.0 SUMMARY, SCOPE, AND APPLICATION

This method may be used for the determination of dissolved, suspended or total elements in non-potable waters, TCLP and EP matrices, and solid materials. Preliminary treatment of the non-potable waters is necessary due to the complexity and variability of the sample matrix. Non-potable waters typically have suspended particulates that must be subjected to a solubilization process before analysis. Groundwater samples that have been pre-filtered and acidified (dissolved samples) will not need acid digestion.

Solid materials are gravimetrically measured and digested to extract the metals component from the aliquot and the digestate is separated from the original solids through filtration, centrifuging, or decanting to eliminate particulates that may impede the instrument operation.

The ICP uses a sequential or simultaneous multielement technique utilizing radial, axial or dual view optical setups to determine trace elements in solution. The basis of this method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the resulting aerosol is transported to the argon plasma where excitation occurs. As the excited-state atoms or ions return to their ground state, energy is emitted in the form of light at wavelengths. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are then dispersed by a grating spectrometer, and the intensities are monitored at specific wavelengths by a photosensitive device. The photocurrents produced are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements.

2.0 INTERFERENCES

2.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

2.1.1 Subtracting the background emission determined by measurements adjacent to the analyte wavelength peak can usually compensate for background emission and stray light. Spectral scans of samples or single element solutions in analyte regions may indicate not only when alternate wavelengths are desirable because of severe spectral interference, but also whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by the measured emission on one side or the other.

2.1.2 Spectral overlaps may be avoided by using an alternate wavelength, or can be compensated for by equations that correct for interelement contributions, which involves measuring known concentrations of common interferents and observing false positive or false negative determinations.

To implement inter-element correction factors (IECs) for the first time, the IEC correction option must be turned off in the instrument software. Known, single element concentrations are analyzed 3-5 times after an acceptable blank sample. A spectral interference is detected if the mean value of the data is +/- 2 times the detection limit. Correction factors are calculated from this data.

$$\mathbf{D/C = X}$$

Where: D is the false positive or negative result in mg/L
C is concentration of the interferent in mg/L

X is the correction factor applied per 1 mg/L of the desired analyte

The correction factors are applied in the instrument software and turned on. The above study is again conducted, and the false readings should be eliminated.

2.1.3 The PE 4300/8300 calculates the IEC automatically, and is applied in the software.

When using interference-correction equations, the interference may be expressed as analyte concentration equivalents (i.e., false positive analyte concentrations) arising from the concentration the standard that was run. For example, if Al was run at 100 mg/L and resulted in an IEC factor of 1.3 on As, 100 mg/L of Al would yield a false positive signal equivalent to an As concentration of 1.3 mg/L. Correspondingly, 10 mg/L of Al would yield a false positive signal for As of 0.13 mg/L.

2.1.4 Multi-element interference check/spectral interference check (IEC/SIC) quality control standards are analyzed daily to verify their accuracy (see Section 8.2.6). Semi-annually, the study is conducted to determine if the IEC/SIC factors need editing.

2.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations.

2.2.1 These interferences can be reduced or eliminated by using a high-solids nebulizer, sample dilution, an appropriate internal standard solution, or a combination of all of the above. The buildup of salts can also have a physical effect, and can be removed though cleaning.

2.2.1.1 Internal Standards restrict physical interferences by the constant addition of an elemental standard into the sample introduction system. The internal standard is monitored throughout the analysis by the software to determine if any drift has occurred. Should physical interferences occur, and the readings of the sample and internal standard are resultantly suppressed, the software will assess a percentage of suppression and apply that to the calculation that determines the final analyte result.

The internal standard must be an obscure element not likely to be found in any samples, such as Yttrium.

2.3 Chemical interferences include molecular compound formation, ionization effects, and solute-vaporization effects.

2.3.1 Typically, this type of interference is not common with the ICP-AES technique. Should it occur, it can be minimized through careful selection of operating conditions, such as incident power and observation position.

2.3.2 Sample matrix matching will reduce the occurrence of chemical interferences.

2.3.3 Should the above measures fail to reduce the interference to acceptable levels, the method of standard additions should be applied.

2.3.3a Use an addition of not less than 50% or more than 100% of the element concentration in the sample so that measurement precision will not be degraded and interferences that depend on element/interferent ratios will not cause erroneous results. Multi-element standard addition can be used if it has been determined that added elements are not interferents.

2.4 Memory interferences may result when analytes in a previously run sample contribute to the signals measured in the following sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer, and from the buildup of sample material in the plasma torch and spray chamber.

2.4.1 In most cases, consistent flushing with a rinse blank between samples will minimize memory effects. The 4300/8300 is capable of adding extended rinse periods should an analyte exceed a prescribed concentration.

2.4.2 Routine rinse times are determined by the regular analysis of blanks after quality control samples containing high concentrations of metals.

3.0 SAMPLE PRESERVATION/STORAGE/HOLDING TIME

3.1 Holding time = 6 months.

3.2 Aqueous samples are pH adjusted <2 with metals grade nitric acid before the appropriate digestion procedure.

3.3 Dissolved samples are filtered prior to preservation through a 0.45-micron filter within 24 hours of sampling. Preserve the sample immediately after filtration to pH<2.

3.4 Solid samples are refrigerated at 4 ± 2 °C upon receipt and are digested within 90 days of collection.

3.5 Aqueous samples are held in storage for a minimum of 30 days before disposal.

3.6 For samples requiring Boron, only plastic or polytetrafluoroethylene (PTFE) should be used for collecting, storing, digestion and handling the sample. This is due to possible contamination by borosilicate glass leaching into the sample. For boron analysis do not use glassware. If necessary to use glass, as in making standards, transfer immediately into a plastic container.

4.0 EQUIPMENT & SUPPLIES

4.1 Perkin Elmer Optima 4300 & 8300 Inductively Coupled Plasma Dual View Optical Emission Spectrometers equipped with Polyscience chillers

- 4.1.1 Winlab 32-bit software and accompanying computers (4300)
- 4.1.2 Syngistix software and accompanying computer (8300)
- 4.1.3 AS 93 plus autosampler with probe/S10 autosampler with probe
- 4.1.4 15 ml disposable sample tubes
- 4.1.5 Orange-Green pump tubing for internal standard introduction
- 4.1.6 Black-Black pump tubing for sample introduction
- 4.1.7 Red-Red pump tubing for drainage
- 4.1.8 PE mixing block for the internal standard and sample combination before delivery to the nebulizer
- 4.1.9 Low Flow Gemcone nebulizer, Miramist nebulizer
- 4.1.10 Cyclonic Spray chamber

5.0 REAGENTS & STANDARDS

Note: When analyzing for Boron, transfer standards immediately after mixing in a clean polytetrafluoroethylene (PFTE) bottle to minimize any leaching of Boron from the glass container. The use of a non-glass volumetric flask is recommended to avoid Boron contamination from the glassware.

Alternative custom mixes from reputable vendors may be used. Calibration and verification standard concentrations may be subject to change.

5.1 Nitric Acid (concentrated) HNO_3 . Trace metals grade; store at room temperature

5.2 Hydrochloric acid (concentrated) HCl - Trace metals grade; store at room temperature

5.3 Type II water or better (ASTM D1193) for preparation of all reagents and standards

5.4 2% HNO_3 / 1% HCl blank – made by adding 20 mL concentrated HNO_3 and 10 mL concentrated HCl to a 1-L volumetric flask containing 400 mL DI. Bring to volume with DI

5.5 Liquid Nitrogen purge gas
- 5.5.1 100 PSI for 4300/8300

5.6 Compressed air shear gas
- 5.6.1 100 PSI for 4300/8300

5.7 Compressed Argon Gas
- 5.7.1 100 PSI for 4300/8300

5.8 Internal Standard Stock solution, 1000 ppm Yttrium traceable ultra-High purity metals grade purchased from a reputable vender

5.9 10 ppm Y, working internal standard solution – made by adding 10 mLs stock standard to a final volume of 1-L volumetrically in 2% HNO_3 /1% HCl DI

5.10 Single element stock standards – varying concentration traceable High purity metals grade purchased from a reputable vender for each analyte.

5.11 3 ppm Pb spike for RLV - made by adding 0.6 mL of 1000 ppm Pb standard to a final volume of 200 mL volumetrically in 2% HNO_3 / 1% HCl DI

5.12 1 ppm axial Mn solution for the X/Y alignment of the torch - Made by adding 1 mL of 1000 ppm Mn stock solution to a final volume of 1-L volumetrically in 2% HNO_3 / 1% HCl DI

5.13 10 ppm radial Mn solution for the X/Y alignment of the torch - Made by adding 10 mLs of 1000 ppm Mn stock solution to a final volume of 1-L volumetrically in 2% HNO_3 / 1% HCl DI

5.14 1000 ppm Na stock solution for sodium bullet test

5.15 Primary multi-element stock standards for calibration: QCS-01 (AccuStandard P/N: QCS-01-5) and QCS-02 (AccuStandardP/N: QCS-02-5), or equivalent from a reputable vendor.

5.16 100 ppm QC-17 custom blend – Al, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, Sb, Se, Tl, V, Zn, purchased from a reputable vender

5.17 Mixed calibration standards – made by combining appropriate volumes of stock solutions in a volumetric flask containing 2% HNO_3 / 1% HCl DI

5.17.1 **Calibration standard 3** – 4mL QCS-01 and 4mL of QCS-02 to a final volume of 40 mL

5.17.2 **Calibration standard 2** – 0.4mL QCS-01 and 0.4mL of QCS-02 to a final volume of 40 mL

5.17.3 **Calibration standard 1** – 2x dilution of calibration standard 2

5.18 1000 ppm QC-26 custom blend - separate source from calibration standards for calibration verification, Al, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, Sb, Se, Tl, V, Zn purchased from a reputable vender.

5.19 QC-17 & Salt/Min Standard (ICV intermediate): made by adding 8mL of each of the following: 1000 ppm QC-16 custom blend stock standard, 1000ppm single element standards Ca, K, Mo, Na, Sn, &Ti; 1.6 mL 5000ppm B and 0.8mL 10000ppm Mg to final volume of 200mL in 2% HNO3/ 1% HCl DI.

5.20 4 ppm ICV (QCS): made by adding 5 mL of QC-17 & Salt/Min standard and 0.20mL of 1000ppm Ag standard to a final volume of 50 mL in 2% HNO_3 / 1% HCl DI volumetrically.

5.21 LCV (90% low level calibration check standard): made by adding 0.09mL of ICP-6010 RL Check Standard and 0.45mL ICP Na/K low level standard to a final volume of 10mL in 2% HNO3/ 1% HCl DI.

5.22 LCV (100% low level calibration check standard): made by adding 0.10mL of ICP-6010 RL Check Standard and 0.50mL ICP Na/K low level standard to a final volume of 10mL in 2% HNO3/ 1% HCl DI.

5.23 Spectral interference/Inter-element interference check (SIC/IEC) stock standard A, purchased from a reputable vender

Analyte	Concentration mg/L
Al	2500
Fe	1000
Ca	2500
Mg	2500

5.24 Spectral interference/Inter-element interference check (SIC/IEC) stock standard B, purchased from a reputable vender

Analyte	Concentration mg/L
Ag	100
Ba	50
Be	50
Cd	100
Co	50
Cr	50
Cu	50
Mn	50
Ni	100
Pb	100
V	50
Zn	100

5.25 SIC/IEC daily check standard A, made by adding 20 mL of SIC/IEC stock standard A to a final volume of 200 mL in 2% HNO_3 / 1% HCl DI volumetrically

5.26 SIC/IEC daily check standard AB, made by adding 4.5 mL of daily check standard A and 0.15 mL SIC/IEC stock standard B to a final volume of 15 mL in 2% HNO_3 / 1% HCl DI volumetrically

5.27 Multi-element reporting limit spike standard, made by adding amounts of single element standards to accommodate variable reporting limits in 5% HNO_3 / 2% HCl DI volumetrically. See Table 1 for a list of reporting limits

5.28 Standard Reference Material (SRM), used for solid matrix LFB/LFB dup purchased from ERA Catalog No. 540, or a reputable vender

5.29 Teflon Chips, used as a control blank for preparation of method blanks when preparing solid matrices

6.0 SAFETY

See Safety Data Sheets (SDS) and Con-Test Chemical Hygiene Plan.

7.0 PROCEDURE

7.1 **Optima 4300** /8300– Calibration and Operation

7.1.1 Turn on the computer and open the Winlab 32/Syngistix software

7.1.2 Open a workspace selecting the instrument method you wish to use

7.1.3 Conduct daily checks

7.1.3.1 Fill rinse containers
7.1.3.2 Check pump tubing, inspect for crimping or clogs and change if necessary
7.1.3.3 Inspect torch and injector and change if necessary
7.1.3.4 Check waste collection, if more than half full, empty into the appropriate disposal system
7.1.3.5 Check the air filters on the instrument (side and back), and on the chiller. Filters should be cleaned weekly
7.1.3.6 Fill the Yttrium internal standard container
7.1.3.7 Prepare calibration and calibration verification check standards (see Section 5)

7.1.4 Tighten pump tubing (shear gas and argon always are on)

7.1.5 In the plasma window, click the "plasma on" button. Observe plasma ignition to ensure the plasma lights correctly

7.1.6 Allow the instrument warm up for 30 minutes - 1 hour to stabilize the plasma and condition the pump tubing

7.1.7 Create a data file to save the results

7.1.8 In the tools folder of Winlab on the software toolbar or from the dropdown menu under the Instrument Tab of Syngistics, select spectrometer control to align the torch

7.1.8.1 Select the axial radio button and aspirate the 1 ppm Mn solution. Once solution has entered the plasma, select align view. The axial alignment is acceptable when X viewing position is set to 0.0 $\pm$0.5 mm and Y viewing position is set to 15.0 $\pm$ 0.5mm
7.1.8.2 After the axial alignment is complete, select the radial radio button and aspirate the 10 ppm Mn solution. Once solution has entered the plasma, select align view. The radial alignment is acceptable when the X viewing position is set to 0.0 $\pm$ 0.5 mm.
7.1.8.3 An error message will flag if there are serious issues with the alignment. Refer to the instrument manual if this occurs. Record the intensity counts daily and monitor for drift

7.1.9 Rinse for 5-10 minutes after alignment. Begin the daily calibration by selecting the calibrate button in the automated analysis control window

7.1.11a. Con-Test only uses a linear calibration algorithm on the 4300/8300, where:

Y = MX + B where:
X = concentration
Y = intensity
M = slope of the calibration curve
B = y-axis intercept

7.1.10 When calibration is complete, evaluate the correlation coefficients (r^2) for acceptability. $r^2 \geq 0.995$ for all methods expect MCP which is ≥ 0.998

7.1.11 If the calibration is acceptable, continue by running the opening calibration verification check standards. Monitor results to ensure QCs are within acceptable limits (see Section 8)

7.1.12 If calibration verification check standards are acceptable, proceed with sample analysis.

7.2 Sample Preparation

7.2.1 Analyze samples after appropriate preparation as specified in the latest revision of the following SOPS:

- Metals in Air, Document # 40
- Dissolved Metals Prep, Document # 394
- Method 3051A and 3015A, Document # 135
- Determination of Metals in Suspended Particulate Matter, Document # 247
- Preservation and Digestion of Aqueous Matrices, Document # 39
- Acid Digestion of Solid Materials, Document # 29

8.0 QUALITY CONTROL

8.1 Definitions

For definitions and explanations of quality control measures (blanks, LCS/QC Reference, LFB, Duplicates, MS/MSD, etc.) refer to the Con-Test Analytical Quality Assurance Manual.

8.2 Quality Control Measures & Acceptance Criteria

Note: All references to spike amounts, spike standards, and concentrations are subject to change. All standards are purchased from a reputable vender. See Table 2 for a summary of QA/QC specifications.

8.2.1 Calibration Curve

A calibration curve must be analyzed daily. The instrument may be calibrated using either a single point or a multipoint calibration curve. A minimum of 3 standards and a calibration blank are required with a correlation coefficient of $\geq$ 0.995 for all methods except MCP which is $\geq$ 0.998. If the calibration coefficient does not pass the criteria, re-calibration is necessary.

8.2.2 Initial Calibration Verification (ICV)

Also known as the external standard or reference standard, the ICV is made from a solution separate from the calibration standards and analyzed after the calibration to ensure proper standard make-up and detect any analytical biases. The ICV is made from a different lot number or a different vender than the calibration. Always verify that the second source is truly a different source than the calibration standard. The acceptable range is ± 10%.

If the calibration cannot be verified within these limits, re-analyze. If the ICV/QCS is still outside the limits, the analysis is stopped, the problem fixed, and the instrument is recalibrated.

For AIHA-LAP, LLC lead program, the ICV shall be measured after calibrating and before measuring samples at a concentration at or below the regulatory level of concern.

Lead Paint = 600 mg/kg (1.2 ppm off instrument)
Lead Wipes = 10ug/ft^2 (0.2 ppm off instrument)
Lead Soil = 400 mg/kg (8ppm off instrument)

8.2.3 **Calibration Blank / Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)**

Analyzed as part of the calibration curve, immediately after the calibration (after the ICV), at the end of sample analysis, and in between every 10 samples or less to determine any bias associated with drift at the RL portion of the curve.

ICB range = -2x RL up to ½ RL for all methods except MCP which is -2x RL up to the RL
CCB range = -2x RL up to the RL

The ICB is run after the ICV

CCBs are analyzed after the CCVs

If the ICB or CCB fail, reanalyze the solution. If the values are not within control limits, the analysis must be stopped and the problem fixed. For an ICB failure, a re-calibration is needed. For a CCB failure, all samples following the last acceptable CCB solution will be re-analyzed or the data qualified

8.2.4 **Low-Level Calibration Verification (LLCV)**

The low level calibration standard is made by diluting the multi-element reporting limit spike standard to accommodate the required reporting limit concentrations. It is run daily at a concentration at or below the reporting limit prior to sample analysis to ensure data validation. See Table 1 for a list of reporting limits. The acceptable range is ± 20% for all elements analyzed for methods 6010D, and ± 30% for MA MCP. For CT RCP, the acceptable range is ± 30% for all metals except Sb, As, Co, and Tl which have a ± 50% limit.

If the reporting limit is included in the low calibration standard, the LLCV does not need to be analyzed for MA MCP or CT RCP.. If a single point calibration is used, then the LLCV must be analyzed with acceptable recoveries of ±20% from the true value.

If the LLCV fails, reanalyze. If the recoveries are still outside control limits recalibrate or qualify on the final report. For MA MCP, data may be reported if an element fails and the sample results are >10x the reporting limit.

8.2.5 **Continuing Calibration Verification (CCV) / Mid-Level Readback or Verification (6010D)**

Per method 6010D, the mid-level readback or verification must be run after the calibration is completed and recover within 90 – 110%.

The CCV is prepared from the same source as the calibration standards and should be at a concentration near the mid-point of the calibration. The CCV is analyzed after every 10 samples or less, and at the conclusion of the analytical run with a range of 90 – 110%.

If the calibration cannot be verified within these limits, re-analyze. If the CCV is still outside the limits, the analysis is stopped, the problem fixed, and the instrument is re-calibrated or the run is resumed. All samples following the last acceptable CCV solution will be re-analyzed.

8.2.6 **Inter-element Correction Verification Standard (IECs) or Spectral Interference Check (SIC) – Multi-element SIC/IEC A and AB**

Analyzed after the calibration (and end of the run if air samples are analyzed), and should be 80-120% of target level of interferent concentration. It is also prudent to monitor concentrations of non-fortified metals to detect possible IEC drift and needed adjustments. Non-fortified elements must be ± 2x the reporting limit.

8.2.7 **Method Blank (MB)**

Matrix matched samples brought through the digestion procedure. At least 1 per batch of 20 or less is prepared and the results should be less than the reporting limit. If the method blank is above the reporting limit, a fresh aliquot should be re-analyzed.

In the case of undigested samples, the calibration blank solution is the method blank.

For dissolved samples, use TYPE II water filtered through the same filters used for dissolved sample filtration. If the samples are digested, the method blank will be digested as well.

If the method blank fails after re-analysis, the outlier is qualified on the final report or samples are re-prepped. If the sample results are >10x the level of contamination detected in the method blank, the data is considered valid and unbiased. If the samples are not >10x the level of contamination in the MB but are non-detect, the data is considered valid. If the samples are detected and are not >10x the level of contamination the sample batch will be re-prepped or the out of control event will be qualified.

8.2.8 **Reporting Limit Verification (RLV)**

The RLV must be prepared with each digestion batch for environmental Pb analysis only. Spiked at the reporting limit, the recovery must be 80 – 120% to ensure accuracy at the reporting limit. If this limit is not met, all Pb samples must be re-digested and reanalyzed or the data qualified.

Soil – 1.5 grams of boiling chips is weighed out into a digestion vessel then spiked with 0.25 mL 3 ppm Pb standard. True value = 0.015 ppm.

Wipe - A blank ghost wipe is put into a digestion vessel then spiked with 0.025 mL 100 ppm QC-26. True value = 0.05 ppm.

Paint - 0.05 grams of Pb free paint powder are weighed into a digestion vessel then spiked with 0.0125 mL 100 ppm QC-26. True value = 0.05 ppm.

8.2.9 **Lab Fortified Blanks (LFB) or Laboratory Control Samples (LCS) / LFB/LCS Duplicates**

Matrix matched blanks are spiked at a frequency of 2 per batch of 20 samples or less for matrices that cannot be spiked, and 1 per digestion batch of 20 or less for those that can. It is the analyst's prerogative to prepare additional LFBs.

LFBs are carried through the entire preparation process, and spiked with a separate source from the calibration prior to preparation. Always verify that the second source is truly a different source than the calibration standard.

Limits for aqueous batches are 80 – 120%. For solid matrices a SRM is used. Control limit criteria are established by the manufacturer.

LCS/LFB duplicates to determine analytical precision must be performed for all MA MCP batches, if a sample duplicate is not performed.

Aqueous	RPD ≤ 20%
Solids	RPD ≤ 30%

Soil - 0.5 grams of a standard reference material are weighed out into a digestion vessel. True values will vary based on makeup of material.

Wipe - 0.5 grams of a standard reference material is weighed out into a digestion vessel. True values will vary based on makeup of material. If using the Pb paint powder SRM, only weigh out 0.05 grams.

Paint
0.05 grams of Pb paint powder is weighed out into a digestion vessel. True values will vary based on makeup of material. If additional metals are requested, 0.25 grams of standard reference material is weighed out into a digestion vessel.

8.2.10 **Matrix Duplicates (DUPS**)

Analyzed one per batch of 20 samples or less to assess precision by use of a calculated RPD. Limits are dependent on the matrix. All methodology states a frequency of one per batch of 20 or less however, a MSD can be prepared in addition or in lieu of a sample duplicate.

If > 5x RL	
Soils	RPD ≤ 35%
Aqueous	RPD ≤ 20%
If < 5x RL	
Soils	difference < 2x RL
Aqueous	difference < RL

Samples that are totally consumed during digestion and cannot be duplicated are either read twice by the instrument or at a 5x dilution to confirm precision.

8.2.11 **Matrix Spikes (MS**)

Spiking occurs prior to sample preparation, and is carried through the entire digestion process, then analyzed with the samples. Spikes are done at a frequency of 1 per batch of 20 or less.

All matrices 75 – 125%

Internal laboratory control limits are generated through a charting program. The recoveries must fall within the tighter of the limits listed above.

Samples that are totally consumed during digestion cannot be spiked.

For MA MCP, if the matrix spike recovers >30% and the LCS is within control limits, qualify on the final report. If the matrix spike recovers <30% and is associated with non-detect results, re-digest and reanalyze sample/MS pair. Both sets of sample/MS data must be reported. (Per EPA Region 1 data validation guidance).

For CT RCP, if the matrix spike recovers >30% and the LCS is within control limits, qualify on the final report. If the matrix spike recovers <30%, re-digest and reanalyze the sample/MS pair.

Soil
1.5 grams of sample is weighed out into a digestion vessel, then spiked with 0.25 mL of 100 ppm QC-26. True value = 0.5 ppm. If Na, Ca, Mg, K are requested, use 1 mL spike of 100 ppm QC-26.

Paint
0.05 grams of a sample is weighed out into a digestion vessel, then spiked with 1 mL of 100 ppm QC-26. True value = 4 ppm.

The concentration of Ca, Mg, and Na, and to some degree Fe, Mn and Al in environmental water samples, along with Fe and Al in solids can vary greatly and are not necessarily predictable. Fortifying these analytes in routine samples at typical spiking concentrations may prove to be of little use in assessing data quality for these analytes.

8.2.12 **Matrix Spike Duplicates (MSDs)**

Matrix spike duplicates can be prepared in addition or in lieu of sample duplicates. Because of the multi-element component of ICP analysis, DUPs are primarily used over the MSDs due to the abundancy of metals with hits > 5x the RL, unless an MSD is requested by the client.

Recovery criteria: 75 – 125%
RPD criteria:

If > 5x RL	
Soils	RPD ≤ 35%
Aqueous	RPD ≤ 20%
If < 5x RL	
Soils	difference < 2x RL
Aqueous	difference < RL

The concentration of Ca, Mg, and Na, and to some degree Fe, Mn and Al in environmental water samples, along with Fe and Al in solids can vary greatly and are not necessarily predictable. Fortifying these analytes in routine samples at typical spiking concentrations may prove to be of little use in assessing data quality for these analytes.

8.2.13 If QC samples generate less than useful data, then the following tests should be performed. At a minimum, these tests should be performed with each batch of samples.

8.2.13.1 **Post digestion spike**

A post digestion spike should be performed on matrices which cannot be spiked.

If the MS/MSD recoveries are unacceptable (<75% or >125%) a post digestion spike should be performed on the QC sample. If there is limited sample this may be performed on another sample from the same batch.

The sample should be spiked at a known concentration and analyzed with a recovery of 80 – 120% for 6010C and 75 – 125% for 6010D. The spike addition should be between 10 and 100 times the lower limit of quantitation.

If the post spike fails, a dilution test may be performed. Otherwise, a matrix effect is confirmed.

***** Not required by MA MCP or CT RCP (recommended per SW-846 methods)

8.2.13.1 **Dilution Test/Serial Dilution**

If a concentration is >50x the RL for a certain analyte, an analysis of a 1:5 serial dilution should be analyzed and agree with the original result within 10% for all methods except 6010D. For 6010D, the results should agree with the original result within 20%. If this criterion is not met, a chemical or physical interference should be suspect.

For MCP data, a dilution test is performed and reported 1 per batch of 20 or less if project-specific MS is requested and the analyte concentration is >50x the RL.

For Category B and data packages, the serial dilution must be included for results >50x the RL.

***** Not required for CT RCP (recommended per SW-846 methods)

8.2.14 **Monitoring Internal Standards**

Yttrium internal standard peak intensities are monitored for every sample introduced into the instrument to verify the absence of interference and/or the integrity of the sample introduction. Any Yttrium internal standard intensity that is significantly different from the calibration is suspect. The sample must be re-analyzed to verify the validity of the initial analysis. If the recovery is still significantly different, a sample dilution must be performed.

8.2.15 **Checking for false Hits**

Since ICP-AES measurements are prone to false positive reporting, any reportable values for Sb, Tl, Se, or Be (elements with frequent potential for false positive identification) require special attention. Spectra are printed out and included in the record; either identifying elevated baselines, contributions from adjacent peak tailing or bonafide identifications. All significant values intended for reporting for these elements may be confirmed by analysis on a different instrument or with a different technique.

8.2.16 **Instrument Detection Limit**s

IDL's are performed to evaluate the instruments change in noise levels over time. 10 replicates of instrument blanks are analyzed with each measurement being taken through the normal sequence of the instrument (i.e., rinses in between samples). The IDL is calculated by taking the mean of the blank results plus 3 times the standard deviation of the 10 replicates. Values of zero are used if the mean is negative. The IDL must be less than the elements MDL.

An IDL study is performed annually, or when conditions are changed due to major maintenance or service to evaluate the instruments change in noise levels over time**.**

8.2.17 **Linear Dynamic Range Analysis (LDR)**

A linear dynamic range study is analyzed every 6 months for each wavelength. It is determined by analyzing a minimum of three concentrations of the analyte of interest until the observed recovery is no more than 10% above or below the stated concentration of the standard.

Sample concentrations that exceed the high calibration standard should be diluted and reanalyzed. Or the analyst may choose to analyze a LDR standard during the run that must recover ± 10%. If the additional LDR standard passes then the sample concentration may be reported up to the LDR standard without dilution.

8.2.18 **Inter-element Spectral Interference Correction Analysis (IEC Study or SIC) – Single-elemen**t

IEC studies are performed on a semi-annual basis (see Section 2.1 for discussion).

The following standards are to be analyzed: Al, B, Ba, Ca, Cu, Fe, Mg, Mn, Mo, Na, Ni, Se, Sn, V, and Zn.

Si is not an analyte of interest and is therefore not analyzed as part of the IEC study.

8.2.19 Method Detection Limit Studies (MDLs)

MDLs are conducted annually or when conditions are changed due to major maintenance or service. (See the Con-Test Analytical Quality Assurance Manual)

Spiking concentrations for MDL determinations shall not exceed 10× the calculated MDL.

9.0 CORRECTIVE ACTIONS/CONTINGENCIES OF HANDLING OUT-OF-CONTROL DATA

9.1 Refer to Con-Test Quality Assurance Manual.

9.2 Refer to Con-Test Corrective Action SOP.

10.0 POLLUTION PREVENTION

10.1 The smallest volume of standard is made up to avoid un-necessary waste.

10.2 Acidic samples and waste are disposed of into the appropriate satellite waste containers.

10.3 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing the waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.

10.4 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many 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 waste generation. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

11.0 REFERENCES

11.1 Con-Test Analytical Chemical Hygiene Plan.

11.2 SW846-6010C "Inductively Coupled Plasma-Atomic Emission Spectrometry," Revision 3, November 2000.

11.3 SW-846 Update V – Method 6010D "Inductively Coupled Plasma – Optical Emission Spectrometry," Revision 4, July 2014.

11.4 Con-Test Analytical Corrective Action SOP.

11.5 Con-Test Analytical Procedure for Maintaining Controlled Documents SOP.

11.4 Con-Test Analytical Quality Assurance Manual.

11.5 Perkin Elmer Instrument Manual Optima 4300 ICP OES DV 2001 1st Ed.

11.6 NELAC SOP # 29 Acid Digestion of Solid Materials.

11.7 NELAC SOP # 16 Metals Turbidity Determination.

11.8 NELAC SOP # 39 Preservation and Digestion of Aqueous Matrices.

11.9 NELAC SOP # 135 Microwave Assisted Digestion of Soils, Sediments, Sludge's and Oils (3051A), and Aqueous Samples and Extracts (3015A).

11.10 NELAC SOP # 40 Metals in Air.

11.11 NELAC SOP # 247 Determination of Metals in Suspended Particulate Matter.

11.12 NELAC SOP # 394 Dissolved metals Prep.

11.13 Quality Assurance and Quality Control Requirements and Performance for SW846 Method 6010C, Trace Metals by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) for the MCP. Massachusetts DEP WSC-CAM-IIIA. Revision 1. July 1 2010.

11.14 CT DEP "Recommended Reasonable Confidence Protocols Quality Assurance and Quality Control Requirements, Determination of Trace Metals by SW-846 Method 6010 Inductive Coupled Plasma-Atomic Emission Spectrometry" Version 2.0, July 2006.

Table 1: ICP Reporting limits.

Analyte	**6010 Waters**	**6010 Soils**		**6010 Oils**		**6010 Wipes**	
	mg/L	**mg/kg**	**mg/L**	**mg/kg**	**mg/L**	**ug/wipe**	**mg/L**
Ag	0.005	0.5	0.01	2.5	0.01	2.5	0.05
Al	0.05	2.5	0.05				
As	0.01	2.5	0.05	5	0.02	2.5	0.05
B	0.1	5	0.1				
Ba	0.05	2.5	0.05	25	0.1	2.5	0.05
Be	0.004	0.25	0.005				
Ca	0.15	7.5	0.15				
Cd	0.004	0.25	0.005	6.25	0.025	2.5	0.05
Co	0.05	2.5	0.05				
Cr	0.01	0.5	0.01	2.5	0.01	2.5	0.05
Cu	0.01	0.5	0.01				
Fe	0.05	2.5	0.05				
K	2	100	2				
Mg	0.15	7.5	0.15				
Mn	0.01	0.5	0.01				
Mo	0.1	5	0.1				
Na	2	100	2				
Ni	0.01	0.5	0.01				
Pb	0.01	0.75	0.015	3.75	0.015	2.5	0.05
Sb	0.05	2.5	0.05				
Se	0.05	5	0.1	12.5	0.05	25	0.5
Sn	0.1	5	0.1				
Tl	0.05	2.5	0.05				
Ti	0.1	5	0.1				
V	0.01	1	0.02				
Zn	0.02	1	0.02				

Table 2: Specific QA/QC Requirements and Performance Standards for Method 6010.

	SW-846 6010C	SW-846 6010D	MCP (w/6010C)	RCP (w/6010B)
r^2	0.995+	0.995+	0.998+	0.995+
ICV	90-110%	90-110%	90-110%	90-110%
ICB	<RL	+/- 1/2RL	<RL	<RL
LCV	Required if Low cal std is not at RL or Single Point Calibration is used 80-120%	80-120%	Not required if Low cal std is at or below RL 70-130%	Not required if Low cal std is at or below RL 70-130% for all except: Sb, As, Co, Tl are 50-150%
CCV	90-110%	90-110%	90-110%	90-110%
ICSA [A]	80-120%	80-120%	80-120%	80-120%
LDR Std		90-110% Not required but may be analyzed to allow reporting over the high calibration standard		
Internal Standard (Con-Test set limit)	+\- 50%	+\- 50%	+\- 50%	+\- 50%
Post Spike needed if:	If MS <74% or >125% or DUP RPD >20%, evaluate the following test on the QC sample for failing metals only **(recommended)**	If MS or DUP are outside control limits or a high concentration is not available for the dilution test, evaluate the following test on the QC sample for elements that failed the MS recovery **(recommended)**		
Post Spike (PS)	80-120%	75-125%	not required	not required
Dilution Test needed if:	If sample concentration is >50x the RL, perform 1:5 on QC sample **(recommended)**	If sample concentration is >50x the RL, perform 1:5 on QC sample **(recommended)**	**Required** if data user specifies QC sample and result is >50x RL. Perform 1:5 serial dilution on the QC sample	
Dilution Test[B]	10% RPD	20% RPD	10% RPD	not required

[A] ICSA non spike elements must be +\- RL
[B] For MCP and RCP, dilution test required if DUP/MS/MSD is requested by client

POLYCHLORINATED BIPHENYLS (PCBs) by GAS CHROMATOGRAPHY

(Method SW846 8082A)

Approved:

Tod Kopyscinski
Laboratory Director

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QA Officer

Revision Number: 13

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Change Record

Revision	Date	Responsible Person	Description of Change
Original	05/05/2003	J. Beane/ S. Kocot	Original, including MCP Data Enhancement Criteria and NELAP format
1	01/13/2004	D.Damboragian	QC criteria updates, for AZ audit
2	8/31/2005	E. Denson	2004 Arizona audit requirements
3	10/27/2005	J. Beane	Updates to extraction and GC parameters
4	11/16/2006	D.Damboragian	Addition of PCB wipe extraction procedure
5	11/12/2008	F. Derose	Updates to extraction and GC parameters
6	10/14/09	F. Derose	Updates
7	4/13/2011	JB	Updates from Annual SOP review: Sec. 9.0 (Instrument Set-up updated), Sec. 6.0 (Reagents section updated), Sec 8.0 updated, and Sec 17.0 (ref. addition)
8	06/19/2012	KFA	Updates from annual review: Sec's 1.0, 2.0, 4.0, 6.18, 11.0, 12.2.5 (Inclusion of PCB Wipes) and Sec 17.10 (new MA MCP rev). Sec 5.24 & Sec 8.3.7 rinse twice with hexane added, Sec 6.10 helium removed, Sec 8.5.3 to 8.5.5 removed and reference to see SOP Florisil Clean-up added.
9	09/19/2013	KFA/CWB	Updates from 2012 annual SOP review: Section 8.3.2 (note added on how to handle sediment on the bottom of sample container), Section 9.1 (deletion of ECD#2) and Section 17.0 (deletion of 5890 reference and addition of Buchi turbovap). Updated section 8.3.9 with new numbering. Added section 8.3.10 to include Buchi Syncore Concentrator. Updated section 8.4.1.
10	03/23/2016	CWB	Removed all Turbo Vap references. Updated Section 9.1 (added Instrument ECD 10), updated column information
11	08/31/2017	KFA	Update from annual internal audit: Sec 9.1 (delete ECD#8 and column 1 is 0.5um df), Sec 12.2.1 (20% ICAL RSD not 15% and 100ug/L ICV not 50ug/L), Sec 12.2.2 (0.03min is default), Sec 12.2.3 (MCP 20% not 15% for CCV), and Sec 12.2.8 (reworded conf. criteria).
12	03/12/2019	Charles Balicki/PJG	Updates from Annual SOP Review: Section 1.0 added 10 ug/L for caulking, paint, and micro extraction waters. Section 3.0 replaced florisil column cleanup with Enhanced Florisil cleanup. Section 4.0 Updated MCP Data Enhancement: removed aqueous samples/no residual chlorine, added "PCB", and changed -10°C to 4°C. Sections 6.17, 6.18, 6.19 Updated volume amounts. Section 8.3.3 changed 1000ug/l to 2000 ug/L. Section 9.1 changed model numbers for column 1 and column 2. Section 11.0 added "^{2}" to Wipe sample concentration formula. Section 12.2.1 changed from 5 point to 6 point. Section 12.2.2 changed default standard deviation from 0.3 to 0.03 minutes. Update for new calibration: Sec 6.16.
13	11/22/19	Todd Gionfriddo	Updates from addition of Low volume: 2.0 Summary of Method 4.0 Sample Preservation/Storage/Holding Time Added 8.3A LOW VOLUME WATER EXTRACTION Added 8.4.7-8.4.10 because it was not in the SOP 8.5 Added TBA Cleanup Note

Distribution/Training List

See Employee Training Record File for signed training statements for trained users.

1.0 SCOPE AND APPLICATION

Method 8082 is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors in extracts from solid, wipes and aqueous matrices. Open-tubular, capillary columns are employed with electron capture detectors (ECD). When compared to packed columns, these fused-silica, open-tubular columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis. The target compounds may be determined by either a single- or dual-column analysis system. The method also may be applied to other matrices such as oils and wipe samples, if appropriate sample extraction procedures are employed. The following analytes can be determined by this method:

PCB-1016	PCB-1254
PCB-1221	PCB-1260
PCB-1232	PCB-1262
PCB-1242	PCB-1268
PCB-1248	

Reporting Limit = 20 ug/L (off of the instrument), 10 µg/L for caulking, paint, and micro-extraction waters, <0.1 mg/Kg and <0.2 ug/L (calculated).

MA CAM RL's = 0.25ug/L and 0.1 mg/kg

2.0 SUMMARY OF METHOD

A measured volume, weight of sample (approximately 1-Liter for liquids, 120mL for low-volume liquids, 10 grams for soils; 0.200 grams for paint; 0.500 grams for caulking; 2.0 grams for product solid), or one wipe is extracted using the appropriate matrix-specific sample extraction technique (e.g. Microwave -3546 or ASE -3545 or Soxhlet -3540C or Liq-Liq 3510C). Aqueous samples are extracted at pH 5-9 with methylene chloride, solid and wipe samples are extracted with 1:1 Acetone: Hexane. Extracts for PCB analysis are subjected to a sulfuric acid clean-up, which will remove many single component organochlorine or organophosphorus pesticides. Therefore, Method 8082 is not applicable to the analysis of such compounds. Instead, use Method 8081. After clean-up, the extract is analyzed by injecting an aliquot into a gas chromatograph with a narrow bore fused silica capillary column and electron capture detector (GC/ECD).

3.0 INTERFERENCES

3.1 Interferences co-extracted from the samples will vary from matrix-to-matrix.

- 3.1.1 Contaminated solvents, reagents, or sample processing hardware.
- 3.1.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.
- 3.1.3 Compounds extracted from the sample matrix to which the detector will respond.
- 3.1.4 Co-elution of target analytes.
- 3.1.5 Clean-up procedures include: Advanced Florisil clean-up, Florisil cartridge clean-up, TBA clean-up (for sulfur interferences: used for either PCBs or pesticides), and sulfuric acid clean-up (only performed for PCBs, never for pesticides).

3.2 Interferences by phthalate esters can pose a major problem in PCB determination. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. For this reason, avoid the use of plastics in the laboratory.

3.3 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Glassware must be scrupulously cleaned.

NOTE: Oven-drying of glassware used for PCB analysis can increase contamination because PCBs are readily volatilized in the oven and spread to other glassware. Therefore, exercise caution, and do not dry glassware from samples containing high concentrations of PCBs with glassware that may be used for trace analyses.

3.4 Subtracting blank values from sample results is not permitted.

4.0 SAMPLE PRESERVATION/STORAGE/HOLDING TIME

Sample Matrix	Container	Preservation	Holding Time
Aqueous*	1-Liter amber glass bottle with Teflon-lined screw cap or 120mL amber glass bottle with Teflon-lined screw cap	Cool to 4°C **	CT = Extract within 7 days of collection; analyze extracts within 40 days following extraction MA = Extract within 1 year and 40 days from extraction to analysis. For states following SW846 guidelines = all matrices no holding times stated.
Soils/Sediments	8-16 oz wide-mouthed amber glass jar with Teflon-lined screw cap	Cool to 4°C **	CT = Extract within 14 days of collection; analyze extracts within 40 days following extraction MA = Extract within 1 year and 40 days from extraction to analysis. For states following SW846 guidelines = all matrices no holding times stated.
Concentrated Waste Samples	125-mL wide-mouth glass with Teflon-lined cap	None Required **	CT = Extract within 14 days of collection; analyze extracts within 40 days following extraction MA = Extract within 1 year and 40 days from extraction to analysis. For states following SW846 guidelines = all matrices no holding times stated.
Wipe sample media (gauze pads)	2-8 oz wide-mouthed amber glass jar with Teflon-lined screw cap	Hexane on media prior to sampling	Extract within 14 days of collection; analyze extracts within 40 days following extraction

* For aqueous samples with a chlorine residual, add 1-3 mL 10% sodium thiosulfate to sampling container prior to filling.
**** MCP Data Enhancement**: Store PCB sample extracts at -4°C, protect from sunlight, and store in sealed vials (screw-cap or crimp-cap vials) with un-pierced PTFE-lined septa.

5.0 EQUIPMENT & SUPPLIES

5.1 Capillary column, gas chromatograph with splitless injector, auto injector, ECD and data system.
5.2 Sample containers - amber glass jars, with Teflon-lined screw caps.
5.3 Buchi Syncore Concentrator and glassware
5.4 Ebulator or boiling chips
5.5 Graduated cylinder - 1-Liter, glass
5.6 Volumetric glassware
5.7 Micro syringes
5.8 Pipettes - 1-mL, volumetric, class A
5.9 Vials, 2-mL snap top
5.10 Water bath
5.11 Filter paper: Grade 413, 11cm
5.12 Glass funnels
5.13 Pasteur pipettes
5.14 Florisil sep packs
5.15 Separatory funnel: 2-Liter
5.16 pH paper
5.17 300-mL BOD bottles
5.18 4-mL screw top vials
5.19 60-mL extraction vials
5.20 10-mL N-EVAP concentrator tubes
5.21 Microwave - CEM – w/ temperature program capable of $\pm$ 2.5° C
5.22 Microwave Vessels – Teflon
5.23 Vials, 12-mL amber vials with Teflon lined caps

Note: All glassware must be rinsed at least twice with methylene chloride and twice with Hexane.

6.0 REAGENTS & STANDARDS

6.1 Reagent Water: deionized water
6.2 Methylene Chloride: pesticide quality
6.3 Hexane: pesticide quality
6.4 Isooctane (2,2,4-Trimethyl Pentane): pesticide quality
6.5 Acetone: pesticide quality
6.6 Sodium Sulfate: ACS grade, granular, anhydrous, baked at 400°C for 4 hours
6.7 Glass Wool: pesticide quality
6.8 Nitrogen: Ultra High Purity
6.9 Sulfuric Acid (concentrated): ACS grade
6.10 Hydrogen: Ultra High Purity
6.11 Sodium Thiosulfate: ACS grade, granular
6.12 Stock Standards: Purchased as certified solutions from Ultra Scientific (or equivalent), 100 ug/mL in either methanol or hexane
Aroclor - 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, 1268
6.13 2-Propanol: Pesticide quality or equivalent
6.14 Tetrabutylammonium hydrogen sulfate: sulfite reagent
6.15 Sodium sulfite: pesticide quality
6.16 Working Stock, 1 ug/mL (1000 ppb): add 500 uL of PCB 1260 and PCB 1016 stock solution [Ultra Scientific (or equivalent) 100ug/mL] and 250 uL of Pesticide Surrogate Mix [Restek (or equivalent) 200 ug/mL] to final volume of 50 mLs in isooctane. Prepared fresh for each new curve; expiration = 6 months. Expiration date to be written on vial.

Dilution	Working Stock (mLs)	Isooctane (mLs)	Final Conc. (ug/L)
2x	20	20	500
5x	8	32	200
10x	4	36	100
20x	2	38	50
50x	0.8	39.2	20
100x	0.4	39.6	10
200x	0.2	39.8	5*

*In surrogate curve only

6.17 Soil Spiking Stock, 2000µg/L: add 1mL of 1000µg/mL of Aroclor 1016/1260 Mix, to a final volume of 500mL with acetone. Spiking standards are obtained from a different source than calibration standards.

6.18 Water and Wipe Spiking Stock, 500 µg/L: add 0.25mL of 1000µg/mL of Aroclor 1016/1260 Mix, to a final volume of 500 mL with acetone. Spiking standards are obtained from a different source than calibration standards.

6.19 Surrogate Standard, 2000 ug/L: add 5 mL of Restek (or equivalent) stock (200 ug/mL in Acetone) to a final volume of 500 mL with Acetone.

7.0 SAFETY

See Material Safety Data Sheets (MSDSs) and Con-Test Chemical Hygiene Plan.

PCBs are absorbed through the skin. Exercise extreme caution when working with concentrated solutions or samples containing or suspected to contain PCBs. Nitrile gloves of sufficient thickness to be impervious to PCBs should be used.

If skin contamination occurs the material should be wiped off immediately and the skin washed with soap and water. Water alone is not sufficient. Contaminated clothing should be removed quickly and disposed of as recommended. Organic solvents should NOT be used to wash the skin.

8.0 SAMPLE EXTRACTION

8.1 Microwave Extraction (Soils and Wipes) – Method 3546 (refer to Microwave Method 3546 SOP)

8.2 Soxhlet Extraction (Soils, Wipes, TO-10A) – Method 3540C (refer to Soxhlet Method 3540C SOP)

8.3 Water Extraction Method SW-846 3510C

8.3.1 The pH of all samples is checked with pH paper at the time of log-in. The pH must be between5-9. If the pH is not in the proper range, adjust accordingly with either 1N NaOH or 1:1 H_2SO_4. Record the volume of acid or base used.

8.3.2 To measure the volume of sample, draw a line on the sample container at the meniscus of the sample. Transfer the entire sample to a separatory funnel. Rinse the sample container with the first 60 mL aliquot of methylene chloride and transfer to the separatory funnel. At a later time, place water in the sample container so the meniscus is up to the line drawn. Measure this volume in a graduated cylinder to the nearest 5 mLs and record. If one liter of sample is not available, record amount of sample used and bring up to one liter with DI water.

Note: If sediment covers the entire bottom of the sample container, be sure to decant sample, rinse container with solvent and decant solvent into separatory funnel leaving sediment in sample container.

8.3.3 Add 1.0 mL of 2,4,5,6-Tetrachloro-m-xylene (TCMX) and Decachlorobiphenyl (DCB) at 2000 ug/L surrogate standard to all samples, spikes and blanks.

8.3.4 Add 1 mL of spike standard to all LFBs ("lab spikes") and matrix spikes. True value = 500 ug/L (50 ug/L off of the instrument). 1016/1260 is used per method. Alternate Aroclors may be warranted based on site specific conditions.

8.3.5 Add 60 mLs of methylene chloride to the separatory funnel. Stopper and shake vigorously for 2 minutes with periodic venting to release excess pressure. Allow the organic layer (bottom layer) to separate from the water phase for a minimum of 10 minutes. If an emulsion exists between layers, the analyst must employ mechanical techniques such as swirling, stirring, and centrifugation, to complete phase separation.

8.3.6 Pass the solvent layer through a glass funnel, lined with filter paper containing anhydrous sodium sulfate into a BOD bottle. Repeat extraction two more times using fresh solvent and combine the three solvent extracts. After the third extraction, pass additional methylene chloride through the sodium sulfate (collecting it in the BOD bottle) to rinse it.

8.3.7 Prepare the evaporation cells by rinsing them twice with methylene chloride and twice with Hexane.

8.3.8 Transfer the extracted samples from the BOD bottles into the rinsed evaporation cells. After adding the sample to the cell, rinse the BOD bottle once with methylene chloride and add that rinseate to the sample.

8A.3 Low Volume Water Extraction Method SW-846 3510C

8A.3.1 The pH of all samples is checked with pH paper at the time of log-in. The pH must be between5-9. If the pH is not in the proper range, adjust accordingly with either 1N NaOH or 1:1 H_2SO_4. Record the volume of acid or base used.

8A.3.2 To measure the volume of sample, draw a line on the sample container (120mL Amber) at the meniscus of the sample. Transfer the entire sample to a separatory funnel. Rinse the sample container with the first 15 mL aliquot of methylene chloride and transfer to the separatory funnel. At a later time, place water in the sample container so the meniscus is up to the line drawn. Measure this volume in a graduated cylinder to the nearest 5 mLs and record.

Note: If sediment covers the entire bottom of the sample container, be sure to decant sample, rinse container with solvent and decant solvent into separatory funnel leaving sediment in sample container.

8A.3.3 Add 200uL of 2,4,5,6-Tetrachloro-m-xylene (TCMX) and Decachlorobiphenyl (DCB) at 2000 ug/L surrogate standard to all samples, spikes and blanks.

8A.3.4 Add 200uL of spike standard to all LFBs ("lab spikes") and matrix spikes. True value = 500 ug/L (50 ug/L off of the instrument). 1016/1260 is used per method. Alternate Aroclors may be warranted based on site specific conditions.

Note: For QC samples, measure 140mls of DI to prepare (this is the maximum volume the 120ml sample bottles hold).

8A.3.5 Add 15mLs of methylene chloride to the separatory funnel. Stopper and shake vigorously for 2 minutes with periodic venting to release excess pressure. Allow the organic layer (bottom layer) to separate from the water phase for a minimum of 10 minutes. If an emulsion exists between layers, the analyst must employ mechanical techniques such as swirling, stirring, and centrifugation, to complete phase separation.

8A.3.6 Pass the solvent layer through a glass funnel, lined with filter paper containing anhydrous sodium sulfate into a BOD bottle. Repeat extraction two more times using fresh solvent and combine the three solvent extracts. After the third extraction, pass additional methylene chloride through the sodium sulfate (collecting it in the BOD bottle) to rinse it.

8A.3.7 Prepare the evaporation cells by rinsing them twice with methylene chloride and twice with Hexane.

8A.3.8 Transfer the extracted samples from the BOD bottles into the rinsed evaporation cells. After adding the sample to the cell, rinse the BOD bottle once with methylene chloride and add that rinseate to the sample.

8.4 Buchi Syncore Concentrator

8.4.1 First the vacuum pump, Syncore platform, and chiller must be turned on. To do so flip the green toggle buttons to the “on” position. Next push the green start button next to the screen on the vacuum pump to turn the chiller on.

Note: The Syncore platform should be set to 55°C.

Note: The chiller’s on/off status is indicated by the snowflake symbol on the vacuum pump screen. When the snowflake is back-lit with a black square, the chiller is on.

8.4.2 Check each individual cell on the Syncore platform so that it reflects the correct concentration glassware being used. If 1.0 ml concentration tubes are used then each cell should have a small orange O-ring at its lowest point. When using 3.0 ml concentration tubes remove the orange O-ring.

Note: Check each individual cell to see if DI water needs to be added to each cell so that the bottom black ring is submerged.

8.4.3 When placing live samples in the Syncore Concentrator, do so one at a time. Remove the sample Id sticker from the glassware before placing the sample in the Syncore Platform. Place the sticker on the sample position grid in order to indicate which sample is in which cell on the Syncore Concentrator.

8.4.4 All samples should have relatively the same volume. Add the appropriate solvent to samples when necessary in order to maintain uniform sample volume.

Note: Maximum sample volume should be below the top heating plate when the Syncore concentrator is running at full speed.

Note: Concentration time will vary based on the program selected and the type of solvent used.

Note: In order to select a desired program, select "menu" on the screen attached to the vacuum pump. Scroll down to "programs" and hit the right arrow button. Continue to scroll down to "open" and use the black knob to select the desired program then hit OK.

Finally, check that the word "gradient" is present in the top left box of the vacuum pump screen. If it is not there go to "menu", "mode", then use the black knob to select "gradient and hit OK.

8.4.5 When starting the Syncore Concentrator place the vacuum plate on top of the concentration tubes and secure firmly using the hand screws. Double check that the correct program is selected for the samples being concentrated. Turn the large black RPM control knob on the Syncore platform to 250. Bring samples to the appropriate final volumes, after sample program on Syncore concentrator has finished.

8.4.6 After samples have been concentrated, empty the solvent collection vessels attached to the condenser. Do so as needed and at the end of each shift.

8.4.7 Replace the samples in the Buchi and concentrate to volume of approximately 8mL.

8.4.8 While the samples in hexane are being concentrated, prepare 10-mL concentration tubes by rinsing them twice with methylene chloride and two times with hexane.

8.4.9 After the samples have been concentrated to 8mL, rinse the cells with the 8mLs and remove the cells from the Buchi. Transfer the sample to the 10-mL concentrator tube using a disposable pipet. Rinse the Buchi cell with approximately 1-2mL of Hexane and add that rinseate to the 10-mL concentrator tube.

8.4.10 Bring the samples up to a final volume of 10-mL using hexane and mix it thoroughly using a disposable pipet. Split the final extract into 12-mL screw-top vials. When completed the extract should be stored in the freezer. Note: For Low Volume Water Extractions bring to a final volume of 2mL and store in a 4mL vial. When completed the extract should be stored in the freezer.

8.5 Sample Extract Clean-Up

8.5.1 An acid clean-up is performed on all PCB samples and their corresponding QC. Never do an acid clean-up on the same sample aliquot that is to be analyzed for pesticides. Pipette approximately 2mLs of sample extract into a 4-mL screw cap vial that contains about 1 mL of sulfuric acid. Cap the vial and vortex for approximately 30 seconds. Allow the layer to separate then pipette off about 1- mL of sample and transfer to a labeled crimp top vial.

TBA Clean-up

8.5.2 Sulfur is removed by Method 3660B; Tetrabutylammonium (TBA) sulfite reagent. Prepare reagent by dissolving 3.39g Tetrabutylammonium hydrogen sulfate in 100 mL organic-free reagent water. To remove impurities, extract this solution three times with 20 mL portions of hexane. Discard the hexane extracts, and add 25g sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a PTFE-lined screw cap. This solution can be stored at room temperature for at least one month. **Note: All Low Volume Water Sample extracts need to be TBA cleaned.**

8.5.2.1 Transfer 1.0mL of sample extract to a 10mL clear vial with a PTFE-lined screw cap.

8.5.2.2 Add 1.0mL TBA sulfite reagent and 2mL 2-propanol, cap vial, and shake for 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present.

8.5.2.3 Add 5mL organic free reagent water and shake for a least 1 min. Allow sample to stand for 5-10 min. Transfer the hexane layer (top) to a 1mL auto sampler vial.

****Florisil Clean-up- Refer to SOP Florsil Clean-Up Method SW-846 3620C****

9.0 PROCEDURE - INSTRUMENT ANALYSIS

9.1 Instrument Set-Up: **HP 6890 (ECD 1 #US10135015)**
HP 6890 (ECD 3 #CN10426061)
HP 7890 (ECD 4 #10715067)
HP 7890 (ECD 5 #10805007)
HP 7890 (ECD 9 #11321159)
HP 7890 (ECD 10 #CN1341002)

Oven

Initial Temp: 125ºC Maximum Temp: 330ºC
Initial Time: 0.25 min Equilibration time: 0.50min
Ramps:

#	Rate	Final temp	Final time
1	30.00	200	0.00
2	20.00	260	0.00
3	45.00	320	2.00
4	0.0 (off)		

Post temp: 0ºC
Post time: 0.00min
Run time: 9.08min

Front Inlet

Initial Temp: 210ºC (On)
Pressure: 13.89 psi (On)
Purge flow: 12.5 mL/min
Purge time: 1.00 min
Total Flow: 25.0 mL/min
Gas type: Hydrogen

Column 1
Model Number: RTX-CL Pesticides: 11139
340ºC 30m x 0.32mmID x 0.5um df

Column 2
Model Number: RTX-CL Pesticides 2: 11324
340ºC 30m x 0.32mmID x .25um df

Front Detector	**Back Detector**
Temperature: 320ºC	Temperature: 320ºC
Combined Flow: 60.0 mL/min	Combined Flow: 60.0 mL/min
Make-up Gas Type: Nitrogen	Make-up Gas Type: Nitrogen

10.0 Sample Analysis

Analyze samples by GC along with solvent blanks, calibration standards, method blanks (extracted blanks) and all appropriate quality control samples.

Sample extracts are generally injected by an auto sampler. If an auto sampler stalls, lab analysts will restart the analysis using two blanks and an acceptable continuing calibration verification standard.

All Aroclor standards must be run for pattern recognition before running samples. Patterns are established before any sample analysis at the beginning of a sequence.

Aroclors are identified based on retention time and PCB pattern matching. All samples are analyzed on a confirmation to verify the correct aroclor is identified. Retention times must fall within established windows on both columns.

11.0 CALCULATIONS

$$\text{Soil concentration, mg/Kg} = \frac{\text{ug/L (from instrument) x (final prep volume, L)}}{\text{initial sample weight, g}}$$

$$\text{Water concentration, ug/L} = \frac{\text{ug/L (from instrument) x (final prep volume, L)}}{\text{initial sample volume, L}}$$

Wipe sample concentration, Total ug = ug/L (from instrument) X (final prep volume, L)

$$\text{ug/area} = \frac{\text{Total ug}}{\text{Area Wiped}} \quad \text{ex. ug/100 cm}^2 \text{ or ug/ft}^2$$

12.0 QUALITY CONTROL

12.1 Definitions

For definitions and explanations of quality control measures, refer to the Con-Test Analytical Quality Control Manual.

12.2 Quality Control Measures & Acceptance Criteria

12.2.1 Calibration Curve

A 6-point calibration curve is used to calibrate the system. The curve must contain Aroclors 1016 and 1260. The low standard must be $\leq$RL. The average response factor over the working range must be $\leq$20%. or ("r" should be $\geq$0.99). The curve must be verified with an independent standard (ICV) prior to sample analysis, (100ug/L). All other Aroclors will also be quantitated from a six-point calibration curve.

If a peak is not properly integrated by the data system, manual integration may be necessary. Manual integrations must comply with the Con-Test SOP on Chromatographic Integration Procedures. The integration of the peaks for the samples and quality control samples must be as consistent as possible with the integration used with the initial calibration. All manual integrations must be documented. In particular, the chromatogram must be expanded to clearly show the specific peak being integrated. A “before” integration is printed, showing the software integration, or lack thereof. An “after” integration showing the action taken by the analyst is printed. The analyst initials and dates both records and they are included with the rest of the documentation for that data file.

The method file used by the data system for the initial calibration should be named with a unique identifier for initial calibration. The initial calibration method file includes a “C” as a suffix to denote that it is the original file. When the retention times change for target compounds due to daily instrument maintenance, the original file is copied to (saved as) a new file with the “C” suffix removed. The method file without the “C” suffix indicates that the retention times have been changed from the initial calibration. The original initial calibration method file with the “C” as a suffix must not be changed.

If the initial calibration does not meet the acceptability criteria, it may not be used for quantitative analyses. Investigate the cause of the problem and perform instrument maintenance if necessary. Then repeat the initial calibration.

12.2.2 Retention Time Windows

Retention time windows will be determined by calculating the mean and standard deviation of the absolute retention times of the surrogate compounds and three (minimum) to five major peaks for each Aroclor.

For the Aroclors, each selected peak will be characteristic of that Aroclor, will be at least 25% of the height of the largest Aroclor peak, and will include at least one peak that is unique to that Aroclor. The retention times used for these calculations should be taken from three injections of the Aroclor standards made over a 72-hour period.

If the standard deviation of the retention times for any peak is 0.000, a default standard deviation of 0.03 minutes may be used. The width of the retention time window for each surrogate and Aroclor peak will be ±3 times the standard deviation of the mean absolute retention time established during the 72-hour period.

12.2.3 Continuing Calibration Check (Calibration Check Standard)

Performed every 12 hours and after no more than 20 samples, and at the end of the analytical sequence. Must be at the mid-point of the curve and contain at least Aroclors 1016 and 1260. For samples run by CT RCP / 8000B protocols, % RSD must be within 15% of the initial calibration. For samples run by MA MCP and 8000C/D protocols % RSD must be $\leq$ 20%. An Aroclor hit in a sample must have calibration verified with a one-point standard of that Aroclor within 12 hours.

The calibration check standard must meet the acceptance criteria before any samples are run. If the calibration check does not meet the acceptance criteria, corrective action is required including instrument maintenance. If the calibration check still fails the acceptance criteria, a new initial calibration is required.

12.2.4 Method Blank

Analyzed on each working day to demonstrate that no contamination is present. The method blank is matrix specific, and extracted with every batch of 20 samples or less. The target compounds and ranges must be $\leq$RL.

12.2.5 Laboratory Control Samples (LCS) / Quality Control Check Samples

Matrix-specific LCS/LCSD's are extracted and analyzed with every batch of 20 samples or less. The concentration should be between the low and mid-level standard, and must contain at least Aroclors 1016 and 1260. Percent recoveries must fall within control limits. Percent recoveries must be 40-140 %R to meet MCP Data Enhancement and RCP criteria. RPD between LCS and LCSD is <20% for waters and <30% for soils.

Water prep: 1 mL of appropriate 500 ppb spike to a final volume of 10 mL. True value = 50 ug/L off of the instrument.

Soil/Solid prep: Add 1-mL of Spike 2000ppb to 10 grams of sample, to a final volume of 10 mL. True value = 200 ug/Kg = 200µg/L off of the instrument.

Wipe prep: Add 1-mL of 500 ppb spike to a final volume of 10 mL. True Value = 50 ug/L off the instrument

12.2.6 Matrix Spikes/Matrix Spike Duplicates

A matrix-specific MS/MSD is extracted and analyzed with every batch of 20 samples or less. It must contain at least Aroclors 1016 and 1260. Percent recoveries must fall within control limits established from historical data. Percent recoveries must be 40-140 %R and MSRPD must be $\leq$50%

12.2.7 Surrogates

Surrogates are added to all blanks, standards, samples, and spikes. Analyze a minimum of two, one that elutes at the beginning of the run and one that elutes at the end of the run (TCMX and DCB). Percent recoveries must fall within control limits established from historical data. Percent recoveries must be 30-150%R in order to meet MCP Data Enhancement and RCP criteria. If the %R is outside of control limits on both columns for the same surrogate, re-extract the sample. If both surrogates are outside limits on one column only, then report any sample results from column within control criteria. If a surrogate is diluted to a concentration below that of the lowest calibration standard, no corrective action, aside from narration, is necessary.

12.2.8 Confirmation

Confirm any hits on a second dissimilar column; report the higher of the two results, unless obvious interference is present on one of the columns, or there were QC outliers on one of the columns. RPD between primary and confirmatory column should be $\leq$40%. All QA/QC parameters (e.g. calibrations, LCSs, etc) must be met on the 2° column as well. For samples the higher of the two results is reported unless requested by client or obvious interference is present from one of the columns.

13.0 DATA PROCESSING

13.1 GC files

A file naming convention is used that allows differentiation between updates to the calibration file performed to adjust target retention times for the changes brought about by daily chromatographic maintenance (no file suffix) and updates due to analysis of a new calibration curve (addition of a “C” suffix to the file identifier)

13.1.1 PCBs

13.2 Reporting Package

The reporting package that is delivered to clients will consist of the sample results, the surrogate recovery results and any matrix spikes, blanks, duplicates and lab fortified blanks that pertain to the clients' samples.

MCP Data Enhancement and RCP projects will include required deliverables plus a case narrative and appropriate checklists.

13.3 Data Filing

13.3.1 Data to be filed in File Boxes labeled as Pest/PCB (date range)

- All raw data

13.3.2 Data to be filed in Laboratory log books

-Records for all types of spike solutions

13.3.3 Backup electronic data filed on DVD

14.0 CORRECTIVE ACTIONS/CONTINGENCIES OF HANDLING OUT-OF-CONTROL DATA

14.1 Refer to Con-Test Quality Assurance Manual.
14.2 Refer to Con-Test Corrective Actions SOP

15.0 POLLUTION PREVENTION

Pollution prevention encompasses any technique that reduces or eliminates the quantity and or eliminates the quantity and or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. Whenever feasible, laboratory personal should use pollution prevention techniques to address waste generation. When it is not feasible to reduce wastes at the source, recycling is recommended as the next best option. Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16.0 WASTE MANAGEMENT

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing the waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.

Any PCB containing samples with over 2.0 ppm are labeled and stored separately for disposal. Used standards are accumulated as a lab-pack and sent out to be disposed properly by a waste management company.

17.0 REFERENCES

17.1 EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW- 846, Rev.7, December 2007, Method 8082, Method 3545, and Method 3546 Rev 0 February 2007.

17.2 EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW- 846, Rev.1, February 2007, Method 8082A.

17.3 Con-Test Analytical Chemical Hygiene Plan.

17.4 Con-Test Analytical Quality Assurance Manual.

17.5 Syncore Application Guide for Buchi Turbo Vap Concentrator, Version A, January 2012.

17.6 HP 6890 Series Gas Chromatograph Operating Manual, Edition 1, January 1990.

17.7 Agilent Technologies 7890 Series II Gas Chromatography Operating Manual, Online

17.8 Dionex ASE 200, Accelerated Solvent Extractor Operator's Manual, February 1996; Doc # 031149-02.

17.9 MA DEP, MCP Data Enhancement Program, "Quality Control Requirements and Performance Standards for the Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography (GC) in Support of Response Actions under the Massachusetts Contingency Plan (MCP)", Rev 1, July 1, 2010.

17.10 Contest document entitled, "Laboratory-Generated Control Limits".

17.11 Con-Test SOP on Procedures for Implementing Corrective Actions

17.12 Con-Test SOP on Chromatographic Integration Procedures

17.13 Con-Test SOP on method 3546.

17.14 Connecticut DEP, Reasonable Confidence Protocol, Method 8082, Ver.2.0 July 2006

17.15 USEPA – "Determinative Chromatographic Separations", SW846, 3rd edition, March 2003, Method 8000C.

17.16 USEPA - – "Determinative Chromatographic Separations", SW846, 2nd edition, December 1996, Method 8000B.

17.17 Con-Test SOP on method 3540C – Soxhlet Extraction

METHOD 3540c
Soxhlet Extraction Procedure for Polychlorinated Biphenyls

Approved: Tod Kopyscinski _____ Katherine F. Allen _____

Tod Kopyscinski
Laboratory Director

Katherine F. Allen
QA Officer

Revision Number: 4

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Change Record

Revision	Date	Responsible Person	Description of Change
Original	3/30/09	F.Derose	Original SOP
1	3/26/2013	Katherine Allen	Updates from annual SOP review: Sec 1.1, 5.3, and 5.4 (addition of fluted filter paper), Sec 2.3 + 5.10 (100 not 500 ml RBF), added sec 2.23 (fluted folding paper), sec 2.9 (deletion of glass wool), sec 2.11+ 6.0(replace sand with sodium sulfate), Sec. 3.0 (updated glassware washing procedure), Sec 5.1 (add 5g for prod/solid and 0.5g for caulking), sec 5.14 (add 12ml vial), sec 5.2 (record lot of NaSO4), deletion of 6.1.5 (LFB) and sec 9.0 (addition of new MCP).
2	03/23/2015	Charles Balicki	Update from annual SOP review: Addition of BUCHI to Sec 2.0, 5.0, and 9.0, and Sec 5.1 (addition of paint).
3	03/15/2017	Katherine Allen	Update from annual Internal audit: Sec 1.4 (20+/-4 hours added), Sec 2.0 (delete Cellulose ext. thimble and Turbovap and add N-EVAP and Dishwasher), Sec 3.0 (ref the Glassware SOP),Sec 3.8 (2:1 hexane:acetone added), Sec 3.9 (dishwasher added), Sec 5.0 (add 1.0ml for spikes, replace water with chiller, add note to put assembly # on bench-sheet, added to cover samples, reworded section, took out cellulose ext. thimble, and remove Turbovap), Sec 5.17.3.1 (add 55c for 55min)
4	1/18/2018	Brianna McLaughlin	Updates from 2017 NY audit: Sec 2.0 (filter paper has lot number which gets documented), Addition of Reagents Section 2.25 and 2.26 as well as note of documentation needed for reagent Section 2.23. Addition of section 5.1.1 (to refer to handling of non-soil samples prior to extraction -shredding of caulk samples).

Distribution/Training List

See Employee Training Record File for signed training statements for trained users.

1.0 SUMMARY OF METHOD

Method 3540C is a procedure for the extraction of organic compounds from soils, clays, sediments, sludge's, PUF's, wipes, and solid wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent. This method is restricted to use by or under the supervision of a trained analyst.

1.1 The solid sample is mixed with anhydrous sodium sulfate, placed in fluted filter paper, and extracted using an appropriate solvent in a Soxhlet extractor.
1.2 The appropriate surrogate and or matrix spike is added to the Soxhlet extractor.
1.3 The appropriate solvent system is added to the round bottom flask. 1:1 Hexane/Acetone. (PCB, PEST).
1.4 Attach the flask to the extractor and extract the sample for 20 +/- 4 hours at 4 – 6 cycles/hour.
1.5 Extract is cooled, dried with anhydrous sodium sulfate, rinsed and is then concentrated and as needed, exchanged into a solvent compatible with its method.

2.0 EQUIPMENT & SUPPLIES

2.1 **Cooled Condenser**: AMK 34/45 #EX01A or equivalent

2.2 **Soxhlet Extractor**: AMK 34/45 #EX01B or equivalent

2.3 **125mL Round Bottom Flask:** AMK #EX01C or equivalent

2.4 **Heating Mantle**: Type "VF" laboratory heating mantle or equivalent

2.5 **Heating Mantle Controller**: Glass-Co #PL3122 or equivalent – regulates temperature control of the mantle.

2.6 **Sodium Sulfate**: ACS Grade, Anhydrous (12-60 mesh)

2.7 **Boiling Chips**: Approximately 10/40 mesh or equivalent

2.8 **Analytical balance**: Capable of weighing to 0.1g, 0.01g (product solid), or 0.001g (paint/caulking)

2.9 **Methylene Chloride**: pesticide quality or equivalent

2.10 **Hexane**: pesticide quality or equivalent

2.11 **Acetone**: pesticide quality or equivalent

2.12 **N-evap Concentrator**

2.13 **Buchi Concentrator Tubes**

2.14 **Buchi Syncore Concentrator Unit**

2.15 **Filter paper**: Whatman No. 41 or equivalent with documented lot number on bench sheet

2.18 **Stock Standards**: Purchased as certified solutions from Ultra Scientific ("or equivalent")

2.19 **Gas Tight Syringes**

2.20 **Vials** – 12ml glass vial with screw top, 2ml crimp top, or 4ml screw top vials.

2.21 **Pasteur Pipettes**: 9inches

2.22 **Disposable Pour-Boat Weighing Dish:** VWR Cat:12577-055 or equivalent

2.23 **Folded Smooth Fluted Filter Paper –** 15.0 cm Grade 313 with documented lot number on bench sheet

2.24 **Dishwasher**

2.25 **PCB Free Gauze Wipe-** When Applicable to matrix of samples. Lot number must be documented on bench sheet.

2.26 **PCB Free Caulking-** When applicable to matrix of samples. Lot number must be documented on bench sheet.

3.0 GLASWARE CLEANING (Also refer to Glassware Cleaning SOP)

3.1 Prepare 2-3% soap solution by adding approximately 10 mLs of Liquinox cleaning soap to 500 mL soap dispenser. Bring to volume with deionized water.

3.2 Add a sufficient amount of soap to glassware and scrub three times using a glassware cleaning brush.

*Note: If not cleaning glassware immediately, it is good to fill a basin tub with hot soapy water to let glassware soak in until cleaning.

3.3 Thoroughly rinse three times with tap water. Take care to rinse off any soap remaining on glass surface at this time.

3.4 Rinse three times with deionized water.

3.5 Place glassware in oven and bake at 103°C until dry. (Teflon or plastic equipment is left on Versi-Dry soaker to air dry).

3.6 Carefully remove dried glassware using appropriate oven mitts and let cool to room temperature.

3.7 If glassware is to be used immediately after washing, Acetone may be used to dry glassware. If Acetone is used to dry glassware, allow to dry in hood. **Do not place in oven – Explosion may result.**

3.8 Prior to use for extraction, glassware must be rinsed with methylene chloride two times followed by 2:1 Hexane:Acetone.

3.9 When available, analysts may use dishwasher. The pre-rinsed glassware should be loaded into the dishwasher. Alcojet soap should be added to dispenser and closed. Run dishwasher on a 0ne-hour quick wash setting.

4.0 SAFETY

See Material Safety Data Sheets (MSDSs) and Con-Test Chemical Hygiene Plan.

Protective gear must always be worn when handling glassware and samples.

Polychlorinated biphenyls have been tentatively classified as known or suspected carcinogens. Then analyst must review the Material Safety Data Sheets (MSDS) for PCBs and all reagents used in the procedure before handling them.

5.0 PROCEDURE FOR EXTRACTION OF SOIL

5.1 Weigh out 10g of soil, 2g for product/solid, 0.500 g caulking, 0.200g paint sample into disposable pour-boat weighing dish.

5.1.1 Note: Per method, product/solid/caulking/paint samples must be cut and or shredded prior to extraction.

5.2 Blend in anhydrous sodium sulfate (make sure sample is free-flowing).

5.3 Place sample in fluted filter paper. The extractor must cycle continuously for the duration of the extraction period.

5.4 Add approximetly 100mL of 70:30 mixture of Hexane/Acetone to a 125mL round bottom flask. Add 2-5 boiling chips. Attach a Soxhlet Extractor on top of the round bottom flask; make sure to slightly twist – ensuring a tight connection.

5.5 Transfer the sample label from the weigh boat onto the round bottom flask. Place the corresponding fluted filter paper into the Soxhlet extractor. Check Soxhlet setup for any cracks or chips which may leak solvent or cause samples to burn out.

5.6 Add 1.0mL of surrogate standard to all samples and QC.

5.7 Add 1.0mL of spike to all LFB's (lab spikes) and MS/D (matrix spikes and duplicates).

5.8 Place the round bottom flask with attached Soxhlet extractor onto a heating mantle and clamp into position. Then, attach condenser unit; make sure to slightly twist – ensuring a tight connection. Turn on chiller to cool the condensers. Chiller should reach at least 8-10°C prior to starting extraction. Note extractor and bulb numbers for each sample on the bench-sheet for tracking purposes.

5.9 Turn on corresponding thermostats. The setting is predetermined during each year's cycle verification testing to achieve 4-6 cycles per hour. At this time, double check Soxhlet for any cracks or chips which may leak solvent or burn out.

5.10 The samples should be extracted for a minimum of 16 hours (20 ± 4 hours). Once the sample has finished extracting, turn the heating mantle off and allow samples to cool to room temperature. Once cool, disengage condenser unit and flush the remaining solvent from the Soxhlet extractor by tipping the Soxhlet. Disengage the Soxhlet extractor from the flask and pour remaining solvent into the bulb and put extractor aside. Using a pair of long-handled tweezers, pull the filter out of the Soxhlet and place in a hood for total solvent evaporation. Repeat for all other samples. Be sure to cover samples while sitting waiting to be concentrated.

5.11 Prepare a glass funnel lined with filter paper and fill half way with sodium sulfate. Saturate sodium sulfate with hexane. Pass the extract through the funnel into a clean Buchi tube. Rinse the 125mL Flask with ~10mLs of fresh solvent and pass it through the funnel. Rinse the funnel with hexane.

5.12 **How to Use the Buchi Syncore Concentrator (In reference to 3510, 3546, and 3540c methods)**

5.12.1 **How to prep a Buchi Syncore in order to concentrate samples for waters and soils.**

Note: Prior to concentrating samples, allow the cooling plate to stabilize to its appropriate temperature.

5.12.2 Chiller should read between 8°C and 10°C before using.

5.12.3 Add at least ¼ inch of de-ionized water to each cell in the concentration platform.
Note: Avoid filling a cell so much that excess DI spills out.

5.12.4 Each day fill the cold-water bath that chills the solvent collection vessel. Run coolant line through the cold-water bath and add ice when necessary.

5.12.5 Before starting, check that the secondary containment solvent vessels are empty! **It is extremely important that this be checked throughout the day!!**

Note: It is important that all of the concentration glassware has the same dimensions. Glassware of different heights can adversely affect sample concentration rates in the Buchi.

5.13 Sample Concentration (Soils)

5.13.1 Refer to section 5.12.1 for prepping the Syncore concentrator before working on samples.

5.13.2 Target sample volume after drying through sodium sulfate should be ~50 mL to avoid the sample going above the level of the cooling plate.

5.13.3 Pour the dried sample into a Buchi Concentration tube. Start the Syncore Concentrator using the following programs where applicable:

5.13.3.1 For **3540c**, use program **"SOX 70/30 HEX/ACE" program. Temperature is set to 55ºC for 55 minutes.**

Note:
Immediately upon completion of a given program, adjust rotation to 0, hit stop on the vacuum pump and then hit start again to restart the chiller. If this is not done, five minutes after a program stops, the chiller will automatically turn off. The result of which may be losing the samples that are being concentrated.

5.18 Using a Pasteur pipette and bulb, transfer the sample extract into a 12mL screw top vial. Rinse the Buchi tube with ~1mL hexane and transfer to vial. Repeat two more times. Bring to a final volume of 10mL with Hexane. Vials are either brought directly to an analyst or placed in freezer. The extraction technician will document rack number on

bench-sheet so the analyst knows where to find the extracts. The extraction technician then changes status in Element to prepared.

6.0 QUALITY CONTROL

6.1 Definitions

For definitions and explanations of quality control measures, refer to the Con-Test Analytical Quality Control Manual.

6.1.1 Method Blank

Analyzed on each working day to demonstrate that no contamination is present. The method blank is matrix specific, and extracted with every batch of 20 samples or less. Sodium Sulfate is used for the solid matrix.

6.1.2 Laboratory Control Sample (LCS) (BS) / Quality Control Check Samples

A matrix-specific LCS is analyzed with every batch of 20 samples or less. Prepared from a different stock than that of the calibration curve. The concentration should be between the low and mid-level standard. Sodium Sulfate is used for the solid matrix.

6.1.3 Matrix Spikes/Matrix Spike Duplicates

A matrix-specific MS/MSD pair is analyzed every batch of 20 samples or less.

6.1.4 Matrix duplicates

Analyze a sample duplicate every 20 samples (when enough aliquot is provided) if requested by client.

6.1.5 Surrogates

Surrogates are added to all blanks, standards, samples, and spikes.

7.0 POLLUTION PREVENTION

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many 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 waste generation. When it is not feasible to reduce wastes at the source, the Agency recommends recycling as the next best option.

8.0 WASTE MANAGEMENT

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing the waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.

9.0 REFERENCES

7.1 EPA, Method 3540C "Soxhlet Extraction"

7.2 Con-Test Analytical Chemical Hygiene Plan.

7.3 Con-Test Analytical Quality Assurance Manual.

7.4 Buchi Syncore Concentrator Manual

7.5 MA DEP, MCP Data Enhancement Program, "Quality Assurance and Quality Control Requirements for SW-846 Method 8082, Polychlorinated Biphenyl's (PCBs) by Gas Chromatography (GC) for the Massachusetts Contingency Plan (MCP)", Rev. 3, May 2003.

7.6 Con-Test SOP on Procedures for Implementing Corrective Actions

7.7 CT RCP, RCP Recommended Reasonable Confidence Program, "Quality Assurance and Quality Control Requirements Polychlorinated Biphenyls by Method 8082, SW-846", Version 2, July 2006.

7.8 MA DEP. MCP Data Enhancement Program, "Quality Control Requirements and Performance Standards for the Analysis of PCB's by GC in Support of Response Actions under the MCP", Rev 1, July 1, 2010.

EXTRACTION PROCEDURE FOR TOXICITY CHARACTERISTIC LEACHING PROCEDURE

Approved:

Tod Kopyscinski	Katherine F. Allen
Laboratory Director	QA Officer

Revision Number: 5

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Change Record

Revision	Date	Responsible Person	Description of Change
Original, Revision 0	9/13/2005	M. Moauro	Original, NELAC Format; Controlled Document Status
1	10/19/2011	F. Derose/PJG	Updates from 07/2011 TRC audit: Section 5.0 (reagents added), Section 8.0 (% solids to determine amount of ext. fluid to use), Section 11.0 (pollution prevention added), and Section 13.5 added (ref. addition)
2	1/13/2015	Charles Balicki	Updates: Section 5.5; Added caution note to sodium hydroxide prep. Added in section 5.6.3 for checking pH of fluid. Revised section 6.3 to update rinsing of vessels with acid/DI. Section 8.4.1: added in note about sample volume. Section 8.6: Added in recording of min/max temps and note about checking the rotators quarterly. Added addendum #1 for pH meter calibration information.
3	01/12/2016	Charles Balicki	Updates from 2015 NY Audit: Section 4.1 updated to include Teflon and HDPE vessels.
4	03/23/2017	Charles Balicki	Updates from Internal Audit. Section 6.3 Changed Acid Rinse/DI Rinse amounts. Section 13.6 Added in new pH meter. Removed Addendum #1.
5	1/23/2018	Brianna McLauglin	Updates from 2017 NY audit: Section 4.0 to include Positive Pressure Manifold apparatus and pH paper, Additions to procedure sections 8.2, 8.7 and 8.8 to include clarity on using positive pressure manifold and preserving/checking pH of leachates Addition of Appendix 1 to include instructions to use positive pressure manifold.

Distribution/Training List

See Employee Training Record File for signed training statements for trained users.

1.0 SUMMARY, SCOPE AND APPLICATION

1.1 This method covers the determination of the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

2.0 INTERFERENCES

2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and or cause elevated baselines in Gas Chromatographs.

2.2 Interferences by Phthalate esters can be a common laboratory problem. Avoiding the use of plastics in the laboratory can best minimize these interferences.

3.0 SAMPLE PRESERVATION/STORAGE/HOLDING TIME

3.1 All samples are stored at 4.0°C ±2°C from the time of collection until extraction.

3.2 Sample holding time:

Volatiles-14 days
Semi-volatiles- 14 days
Mercury- 28 days
Metals (except mercury) - 180days

4.0 EQUIPMENT & SUPPLIES

4.1 Extraction Vessels: Teflon (PTFE) vessels must be used when organic test choices are requested. The HDPE vessels are to be used for metals only.

4.2 Filter holder

4.3 Filters, made of borosilicate glass fiber with a pore size of 0.6 to 0.8 µm

4.4 Reagent grade chemicals

4.5 pH meter

4.6 Laboratory balance, accurate to within $\pm$ 0.01 grams.

4.7 Beaker or Erlenmeyer flask, glass, 500mL.

4.8 Vacuum pump

4.9 Positive Pressure Filtration Unit

4.10 pH Paper

5.0 REAGENTS:

5.1 Reagent Water (Deionized water)

5.2 Hydrochloric acid (1N), HCL, made from ACS reagent grade

5.3 Concentrated Nitric Acid (1N), HNO_3, made from ACS reagent grade.

5.4 1:1Nitric Acid: Deionized water prepared by adding 500mL concentrated Nitric Acid to 500mL Deionized water.

5.5 Sodium hydroxide (10N), NaOH, made from ACS reagent grade. Prepared by adding 400.0 grams NaOH pellets to 1.0 Liter Deionized water. **(Caution, solution gets extremely hot while dissolving so make in an ice bath.)**

5.6 Glacial Acetic Acid, CH_3CH_200H, ACS reagent grade.

5.7 Extraction fluid Preparation:

5.6.1 Extraction fluid # 1: Add 5.7 mL glacial CH_3CH_200H to 500mL of reagent water. Add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. **Correct preparation will produce a pH of 4.93 $\pm$ 0.05. The pH of the fluid must be checked before use!**

5.6.2 Extraction fluid # 2: Dilute 5.7mL glacial CH_3CH_200H with reagent water to a volume of 1 liter. **Correct preparation will produce a pH of 2.88 $\pm$ 0.05. The pH of the fluid must be checked before use!**

5.6.3 **These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.**

6.0 GLASSWARE CLEANING & ACID RINSING

6.1 All equipment must be washed with Liquinox and DI water.

6.2 Rinsed with DI water.

6.3 Acid rinse all glassware, filtering devices, extraction vessels, and glass fiber filters with 50:50 DI: HNO_3 3 times, and then rinse 3 times with DI water before each use. All of the acid rinse must be removed so the pH of the samples is not affected! **This is extremely important!**

7.0 SAFETY

See Material Safety Data Sheet (MSDS's) and Con-Test Chemical Hygiene Plan.

8.0 PROCEDURE:

Note: For liquid wastes containing less than 0.5% dry solid material, filter through a 0.6 to 0.8 um glass fiber filter. Liquid collected is defined as the TCLP extract.

Note: For wastes containing a liquid and solid phase; the liquid phase, if any, is separated from the solid phase and stored for later analysis. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase.

8.1 Perform preliminary TCLP evaluations on a minimum 100-gram aliquot of sample. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) Determination of the percent Solids, (2) Determination of whether the waste contains insignificant solids and is, its own extract after filtration (3) Determination of whether the solid portion of the waste requires particle size reduction and (4) determination of which of the two extraction fluids are to be used for the non-volatile TCLP extraction.

8.2 Determination of Percent Solids: See Percent Solids SOP. Percent Solids needs to be determined before proceeding with further preliminary evaluations.

If the percent solids determined is equal to or greater than 0.5% then proceed to (Section 8.2) determine whether the solid material requires particle size reduction.

If the percent solids determined is less than 0.5%, the liquid portion of the waste, after filtration, is defined as the TCLP extract. The solid portion can be extracted utilizing the positive pressure manifold.

Note: If a notable amount of water exists in the sample container that shows significant multiphasic properties, a positive pressure system will be used to separate the extract prior to extraction. If analyst is unsure of the layers of the sample, they should seek out guidance from a Supervisor or Quality Assurance Personnel before proceeding. See Appendix 1 for the procedure using the positive pressure manifold.

8.2 Determination of particle size reduction: Evaluate the waste sample particle size. Particle size reduction is required, unless the solid is capable of being passed through a 9.5mm (0.375 inch) standard sieve. If the particles in the sample are not able to pass through the sieve, prepare the sample by crushing, cutting, or grinding the waste to a particle size as described above.

8.3 Determination of appropriate extraction fluid: This is necessary for all nonvolatile samples. TCLP extraction for volatile constituents uses only extraction fluid #1.

8.3.1 Weigh out 5.0 grams of sample to be extracted into a beaker.

8.3.2 Add 96.5 mL of reagent water to beaker and stir for 5 minutes.

8.3.3 Calibrate the pH meter according to manufacturer's instructions. This needs to be done every day prior to taking the pH of any fluid. (See Addendum #1 for information)

8.3.4 Measure and record pH in TCLP log book. If the pH is <5.0, use extraction fluid #1. If pH is >5.0 add 3.5 mL 1N HCL to sample, slurry briefly, cover with watch glass, and heat at 50 °C for 10 minutes. Allow sample to cool and record pH. If pH <5.0 use extraction fluid #1. If pH is >5.0 use extraction fluid #2.

8.4 Weigh out samples for extraction and record all weights in TCLP log book.

8.4.1 N**onvolatile samples**: Weigh out a 100-gram aliquot of the TCLP sample to be extracted into the rinsed extraction vessel. One sample of each matrix type soil, clay, sand, and loam, out of every ten will be labeled a matrix spike. A method blank is required for every twenty samples. The extraction vessel for the method blank will contain only extraction fluid.
NOTE: If there is not a sufficient amount of sample (100-gram aliquot + 5 grams for initial pH), the Project Manager must be informed.

8.4.2 **Volatile samples**: (See ZHE SOP)

8.5 Determine and record the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of Extraction Fluid (mLs)} = \frac{20 \times \text{Percent solids (\%)} \times \text{weight of waste filtered (g) (if any)}}{100}$$

Example: Sample 1-

Determined Percent Solids Dry weight = 85% Dry
Determined Particle size reduction was not needed.
Determined to use Extraction Fluid #1.
Now determined how much extraction fluid is needed for a 100g minimum aliquot of the sample:

$$\text{Weight of Extraction Fluid \#1} = \frac{20 \times 85 \times 100}{100} = 1700 \text{ mLs of Extraction Fluid to be used}$$

Example: Sample 2-

Determined Percent Solids Dry weight = 100% Dry
Determined Particle size reduction was not needed.
Determined to use Extraction Fluid #1.
Now determined how much extraction fluid is needed for a 100g minimum aliquot of the sample:

$$\text{Weight of Extraction Fluid \#1} = \frac{20 \times 100 \times 100}{100} = 2000 \text{ mLs of Extraction Fluid to be used}$$

Add the appropriate amount of extraction fluid to sample vessel and tightly seal the lid of the vessel.

8.6 Secure the extraction vessel in a rotary agitation device and tumble for 18 $\pm$ 2 hrs. At this time record the following in the TCLP log book:

(1) Room temperature; should be 23°C $\pm$ 2;
(2) Rotator; Revolutions per Minute should be 30 $\pm$ 2 RPM.
(3) Record MIN/MAX Temperatures

****Note: It is required that the RPM's of the rotators be checked quarterly to ensure they are not outside of the 30±2 RPM criteria. This can be done using a stopwatch for one minute.**

8.7 After 18$\pm$2 hours of agitation remove TCLP samples from agitation device and record the room temperature. Use vacuum pump device to filter the samples. *Note: If initial positive pressure manifold was used, add the initial liquid filtrate to the sample before dispersing to additional containers in the next step.

8.8 Transfer samples from filtering apparatus into the appropriate sample containers; plastic containers for metals analysis, glass for organic extractions. Record the pH of the extract in the TCLP log book.

Note: For metals leachates, they must be filtered into Nitric Acid preserved 250mL plastic containers. The extract pH should be verified to be <2 using litmus paper and documented in Element on the sample extract created for the leachate.

9.0 QUALITY CONTROL:

For definitions and explanations of quality control measures (blanks, LCS/QC Reference, LFB, Duplicates, MS/MSD) refer to the Con-Test Analytical Quality Assurance Manual.

9.1 Extract a method blank (Mb) for every twenty samples, (nonvolatile: 2 L of appropriate extraction fluid).
9.2 Extract a matrix spike (MS) for every ten samples extracted.

10.0 CORRECTIVE ACTIONS/CONTIGENCIES OF HANDLING OUT-OF-CONTROL DATA

10.1 Refer to Con-Test Quality Assurance Manual.
10.2 Refer to Con-Test Corrective Action SOP.

11.0 POLLUTION CONTROL

Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Many 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 waste generation. When it is not feasible to reduce wastes at the source, the Agency recommends recycling as the next best option.

12.0 WASTE MANAGEMENT

It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.

13.0 REFERENCES

13.1 USEPA - "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods", Third Edition, November 1986 (SW846 Method 1311).

13.2 Con-Test Analytical Quality Assurance Manual.

13.3 Con-Test Analytical Chemical Hygiene Plan

13.4 Con-Test Analytical Corrective Action SOP.

13.5 SW-846 Method 1311, Toxicity Characteristics Leaching Procedure, Revision 0, July 1992.

13.6 Thermo Orion Star A111 pH meter manual.

Appendix 1

1. **Pre-weigh the filter and the container that will receive the filtrate and record the weights. Assemble the filter holder within the positive pressure filtration apparatus.**
2. **Weigh out a subsample of the waste to be filtered at 100.00g minimum and record the weight.**
3. **Sample should then be spread evenly over the filter.**
    a. **If sample residue remains on the vessel, it is to be weighed and recorded and eliminated from the sample aliquot in calculations.**
4. **Gradually apply pressure between 1-10 psi and allow sample to filter through. The pressure can be increased in 2 minute intervals up to 50 psi to remove liquid from the sample, 10 psi at a time.**
    a. **Do not instantaneously apply pressure to the unit as this will compromise the integrity of the glass fiber filter.**
5. **Determine the weights of each phase by subtracting the weight of the receiving vessel from that of the liquid portion and respectively subtracting the weight of the filter from the solid portion of the sample.**
6. **The percent solid can be calculated for this solid sample. Set the initial filtrate liquid aside for a later step. Then, proceed to section 8.2 in the SOP.**

PETROLEUM HYDROCARBONS (BY GC/FID)

(Method SW846 8100M/8015D/8015D DRO/8015C/8015C DRO)

Approved:

Tod Kopyscinski
Laboratory Director

Katherine Allen
QA Officer

Revision Number: 13

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Change Record

Revision	Date	Responsible Person	Description of Change
1	03/05/2003	S. Kocot	Updates for NELAC format
2	03/01/2007	C. Merchant	Updates for annual SOP review: section 5.0 add'n of acetone; section 7.0 instrument set-up; section 7.3.2 microwave prep; section 8.2.4 acetone used; section 12.0 added microwave SOP as a reference
3	05/11/2007	D. Damboragian	corrections
4	02/11/2009	P. Gryszkiewicz	corrections
5	08/25/2009	F.Derose	Updates
6	10/07/2009	F.Derose	Corrections
8	9/18/2013	KFA	Updates from annual SOP review: RL updated for soil. Sec9.1.1 bulk sample updated. ASE extraction section deleted.
9	03/23/2015	CWB	Update from annual SOP review: Sec 5.8 (addition of Buchi), Sec 9.1.1 (addition of procedure to weigh), Sec 9.1.2.1 (note added wet samples may need more solvent and Buchi added), Sec 9.1.3(Buchi added) and Appendix added for full Buchi instruction.
10	08/04/2015	CWB	Update from Internal Audit: Table 7.3 CT ETPH Alkane Standard final concentration changed from 10,000 ug/ml to 3,000 ug/ml.
11	11/15/2017	BM	Update for change in procedure: Acidification of samples prior to extraction. Added 6.12 to section 6.0 and edited section 9.0
12	02/19/2019	Charles Balicki	Updates from Annual SOP Review: Section 6.8 Changed OTP to 2-Fluorobiphenyl. Section 7.1 Updated Surrogate Table. Section 9.1.2.6 Changed OTP to 2-Fluorobiphenyl @ 100 µg/mL
13	09/25/2019	Rachel Wilson	Updates to procedure: Section 7.2 (deleted spikes not used anymore), Section 7.3 (deleted spikes not used anymore and changed OTP to 2-Fluorobiphenyl and changed wording for a7-point curve instead of 6-points), Section 10.0 (New Instrument conditions) and Section 11.2.4 (7-point curve not 6-points).

Distribution/Training List

See Employee Training Record File for signed training statements for trained users.

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of Petroleum Organics.

1.2 Samples can be qualitatively and/or quantitatively determined by these methods. Method 8100M is used to determine petroleum hydrocarbons in the range of C_9-C_{36}, using #2 fuel oil as a calibration standard. Method 8015 (GC fingerprint) is used to determine the presence of gasoline, kerosene, jet fuel, #2/#4 fuel oil (C_9-C_{36}), #6 fuel oil, and other petroleum hydrocarbons. Method 8015 DRO is used to determine diesel range organics (C_{10}-C_{28}). An n-hydrocarbon standard is used to determine the correct retention times for C_9, C_{10}, C_{28}, and C_{36}. These retention times are then used to determine the C_9-C_{36} quantitation range for method 8100M and the C_{10}-C_{28} range for method 8015 DRO.

1.3 This method is based on direct inject gas chromatography, using a Flame Ionization Detector (FID).

2.0 SUMMARY OF METHOD

2.1 1 µl of sample extract is injected into the GC injection port, where it is volatilized from the liquid phase to the gas phase. The gas is directed from the injection port liner and focused onto the capillary column. The gas chromatograph is temperature programmed to achieve separation of the organic compounds. The separated components then pass into a flame-ionization detector (FID). The FID chromatogram is used to determine the concentration of petroleum hydrocarbons.

2.2 Reporting Limit = 250 µg/mL off instrument for soils = 8.33 mg/kg
200 µg/mL off instrument for waters = 0.200 mg/L

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.3 Interferences co-extracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

3.4 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. To reduce the potential for carryover, the sample syringe is rinsed out between samples with an appropriate solvent. Whenever an unusually concentrated sample is encountered, it should be followed by injection of a solvent blank to check for cross contamination.

3.5 The flame ionization detector (FID) is a non-selective detector. There is a potential for compounds present in samples to cause interference.

4.0 SAMPLE PRESERVATION/STORAGE/HOLDING TIME

4.1 A chain-of-custody form must accompany all sampling vials and must document the date and time of sample collection and preservation used.

4.2 Aqueous and Soil/Sediment samples must be stored at 4 ± 2ºC.

4.3 Aqueous samples must be extracted within 7 days of collection and analyzed within 40 days of extraction.

4.4 Soil/Sediment samples must be extracted within 14 days of collection and analyzed within 40 days of extraction.

5.0 EQUIPMENT & SUPPLIES

5.1 Gas Chromatograph with Flame Ionization Detector, integrator, and column; Hewlett-Packard Model 5890

5.2 Capillary column: Restek, Rtx-5Sil MS, 15m x 0.25mm x 0.25µm, or equivalent

5.3 Glass vials - 2 mL crimp-top and 4 mL screw cap

5.4 Syringes - 1 mL (for standards)

5.5 2 Liter separatory funnels

5.6 Graduated cylinders - 100 mL

5.7 Glass powder funnels

5.8 Concentration workstation – Buchi Syncore, and associated glassware.

5.9 Concentration workstation – Zymark or equivilant.

5.10 Filter paper - qualitative

5.11 Volumetric flasks - 5 mL, 20mL, 50 mL, 100 mL

6.0 REAGENTS & STANDARDS

6.1 Methylene Chloride - pesticide grade

6.2 Acetone - pesticide grade

6.3 Nitrogen - ultra high purity

6.4 Helium - ultra high purity

6.5 Hydrogen - ultra high purity

6.6 Air - ultra high purity

6.7 Sodium Sulfate - reagent grade

6.8 Surrogate Stock – 2-Fluorobiphenyl

6.9 Spiking Solutions

6.10 Petroleum Standards - gasoline, jet fuel / kerosene, #2 fuel oil, #6 fuel oil

6.11 Reference Standards – including but not limited to motor oil, mineral spirits, #4 fuel oil, PCB free transformer oil, weathered #2 fuel oil, weathered gasoline, weathered kerosene.
Reference standards are used for identification purposes and are quantitated using the #2 fuel oil curve.

6.12 Sulfuric acid: (1:1) – slowly add 100mL of H2SO4 to 100mL of reagent water

7.0 PREPARATION OF STANDARDS AND STOCK SOLUTIONS

7.1 Surrogate

Compound	Vendor (Catalog #)	Stock Volume / Weight	Final Volume (in acetone)	Final Concentration
2-Fluorobiphenyl	Aldrich 102741	0.10 g	1000 mL	100 µg/mL

7.2 Spiking Solutions

Compound	Vendor (Catalog #)	Stock Volume / Weight	Final Volume (in acetone)	Final Concentration
Diesel Fuel #2 Composite Standard 50,000 µg/mL	Restek (31259)	5.0 mL	250 mL	1000 µg/mL

These spiking solutions are also used as second sources to verify initial calibration curves.

7.3 Calibration Standards

Compound	Vendor (Catalog #)	Stock Volume/ Weight	2-Fluorobiphenyl (@5000 µg/mL)	Final Volume (in methylene chloride)	Final Concentration
#2 Diesel Fuel	Accustandard (DRO-AK-102-LCS-10X-R1-PAK)	1.0 mL	1.0 mL	5.0 mL	10,000 µg/mL (1000 µg/mL 2-Fluorobiphenyl)
Connecticut ETPH Calibration Mixture	Restek (31614)	1.0 mL	200 µL	5.0 mL	3,000 µg/mL (200 µg/mL 2-Fluorobiphenyl)

The #2 Diesel Fuel stock is further diluted to produce a seven-point calibration curve. The seven points in the calibration curve are: 10, 200, 250, 500, 1000, 5000, and 10,000 µg/mL. The first point is only used for the calibration of 2-Fluorobiphenyl. As stated previously, the Connecticut ETPH Calibration Mixture is used to determine the correct retention times for C_9, C_{10}, C_{28}, and C_{36}. These retention times are then used to determine the C_9-C_{36} quantitation range for method 8100M, and the C_{10}-C_{28} range for method 8015 DRO. For continuing calibration verification, single point reference standards (1000 µg/mL) are used.

8.0 SAFETY

See Material Safety Data Sheets (MSDSs) and Con-Test Chemical Hygiene Plan.

9.0 PROCEDURE

9.1 Sample Prep - Sample can be a bulk material, a soil, or a water. Extraction procedure is matrix-dependent.

9.1.1 Bulk sample (oil) – Method 3580

Client requests identification of bulk sample or comparison of a different sample to a provided bulk sample.

To run a bulk sample, accurately weigh 0.100g of sample. Add 2.0 ml of surrogate and bring to a 10.0 ml final volume. (LCS gets 2.0 ml of surrogate and 2.0 ml of spike).

If sample is wet, add a small amount of sodium sulfate.

Shake until dissolved and inject. Use this chromatogram (representing a concentration of approximately 1000 µg/mL) as a reference if another sample is to be compared to the bulk.

For identification, compare to other petroleum standards (run at 1000 µg/mL).

Compare profile of chromatogram, keeping in mind that age and weathering will affect the consistency of the hydrocarbons, particularly C_{18} hydrocarbons and lower.

9.1.2 Soil / Sediment sample

9.1.2.1 Microwave extraction procedure for soil samples – Method 3546

Microwave sample preparation imposes a unique set of safety considerations. Never heat liquids in a sealed vessel or container that is not equipped with a pressure relief valve. Microwave heating of alkaline or salt solutions in closed vessels will concentrate these solutions, causing precipitation of salts and formation of crystal deposits on vessel walls. These crystal deposits will absorb microwave energy, causing localized heating, which may char and damage vessel components. Because samples are extracted at high temperatures, exercise extreme caution when removing a vessel. **Never open a hot vessel, wait until vessel has cooled (approx. 10min**). Protective gear should always be worn. (Gloves, Protective Lab Coat, and Protective Eyewear)

9.1.2.2 All cells are washed with soap and warm water, rinsed with reagent grade water, and then solvent rinsed first with acetone, and then with methylene chloride.

9.1.2.3 Weigh out desired amount of sample (30g) into a weigh boat.

9.1.2.4 Add sodium sulfate, mix well adding more if needed, making sure sample is free flowing.

9.1.2.5 Load pre-weighed soil sample into a clean microwave vessel.

9.1.2.6 Add 1.0mL of surrogate (2-Fluorobiphenyl @ 100ug/mL)

9.1.2.7 Add 1.0mL of matrix spike (#2 Fuel Oil @ 1000ug/mL) to all LCSs (laboratory control blanks) and Matrix spikes and Matrix spike duplicates.

9.1.2.8 Add 25mLs of 1:1 Methylene Chloride: Acetone. **Note:** Wet sample may require more solvent to extract)

9.1.2.9 The vessel is then capped, first adding the Teflon insert, then adding the screw cap. The vessel is then tightened using the CEM Capping Station **or** the hand tool for tightening. **DO NOT OVERTIGHTEN!!!**

9.1.2.10 Invert vessel, making sure sample and solvent are mixed well.

9.1.2.11 The vessel is put into the appropriate numbered slot in the carrousel, and the position is entered into the ETPH log book.

9.1.2.12 The carrousel is then put into the oven.

9.1.2.13 Method 3546 – is loaded and the method is started by pressing the green button

- Microwave Oven Parameters: **Method 3546**
- Ramp to Temperature: 115°C
- Time at Temperature: 10 minutes
- Pressure: 50 – 150 psi
- Cooling: 10minute cooling down

Note: Do not open vessels when contents are hot. Solvent burns can occur.

9.1.2.14 The sample is filtered through a glass funnel containing filter paper and sodium sulfate, into a clean Buchi concentration tube.

9.1.2.15 The extract is then concentrated in a concentrator tube to 1mL.

9.1.2.16 Extract is then transferred to a 2mL target vial.

9.1.3 Water Extraction Procedure

9.1.3.1 All glassware should be cleaned and rinsed with methylene chloride.

9.1.3.2 Pour 1000 mL of water sample into a 2-liter separatory funnel. Check pH with pH paper, and record on bench sheet. Adjust pH to <2 using 1:1 Sulfuric Acid. Check pH with pH paper and record on bench sheet.

9.1.3.3 Add 1 mL of surrogate spike.

9.1.3.4 Add 60mLs of methylene chloride to the sample container, seal, and rinse the inner walls of the container. Transfer to the separatory funnel. Cap funnel and shake, periodic venting to release excess pressure. Shake vigorously for 2 minutes. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If an emulsion exists between the two layers, the analyst must employ mechanical techniques to complete phase separation.

9.1.3.5 Buchi Syncore Concentrator Procedure. See Appendix I.

9.1.3.6 Concentrate to 1 mL by Turbo-vap concentration. Passing solvent through a glass funnel lined with filter paper and sodium sulfate into a 250mL Turbo-vap concentrator tube.

9.1.4 Analysis

9.1.4.1 Compare sample chromatograms run by GC/FID-direct injection with standard reference chromatograms.
9.1.4.2 Determine the identity of the unknown materials by comparing fingerprint by retention times,
9.1.4.3 Quantitate by comparing peak areas.
9.1.4.4 All peak areas are summed to baseline using retention time markers as specified below.

9.1.5 Interpretation of Data
Results should be reported as follows:

9.1.5.1 Match: Profile of chromatogram has a perfect or near perfect match to a standard or bulk.

9.1.5.2 Probable Match: Profile of chromatogram has similar appearance to a standard or bulk.

9.1.5.3 Indeterminate: Possibly a standard or match with bulk but weathering and/or interferences prevents a firm conclusion.

9.1.5.4 Mismatch: Unlike any of the standards or bulk, if provided (i.e. no match found with diesel, unleaded gasoline, #2 fuel oil, etc.). (If no hydrocarbons are detected, report as "other " and provide detection limit.) Area is quantitated against a #2 diesel fuel standard.

9.1.5.5 Samples are quantitated against standards and reported as:

Method 8100M (C9-C36) - #2 fuel oil

Method 8015 (GC fingerprint) - gasoline, kerosene, jet fuel, #2/#4 fuel oil (C9-C36), and / or #6 fuel oil.

Method 8015 DRO (C10-C28) - #2 fuel oil

10.0 INSTRUMENT CONDITIONS

10.1 Instrument Set-Up: Dual FID HP5890

10.1.1 Column: Restek; Rtx-5Sil MS, 0.25 mmID x 0.25 µm x 15 m, or equivalent **OR** Rxi-5Sil MS, 15m x 0.25mm x 0.25µm, or equivalent.
(Front and Back)

10.1.2 Column Flow: Front: Constant flow – 3.0 mL/min
Rear: Constant flow – 3.0 mL/min

10.1.3 Injection Temperature: 290°C (Front and Rear)

10.1.4 Detector Temperature: 325°C (Front and Rear)

10.1.5 Injection Volume: 1µL (Front and Rear)

10.1.6 Temperature Program:
60°C hold for 1.5 min
40°C/min to 200°C hold 0 min
15°C/min to 230°C hold 0 min
20°C/min to 310°C hold 4 min

Inlet flows: Split ratio 18:1, gas saver of 20.0mL/min at 1.0 min. (Optional)

11.0 QUALITY CONTROL

11.1 **Definitions**

For definitions and explanations of quality control measures, refer to the Con-Test Analytical Quality Assurance Manual.

11.2 **Quality Control Measures & Acceptance Criteria**

11.2.1 **Method Blank (MB)**

A matrix-specific method blank must be analyzed 1 per batch of 20 samples or less, prior to running samples and after calibration standards. Target analytes must be <RL.
If the method blank does not meet these criteria, appropriate corrective action is taken (bake the trap or column, flush the transfer lines, etc.). An acceptable method blank must be analyzed prior to sample analyses.

11.2.2 **Laboratory Control Samples (LCS/LCSD)**

Analyzed with every batch of 20 or less. A #2 fuel oil matrix spiking solution in acetone can be used as the spiking stock. Percent recovery must fall within method established limits of 40 - 140%.

11.2.3 **Matrix Spikes (MS/MSD)**

Analyzed with every batch of 20 or less samples. A #2 fuel oil spiking solution in acetone can be used as the matrix spike stock. Percent recovery must fall within method established limits of 40 - 140%.

11.2.4 **Calibration Curve**

A seven-point calibration curve is used to calibrate the system. %RSD must be ≤20% for response factors, or linear regression must be used with correlation coefficient ≥0.99.

11.2.5 **Calibration Check Standard**

Method 8100M / 8015D DRO / 8015C DRO

A #2 fuel oil standard is analyzed at a concentration of 1000 µg/mL at the beginning of each analytical batch, after every 20 samples, at the end of the analytical batch, and at least every 12 hours. Percent recovery must fall within method established limits of 80 - 120%.

Method 8015D / 8015C

Analyze at least two hydrocarbon standards with each run (use #2fuel oil or gasoline if needed) at a concentration of 1000 µg/mL at the beginning of each analytical batch. Analyze after every 20 samples, at the end of the analytical batch, and at least every 12 hours. Percent recovery must fall within method established limits of 80 - 120%.

12.0 CORRECTIVE ACIONS/CONTINGENCIES OF HANDLING OUT-OF-CONTROL DATA

Refer to Con-Test Quality Assurance Manual.
Refer to Con-Test Corrective Action SOP.

13.0 POLLUTION PREVENTION

Pollution prevention encompasses any technique that reduces or eliminates the quantity and or eliminates the quantity and or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. Whenever feasible, laboratory personal should use pollution prevention techniques to address waste generation. When it is not feasible to reduce wastes at the source, recycling is recommended as the next best option. Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

14.0 WASTE MANAGEMENT

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing the waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.

15.0 REFERENCES

15.1 ASTM designation: D3328-78 (Reapproved 1982): "Comparison of waterborne petroleum oils by gas chromatography".

15.2 Con-Test Analytical Chemical Hygiene Plan.

15.3 Con-Test Analytical Quality Assurance Manual.

15.4 HP 5890 Series II Gas Chromatograph Operating Manual, Edition 2, 1989.

15.5 Con-Test Analytical SOP, “Method 3546, Microwave Extractions Procedure”.

15.6 Con-Test Analytical Corrective Action SOP.

15.7 Procedure for Maintaining Controlled Documents SOP.

15.8 Con-Test SOP on Chromatographic Integration Procedures.

15.9 Con-Test Analytical SOP, “CT ETPH: Analysis of Extractable Petroleum Hydrocarbons (ETPH) Using Methylene Chloride; GC/FID”.

15.10 USEPA – “Determinative Chromatographic Separations”, SW846, 3rd edition, March 2003, Method 8000C.

15.11 USEPA – “Method 8015D – Non Halogenated Organics using GC/FID”, SW846, 4th edition, June 2003.

15.12 USEPA – “Method 8000 B - Determinative Chromatographic Separations”, SW846, 2nd edition, December 1996.

15.13 USEPA – “Method 8015C – Non Halogenated Organics using GC/FID”, SW846, 3rd edition, February 2007.

Appendix I

How to Use the Buchi Syncore Concentrator (In reference to 3510, 3546, and 3540c methods)

1.0 How to prep a Buchi Syncore in order to concentrate samples for waters and soils.

Note: Prior to concentrating samples, allow the cooling plate to stabilize to its appropriate temperature.

1.1 Turn the chiller and vacuum pump on via the green toggle switch on each device. Next press the start button on the vacuum pump. Allow the temperature to reach 9°C.

1.2 Add at least ¼ inch of de-ionized water to each cell in the concentration platform. **Note: Avoid filling a cell so much that excess DI spills out.**

1.3 Each day fill the cold water bath that chills the solvent collection vessel. Run coolant line through the cold water bath and add ice when necessary.

1.4 Before starting, check that the secondary containment solvent vessels are empty! **It is extremely important that this be checked throughout the day!!**

2.0 Sample Concentration (Waters)

Note: All glassware should be similar in length to ensure a proper seal when under vacuum.

2.1 Rinse all concentration glassware with Acetone 2 times and Methylene Chloride 2 times. (Enough to coat glassware to ensure sufficient rinsing)

2.2 Transfer sample extract from the BOD bottle to Buchi concentration glassware. Rinse the BOD bottle 2 times with Methylene Chloride and add rinseate to sample.

2.3 Place samples in the Syncore, cover with the top cooling plate and hand tighten.

2.4 Turn the Syncore concentration platform on via the green toggle switch. Press the start button and adjust the rotation dial to 0.

2.5 Check that **"Gradient"** is shown in the upper left corner of the display on the vacuum unit. If it is not selected, push the menu button and adjust the black dial until **"Gradient"** is selected, hit OK.

2.6 Check that the **"Water Met Final 1 ml" program** is selected and hit start.

2.7 Adjust the concentration platform to "250" using the black Dial.

2.8 For samples that require a solvent exchange: (3546 and 3510c soils and waters)

2.9 Run the **"Waters Met Final 1 ml" program** (1 hr. 22 min.). Add 50 mls of hexanes to each sample and aspirate. Select **"Hex Exchange Final" program** (22 min.) and hit start. When the program has finished, bring samples to their appropriate final volume and vial.

2.10 After the program finishes, adjust the concentration platform so that 0 is displayed and it is no longer moving. Check that the vacuum is steady at ambient pressure and remove the top plate. Bring samples to their appropriate final volume and vial.

3.0 Sample Concentration (Soils)

3.1 Refer to section 1 for prepping the Syncore concentrator before working on samples.

3.2 Target sample volume after drying through sodium sulfate should be ~50 mL to avoid the sample going above the level of the cooling plate.

3.3 Pour the dried sample into a Buchi Concentration tube. Start the Syncore Concentrator using the following programs where applicable:

3.3.1 For **ETPH/8100 and 8270**, use program **"Soil Met in Use."** (43 min.)
3.3.2 For **8081/8082** use program **"Soil Pest/PCB 2 ml." (**32 min.)
3.3.3 For **EPH** first use program **"Soil Met in Use."** After the program finishes, perform a solvent exchange run the Syncore using program **"Hex exchange 2 ml final."** (22 min.)

Note:
If samples cannot be vialed immediately upon completion of a given program, hit "stop" on the concentration platform and adjust rotation to 0. Next hit stop on the vacuum pump and then hit start again to restart the chiller. If this is not done, five minutes after a program stops, the chiller will automatically turn off. The result of which may be losing the samples that are being concentrated.

IGNITABILITY OF SOLIDS

Approved:

Tod Kopyscinski
Laboratory Director

Katherine F. Allen
QA Officer

Revision Number: 5

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Change Record

Revision	Date	Responsible Person	Description of Change
0	03/20/2007	Katherine Delisle	Original SOP
1	04/14/2009	Katherine Delisle	Updates from annual SOP review: Sec. 9.0 (inclusion of pollution prevention sec.).
2	06/20/2012	J Pace	Updates due to internal audit: Section added for preservation/holding time/and storage
3	05/08/2014	K. Allen	Update from annual SOP review: Sec. 3.0 (include size of markings).
4	03/15/2017	K. Allen	Update from annual SOP review: Sec 3.0 and 6.4 (blow torch used not Bunsen burner)
5	03/12/2019	K. Allen	Updates from annual internal audit: Sec 6.2 (note to only measure out one sample at a time), Sec 6.7 (add clarification of timing), add sec 6.9 (to let samples cool, how to dispose sample and how to clean tile).

Distribution/Training List

See Employee Training Record File for signed training statements for trained users.

1.0 SUMMARY, SCOPE, AND APPLICATION

This method is suitable for the determination of the ignitability of solids and is appropriate for pastes, granular materials, solids that can be cut into strips, and powdery substances. If it is impractical to perform the test because of the physical form of the sample, generator knowledge should be used to determine the ignitability hazard posed by the material.

The test material is formed into an unbroken strip or powder train 250 mm in length. An ignition source is applied to one end of the test material to determine whether combustion will propagate along 200 mm of the strip within 2 minutes. If test material burns along 200 mm of the strip, it is considered present. If it does not propagate along 200 mm of the strip, it is absent.

2.0 SAMPLE PRESERVATION/STORAGE/HOLDING TIME

All samples are tested on as-received basis unless requested otherwise. No sample preservation is required, but sample containers should be completely filled and tightly sealed to preserve sample integrity.

Samples should be tested as soon as possible after removal from the sample container.

Samples that are chilled or cooled upon receipt to the laboratory should be allowed to equilibrate to the ambient laboratory temperature in the sample container.

3.0 EQUIPMENT & SUPPLIES

Low-heat conducting, non-combustible, impervious ceramic tile or equivalent material, of approximate dimension of 25 cm x 25 cm x 2.5 cm (the tile must be at least 25 cm in length to support a 25mm test sample). Mark a test line strip to indicate a length of 250mm on the tile.

High Temperature marker or equivalent marking device for marking ceramic plates.

A blow torch with a minimum diameter of 5mm capable of attaining a temperature of at least 1,000 °C.

Stop Watch

4.0 REAGENTS & STANDARDS

No special reagents are required to conduct this test.

5.0 SAFETY

See Material Safety Data Sheets (MSDS's) and Con-Test Chemical Hygiene Plan.

Prior to starting the test, all sample materials must be tested to determine if that material is explosive or extremely flammable. Use a very small portion of material (1 gram or less). If the sample displays explosivity or extreme flammability, do not conduct this test.

6.0 PROCEDURE

6.1 The ignitability test is conducted on all waste materials. On a clean, impervious ceramic tile (or equivalent), clearly mark a 250mm long test path. Make another mark at exactly 200 mm from the start of the sample path.

6.2 Samples that are chilled or cooled upon receipt to the laboratory should be allowed to equilibrate to the ambient laboratory temperature in the sample container.\

Prepare the test material in its “as received” form by forming an unbroken strip or powder train of sample 250 mm long by 20 mm wide by 10 mm high on the ceramic tile.

Only prepare one sample at a time as, samples should be tested as soon as possible after removal from the sample container.

6.3 Place the ceramic tile with the loaded sample in a fume hood about 20 cm from the front of the hood and in an area of laminar airflow. Position the sample perpendicular to the airflow. The airflow across the perpendicular axis of the sample should be sufficient to prevent fumes from escaping into the laboratory and should not vary during the test. The air velocity should be approximately 0.7 meters/second.

6.4 Light the blow torch. The temperature of the flame must be at least 1000° C.

6.5 Apply the tip of the flame to one end of the sample strip. The test period will depend on the sample matrix as follows:

6.6 If the waste is non-metallic, hold the flame tip on the sample strip until the sample ignites or for a maximum of 2 minutes. If combustion occurs, begin timing with a stop watch and note whether the combustion propagates up to the 200mm mark within the 2minute test period.

6.7 If the waste is a metal (ex. metal shavings) or metal-alloy powder, hold the flame tip on the sample strip until the sample ignites or for a maximum of 5 minutes. If combustion occurs reset timer/stop watch and begin timing again and note whether the combustion propagates up to the 200mm mark within the 20minute test period.

6.8 If the waste does not ignite and propagate combustion either by burning with open flame or by smoldering along 200 mm of the sample strip within the 2minute test period (or by 20minute test period for metal powders), the waste is not considered flammable.

6.9 Allow sample to cool before disposal. If sample is combustible or smells strongly refer to waste personnel for disposal, otherwise dispose of in the trash receptacle. Wipe the tile down with a wet paper towel and store in cabinet.

7.0 CALCULATIONS

Report Absent or Present.

8.0 QUALITY CONTROL

8.1 There is no outside QC needed for this test

9.0 CORRECTIVE ACTIONS/CONTINGENCIES OF HANDLING OUT-OF-CONTROL DATA

9.1 Refer to Con-Test Quality Assurance Manual.
9.2 Refer to Con-Test Corrective Action SOP.

10.0 POLLUTION PREVENTION

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many 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 waste generation. When it is not feasible to reduce wastes at the source, the Agency recommends recycling as the next best option.

11.0 WASTE MANAGEMENT

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing the waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.

12.0 REFERENCES

12.1 EPA Test Methods for Evaluating Solid Wastes (SW-846, Rev. 0 December 1996), Method 1030.

12.2 Con-Test Analytical Chemical Hygiene Plan.

12.3 Con-Test Analytical Quality Assurance Manual.

12.4 Con-Test Analytical Corrective Action SOP.

12.5 Con-Test Analytical Controlled Document SOP.

pH

Approved:

Tod Kopyscinski
Laboratory Director

Katherine F. Allen
QA Officer

Revision Number: 10

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Change Record

Revision	Date	Responsible Person	Description of Change
2	08/11/2003	Sondra S. Kocot	Updates for NELAC format
3	09/21/2005	Sondra S. Kocot	Updates for "Controlled Copy Status"; section 1.0 (deleted mention of portable pH probe); section 4.0 (new meter/probe); section 7.0 (procedure for new meter); section 8.0 (reporting); section 13.0 (ref. to new instr. Manual, lab gen limits, SM19th ed., corr action SOP)
4	04/22/2008	Katherine F. Delisle	Updates from internal audit findings and 03/08 NY Audit, sections 7.0 and 9.2.4(slope criteria), section 7.2(3-pt. Cal.), sections 7.4 and 7.5 (pH electrode main.), section 8.2(Potable Water HT), section 11.0 (addition of pollution prevention), and section 13.0 (ref. addition).
5	11/04/2008	Katherine F. Delisle	Update from EPA "Method Update Rule": Omit pH reference of method 150.1 (Sec. 13.0)
6	03/30/2011	Katherine F. Allen	Update from pH Internal Audit: Sec. 7.0(ph to pH), Sec. 7.3 (prep 20 grams not 10 grams), Sec. 8.2 (change pH analysis to pH holding time), and Sec. 13.0 (addition of method 9045D and 21st ed of SM).
7	04/01/2013	Andrea Palpini	Update from annual SOP review: Sec's 7.2.1 and 7.2.6 (changed concentration of check std), Sec. 7.3 (changed vol of DI), Sec. 8.2 (changed qualifier addition to be 15 min. for all samples), Sec. 9.2.1 (typo and added 4th std for LCS check for 3-pt cal).
8	02/18/2014	Katherine Allen	Updates from annual SOP review: Sec. 13.0 (addition of SM 22nd edition).
9	02/14/2018	Katherine Allen	Update from annual SOP review: Sec 3.0 (add soil HT of 24hours), Sec 7.0 (slope recorded at least monthly), and Sec 8.2 (qualifier on each water sample with 15 min requirement)
10	03/27/2019	Charles Balicki	Updates from pH Internal Audit: Section 4.2 Updated instrument. Section 5.1 Removed 2.00 and 11.00. Section 7.1.2 updated instrument. Section 7.1.2.1 updated pH buffers. Sections 7.1.2.2, 7.1.2.3, 7.1.2.4, 7.1.2.5, 7.1.2.6, and 7.1.2.8 updated pH meter calibration instructions. Removed Section 7.2. Section 7.4 updated instrument. Section 13.4 Updated instrument manual information and Sec 13.0 – Addition of SM 23rd ed.

Distribution/Training List

See Employee Training Record File for signed training statements for trained users.

1.0 SUMMARY, SCOPE, AND APPLICATION

The intensity of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. The pH or negative logarithm of the Hydrogen concentration is defined as:

$$pH = -\log_{10}[H^+] = \log_{10} 1/[H^+]$$

A solution with a higher pH has a lower concentration of H^+ ions and a higher concentration of OH^- ions than a solution with a lower pH. The pH meter determines the free H^+ and OH^- ion levels. Upon immersion of the electrode in a solution, the outer bulb surface becomes hydrated and exchanges sodium ions for hydrogen ions. This action (along with the repulsion of anions by fixed, negatively charged silicate sites) produces a potential that is a function of hydrogen ion activity in the solution at the glass-solution interface.

This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes, and solids.

Operating resolution is 0.01 pH units.

2.0 INTERFERENCES

2.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.

2.2 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by deionized water rinsing. Refer to electrode manual for cleaning details.

2.3 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. Note also that heat is generated from any stir plate being used: insulating material (a thin piece of cork, or paper towel) may be placed between the beaker and the plate. The second source is the change in pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled, it should therefore be noted by reporting both the pH and temperature at the time of analysis.

3.0 SAMPLE PRESERVATION/STORAGE/HOLDING TIME

Preservation = cool to 4°C
Store at 4 °C.
Water Holding time = analyze immediately (ASAP)
Soil Holding Time = 24 hours

4.0 EQUIPMENT & SUPPLIES

4.1 pH meter (Orion Expandable Ionanalyzer, EA 920, or a portable pH probe)
4.2 pH meter (Orion Versa Star)

4.3 pH electrode – Standard Polymer – body Gel-filled Combination Electrode, Accumet
4.4 pH electrode – Orion Triode pH Electrode, Thermo Electron Corporation
4.5 ATC (Automatic Temperature Compensation) probe, Epoxy model – ThermoOrion
4.6 Stir Plate

5.0 REAGENTS & STANDARDS

5.1 pH Buffers - 4.00, 6.00, 7.00, 9.00, 10.00 - certified, purchased.

6.0 SAFETY

See Material Safety Data Sheets (MSDS's) and Con-Test Chemical Hygiene Plan.

7.0 PROCEDURE - CALIBRATION & ANALYSIS

The pH meter is to be calibrated using standard buffers daily or with each use, whichever is less frequent.

NOTE: Stir buffers and sample solutions slowly with teflon coated magnetic stir bars while measurements are being made. Ensure enough clearance between the electrodes (pH and ATC) and stir bar. Rate of stirring should minimize the air transfer rate at the air water interface of the sample. Also ensure no air bubbles are "stuck" to the bottom of the probes.

For the pH meter with slope adjustment, the slope is created using standard pH buffers at the extremes of the normal working range (e.g. pH 6.00 and pH 9.00). The slope is then checked using a standard buffer at the middle of the working range (e.g. pH 7.00). An acceptable actual reading is target value +/- 0.05 pH units. Using a two-point standardization, an efficiency >0.95 or slope >95% indicates proper response. Record the slope at least monthly in the calibration section of pH bench sheet per MA DEP.

If the sample result is outside the calibrated usual working range, check the calibration with another buffer which would create a range the sample would fall within (using +/- 0.20 pH units acceptance criteria). If the acceptance criteria are not met, recalibrate the pH meter into a range which will include the sample result. Be sure to record initial calibrations, recalibrations and outside-range calibration checks in the pH bench sheet.

7.1 Two-Point Calibration

7.1.1 Orion EA 920

Calibrate the pH meter with 6.0 pH buffer standard, 9.0 pH buffer standard, and check with the 7.0 pH buffer standard. ***Make sure standards are not expired***.

7.1.1.1 Immerse the electrode in 6.00 pH buffer. Hold the function button until "STD 1" appears in the function column. Wait for the meter to stabilize. If the meter does not read 6.00, use the arrow keys to adjust pH reading higher or lower until a constant reading of 6.00 is obtained. When it is steady for several minutes, the "**Ready**" light will appear. Press "**Enter**" and the meter automatically switches to "STD 2". Remove the electrode from the 6.00 pH buffer. Rinse the electrode twice with deionized water between solutions. After rinsing, wipe electrode with a Kimwipe.

7.1.1.2 Repeat the above procedure with pH buffer 9.00. When "enter" is pressed the meter automatically switches to "SAMPLE".

7.1.1.3 Check the calibration with another buffer, pH 7.00. Refer to acceptable limits stated at the beginning of section 7.0. Recalibrate if necessary.

7.1.1.4 Record calibration information in the back section of the pH bench sheet.

7.1.1.5 Shake samples well before pouring off into analysis beaker. Stir at a constant, slow rate, without the electrodes touching the stir bar or the beaker sides.

7.1.1.6 Record pH, time and temperature (obtained from the instrument read-out display) in the pH bench sheet.

7.1.1.7 Perform a CCV (usually a mid-range buffer) after each batch, or on a 10% basis.

7.1.2 Orion Versa Star Calibration Procedure

7.1.2.1 Calibrate the pH meter with pH buffer standards 4.0, 10.0, 7.0 (check slope), and check with the 6.0 pH buffer standard. ***Make sure standards are not expired***.

7.1.2.2 Press **F1** until the pH Calibration is displayed.

7.1.2.3 Immerse the electrode in 4.0 pH buffer. Press **F3** to begin calibration. READY is displayed next to the reading, indicating electrode stability. For manual calibration use the **F3** key and enter value, then press **F2** to accept each digit. After accepting each digit, press **next**. Remove the electrode from the 4.0 pH buffer. Rinse the electrode twice with deionized water between solutions. After rinsing, wipe the electrode with a Kimwipe.

7.1.2.4 Repeat the above procedure with pH buffers 10.0 and then 7.0.

7.1.2.5 After entering the final buffer value, press **F3**. The electrode slope will be displayed. Average Slope appears in right if the display. After the third buffer point, the meter automatically displays the calibration slope. Press F3 to finish calibrating.

7.1.2.6 Check the calibration with another buffer, pH 6.0. Press **Measure** and wait for the meter to stabilize. Once the meter stabilizes the display will say "Ready" above the pH measurement. Record this number into the pH Logbook. Refer to acceptable limits stated at the beginning of section 7.0. Recalibrate if necessary.

7.1.2.7 Record calibration information in the back section of the pH bench sheet.

7.1.2.8 Rinse electrode and place into sample and press **Measure**. Record pH directly from the main meter display. Temperature is displayed in the right side of the pH reading.

7.1.2.9 Shake samples well before pouring off into analysis beaker. Stir at a constant, slow rate, without the electrodes touching the stir bar or the beaker sides.

7.1.2.10 Record pH, time and temperature (obtained from the instrument read-out display) in the pH bench sheet.

7.1.2.11 Perform a CCV (usually a mid-range buffer) after each batch, or on a 10% basis

7.2 Solid Matrix Analysis

Mix 20.0 grams sample with 20 mL deionized water. For soils, stir 15 min. and let settle for 1 hour prior to analysis. For waste, stir 15 min. and let settle for 15 min. prior to analysis. Record sample weight on pH bench sheet. Immerse calibrated probe into slurry and analyze as in above sections.

7.3 pH Electrode Maintenance for Orion Versa Star

7.3.1 Weekly, inspect the electrode for scratches, cracks, salt crystal build-up, or membrane/junction deposits.

7.3.2 Rinse off any salt build-up with distilled water, and remove any membrane/junction deposits as directed in cleaning procedures below.

7.3.3 Drain the reference chamber, flush it with fresh filling solution and refill the chamber.

7.3.4 Document cleaning procedure in pH meter maintenance logbook.

7.3.5 **Cleaning Procedure:**

7.3.5.1 **General-** Soak in a 1:10 dilution of Cleaning Solution C (Orion 900023) for a half- hour or to clean microbiological contaminants, soak in a 1:100 dilution of Cleaning Solution B (Orion 900022) for 15 minutes with stirring.

7.3.5.2 **Removal of Membrane/Junction Deposits-**
Protein- Soak in Cleaning Solution A (Orion 900021) for 15 minutes.
Inorganic- Soak in 0.1 M tetrasodium EDTA solution for 15 minutes.
Grease and Oil- Rinse with Cleaning Solution D (Orion 900024) or methanol solution.

7.3.5.3 After any of these cleaning procedures, drain and refill the reference chamber and soak the electrode in storage for at least one hour.

7.4 pH Electrode Maintenance for Orion EA 920

7.4.1 A dirty glass membrane is usually indicated by beads of water forming on the bulb when it is rinsed with distilled water. The bulb can be cleaned as follows:

7.4.1.1 For protein layers – soak in a freshly prepared solution of pepsin in 0.1N HCL (approximately ¼ teaspoon/100 ml) for 30 minutes.

7.4.1.2 For Inorganic deposits – wash with EDTA, ammonia, or acids.

7.4.1.3 For Grease and similar films – wash with acetone, methanol, etc.

7.4.2 Unblocking the Junction – If the junction should become blocked or partially plugged, perform the following:

7.4.2.1 Inspect the reference cavity for crystallization. If crystallization is present, go to the next step (7.5.2.2); if not, proceed to step 7.5.2.3.

7.4.2.2 Remove crystals as follows – Remove the filling solution by shaking it out through the fill hole. Repeatedly rinse the reference cavity with distilled water until all crystals are dissolved. Empty the reference cavity and refill it with SP135. Pressurize the electrode and determine if flow is re-established. If no flow is found, proceed to the next step (7.5.2.3).

7.4.2.3 Perform the following procedures in sequence and as needed, depending upon the severity of the blockage. – Soak electrode tip in warm water and apply pressure to filling hole. Soak the electrode tip in concentrated ammonium hydroxide for 5 to 10 minutes. Rinse with DI water. Then, apply pressure to filling hole.

8.0 CALCULATIONS

8.1 RELATIVE PERCENT DIFFERENCE

RPD = [(A – B)/C] x 100
where:

A = sample result or duplicate result (whichever is larger)

B = sample result or duplicate result (whichever is smaller)

C = average of sample and duplicate results

8.2 REPORTING

When reporting results, record analysis date, time, and temperature in the bench sheet and in the LIMS. A qualifier is always added to each water sample result that states “Holding time exceeded – Recommended holding time - 15 minutes”. The temperature is entered into the “response” field in Element.

This is meet both the EPA Clean Water act for non-potable waters and the NELAC acceptance requirements for potable water.

9.0 QUALITY CONTROL

9.1 Definitions

For definitions and explanations of quality control measures (LCS/QC Reference, Duplicates) refer to the Con-Test Analytical Quality Assurance Manual.

9.2 Quality Control Measures & Acceptance Criteria

9.2.1 LCS (Laboratory Control Sample)

Also known as External Standard/ QC Reference Material.
Analyze once daily to determine any bias of the analysis. The LCS is from an independent source (i.e. external to the calibration curve stock), and is thus a true validation of the analytical system. In general, use the laboratory-generated limits for acceptance criteria, or if none are available, use those provided by the supplier.

NOTE: The LCS must pass acceptance criteria before any further analysis can take place. Perform corrective actions if necessary.

The third or fourth (fourth for the 3-point calibration) buffer analyzed at calibration is considered the LCS, as it is not used in the calibration.

9.2.2 Matrix duplicates

Analyze on $\geq$ 10% basis (one per batch of 10 or less samples) to assess precision by use of a calculated RPD. Follow laboratory-generated control limits.

9.2.3 CCV (Continuing Calibration Verification)

CCV's are standards which determine the validity and stability of the initial calibration of an instrument. Analyze on a 10% basis, or after each batch. Choose a mid-level standard as the CCV.

Acceptable range = true value +/- 0.05 pH units.

If, after corrective action(s) the CCV still falls outside the acceptance criteria, a new calibration curve must be reanalyzed and all samples since the last successful calibration verification standard also reanalyzed.

9.2.4 SLOPE

Record the slope of each pH meter monthly in the pH bench sheet, per "Revised Massachusetts Regulations for the Certification and Operation of Environmental Analysis Laboratories", 310 CMR 42.00 (March 2008).

10.0 CORRECTIVE ACTIONS/CONTINGENCIES OF HANDLING OUT-OF-CONTROL DATA

10.1 Refer to Con-Test Quality Assurance Manual.
10.2 Refer to Con-Test Corrective Action SOP.

11.0 POLLUTION PREVENTION

11.1 The reagents used in this method pose little threat to the environment when recycled and managed properly.

11.2 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

12.0 WASTE MANAGEMENT

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing the waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.

13.0 REFERENCES

13.1 APHA "Standard Methods for the Examination of Water and Wastewater", 18/19th /21st/22nd /23rd edition, 1992/1995/2005/2012/2017, Method 4500 H^+.

13.2 EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW-846, January 1995, Rev. 3, Method 9045C.

13.3 EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW-846, November 2004, Rev. 4, Method 9045D.

13.3 Instrument Manual, Orion EA 920 Expandable IonAnalyzer, Orion Research Inc., c.1985.

13.4 Instrument Manual, Orion Versa Star Thermo Fisher Scientific, Document #68X000791 Revision B, 2018.

13.5 pH Electrode Manual (Fisher, Accumet model), Accumet, Nov. 1993.

13.6 pH Electrode Manual (Thermo Electron Corporation, document #212957-001 Rev.D, 2003.

13.7 ATC probe Manual, ThermoOrion, 2001.

13.8 Con-Test Analytical Chemical Hygiene Plan.

13.9 Con-Test Analytical Quality Assurance Manual.

13.10 Con-Test Analytical Corrective Action SOP.

13.11 Con-Test Document, "Laboratory-Generated Control Limits".

13.12 EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW-846, November 2004, Rev. 3, Method 9040C.

REACTIVITY

Approved:

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Laboratory Director

Katherine F. Allen
QA Officer

Revision Number: 6

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Change Record

Revision	Date	Responsible Person	Description of Change
0	09/27/2005	Sondra S. Kocot	Original
1	09/24/07	Sondra L. Slesinski	Edits per corrective actions: stdz'n of sulfide stock (section 4.10); Rxt CN false positives due to sulfide interferences (sections 4.11, 4.12, 6.1); delete reference to EPA 376.1 (as per EPA Method Update Rule)
2	3/30/2011	J. Morrow	Updates from internal audit: Replaced 0.005M H2SO4 with 0.01N H2SO4, Add comment to use lead acetate paper for only for sulfide water samples, add titration blank section to analysis of Rx Sulfide, for analysis of reactive sulfide amount of 6N HCl goes from 2mL to 5mL, add step to Rx Sulfide to add small scoop of Thyodene, remove distillation blank from QC section, replace LFB section with LCS in QC section, and add 21st ed. of SM in ref. section.
3	10/24/2012	J. Pace	Edits from internal audit: Sec 4.0: 1.25N NaOH removed and 0.25N NaOH recipe updated. Sec 6.2.1: replace term separatory funnel with condenser tube. Sec 6.3.1:Replace sulfide waste drum with pH <2 waste drum. Sec 10 add to put acidic waste from distillations into pH <2 waste drum.
4	06/05/2013	J. Pace	Edits from internal audit: Sec 6.1.1 changed 50mL of 0.25N NaOH to 20-30mL. Sec 6.2.6 had incorrect volumes of titrant used and waste section was removed. Sec 8.2.2 A note was added to run an annual distilled LCS.
5	03/15/2017	Katherine Allen	Update from annual SOP review: Sec 6.2 (order of steps changed), Sec 6.3.3 (salmon color not orange), Sec 8.2.4 (new CCV criteria of 90-110%) and Sec 12.0 (addition of SM 22nd edition and SM 4500 S2-F).
6	03/12/2019	Charles Balicki	Updates from Annual SOP Review. Section 4.3.6 updated CN stock volume to 100 mls from 250. Section 12.1 and 12.2 added 23rd edition. Section 3.8 Added Balance information. Added Section 12.8 added balance manual.

Distribution/Training List

See Employee Training Record File for signed training statements for trained users.

1.0 SUMMARY, SCOPE, AND APPLICATION

A solid waste exhibits the characteristic of reactivity if a representative sample of the waste has any of the following properties:

- it is normally unstable and readily undergoes violent change without detonating
- it reacts violently with water
- it forms potentially explosive mixtures with water
- when mixed with water, it generates toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or to the environment
- it is a cyanide- or sulfide-bearing waste, that, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or to the environment.
- it is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement.
- it is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.
- it is a forbidden explosive, as defined in 49 CFR 173.51, or a Class A explosive, as defined in 49 CFR 173.53, or a Class B explosive, as defined in 49 CFR 173.88
- a solid waste that exhibits the characteristic of reactivity, but is not listed as a hazardous waste in Subpart D, has the EPA Hazardous Waste Number of D003.

This method is applicable to all wastes, with the condition that wastes that are combined with acids do not form explosive mixtures. This method provides a way to determine the specific rate of release of hydrocyanic acid and hydrogen sulfide upon contact with an aqueous acid.

This test measures only the hydrocyanic acid and hydrogen sulfide evolved at the test conditions. It is not intended to measure forms of cyanide and sulfide other than those that are evolved under the test conditions.

An aliquot of the waste is acidified to pH 2 in a closed system. The gas generated is swept into a scrubber. The analyte is quantified. The procedure for quantifying the cyanide is EPA SW-846 Method 9014. The procedure for quantifying the sulfide is EPA SW-846 Method 9030.

Reporting Limit	Reactive Cyanide = 4 mg/Kg Reactive Sulfide = 20 mg/Kg
EPA Action Level	Reactive Cyanide = 250 mg/Kg Reactive Sulfide = 500 mg/Kg

2.0 SAMPLE PRESERVATION/STORAGE/HANDLING

2.1 Samples containing, or suspected of containing, cyanide, sulfide, or a combination of the two, should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all headspace, and capped. Analysis should commence as soon as possible, and samples should be kept in a cool, dark, place (Refrigerate at 4 °C) until analysis begins.

2.2 It is suggested that samples of cyanide and sulfide wastes be tested as quickly as possible. Although liquid samples can be preserved as for total cyanide and total sulfide, this will cause dilution of the sample, increase the ionic strength, and possibly change other physical or chemical characteristics of the waste which may affect the rate of release of hydrocyanic acid and hydrogen sulfide.

2.3 Distillation should be performed in a ventilated hood.

3.0 EQUIPMENT & SUPPLIES

3.1 Round-bottom flask – 500 mL, three-neck, with 24/40 ground-glass joints
3.2 Separatory funnel with 24/40 glass joint and Teflon stopcock.
3.3 Scrubber and receiver tube
3.4 Stir plate (to achieve approximately 30 rpm)
3.5 Nitrogen gas
3.6 Buret - 50 mL
3.7 Glassware - volumetric and non-volumetric
3.8 Analytical balance: AND Model HR-200, Ser.# 12336744

4.0 REAGENTS & STANDARDS

4.1 Sulfuric Acid, 0.01N – add 20 mL of prepared 1.0N H_2SO_4 to 2L deionized water.

4.2 Sodium Hydroxide, 0.25N – dilute 50 mL of 10 N NaOH volumetrically to 1-L with deionized water.

4.3 **Cyanide Stock & Standardization Reagents**

4.3.1 Standard Silver Nitrate Solution, 0.0192N -Prepare by crushing approximately 5 g $AgNO_3$ (ACS grade) crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in distilled water in a 1 liter volumetric flask, and dilute to volume.

Standardize monthly:

Fill a 25 ml buret with 0.0192 N $AgNO_3$ solution.

Measure 10 mls of the 0.0141 N NaCl solution to a 125 ml Erlenmeyer flask.

Add a few drops of Potassium Chromate Indicator solution.

Titrate with $AgNO_3$ to pinkish yellow end point (sample becomes a cloudy yellow instead of bright yellow).

$$\text{N of AgNO3} = \frac{(\text{mls of sample})\ (\text{N of NaCl solution})}{(\text{mls of } AgNO_3 \text{ titrated})}$$

Where: mls of sample = 10 mls
N of NaCl = 0.0141

Record Standardization in Standardization Logbook.

4.3.2 Standard Sodium Chloride, 0.0141 N - Dissolve 0.8241 g of NaCl (anhydrous), ACS grade, in deionized water in a 1-L volumetric flask. Dilute to volume with deionized water.

4.3.3 Potassium Chromate Indicator Solution - Dissolve 50 g of K_2CrO_4 in deionized water. Add $AgNO_3$ solution until a definite red precipitate forms. Let stand 12 hours, filter, and dilute to 1-L with deionized water.

4.3.4 Rhodanine Indicator - Dissolve 20 mg (0.020g) of paradimethylaminobenzalrhodanine (ACS grade) in 100 mLs acetone (ACS grade). Store in a glass bottle.

4.3.5 10 N NaOH - Dissolve 40 g NaOH (ACS grade) in a 100 mL volumetric flask with deionized water.

4.3.6 Stock CN Solution, 2000 mg CN/L (actual), 1000 mg CN/L (pre-distillation equivalent) -In a 1-L volumetric flask, dissolve 2.0 g potassium hydroxide (KOH) (ACS grade) in approximately 500 mls of deionized water. Add 5.01 g potassium cyanide (KCN) (ACS grade) . Dilute to the mark with deionized water and mix. **Standardize weekly.**

CAUTION; KCN IS HIGHLY TOXIC. AVOID INHALATION OF DUST OR CONTACT WITH THE SOLID OR SOLUTIONS.

Standardization:

Measure 10 mls of Cyanide Stock solution into an Erlenmeyer flask. Add 0.25 mls of Rhodanine Indicator Solution , titrate with 0.0192 N $AgNO_3$ until the color changes from a canary yellow (which get cloudy) and to a salmon hue.

Titrate a Blank consisting of 0.10 mls of 10 N NaOH in 10 mls of deionized water to which has been added 0.25 mls of Rhodanine Indicator Solution.

$$\text{Mg/L CN} = \frac{(\text{ml } AgNO_3 \text{ titrated-blank})(\text{N of } AgNO_3)\ (5.204)\ (10{,}000)}{(10 \text{ mLs})}$$

Based on the calculated concentration, determine the volume of CN stock solution needed to make 100 mls working standard at 10 mg/L.
(Refer to Standardization Logbook).

Record standardization in Standardization Logbook.

4.5 Standard Iodine Solution, 0.025N - Using a 1-Liter volumetric flask, dissolve 20.0 to 25.0g KI (Potassium Iodide) (ACS grade) in approximately 200 mls deionized water. Add 3.2g iodine (ACS grade). Allow ample time for the iodine to dissolve, mix and then dilute to mark with deionized water.

Alternatively, make a 4x dilution of purchased, certified 0.1N Iodine Solution (i.e. dilute 250 mLs of 0.1N Iodine Solution volumetrically to 1-L with deionized water).

This solution must be standardized monthly against 0.025 N sodium thiosulfate.

Standardization:

Dissolve approximately 2g of Potassium Iodide (KI) (ACS grade) in a 500 ml Erlenmeyer flask with 150 mls of deionized water. Add 1.0 ml of 6N HCL and 20.0 mls of 0.025N iodine solution. Dilute to approximately 200 mls with deionized water. Add a stir bar and titrate the solution with 0.025N sodium thiosulfate titrant, adding a small scoop (0.3-0.5 grams) of Thyodene starch indicator when a pale straw color is reached near end of titration. Add enough starch indicator so that the solution is dark blue in color. Continue titrating until the blue color does not persist (i.e. the solutions goes "clear"). Note: At end point color, the sample may not appear entirely clear due to small blue precipitated particles. Approximately 15 to 25 mls should be used.

$$\text{N, Iodine} = \frac{\text{mls of titrant X Normality of titrant (0.0250N)}}{\text{Iodine Solution sample size (mls)}}$$

Record standardization information in the Standardization Logbook.

4.6 Sodium Thiosulfate Solution, 0.0250N - Purchased. **Standardize monthly against 0.1N Potassium Biiodate.**

Standardization:

In a 250 ml Erlenmeyer flask, dissolve 2 g KI (ACS grade) in 150 mls deionized water. Add 10 of 10% H2SO4 (prepared from ACS grade) and 10 mls of the 0.100 N Potassium biiodate (prepared from ACS grade). Bring the volume to 200 mls with deionized water.

Immediately titrate with 0.025 N sodium thiosulfate to a straw-yellow color. Add 1 scoop of starch indicator (thyodene) and continue titrating with the 0.025 N thiosulfate to a clear, water-white endpoint.

Calculate normality using the formula:

$$\text{N, } Na_2S_2O_3 = [\ A \times 0.1\ N\ (KH\ (IO_3)_2\ ]\ /\ B$$

Where:

A = the volume of 0.1 N $KH(IO_3)_2$
B = the volume of $Na_2S_2O_3$
Record standardization information in the Standardization Logbook.

4.7 Potassium Biiodate, 0.1 N - (For standardization of the sodium thiosulfate titrant). Into a 1L volumetric flask add 3.2490 g potassium biiodate (ACS grade). Dilute to volume with deionized water.

4.8 Hydrochloric Acid, 6N - Slowly add 50 mL concentrated HCl (ACS grade) to 50 mL deionized water.

4.9 Starch Indicator - "Thyodene", purchased from Fisher Scientific.

4.10 Sulfide Reference Solution - Sodium Sulfide Nonahydrate ($Na_2S \bullet 9H_2O$). Dissolve 4.02g of Sodium Sulfide (ACS grade) in deionized water at pH 9-11 using a 1-L volumetric flask. The true value of this solution is 570 mg/L Hydrogen Sulfide. Store solution in an amber glass bottle at 4°C. **This solution is not stable for long periods of time. Dilute this solution 1:10 or 1:100 in a final volume of 100 ml and analyze for reference value determined, daily.**

4.11 Lead acetate paper (VWR Scientific/ Fisher Scientific)

4.12 Bismuth Nitrate – ACS grade

5.0 SAFETY

See Material Safety Data Sheets (MSDS's) and Con-Test Chemical Hygiene Plan.

Exercise caution when handling acids.

6.0 PROCEDURE

6.1 Distillation

6.1.1 Add 20-30 mL of 0.25 N NaOH solution to a scrubber tube. Ensure that adequate depth of liquid exists.
6.1.2 Add 250 mL 0.01N H_2SO_4 to the condenser tube.

6.1.3 Check samples for sulfide, prior to distillation, with lead acetate paper, **for water samples only.**

6.1.3.1 If lead acetate paper indicates sulfide, add bismuth nitrate to the sample prior to distillation.
6.1.3.2 If the sample is treated for sulfide, then a separate (untreated) aliquot must be distilled for Rxt. Sulfide.
6.1.3.3 Record use of bismuth nitrate on the bench sheet.

6.1.4 Add ~25.0 g weighed sample and stir bar to the round bottom flask.
6.1.5 Close the system and adjust the flow rate of nitrogen (~60 mL/min).
6.1.6 With the nitrogen flowing, add enough acid to fill the system half full, while starting the 30-minute test period.

6.1.7 Begin stirring while the acid is entering the round-bottomed flask.
6.1.8 After 30 minutes, close of the nitrogen and disconnect the scrubber; dilute the scrubber volume to 250 mL with 0.25N NaOH.
6.1.9 Record distillation information on the bench sheet.

6.2 Analysis – Reactive Sulfide Distillates

6.2.1 Place 100 mL of sample into the titration vessel.

6.2.2 Place a known amount of 0.025N Iodine Solution in the titration vessel. The amount should be estimated to be in excess of the amount of sulfide expected.

6.2.3 Add 5 mL of 6N HCl and then add a small scoop of Thyodene starch indicator.

6.2.4 If the iodine color disappears, add more iodine until the color remains. Record the total mLs 0.025N iodine added. Note: prior to iodine addition, check the pH of the sample with pH paper (if it is not acidic, the iodine color will disappear: add more 6N HCl if needed).

6.2.5 Titrate with 0.025N sodium thiosulfate, using starch indicator, until the blue color disappears. Record the mLs of titrant used.

6.2.6 Note: The blank and samples will take ~4.5-5.2 mL of titrant. The standard will take ~16-17 mLs of titrant.

6.3 Analysis – Reactive Cyanide Distillates

6.3.1 Pour off 100 mL distillate into the titration vessel.
- 6.3.1.1 Titration blank = 100 mL 0.025N NaOH
- 6.3.1.2 Titration standard = 530 uL of Cyanide stock into 100 mL 0.25N NaOH = 10 mg/L.

6.3.2 Add 0.5-1.0 mL rhodanine indicatior to each flask (the color will be yellow).

6.3.3 Titrate with 0.019 N AgNO3 titrant, until a “pink salmon” endpoint is reached.

6.3.4 Note: The blank will take only one drop (~0.05 mL) of titrant; most samples will only take one drop. The standard will take about 1.00-1.10 mLs of titrant: dispose of this titrated standard in the Cyanide waste drum.

7.0 CALCULATIONS

7.1 SULFIDE CALCULATION

One milliliter 0.0250N iodine solution reacts with 0.4 mg S^{2-}

$$\text{mg } S^2/L = \frac{[(A \times B) - (C \times D)] \times 16\,000}{\text{mLs sample titrated}}$$

Where: A = mLs iodine solution
B = normality of iodine solution
C = mL $Na_2S_2O_3$ solution
D = normality of $Na_2S_2O_3$

Calculate the specific rate of release of H_2S:

$$R = \frac{X \times L}{W \times S}$$

Where: R = Specific rate of release (mg/Kg/sec)
X = Concentration of H_2S in scrubber (mg/L)
L = Final volume of solution from scrubber (0.250 Liters)
W = Weight of waste used (kg)
S = Time of experiment (sec.)

Total releasable H_2S (mg/Kg) = R x S
(Note that "S" cancels in this equation, therefore the final result is determined by the equation, {X x L}/ W).

7.3 CYANIDE CALCULATION

$$\text{Mg CN/L} = \frac{(A-B)(C)(52040)}{\text{mLs titrated}}$$

Where: A = mLs titrated for sample
B = mLs titrated for blank
C = normality of $AgNO_3$

Calculate the specific rate of release of HCN:

$$R = \frac{X \times L}{W \times S}$$

Where: R = Specific rate of release (mg/Kg/sec)
X = Concentration of HCN in scrubber (mg/L)
L = Final volume of solution from scrubber (0.250 Liters)
W = Weight of waste used (kg)
S = Time of experiment (sec.)

Total releasable HCN (mg/Kg) = R x S
(Note that "S" cancels in this equation, therefore the final result is determined by the equation, {X x L}/ W).

7.4 RELATIVE PERCENT DIFFERENCE

$$RPD = [(A - B)/C] \times 100$$

Where:

A = sample result or duplicate result (whichever is larger)
B = sample result or duplicate result (whichever is smaller)
C = average of sample and duplicate results

7.5 PERCENT RECOVERY

$$\%R = [(A - B)/C] \times 100$$

Where:

A = matrix spike result
B = sample result
C = true value of spike

7.6 REPORTING

When reporting results, record analysis date and time on the bench sheet.

8.0 QUALITY CONTROL

8.1 Definitions

For definitions and explanations of quality control measures (blanks, LCS/QC Reference, LCS Duplicates, MS/MSD) refer to the Con-Test Analytical Quality Assurance Manual.

8.2 Quality Control Measures & Acceptance Criteria

8.2.1 Reagent (Titration) Blank

Analyze once daily, to determine any bias associated with reagents. Apply the necessary correction to analyte determination.

8.2.2 LCS (Laboratory Control Sample)/LCS Duplicate (Laboratory Control Sample Duplicate)

Also know as External Standard/ QC Reference Material. This is an un-distilled LCS/LCS Dup. Use the Sulfide or Cyanide Reference Sample as the LCS/LCS Dup. Analyze once daily to determine any bias of the analytical method. The LCS is from an independent source and is thus a true validation of the analytical system. In general, use the laboratory-generated limits for acceptance criteria, or if none are available, use those provided by the supplier.

NOTE: The LCS/LCS Dup. must pass acceptance criteria before any further analysis can take place. Perform corrective actions if necessary.

NOTE: An annual Distilled LCS needs to be run and documented.

8.2.4 CCV (Continuing Calibration Verification)

CCV's are un-distilled standards which determine the validity and stability of the initial calibration of an instrument. Analyze on a $\geq$ 5% basis (at the end of a batch of 20 or less samples); it is advisable to analyze on a 10% basis. Choose a mid-level standard as the CCV.

Acceptance criteria = 90-110%

If, after corrective action(s) the CCV still falls outside the acceptance criteria, a new calibration curve must be reanalyzed and all samples since the last successful calibration verification standard also reanalyzed.

9.0 CORRECTIVE ACTIONS/CONTINGENCIES OF HANDLING OUT-OF-CONTROL DATA

9.1 Refer to Con-Test Quality Assurance Manual.
9.2 Refer to Con-Test Corrective Action SOP.

10.0 POLLUTION PREVENTION

10.1 Make Sulfide Reference Solution in small aliquots, as it degrades quickly and needs to be re-made; this will result in less waste for disposal. Do not dispose of samples down the general sink; use the neutralization tank drain under a ventilation hood.
10.2 Do not prepare a higher concentration of Cyanide stock than is needed. All cyanide solutions need to go into the cyanide waste drum.
10.3 For distillation waste pour acidic waste into pH <2 drum.

11.0 WASTE MANAGEMENT

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing the waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.

12.0 REFERENCES

12.1 APHA "Standard Methods for the Examination of Water and Wastewater", 18/19th /21st /22nd /23rd Edition, 1992/1995/2005/2012/2017, Method 4500 S^{2-} F.

12.2 APHA "Standard Methods for the Examination of Water and Wastewater", 18/19th /21st /22nd /23rd Edition, 1992/1995/2005/2012/2017, Method 4500 CN-D.

12.3 EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW-846, Rev.0, December 1986, Methods chapter 7: 7.3.3.2/ 7.3.4.2 (distillation) and Methods 9014 / 9030A (titration).

12.4 Con-Test Analytical Chemical Hygiene Plan.

12.5 Con-Test Analytical Quality Assurance Manual.

12.6 Con-Test Analytical Corrective Action SOP**.**

12.7 Con-Test Document "Laboratory-Generated Control Limits".

12.8 Balance Manual, AND Model HR-200, S/N 12336744.

SHEALY ENVIRONMENTAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

Determination of Per- and Polyfluoroalkyl Substances (PFAS) by LC/MS/MS (Isotope Dilution)
QSM 5.3 Table B-15

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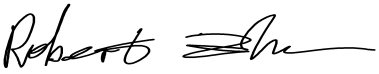
Daniel J. Wright
Laboratory Director

12/13/2019 9:09:01 AM
Stephanie L. Atkins
Quality Assurance Officer



12/16/2019 1:22:06 PM
Robert Zhu
Technical Director

12/9/2019 10:17:28 AM
Bradley E. Belding
Operations Director

12/13/2019 2:51:01 PM
Stephen E. Somerville
Analyst

TABLE OF CONTENTS

1. SCOPE AND APPLICATION

NOTE: Refer to appendices for state and/or program specific method criteria, which supersede and/or supplement the method criteria prescribed in this SOP.

1.1. The main body of this SOP describes a Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) method for the determination of selected Per- and Polyfluorinated Alkyl Substances (PFAS) in aqueous and solid samples using isotope dilution (ID) quantitation. This method is referred to as ID (ID-AQ, ID-Solid, ID-SD). Refer to Table 1 for target analytes.

1.2. The requirements contained in this SOP conform to those presented in the Department of Defense-Quality Systems Manual (DoD-QSM) Version 5.3, Table B-15 (2018), which are listed in Appendix F of this SOP, for reference.

2. SUMMARY OF METHOD

NOTE: Refer to appendices for state and/or program specific method criteria, which supersede and/or supplement the method criteria prescribed in this SOP.

2.1. ***PFAS Isotope Dilution method (aqueous; ID-AQ)*** - A 250-mL water sample is fortified with surrogates (SUR; isotope dilution standards) and passed through a solid phase extraction (SPE) cartridge (Phenomenex Strata-XL-AW or equivalent) to extract the method analytes and SUR. The compounds are eluted from the Strata-XL-AW cartridge with 4-mL of methanol and 4-mL of ammonia-methanol (0.3%). Samples are then filtered by SPE (Strata-GCB or equivalent), with a tube rinse of 2-mL of clean MeOH. With the SPE-Strata-GCB tube rinse, the final extract volume is approximately 10 mL. An aliquot of the extract is fortified with internal standards (IS). 10-µL of the fortified aliquot is injected on an LC equipped with a C18 column that is coupled to an MS/MS detector. The analytes are separated and identified by comparing the acquired mass spectra and retention times to the reference spectra and retention times for calibration standards acquired under identical LC/MS/MS conditions. The concentration of each analyte is determined by using the internal standard isotope dilution technique.

2.2. ***PFAS Isotope Dilution method (solid; ID-Solid)*** - Approximately 1g of solid sample is mixed with 8mL of methanol containing surrogates (SUR; isotope dilution standards). It is shaken on an orbital shaker and then sonicated and centrifuged. The extract is filtered by SPE (Strata-GCB or equivalent), with a tube rinse of 2-mL of clean MeOH. The final extract volume following the filtration step is approximately 10 mL. An aliquot of the extract is fortified with internal standards (IS). 10-µL of the fortified aliquot is injected on an LC equipped with a C18 column that is linked to an MS/MS detector. The analytes are separated and identified by comparing the acquired mass spectra and retention times to the reference spectra and retention times for calibration standards acquired under identical LC/MS/MS conditions. The concentration of each analyte is determined by using the internal standard isotope dilution technique. See Appendix B for specific procedures for preparing and analyzing solid samples by ID-Solid.

2.3. ***PFAS Isotope Dilution method (Aqueous Serial Dilution; ID-SD)*** - Samples of known high PFAS concentrations, such as AFFF pure product formulations, can be prepared by serial dilution instead of SPE, with documented project approval. The sample serial dilutions will be prepared in 96% MeOH: 4% water. IS and SUR will be spiked into the diluted sample (not the original sample collected) in the preparation vial. Any target analytes found to be ND in any samples shall be spiked at the LOQ level (post-spike) in those samples at the dilution reported, and analyzed again. Recovery for the post-spiked analytes must fall within 70-130% of the expected value; if these criteria are not met, the post-spike analysis will be repeated at successively higher dilutions until recovery is acceptable. The spiking concentration will be used to calculate the project-specific LOQ for each analyte. 10-µL of the prepared dilution aliquot is injected on an LC equipped with a C18 column that is coupled to an MS/MS detector. The analytes are separated and identified by comparing the acquired mass spectra and retention times to the reference spectra and retention times for calibration standards acquired under identical LC/MS/MS conditions. The concentration of each analyte is determined by using the internal standard isotope dilution technique. See Appendix C for specific procedures for preparing and analyzing serial dilution samples by ID-SD.

3. DEFINITIONS

NOTE: Refer to the *Quality Assurance Management Plan* [QAMP ME0012K] to reference additional terms used in this procedure.

3.1. ***Analysis Batch*** – A set of samples that is analyzed on the same instrument during a 24-hour period, including no more than 20 field samples, that begins and ends with the analysis of the appropriate Continuing Calibration Verification (CCV) standards. Additional CCVs may be required depending on the length of the analysis batch and/or the number of

field samples.

3.2. ***Collisionally Activated Dissociation (CAD)*** – The process of converting the precursor ion's translational energy into internal energy by collisions with neutral gas molecules to bring about dissociation into product ions.

3.3. ***Extraction Batch*** - A set of up to 20 field samples (count does not include QC samples) extracted together by the same person(s) during a work day using the same lot of SPE devices, solvents, surrogates, internal standards and fortifying solutions. Required QC samples include Method Blank, Laboratory Control Sample, Matrix Spike, and either a Field Duplicate or Matrix Spike Duplicate.

3.4. ***Internal Standard (IS)*** – A pure chemical added to an extract or standard solution in a known amount(s) and used to measure the relative response of other method analytes and surrogates that are components of the same solution. The internal standard must be a chemical that is structurally similar to the method analytes, has no potential to be present in water samples, and is not a method analyte. For the ID methods, the IS is used to monitor consistency of instrumentation performance.

3.5. ***Surrogate (SUR)*** – A pure chemical which chemically resembles method analytes and is extremely unlikely to be found in any sample. This chemical is added to a sample aliquot (field and QC) in known amount(s) before the extraction and analysis processes. The purpose of the SUR is to monitor method performance from extraction to final chromatographic measurement. For the ID methods, the SUR is used as an isotope dilution standard for measuring the relative response and quantification of other method analytes.

3.6. ***Field Duplicates (FD1 and FD2)*** – Two separate samples collected at the same time and place under identical circumstances, and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

3.7. ***Precursor Ion*** – The precursor ion is typically the deprotonated molecule ([M-H]-) of the method analyte. In MS/MS, the precursor ion is the mass selected and fragmented by collisionally activated dissociation to produce distinctive product ions of smaller m/z.

3.8. ***Product Ion*** – A product ion is one of the fragment ions produced in MS/MS by collisionally activated dissociation of the precursor ion.

3.9. ***Non-conformance Memo (NCM)*** - A form used to document a non-conforming event. An analyst must document a non-conformance memo when a non-conforming event occurs. A non-conforming event may include the reporting of analytical data outside of method or SOP criteria, or when there is a deviation from a written policy or procedure. Information in an NCM may be used by project managers to flag data in the report narrative, or by the quality department to track trends and initiate corrective actions, where applicable. Additional information on the NCM policy and procedure is located in the *Nonconformance and Corrective Action* SOP [QA SOP ME0012BO].

4. INTERFERENCES

4.1. Non-volumetric glassware can be solvent rinsed or heated in a muffle furnace at 400 °C for 2 h. Volumetric glassware should be solvent rinsed and can be heated in an oven at a temperature below 120°C. Store clean glassware inverted or capped. Do not cover with aluminum foil since PFAS may potentially be transferred from the aluminum foil to the glassware.

NOTE: PFAS standards, extracts and samples should not come in contact with any glass containers or pipettes as these analytes can potentially adsorb to glass surfaces. PFAS analyte, internal standards (IS) and surrogate standards (SUR) commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be prepared and stored in HDPE or polypropylene containers.

4.2. Method interferences may be caused by contaminants in solvents, reagents (including reagent water), sample containers and caps, and other sample processing equipment that lead to discrete artifacts and/or elevated baselines in the chromatograms. The method analytes in this method can also be found in many common laboratory supplies and equipment, such as PTFE (polytetrafluoroethylene) products, LC solvent lines, methanol, aluminum foil, SPE sample transfer lines, etc. All items such as these must be routinely demonstrated to be free from interferences (less than 1/2 the LOQ for each method analyte) under the conditions of the analysis by analyzing method blanks as described in Section 9. Subtracting blank values from sample results is not permitted.

4.3. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the water. Humic and/or fulvic material can be co-extracted during SPE and high levels can cause enhancement and/or suppression in the electrospray ionization source or low recoveries on the SPE sorbent.

4.4. SPE cartridges/tubes can be a source of interferences. The analysis of field and laboratory reagent blanks can provide important information regarding the presence or absence of such interferences. Brands and lots of SPE devices should be tested to ensure that contamination does not prevent analyte identification and quantitation.

5. SAFETY

5.1. Procedures must be carried out in a manner protective of the health and safety of all Shealy personnel. All work must be stopped in the event of a known or potential compromise to the health and safety of a Shealy employee. The situation must be reported immediately to the Environmental Health and Safety Officer (EHSO).

5.2. As stated in the *Shealy Comprehensive Chemical Hygiene, Safety, and Hazard Communication Plan* (ME0012D), eye protection that satisfies ANSI Z87.1, laboratory coat, and at least latex gloves must be worn while samples, standards, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in these procedures have not been fully defined. Additional health and safety information can be obtained from safety data sheets (SDS) maintained electronically in the public directory. Physical and health hazards specific to this procedure:

5.3.1. The following chemical(s) is known to be **flammable**: Glacial acetic acid, methanol, isopropyl alcohol.

5.3.2. The following chemical(s) is known to be **corrosive**: Glacial acetic acid, ammonium hydroxide.

5.3.3. The following chemical(s) is known to present a **health hazard**: ammonium hydroxide.

5.3.4. PFOA has been described as **carcinogenic** to humans. Primary standards should be purchased in solution. If neat materials must be obtained, they shall be handled in a fume hood.

5.4. Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers must be kept closed unless transfers are being made.

5.5. To ensure safe operation, analysts must adhere to safety notices and labels located on the equipment utilized during the processes outlined in this procedure.

6. EQUIPMENT AND SUPPLIES

NOTE: Refer to the *Major Operational Equipment List* [QA Control Log ME001PM] for specific details regarding the equipment and data processing software utilized during this procedure.

NOTE: Due to the possibility of adsorption of analytes onto glass, HDPE containers are used for all standard, sample and extraction preparations. Any time a new lot of SPE cartridges/tubes, solvents, cryovials, or autosampler vials are used, it must be demonstrated that a MB is reasonably free of contamination and that the criteria in Section 9.6.1 are met.

6.1. ***Extract/Standard storage containers*** – 15-mL, 8-mL, or 4-mL narrow-mouth HDPE container - Thermo Scientific item# 2002-9050, 2002-9025, 2002-9125; 2.0-mL screw-top polypropylene cryogenic vials – Grainger item# 6EMV1;1.5-mL snap-cap polypropylene microcentrifuge tubes - Fisher item# 05-408-129; or equivalent.

6.2. ***Centrifuge Tubes*** – 15-mL conical polypropylene tubes with (Falcon) or without (MoldPro) polypropylene screw caps for storing standard solutions and for collection of extracts (Falcon catalog #: 21008-931; MoldPro, Inc. item# MP-100, 17x100mm sample tubes, alternate extract collection tubes).

6.3. ***Autosampler Vials*** – Polypropylene vials (Agilent part# 5188-2788) with polypropylene caps (Agilent part# 5182-0542), or equivalent.

NOTE: Polypropylene vials and caps are necessary to prevent contamination of the sample from PTFE coated septa.

However, polypropylene caps do not reseal, so evaporation occurs after injection. Thus, multiple injections from the same vial are not advisable.

6.4. ***Polypropylene Graduated Cylinders*** – Suggested sizes include 25, 50, 100 and 1000-mL cylinders

6.5. ***Micropipettes*** – Range of volumes (see section 7 for volumes needed)

6.6. ***Plastic Pipettes*** – Polypropylene or polyethylene disposable pipettes, Fisher Cat# 13-711-7M or equivalent.

6.7. ***Analytical Balance*** – Capable of weighing to the nearest 0.0001 g

6.8. ***Solid Phase Extraction (SPE) Apparatus***

6.8.1. SPE Cartridges Strata-XL-AW 100um Polymeric Weak Anion (0.5 g, 6mL) (Phenomenex Part # 8B-S051-HCH) or equivalent

6.8.2. Strata-GCB filtration tubes, 250mg/6mL, Phenomenex part# 8B-S528-FCH, or equivalent.

6.8.3. Vacuum Extraction Manifold – 24-port SPE manifold, Phenomenex part# AH0-6024, or equivalent. Care must be taken with automated SPE systems to ensure the PTFE commonly used in these systems does not contribute to unacceptable analyte concentrations in the MB.

6.8.4. SPE reservoirs – 60mL polypropylene, Phenomenex part# AH0-7189, or equivalent.

6.8.5. SPE adapter caps – Phenomenex Part# AH0-7191 (Adapter cap for 1, 3, 6mL SPE tubes)

6.8.6. Vacuum tubing – 1/4” ID, 5/8” OD, 3/16” wall; Fisher Scientific part# 14-176-6B or equivalent

6.9. ***Vacuum Pump*** – Sufficient capacity to maintain a vacuum of approximately 10 to 15 inches of mercury for extraction cartridges. Millipore model# WP6111560, 115V, 60Hz, 3.5A.

6.10. ***Liquid Chromatography (LC)/Tandem Mass Spectrometer (MS/MS) with Data System***

6.10.1. LC System – Agilent Model 1260, with Degasser (G4225A), Binary Pump (G1312B), Autosampler (G1329B), Thermostat (G1330B), Column Compartment (G1316A).

NOTE: PFAS can build up in the PTFE solvent transfer lines and PTFE solvent frits. To prevent long delays in purging high levels of PFAS from the LC solvent lines, PEEK tubing and stainless-steel frits are used.

6.10.2. Tandem Mass Spectrometer (MS/MS) – Sciex 4500 MS/MS, in negative ion electrospray ionization (ESI) mode. A minimum of 10 scans across the chromatographic peak is required to ensure adequate precision.

6.10.3. Analytical Column – Phenomenex Gemini® 3µm C18 110Å LC column 50 x3mm, (part# 00B-4439-Y0). Any column that provides adequate resolution, peak shape, capacity, accuracy, and precision may be used.

6.10.4. Mixing/Guard Column – Phenomenex Luna 5µm C18 100Å LC column 30 x 3mm (part# 00A-4252-Y0) or equivalent.

6.10.5. Guard cartridge – SecurityGuard Cartridges: Gemini C18, 2-3mm ID, 10/pk; Part# AJ0-7596; Phenomenex Part# KJ0-4282 (SecurityGuard Guard Cartridge Kit)

6.11. ***Vortex Mixer*** - Bibby Scientific/Stuart Vortex Mixer, Model SA8, or equivalent.

6.12. ***Orbital shaker table*** - VWR Model 3500 Standard Shaker, 120V, or equivalent

6.13. ***Centrifuge*** - VWR Clinical 200, or equivalent

6.14. ***Sonicator*** - VWR Model 97043-976, or equivalent

6.15. ***Ottawa Sand*** - for solid QC preparation (VWR catalog #: EM-SX0075-3 or equivalent)

7. REAGENTS AND STANDARDS

NOTE: Refer to appendices for state and/or program specific method criteria, which supersede and/or supplement the method criteria prescribed in this SOP.

7.1. Reagent grade or better chemicals should be used. Unless otherwise indicated, it is intended that ACS reagents be used, where such specifications are available. Other grades may be used, provided it is first determined that the reagent is of sufficiently high purity to permit its use without lessening the quality of the analysis.

7.2. ***Reagent Water*** – Optima LC/MS water, Fisher part# W6-4 or equivalent.

7.2.1. The reagent water should not contain any measurable quantities of any method analytes or interfering compounds greater than 1/2 the LOQ for each analyte of interest.

7.3. ***Methanol (MeOH, CH_3OH, CAS#: 67-56-1)*** – HPLC grade, demonstrated to be free of analytes and interferences (Fisher part# A452-4 or equivalent).

7.4. ***Ammonium Acetate ($NH_4C_2H_3O_2$, CAS#: 631-61-8***) – LC/MS grade, demonstrated to be free of analytes and interferences (Fisher part# A114-50 or equivalent).

7.5. ***20 mM Ammonium Acetate*** – To prepare 1 L, add 1.54 g ammonium acetate to 1L of reagent water (0.77g into 0.5L reagent water). This solution is prone to volatility losses and should be replaced at least every 48 hours.

7.6. ***Ammonia-Methanol (Amm-MeOH, 0.3%)*** – In a 1000 mL graduated cylinder, add 13.52 mL NH4OH (Ammonium Hydroxide) and fill to volume with methanol (986.48 mL reagent MeOH). Invert to mix.

7.7. ***Ammonium Acetate/Acetic Acid buffer (25mM, pH 4)*** – In a 1000 mL graduated cylinder, add 1.16 mL acetic acid and 0.40 g ammonium acetate then fill to volume with reagent water (998.84 mL reagent water). Invert to mix.

7.8. ***Nitrogen*** – Nitrogen aids in aerosol generation of the ESI liquid spray and is used as collision gas in some MS/MS instruments. The nitrogen used should meet or exceed instrument manufacturer's specifications.

7.9. ***Standard Solutions*** – When a compound purity is assayed to be 96% or greater (standards purchased from Wellington are >98%), the weight can be used without correction to calculate the concentration of the stock standard. PFAS analyte, IS, and SUR standards commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be prepared and stored in HDPE containers. Solution concentrations listed in this section were used to develop this method and are included as an example. Alternate concentrations may be used as necessary depending on instrument sensitivity and the calibration range used. Standards for sample fortification generally should be prepared in the smallest volume that can be accurately measured to minimize the addition of excess organic solvent to aqueous samples.

NOTE: The final compositions for all standards in section 7.9 contain 96:4% (v/v) methanol/water. The solutions are stored at 2-6°C in HDPE containers.

7.9.1. ***Internal Standards (IS) Stock Standards*** – The stocks are obtained from Wellington Labs (catalog # MPFHxA and catalog # MPFAC-C-IS). IS stock standard solutions are stable for 12 months when stored at 2-6°C. The internal standards used for Method 537-MOD ID are comprised of the following compounds:

- Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid (13C2-PFHxA)
- Perfluoro-n-[1,2-$^{13}C_2$] octanoic acid (13C2-PFOA)
- Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate (13C4-PFOS)
- Perfluoro-n-[2,3,4-$^{13}C_3$] butanoic acid (13C3-PFBA)
- Perfluoro-n-[1,2-$^{13}C_2$] decanoic acid (13C2-PFDA)

7.9.2. ***Internal Standard (IS) 50X Mix*** - Dilute the stock standard with methanol/water in accordance with the table below:

IS 50X Mix Preparation (Aqueous)

Standard Name	Conc. of Stock Std. (µg/mL)	Aliquoted Volume (µL)	Dilution Volume (mL)	Final Conc. (µg/mL)
Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid (13C2-PFHxA)	50	200	10	1.0

7.9.3. ***Internal Standard (IS) 20 ppb Mix*** - Combine the IS 50X Mix and Wellington Labs stock standard part# MPFAC-C-IS and dilute with methanol/water in accordance with the table below:

20 ppb IS Mix Preparation (Aqueous)				
Standard Name	**Conc. of Stock Std. (µg/mL)**	**Aliquoted Volume (µL)**	**Dilution Volume (mL)**	**Final Conc. (µg/mL)**
IS 50X Mix	1	300	15	0.02
MPFAC-C-IS Stock	2	150	15	0.02

NOTE: The complete list of compounds included in the ID (Aqueous and Solid) 20 ppb IS Mix are found in Table 5.

7.9.4. ***Surrogate (SUR) Stock Standard Solutions*** – The SUR standard stocks are obtained from Wellington Labs (catalog #s: M2PFHxDA, M2-4:2FTS, M2-6:2FTS, M2-8:2FTS, M8FOSA-I, d-N-EtFOSA-M, d-N-MeFOSA-M, d5-N-EtFOSAA-M, d3-N-MeFOSAA-M and MPFAC-C-ES). SUR stock standard solutions are stable for 12 months when stored at 2-6°C.

7.9.5. ***SUR 50X Mix*** - Dilute the stock standards with methanol/water in accordance with the table below:

SUR 50X Mix Preparation (Aqueous)				
Standard Name	**Conc. of Stock Std. (µg/mL)**	**Aliquoted Volume (µL)**	**Dilution Volume (mL)**	**Final Conc. (µg/mL)**
Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-$^{13}C_2$] hexane sulfonate (13C2-4:2FTS)	50	1000	10	5.0
Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-$^{13}C_2$] octane sulfonate (13C2-6:2FTS)	50	1000	10	5.0
Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-$^{13}C_2$] decane sulfonate (13C2-8:2FTS)	50	1000	10	5.0
Perfluoro-1-[$^{13}C_8$] octanesulfonamide (13C8-PFOSA)	50	200	10	1.0
N-ethyl-d5-perfluoro-1-octanesulfonamide (d5-EtFOSA)	50	200	10	1.0
N-methyl-d3-perfluoro-1-octanesulfonamide (d3-MeFOSA)	50	200	10	1.0
N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid (d5-EtFOSAA)	50	1000	10	5.0
N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid (d3-MeFOSAA)	50	1000	10	5.0
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-$^{13}C_3$-propanoic acid (13C3-GenX)	50	1000	10	5.0
2-(N-methyl-d3-perfluoro-1-octanesulfonamido) ethan-4-ol (d7-MeFOSE)	50	200	10	1.0

2-(N-ethyl-d5-perfluoro-1-octanesulfonamido) ethan-4-ol (d9-EtFOSE)	50	200	10	1.0

7.9.5.1. ***20 ppb SUR Mix*** - combine the SUR 50X mix and Wellington Labs standard part# MPFAC-C-ES and dilute with methanol/water in accordance with the table below:

20 ppb SUR Mix Preparation (Aqueous)				
Standard Name	**Conc. of Stock Std. (µg/mL)**	**Aliquoted Volume (µL)**	**Dilution Volume (mL)**	**Final Conc. (µg/mL)**
SUR 50X Mix	1	200	10	0.02
MPFAC-C-ES Stock	2	100	10	0.02

7.9.5.2. ***100 ppb SUR Mix*** - Combine the SUR 50X mix and Wellington Labs standard part# MPFAC-C-ES and dilute with methanol/water in accordance with the table below:

100 ppb SUR Mix Preparation (Aqueous)				
Standard Name	**Conc. of Stock Std. (µg/mL)**	**Aliquoted Volume (µL)**	**Dilution Volume (mL)**	**Final Conc. (µg/mL)**
SUR 50X Mix	1	1500	15	0.10
MPFAC-C-ES Stock	2	750	15	0.10

NOTE: The complete list of compounds included in the ID (Aqueous and Solid) 100 ppb and 20 ppb SUR Mixes are found under Table 5.

7.9.6. ***Analyte Primary Dilution Standards (PDS)*** – Analyte standards are purchased from Wellington Labs as ampoulized solutions. The PDS standards are stable for 12 months when stored at 2-6°C. For Method 537-MOD ID (Aqueous/Solid), a list of these solutions is provided below:

- PFAC-24PAR (24 compound mix of native PFAS)
- N-MeFOSA-M
- N-EtFOSA-M
- 10:2FTS
- HFPO-DA (GenX)
- N-MeFOSE-M
- N-EtFOSE-M
- NaDONA
- 9Cl-PF3ONS
- 11Cl-PFOUdS

7.9.6.1. PFHxS, PFOS and other sulfonic acids are not available as the acid form, but rather as their corresponding salts, such as Na+ and K+. These salts are acceptable for use as stock standards as long as the weight is corrected for the salt content according to the equation below.

$$\text{Mass}_{acid} = \text{Measured Mass}_{salt} \times \frac{\text{MW}_{acid}}{\text{MW}_{salt}}$$

Where:
MW_{acid} = the molecular weight of PFAA

MW_{salt} = the molecular weight of purchased salt

7.9.7. ***10X Stock Analyte PDS*** – Contains all target analytes at 0.2 ug/mL, except GenX which is present at 0.4 ug/mL. Prepare as outlined below:

7.9.7.1. 1 mL of the primary lot of PFAC-24PAR standard mix, 40 uL of MeFOSA, EtFOSA, 10:2 FTS, MeFOSE, EtFOSE, NADONA, 9Cl-PF3ONS, and 11Cl-PF3OUDS primary standards, and 80 uL of GenX primary standard are diluted to 10 mL with 8.2 mL of methanol and 400 uL reagent water.

7.9.8. ***100X Analyte PDS*** - Contains all target analytes at 20 ng/mL, except GenX which is present at 40 ng/mL. Prepare as outlined below:

7.9.8.1. 1 mL of Stock (10X) Analyte PDS is diluted to 10 mL with 9 mL of 96% MeOH

7.9.9. ***1000X Analyte PDS*** - Contains all target analytes at 2.0 ng/mL, except GenX which is present at at 4.0 ng/mL. Prepare as outlined below:

7.9.9.1. 1 mL of 100X Analyte PDS is diluted to 10 mL with 9 mL of 96% MeOH

7.9.10. ***Initial Calibration Standards (ICAL)*** – According to the table below, prepare calibration standards at the following concentrations in pg/mL (ng/L): 50, 100, 200, 500, 1000, 2000, 5000, 10000, and 20000, except for GenX which will be at double these concentrations. The ICAL standards are stable for two weeks when stored at room temperature, or 12 months when stored at 2-6°C. The final composition of the above solutions contains 96:4% (vol/vol) methanol: water. See Table 5 for a list of analytes and exact concentrations.

ICAL Preparation (Aqueous)								
PFAS Conc. (pg/mL)	**SUR Conc. (pg/mL)**	**IS Conc. (pg/mL)**	**PFAS FL PDS 10X (mL)**	**PFAS FL PDS 100X (mL)**	**PFAS FL PDS 1000X (mL)**	**20 ppb SUR (mL)**	**20 ppb IS (mL)**	**Final Volume (mL)**
50	1000	1000	-	-	0.125	0.25	0.25	5
100	1000	1000	-	-	0.250	0.25	0.25	5
200	1000	1000	-	-	0.500	0.25	0.25	5
500	1000	1000	-	0.125	-	0.25	0.25	5
1000	1000	1000	-	0.250	-	0.25	0.25	5
2000	1000	1000	-	0.500	-	0.25	0.25	5
5000	1000	1000	0.125	-	-	0.25	0.25	5
10000	1000	1000	0.25	-	-	0.25	0.25	5
15000	1000	1000	0.375	-	-	0.25	0.25	5
20000	1000	1000	0.50	-	-	0.25	0.25	5

7.9.11. ***100X ICV Mix*** - Second source standard containing required target analytes at 0.02 ug/mL or 20ppb. Prepare as outlined below:

7.9.11.1. 100 uL of the secondary lot (different than the lot used to prepare the PDS solutions) of PFAC-24PAR standard mix and 20 uL of GenX secondary standard is diluted to 10 mL with 9.88 mL of methanol. The PFAC-24PAR standard includes all analytes listed in Table 5 except the following: MeFOSA, EtFOSA, 10:2FTS, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUDS, MeFOSE, and EtFOSE.

7.9.12. ***ICV Sample Solution (500ppt)*** – Prepare according to the table below. The final solvent composition of this solution should be 96:4% MeOH: water.

ICV Preparation (Aqueous)

Standard Name	Conc. of Stock Std. (pg/mL)	Aliquoted Volume (µL)	Dilution Volume (mL)	Final Conc. (pg/mL)
PFAS ICV 100X Mix	20000	25	1.0	500
Full List SUR mix, 20ppb	20000	50	1.0	1000
Full List IS mix, 20ppb	20000	50	1.0	1000

7.9.13. ***Isomer check*** – For target compounds which have multiple chromatographic peaks due to branched and linear isomers, but for which quantitative standards are not available, a qualitative check is analyzed with each calibration event to demonstrate the peak shape and retention time of the branched isomers. See Sec. 12.5 for integration information.

7.9.13.1. ***Isomer Check 50X Mix*** – 20 µL each of TPFOA, br-MeFOSAA, and br-EtFOSAA standards (Wellington Laboratories item #s T-PFOA, br-MeFOSAA, and br-EtFOSAA) are diluted to 1 mL with 900 µL of MeOH and 40 µL of reagent water. Final solvent composition is 96:4% MeOH:water. This solution is used to create the actual isomer check standard to be analyzed with each ICAL.

7.9.13.2. ***Isomer Check Standard*** - 10 µL of the Isomer Check 50X Mix plus 50 µL each of the 20 ppb IS and 20 ppb SUR are diluted to 1 mL with 890 µL of 96% MeOH. The concentrations of the isomer components should be approximately 10000 ppt. Final solvent composition is 96:4% MeOH:water. This sample will be analyzed with each calibration event to demonstrate peak shape and retention time of the additional branched isomers of the included compounds.

7.10. ***Instrument Blank (IBLK)*** – The instrument blank is prepared by spiking 180 µL 96% MeOH with 10 µL of 20 ppb IS Mix and 10 µL of 20 ppb SUR Mix in an autosampler vial. Cap and vortex to mix. Alternatively, spike 900 µL of 96% MeOH with 50 µL of IS 20ppb mix and 50 µL of SUR 20ppb; cap and vortex to mix, then aliquot into auto-sampler vial.

7.11. ***Method Blank (MB)*** – Spike 250 mL reagent water with 110 µL of the 100ppb SUR Mix. Mix well, extract as normal alongside client samples.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

NOTE: Refer to appendices for state and/or program specific method criteria, which supersede and/or supplement the method criteria prescribed in this SOP.

8.1. Sample Containers and preservatives

8.1.1. Method ID-AQ - Aqueous samples must be collected in a 250mL HDPE bottle fitted with a polyethylene screw-cap.

8.1.2. Method ID-Solid - Solid samples must be collected in a 4 oz. HDPE bottle fitted with a polyethylene screw-cap.

8.2. Sample temperature must be confirmed to be at or below 6°C when the samples are received at the laboratory. Samples stored in the lab must be stored at 4 ± 2°C.

8.3. Aqueous samples must be extracted within 28 days of collection and solid samples must be extracted within 28 days of collection. All sample extracts must be stored at room temperature and analyzed within 28 days after extraction.

9. QUALITY CONTROL

NOTE: Refer to appendices for state and/or program specific method criteria, which supersede and/or supplement the method criteria prescribed in this SOP.

9.1. ***Initial and Continuing Demonstrations of Capability (IDOC and CDOC)*** – To establish the ability of an analyst to generate acceptable accuracy, each analyst must make a satisfactory initial demonstration of capability prior to using any method and at any time there is a change in instrument type or method. Thereafter, a continuing demonstration of capability is required annually. Refer to the *Demonstration of Capability* SOP [QA SOP ME001F2] for additional information.

9.2. ***Instrument Blank (IBLK)*** – One instrument blank (IBLK) is analyzed immediately following the highest ICAL standard analyzed and also on a daily basis prior to sample analysis, to check for carryover and instrument contamination. The concentration of each analyte must be ≤ 1/2 the LOQ. If the instrument blank does not pass this requirement after the highest ICAL standard, the calibration must be performed using a lower concentration for the highest standard until the acceptance criteria is met.

9.3. ***Method Blank (MB)*** – One method blank (MB) must be processed with each extraction batch. If more than 20 samples are included in a batch, analyze an MB for every 20 samples. The MB is to contain all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis.

9.3.1. The MB must not contain any analyte of interest at or above 1/2 of the LOQ or project specific-requirements. (Note: see appendices for state or program specific requirements). If the MB contains an analyte of interest at or above 1/2 of the LOQ, then the MB and associated samples must be reanalyzed. If the MB contamination is confirmed, the entire batch must be re-prepared and reanalyzed. Reanalysis or re-extraction is not required if the samples are not impacted. Samples are not impacted when:

9.3.1.1. The MB detection is not present in the sample.

9.3.1.2. The sample concentration is ≥10x the concentration of the detection in the MB.

9.3.2. The MB must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, sample analysis should stop immediately. Corrective action should be taken. The MB should be reanalyzed if the analyst feels that the failure could be attributed to instrument problems. If the analyst feels that the failure is due to a poor extraction, entire batch must be sent for re-extraction.

9.4. ***Laboratory Control Sample (LCS)*** – An LCS is required with each extraction batch. The spiked concentration of the LCS will be at a mid-point concentration of the calibration curve. See DoD acceptance criteria for LCS targets in Table 6. If the LCS results do not meet the criteria listed in Table 6 for method analytes, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch. For target analytes not included in the DoD Limits for batch control table (Appendix C of QSM 5.3), in-house limits of 70-150% recovery will be used as acceptance criteria.

9.4.1. The LCS for ID-AQ is prepared by spiking 250 mL of reagent water with 250 µL of the 100X PDS mix (20 ppb) for a concentration of 20 ppt (GenX at 40 ppt). The LCS is also spiked with 110 µL of Full List 100 ppb SUR mix and extracted as normal alongside client samples.

9.5. ***Internal Standards (IS)*** – The analyst must monitor the peak areas of the IS in all injections during each analysis day. The IS responses (peak areas) in any chromatographic run must not deviate by more than 50% from the area measured during initial analyte calibration or the daily CCV. If the IS areas in a chromatographic run do not meet these criteria, inject a second preparation of that extract prepared in a new capped autosampler vial. Loss due to evaporation has been observed when using polypropylene caps which can cause high IS response.

9.5.1. If the reinjected aliquot produces an acceptable IS response, report the results for that aliquot.

9.5.2. If the reinjected extract fails again, the analyst should check the calibration by reanalyzing the most recently acceptable ICAL standard. If the ICAL standard fails the criteria of Section 10.2.4, recalibration is needed. If the ICAL standard is acceptable, extraction of the sample may need to be repeated provided the sample is still within the holding time. Otherwise, report results obtained from the reinjected extract, but write an NCM as to the circumstances under which the results are reported. Alternatively, a new sample can be collected and re-analyzed.

9.6. ***Surrogates (SUR)*** – The surrogate (also referred to as extracted internal standard [EIS] or isotope dilution standard [IDS]) standard is fortified into all samples, MBs, LCSs, MSs, MSDs prior to extraction. It is also included in the ICAL standards.

9.6.1. The analyst must monitor the peak areas of the SUR in all injections during each analysis day. The SUR responses (peak areas) in any chromatographic run must not deviate by more than 50% from the area measured during initial calibration or the daily CCV. When the SUR recovery from a sample, blank, or CCV is not within this range check the following: calculations to locate possible errors, standard solutions for degradation, contamination, and instrument performance. Correct the problem and inject a second preparation of that sample

extract (or blank or CCV) prepared in a new capped autosampler vial. Loss due to evaporation has been observed when using polypropylene caps which can cause high SUR response.

9.6.1.1. If the extract reanalysis meets the surrogate recovery acceptance criteria, report only the data for the reanalyzed extract.

9.6.1.2. If the extract reanalysis fails the 50-150% acceptance criteria, the analyst should check the calibration by injecting the last ICAL standard that passed. If the ICAL standard fails the criteria of Section 10.2.4, recalibration is in order. If the ICAL standard is acceptable, extraction of the sample should be repeated provided the sample is still within the holding time. If the re-extracted sample also fails the recovery acceptance criteria, write an NCM describing that the results are suspect due to surrogate recovery. Alternatively, a new sample can be collected and re-analyzed.

9.7. ***Ion Ratios*** – In analytes for which two ion transitions (quantitation and confirmation) are analyzed, the area ratio between the confirmation and quantitation transitions shall be monitored and documented. The ion ratio for all analytes in each injection should be within 50-150% of the average ion ratio for the same analyte in the ICAL. On days ICAL is not performed, the ion ratio should be within 50-150% of the initial CCV standard. Targets detected and identified with ion ratios that fail these acceptance criteria will be flagged, but not disqualified.

9.8. ***Matrix Spike (MS)*** – Analysis of an MS is required in each extraction batch. Assessment of method precision can be accomplished by analysis of a duplicate collected in the field; however, infrequent occurrence of method analytes might hinder this assessment. If the occurrence of method analytes in the samples is infrequent, or if historical trends are unavailable, a matrix spike duplicate (MSD), must be prepared, extracted, and analyzed. Extraction batches that contain MSD will not require the extraction of an FD.

9.8.1. Within each extraction batch, a minimum of one sample is spiked as an MS for every 20 samples analyzed. Client samples are spiked in the same manner as the LCS. 250mL of sample is spiked with 250 µL of 100X PDS mix (20 ppb) plus 110 µL of Full List 100 ppb SUR mix and extracted as normal alongside other client samples.

9.8.1.1. Analyte recoveries may exhibit matrix effect. For matrix spike samples, recoveries should range between 70-150%. If the % recovery falls outside of the acceptable range, corrective action must occur. The initial corrective action will be to check all calculations. If the calculations are correct, check the recovery of that analyte in the LCS. If the recovery of the analyte in the LCS is within limits, then matrix interference has been demonstrated and the laboratory operation may proceed. Analytical reports will show qualifier flags in such cases.

9.8.1.2. If the recovery for any analyte is outside the acceptance criteria for the matrix spike and the LCS, the laboratory is out of control and corrective action will be taken. Corrective action may include re-preparation and reanalysis of the batch. An NCM will be generated to document the corrective action taken.

9.9. ***Field Duplicate (FD) or Matrix Spike Duplicate (MSD)*** – Within each extraction batch (not to exceed 20 Field Samples, Sect. 3.4), a minimum of one FD or MSD must be analyzed. If method analytes are not routinely observed in field samples, an MSD should be analyzed rather than an FD.

9.9.1. Relative Percent Differences (RPDs) – FDs should have RPDs that are ≤30% between the original sample and the FD. If the RPD of any analyte falls outside the acceptance criteria, and the laboratory performance for that analyte is shown to be in control in the LCS, the recovery is judged to be matrix biased. An NCM is written describing that the result for that analyte in the unspiked sample is suspect due to matrix effects.

9.9.2. RPDs for MS/MSDs should be ≤30%. If the RPD falls outside of the acceptable range, corrective action must occur. The initial corrective action will be to check all calculations. If the calculations are correct, check the recovery of that analyte in the LCS. If the recovery of the analyte in the LCS is within limits, then matrix interference has been demonstrated and the laboratory operation may proceed. Analytical reports will show qualifier flags in such cases.

9.9.3. Every effort is made to ensure that an MS/MSD or an FD is included in every batch. In the event that there is insufficient sample to analyze an MS/MSD pair or if no FD is available, a duplicate LCS (laboratory control sample duplicate (LCSD)) is included in the batch. The MS/MSD must be analyzed at the same dilution as the

most concentrated reportable analysis of the parent sample (the un-spiked sample).

9.10. ***Trip Blank (TB)*** – The purpose of the TB is to ensure that PFAS measured in the samples were not inadvertently introduced into the sample during sample collection/handling. Analysis of the TB is required only if a sample contains a method analyte or analytes at or above the LOQ. The TB is processed, extracted and analyzed in exactly the same manner as the samples. If an analyte found in the sample is present in the TB at a concentration greater than 1/2 the LOQ, then all samples collected with that TB are invalid and must be recollected and reanalyzed.

9.11. ***Deionized (DI) Water Contamination Testing*** – DI water from the laboratory in-house DI system, confirmed to be reasonably free of PFAS compounds, will be used for QC samples (MB/LCS/LCSD) in extraction batches and also sent to clients for use as trip blanks (TB), field blanks (FB), and equipment blanks (EB). Clean DI water may also be sent to client sampling sites for other uses. DI water used for these purposes will be tested by the lab to confirm the absence of PFAS compounds prior to shipping to clients or being used for QC samples. DI water taps in the lab will be used to fill multiple carboys (approximate volume of 6L) at once, each of which will be logged into the LIMS system with an individual sample identifier (example: UB20091-001). One sample bottle per carboy will be filled and tested as a sample using the ID-AQ method. These test samples will be treated exactly the same as all other client samples, taken through the entire extraction and analysis process. Should any PFAS contamination be detected in any of the carboys, the water in those carboys will not be used further and will be dumped and the carboy refilled, logged as a new sample, and tested again.

10. CALIBRATION AND STANDARDIZATION

NOTE: Refer to appendices for state and/or program specific method criteria, which supersede and/or supplement the method criteria prescribed in this SOP.

NOTE: Refrigerator units are maintained and verified as required by the *Quality Assurance Management Plan* [QAMP ME0012K].

NOTE: The balance is verified at the beginning of each analytical day using a certified weight set. Refer to the *Equipment and Instrumentation* SOP [QA SOP ME002JT] for balance verification procedures and acceptance criteria.

NOTE: Bottletop dispensers, pipettes, and thermometers are maintained and verified as required by the *Equipment and Instrumentation* SOP [QA SOP ME002JT].

10.1. Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed. After the initial calibration is successful, a CCV is required at the beginning and end of each period in which analyses are performed, and after every tenth field sample.

10.2. ***Initial Calibration (ICAL)***

10.2.1. Mass Calibration – calibrate the mass scale of the MS with the calibration compounds and procedures prescribed by the manufacturer. Mass calibration/mass tune will be performed any time major maintenance is performed on the MS, or following any catastrophic instrument failure (power loss, etc.)

10.2.2. Mass Calibration verification – a mass calibration verification will be analyzed following mass calibration/mass tune, prior to each ICAL. A prepared standard containing PFAS targets will be injected using the normal LC parameters for analysis, but set up to perform a product ion (MS2) scan for the quantitation product ions of PFOA (m/z 369) and PFOS (m/z 80). If these target product ions are detected at the expected RT, the mass calibration has been verified. A chromatogram image will be included in each data package as documented verification of appropriate mass calibration.

10.2.3. Prepare a set of at least five ICAL standards (six ICAL standards for quadratic regressions) as described in Section 7. The lowest concentration ICAL standard must be at or below the LOQ, which may depend on system sensitivity. It is recommended that at least four of the ICAL standards are at a concentration greater than or equal to the LOQ.

10.2.4. The LC/MS/MS system is calibrated using the IS technique. Generate a linear regression calibration curve for each of the analytes. This curve will typically be forced through zero and may be concentration weighted, if necessary. Forcing through zero allows for a better estimate of the background levels of method analytes.

10.2.4.1. The linear regression curve is expressed as below:

$y = ax + b$

Where a is the slope and b is the y-intercept. When forced through 0, b=0.

$y = A_S/A_{SUR}$ $x = C_S/C_{SUR}$

A_S is peak response of target analyte in calibration standards
A_{SUR} is peak response of surrogate standard (SUR) in calibration standards
C_S is concentration of target analyte in calibration standards
C_{SUR} is concentration of surrogate standard (SUR) in calibration standards

10.2.5. Calibration Acceptance Criteria – When quantitated using the ICAL curve, each calibration level for each analyte should calculate to be within 70-130% of its true value. For calibration curves produced using average response factors, the percent relative standard deviation (%RSD) of the RFs for all analytes must be <20%. Linear or non-linear regressions must have $r^2 \geq 0.99$ ($r \geq 0.995$) for each analyte. Weighting (typically 1/x or $1/x^2$) is allowed for linear and non-linear regressions. If these criteria cannot be met, the analyst will have difficulty meeting ongoing QC criteria. It is recommended that corrective action is taken to reanalyze the ICAL standards, restrict the range of calibration, or select an alternate method of calibration (forcing the curve through zero is still recommended).

10.2.5.1. Calibration results for labeled Surrogate and Internal Standard compounds will be evaluated by comparing the area response of each level to the ICAL midpoint level (L5 – 1000ppt). Any ICAL points for which SUR or IS responses fall outside of 50-200% of the midpoint ICAL shall be removed. If any more than two ICAL points fail these criteria, the system should be inspected and maintenance should be performed if needed. A new ICAL will then be analyzed following any maintenance.

NOTE: When acquiring MS/MS data, LC operating conditions must be carefully reproduced for each analysis to provide reproducible retention times. If this is not done, the correct ions will not be monitored at the appropriate times. As a precautionary measure, the chromatographic peaks in each window must not elute too close to the edge of the segment time window.

10.3. ***Initial Calibration Verification (ICV)*** – As part of the IDOC, each time a new Analyte PDS is prepared, and once after each ICAL, analyze an ICV sample from a second source (different from the source of the ICAL standards). If a second vendor is not available, then a different lot of the standard should be used. The ICV should be prepared and analyzed just like a CCV. Acceptance criteria for the ICV are identical to the CCVs; the calculated amount for each analyte must be ± 30% of the expected value. If measured analyte concentrations are not of acceptable accuracy, correct the problem and rerun the ICV. If the problem persists, repeat the ICAL. Samples are not to be analyzed until the ICAL has been verified by acceptable ICV accuracy.

10.4. ***Continuing Calibration Verification/Instrument Sensitivity Check (CCV/ISC)*** – CCV Standards are analyzed at the beginning of each analysis batch, after every 10 samples, and at the end of the analysis batch. In this context, a "sample" is considered to be a field sample. MBs, CCVs, LCSs, MSs, FDs, TBs and MSDs are not counted as samples. In the event that 10 field samples and various non-field sample QC (MBs, CCVs, LCSs, MSs, FDs, TBs and MSDs) are injected between a set of CCVs, the maximum injections between CCVs is limited to 20. Inject an aliquot of the appropriate concentration ICAL standard and analyze with the same conditions used during the initial calibration.

10.4.1. The daily Instrument Sensitivity Check (ISC; DOD required) will be used as the daily opening CCV, and will be analyzed at a concentration at or below the LoQ (100ppt and 200ppt), using prepared ICAL standards.

10.4.2. The prepared ICAL solution at 1000ppt will be analyzed for subsequent and closing CCVs.

10.4.3. Determine that the absolute areas of the quantitation ions of the IS(s) are within 50-150% of the areas measured in the most recent CCV, or, if ICAL was performed the same day, IS areas must be within 50-150% of the midpoint of the ICAL range (1000ppt). If any of the IS areas has changed by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may include cleaning of the MS ion source, or other maintenance. Major instrument maintenance requires recalibration and verification of sensitivity by analyzing a CCV at or below the LOQ. Control charts are useful aids in documenting system sensitivity changes.

10.4.4. Calculate the concentration of each analyte and surrogate in the CCV. The calculated amount for each analyte must be within ± 30% of the true value. The calculated amount for each surrogate compound must be within ±50%. If these conditions do not exist, then all data for the problem analyte must be considered invalid, and remedial action should be taken which may require recalibration. Any field or QC samples that have been analyzed since the last acceptable calibration verification should be reanalyzed after adequate calibration has been restored, with the following exception: if the CCV fails because the calculated concentration is greater than 130% for a particular method analyte, and the field sample extracts show no detection for that method analyte, non-detects may be reported without re-analysis.

10.4.5. Remedial Action – Failure to meet CCV QC performance criteria may require remedial action. Major maintenance, such as cleaning the electrospray probe, atmospheric pressure ionization source, cleaning the mass analyzer, replacing the LC column, etc., requires recalibration and verification of sensitivity by analyzing a CCV at or below the LOQ.

10.4.6. If reanalysis cannot be performed, the data must be qualified. An NCM must be generated which describes the reason that reanalysis is not being performed.

10.5. ***Correction Factors*** – Correction Factors (CF) will be used to calculate original sample concentration. The CF is the inverse of the concentration factor (sample volume / extract final volume) times the dilution factor (DF). For undiluted analysis, the extract is prepared for injection by adding 182 µL of sample extract, 8 µL of reagent water, and 10 µL of 20ppb IS mix to a polypropylene autosampler vial. Sample vial must then be capped and vortexed thoroughly. An extract correction factor of 0.91 (182 µL / 200 µL = 0.91) applies. The CF is calculated as follows:

$CF = DF \times FV / V_o$

Where:

FV is the volume of extract (mL)

V_o is the initial sample volume (mL)

DF is the dilution factor. For undiluted analysis, DF = 1/0.91

11. PROCEDURE

11.1. Some of the PFAS adsorb to surfaces, including polypropylene and HDPE. Therefore, aqueous sample containers must be rinsed with the elution solvent. The container rinse is passed through the cartridge to elute the method analytes and is then collected.

NOTE: The SPE cartridges, reservoirs, and sample containers described in this section are designed as single use items and should be discarded after use. They may not be refurbished for reuse in subsequent analyses.

11.2. Sample Preparation (aqueous)

11.2.1. Spike the sample containers with 110 µL of the 100 ppb SUR Mix. Invert the sample to mix. Inversion will be omitted if solids are present in sample container.

11.2.2. Spike the LCS/LCSD, MS, and either FD or MSD appropriately according to the corresponding section under Reagents and Standards

11.2.3. Attach the SPE extraction cartridges (Strata-XL-AW) to the converter caps and the reservoirs. Place the cartridge setups in the active SPE manifold ports.

11.2.4. Wet the rim of the manifold body with DI water to form a proper seal with the manifold top.

11.2.5. Place the top on the SPE manifold, start the vacuum pump, and ensure the vacuum is approximately 5in. Hg.

11.2.6. Condition each SPE cartridge in individual steps with the following solvents (**do not allow to go dry during conditioning**):

11.2.6.1. Conditioning step 1 - 4mL Ammonia-MeOH (0.3%) + 4mL MeOH
11.2.6.2. Conditioning step 2 - 4mL Ammonium acetate/acetic acid buffer

If the SPE cartridge goes dry during any step of the conditioning process, restart conditioning with first step (Amm-MeOH)

11.2.7. Weigh the full sample container.

11.2.8. Add the entire water sample to the SPE tube/reservoir (**do not allow to go dry during sample loading**).

11.2.9. Adjust the pressure/SPE stopcocks to load the sample at ~10-15mL/min; this rate equates to loading time of 17-25 mins for a 250mL sample.

11.2.10. Weigh the empty container and document the weight.

11.2.11. The difference between the weights from sections 11.2.7 and 11.2.10 is the sample volume (assuming 1g/mL density). Sample volumes will be rounded to the nearest 1.0 mL for use in calculations.

11.2.12. Once entire sample has passed through the SPE cartridge, wash the cartridge with 4 mL of the Ammonium Acetate/acetic acid buffer.

11.2.13. Use the vacuum to dry cartridges under high vacuum (≤20in. Hg) for ~5mins.

11.2.14. Release the vacuum, remove the top from the SPE manifold and wet the rim of the manifold. Place the rack with the eluent collection tubes in the manifold and replace the top, ensuring that the active SPE ports are set in the corresponding collection tubes and a proper seal is formed. Turn the pump back on and ensure the pressure is approximately 5in. Hg.

11.2.15. Add 4mL MeOH to each empty sample container, cap, and shake the bottle to ensure all interior surfaces get rinsed. Transfer rinsate to the SPE, using a pipette to swirl MeOH along the sides of the reservoir to rinse.

11.2.16. Rinse each empty sample container a second time with 4mL Ammonia-MeOH (0.3%). Transfer to the SPE, using a pipette to swirl the Ammonia-MeOH solution along the side of the reservoir to rinse.

11.2.17. Collect the total eluent in the previously positioned collection tubes. Adjust the pressure/SPE stopcock to elute in a ***slow*** dropwise fashion.

11.2.18. Release the vacuum and remove the collection tube rack.

11.2.19. Replace the extraction cartridge setups (Strata-XL-AW and reservoirs) with Strata-GCB cleanup SPE tubes; place the manifold top on the manifold body and resume the vacuum, ensuring a proper seal and pressure.

11.2.20. Condition the Strata-GCB SPE tubes with 3 mL MeOH, but do not dry the tubes fully. **If the SPE cartridge goes dry during the conditioning process, restart conditioning.**

11.2.21. Release the vacuum, remove the top, and place the collection rack with clean, empty collection tubes in the manifold body, ensuring the proper alignment of the SPE ports with collection tubes. Resume the vacuum, ensuring a proper seal and pressure. Filter the extract through the Strata-GCB SPE tubes under vacuum and collect the eluent.

11.2.22. Rinse the GCB tubes with 2mL of fresh MeOH and collect the eluent in a ***slow*** dropwise fashion.

11.2.23. In a polypropylene autosampler vial, combine 8 µL water, 10 µL (20ppb) IS mix, and 182 µL of sample extract. Cap and vortex thoroughly to mix. This aliquot is ready for analysis.

11.2.24. Transfer the remaining extracts to 8 mL HDPE containers for storage at room temperature.

11.2.25. Manifold cleanup – use the methanol squirt bottle to thoroughly rinse all stopcocks on the vacuum manifold top. The stopcocks should be rotated while methanol is squirted into/through the stopcocks so that the entire body of the stopcock housing and rotor are cleaned well. The rotor should be rotated **several times in both directions** to ensure the stopcock is thoroughly decontaminated.

11.2.26. Correction Factors – Correction Factors (CF) will be used to calculate original sample concentration. The CF is the inverse of the concentration factor (sample volume / extract final volume) times the dilution factor (DF). For undiluted analysis, the extract is prepared for injection by adding 182 µL of sample extract, 8 µL of reagent water, and 10 µL of 20ppb IS mix to a polypropylene autosampler vial. An extract correction factor of 0.91 (182 µL / 200 µL = 0.91) applies. The CF is calculated as follows:

$CF = DF \times FV / V_o$

Where:

FV is the volume of extract (mL)

V_o is the initial sample volume (mL)

DF is the dilution factor. For undiluted analysis, DF = 1/0.91

11.2.27. For samples that show analyte detections above the range of the ICAL, sample dilutions will need to be prepared. See Appendix D for dilution preparation scheme.

11.3. Analytical Procedure

11.3.1. Column Flush – Each day of analysis, the column must be thoroughly flushed with 100% MeOH for at least 20 minutes to clear any accumulated impurities and interferents from the sample pathway. It is also good practice to open the purge valve on the pumps for the first ~1min of flush time. The column should then be equilibrated to the analysis starting conditions by flushing for 10 mins with 50:50 Ammonium Acetate: MeOH and finally 10 mins with 95:5 Ammonium acetate: MeOH. Ensure that pressure is stable.

11.3.2. Analytical Sequence – Following the daily column flush, three (3) high ICAL standard (L8 or L9) injections and one blank injection will be made in order to prime the system before analyzing opening QC and client samples. Following these opening injections, Instrument Sensitivity Check (ISC) samples will be analyzed as the opening CCV (Sec. 7.11; 10.4). When a passing ISC sample has been evaluated, an instrument blank will be analyzed to demonstrate the absence of system contamination. After system contamination is determined to be acceptable (no target analyte concentrations >1/2 LOQ), samples may be analyzed. After every tenth field sample analyzed in a sequence, a CCV will be analyzed (Sec. 7.11; 10.4), as well as at the end of the sequence.

11.3.3. Chromatographic Conditions

Step	Total Time (min)	Flow Rate (uL/min)	A: 20mM Ammonium Acetate (%)	B: Methanol (%)
0	0.00	1200	95.0	5.0
1	0.10	1200	45.0	55.0
2	4.50	1000	1.0	99.0
3	6.00	1000	1.0	99.0
4	6.10	1000	95.0	5.0
5	8.10	1000	95.0	5.0

11.3.4. Mass Spectrometric Conditions

Parameter	Setting or Value
Syringe Size	100 µL
Injection Volume	10 µL
Draw Speed	50.0 µL/min
Eject Speed	50.0 µL/min
Needle Level	3.0 mm
Column Oven Temperature	40°C
MRM Scan Window	60 sec
Curtain Gas (CUR)	30.0
Collision Gas (CAD)	9
Ion Spray Voltage (IS)	-4500.0 V
Temperature (TEM)	450.0°C
Ion Source Gas 1 (GS1)	40.0
Ion Source Gas 2 (GS2)	60.0

12. DATA ANALYSIS AND CALCULATION

NOTE: The surrogate (SUR) standard is used for quantitation in the PFAS ID methods.

12.1. Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations using MS/MS. Concentrations are calculated by measuring the product ions (Q3 Mass) listed in Table 4. Other ions may be selected at the discretion of the analyst.

12.2. Calculate analyte and surrogate concentrations using the multipoint calibration established in Section 10.2. Do not use daily calibration verification data to quantitate analytes in samples. Using the calculated CF (Sec. 11.2.26), adjust final analyte concentrations to reflect the actual sample volume determined in Section 11.

Sample concentration for aqueous samples:

$$\text{Concentration (ng/L)} = (Cs)(DF)$$

Where:
DF = dilution factor
Cs – see section 12.2.2

From the equation in section 12.2.1, Cs is calculated as follows:

$$Cs = \left(\frac{As}{Asur} - b\right) \bullet \left(\frac{Csur}{a}\right)$$

Where:
A_s is peak response of target analyte in the sample
A_{sur} is peak response of internal standard in the sample (SUR for isotope dilution methods)
C_s is concentration of target analyte in the sample
C_{sur} is concentration of internal standard in the sample (SUR for isotope dilution methods)
a is the slope from the ICAL linear regression
b is the y-intercept from the ICAL linear regression

12.3. Prior to reporting the data, the chromatogram should be reviewed for any incorrect peak identification or poor integration.

12.4. Dilution - When the concentrations of target analytes on-column exceed the highest concentration of initial calibration standard, dilution analyses are required. An appropriate dilution should be in the upper half of the calibration range, or close to the CCV. The diluted extract must maintain the same methanol/water ratio as the original extract. If a dilution of the extract is required, fortification of the diluted extract is necessary. Refer to Appendix D for dilution preparation

information.

12.5. PFHxS and PFOS have multiple chromatographic peaks using the LC conditions in Table 4 due to the linear and branched isomers of these compounds. The areas of all the linear and branched isomer peaks observed in the ICAL standards for each of these analytes must be integrated together and summed. The concentrations are reported as a total for each of these analytes. Purchased standards contain both linear and branched isomers; therefore, individual ICALs for the linear and branched isomers will not be possible. PFOA also has multiple chromatographic peaks using the LC conditions in Table 4 due to linear and branched isomers of this compound. However, a quantitative standard containing both linear and branched isomers is not currently available, so ICAL standards will not show multiple peaks for PFOA. A technical (qualitative) standard is analyzed with each calibration event to identify where the branched isomer peak elutes, relative to the linear isomer peak. In client samples, the areas of the linear and branched isomer peaks observed must be integrated together and summed. The concentration of PFOA in client samples will be reported as a sum total of branched and linear isomers. As more standards (quantitative or qualitative) containing both branched and linear isomers for other target analytes become available, these will be used in the same way as for PFHxS/PFOS or PFOA. Following the same procedure, any target analyte for which a standard has been purchased and analyzed will be integrated and reported as a sum total of branched and linear isomers.

12.5.1. MeFOSAA and EtFOSAA standards containing branched and linear isomers have been added to the Isomer Check solutions.

12.6. Integration - Sample integration is performed automatically by quantitation software and reviewed by the analyst for any incorrect analyte identification or poor integration. A peak is considered a positive detection if the primary (quantitation) ion transition peak shows a signal-to-noise ratio (S/N) of at least 10.0:1 and is defined by at least 10 MS scans (data points) across the baseline of the peak. For analytes with a secondary (confirmation) ion transition, the primary and secondary ion transitions must elute at nominally the same retention time. Further, the secondary transition must show a S/N of at least 3.0:1.

12.6.1. Retention Time (RT) acceptance – RT of each analyte, SUR, and IS must fall within 0.4 minutes (±0.2 mins) of the corresponding RTs from the ICAL midpoint, or the daily ISC on days when ICAL is not performed. Analytes with matched (labeled analogue) SUR compounds must elute within 0.1 mins of the associated SUR.

12.7. Calculations must utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty), typically two, and not more than three significant figures.

12.8. Calculate the % recovery for the SUR and LCS using the following equation:

$$\%\ \text{Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100$$

12.9. Calculate the MS % recovery for each analyte using the equation:

$$\%\ \text{Recovery} = \frac{Xs - X}{t} \times 100$$

Where:
X_s = measured concentration in the spiked sample
X = measured concentration in the unspiked sample
t = spike concentration

12.10. Calculate the relative percent difference (RPD) for duplicate measurements (FD1 and FD2 or MS and MSD) using the equation:

$$\text{RPD} = \frac{|X1 - X2|}{\frac{(X1 + X2)}{2}} \times 100$$

Where:

X1 = FD1 or MS result
X2 = FD2 or MSD result

12.11. Calculate the percent relative standard deviation (%RSD) for calibration curves produced using average response factor using the equation:

$$\%\,\mathrm{RSD} = \frac{\mathrm{SD}}{\mathrm{AVG}} \times 100$$

Where:
SD = the standard deviation of the curve
AVG = the average response factor for the curve (y = AVG*x)

13. METHOD PERFORMANCE

13.1. Prior to institution of any method for which data will be used for compliance reporting, the method must be validated; routine quality control procedures are utilized to monitor the validity of the method. Refer to the *Quality Assurance Management Plan* [QAMP; ME0012K] for information regarding method performance and data quality objectives.

13.2. Method Detection Limit – An acceptable MDL study is required before analysis of samples may begin. Refer to the *Method Validation Policy* [QA Policy ME003BF] for additional information.

13.2.1. The MDL is prepared by spiking 250 mL of reagent water with 50 µL of 100X PDS mix (20ppb), for a concentration of 4 ppt (100 ppt on column), plus 110 µL of Full List 100ppb SUR mix and extracted as normal. An equal number of MB (see section 7.10 above) will be extracted and analyzed with MDL samples.

13.2.2. For non-standard, non-regulatory analytes, an MDL study should be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client.

13.3. Initial Demonstration of Capability (IDOC) – Each analyst must make an initial demonstration of capability for each individual method. An IDOC for both solid and water matrices is required. This requires analysis of the LCS containing a representative list of analytes for the method.

13.3.1. Four aliquots of the LCS are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the LCS sample should be in the middle of the ICAL range.

13.3.1.1. The analysis of a MB must pass the criteria in Section 9.6.

13.3.1.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given below.

13.3.1.3. The relative standard deviation (RSD) of the results of the replicate analyses must be less than 20%.

13.3.1.4. The average recovery of the replicate values must be within ± 30% of the true value.

13.3.2. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3.3. An IDOC must be performed for any new analyst being trained to perform the method. The IDOC demonstrates that the analyst can perform the method, or portion of the method they are responsible for. An IDOC must also be performed if there is any major change in preparation procedure, such as change in solvent. A continuing demonstration of capability (CDOC) must be performed annually. The CDOC is established either by the procedure in section 13.2 or via participation in a passing proficiency test (PT).

13.3.4. A continuing demonstration of capability (CDOC) is required annually.

13.4. Training Qualification – The department group leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method utilizes SPE to extract analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes, thereby minimizing the potential hazards to both the analyst and the environment as compared to the use of large volumes of organic solvents in conventional liquid-liquid extractions.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure must be segregated and disposed according to the *Shealy Hazardous and Non-Hazardous Laboratory Waste Management Plan* [HS SOP ME0012A]. The Waste Manager should be contacted if additional information is required.

16. REFERENCES

NOTE: Where references exclude a date or edition, the latest edition of the referenced document adopted/recognized by the laboratory's accreditation bodies applies. Refer to the *Quality Assurance Management Plan* [QAMP ME0012K] for details.

16.1. Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography / Tandem Mass Spectrometry (LC/MS/MS), USEPA, Method 537.1, Version 1.0, November 2018.

16.2. Department of Defense Department of Energy Consolidated Quality Systems Manual (QSM) for Environmental Laboratories

16.3. Water Quality – Determination of Perluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA) – Method for Unfiltered Samples Using Solid Phase Extraction and Liquid Chromatography/Mass Spectrometry, ISO 25101:2009(E).

16.4. Solvent-Extractable Nonvolatile Compounds by High-Performance Liquid Chromatography /Thermospray/Mass Spectrometry (HPLC/TS/MS) or Ultraviolet (UV) detection, USEPA, SW846, Method 8321B, Revision 2, February 2007.

16.5. Knepper, T.P. (2003) Analysis and Fate of Surfactants in the Aquatic Environment. Amsterdam, The Netherlands: Elsevier Science B.V.

16.6. Knepper, T.P. (2012) Polyfluorinated Chemicals and Transformation Products. Berlin, Germany: Springer-Verlag Berlin Heidelberg.

16.7. Rapid Commun Mass Spectrom. 2007;21 (23):3803-14.

17. MISCELLANEOUS

17.1. Method Modifications – The analyst is permitted to modify LC columns, LC conditions, internal standards or surrogate standards, and MS and MS/MS conditions. Each time such method modifications are made, the analyst must repeat the procedures of the IDOC. **Modifications to LC conditions should still produce conditions such that co-elution of the method analytes is minimized to reduce the probability of suppression/enhancement effects.**

APPENDIX A: TABLES

TABLE 1 – TARGET ANALYTE LIST

Analyte Name	Analyte Acronym	CAS Number	Method 537.1	ID (Aqueous)	DAI	ID (Solid)
Fluorotelomer sulfonate 4:2 [1H,1H,2H,2H-perfluorohexane sulfonate]	4:2 FTS	757124-72-4*	No	Yes	No	Yes
Fluorotelomer sulfonate 6:2 [1H,1H,2H,2H-perfluorooctane sulfonate]	6:2 FTS	27619-97-2	No	Yes	No	Yes
Fluorotelomer sulfonate 8:2 [1H,1H,2H,2H-perfluorodecane sulfonate]	8:2 FTS	39108-34-4	No	Yes	No	Yes
1H,1H,2H,2H-perfluorododecane sulfonic acid	10:2FTS	120226-60-0*	No	Yes	No	Yes
N-ethylperfluoro-1-octanesulfonamidoacetic acid	EtFOSAA	2991-50-6	Yes	Yes	No	Yes
N-methylperfluoro-1-octanesulfonamidoacetic acid	MeFOSAA	2355-31-9	Yes	Yes	No	Yes
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5	Yes	Yes	Yes	Yes
Perfluoro-n-butanoic acid	PFBA	375-22-4	No	Yes	Yes	Yes
Perfluoro-1-decanesulfonic acid	PFDS	335-77-3	No	Yes	No	Yes
Perfluoro-n-decanoic acid	PFDA	335-76-2	Yes	Yes	Yes	Yes
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1	Yes	Yes	No	Yes
Perfluoro-1-heptanesulfonic acid	PFHpS	375-92-8	Yes	Yes	No	Yes
Perfluoro-n-heptanoic acid	PFHpA	375-85-9	Yes	Yes	Yes	Yes
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4	Yes	Yes	Yes	Yes
Perfluoro-n-hexanoic acid	PFHxA	307-24-4	Yes	Yes	Yes	Yes
Perfluoro-1-nonanesulfonic acid	PFNS	68259-12-1	Yes	Yes	No	Yes
Perfluoro-n-nonanoic acid	PFNA	375-95-1	Yes	Yes	Yes	Yes
Perfluorooctanesulfonic acid	PFOS	1763-23-1	Yes	Yes	Yes	Yes
Perfluoro-1-octanesulfonamide	PFOSA	754-91-6	No	Yes	No	Yes
Perfluoro-n-octanoic acid	PFOA	335-67-1	No	Yes	Yes	Yes
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3	Yes	Yes	Yes	Yes
Perfluoro-1-pentansulfonic acid	PFPeS	2706-91-4	Yes	Yes	No	Yes
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7	Yes	Yes	No	Yes
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8	Yes	Yes	No	Yes
Perfluoro-n-undecanoic acid	PFUdA	2058-94-8	Yes	Yes	No	Yes
N-methylperfluoro-1-octanesulfonamide	MeFOSA	31506-32-8	No	Yes	No	Yes
N-methylperfluoro-1-octanesulfonamide	EtFOSA	4151-50-2	No	Yes	No	Yes
Hexafluoropropylene oxide dimer acid	GenX	13252-13-6	Yes	Yes	No	Yes

4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	Yes	Yes	No	Yes
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9Cl-PF3ONS	756426-58-1	Yes	Yes	No	Yes

* CAS Numbers are for the acid and not the salt.
NOTE: Methods 537.1 and DAI are addressed in SOPs ME002I6 and ME002I7 respectively.

TABLE 1 – TARGET ANALYTE LIST CONT.

Analyte Name	**Analyte Acronym**	**CAS Number**	**Method 537.1**	**ID (Aqueous)**	**DAI**	**ID (Solid)**
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUDS	763051-92-9	Yes	Yes	No	Yes
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	MeFOSE	24448-09-7	No	Yes	No	Yes
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	EtFOSE	1691-99-2	No	Yes	No	Yes

TABLE 2A – REPORTING LIMITS (LOQ) – PFAS ISOTOPE DILUTION – AQUEOUS MATRIX

Analyte Acronym	Analyte Name	CAS Number	Spiked Conc[1] (ng/L)	DL (ng/L)	LOD (ng/L)	LOQ (ng/L)
EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid	2991-50-6	4.0	2	4	8
8:2 FTS	Fluorotelomer sulfonate 8:2 [1H,1H,2H,2H-perfluorodecane sulfonate]	39108-34-4	3.832	2	4	8
4:2 FTS	Fluorotelomer sulfonate 4:2 [1H,1H,2H,2H-perfluorohexane sulfonate]	757124-72-4[2]	3.736	2	4	8
6:2 FTS	Fluorotelomer sulfonate 6:2 [1H,1H,2H,2H-perfluorooctane sulfonate]	27619-97-2	3.792	2	4	8
MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid	2355-31-9	4.0	2	4	8
PFBS	Perfluoro-1-butanesulfonic acid	375-73-5	3.536	1	2	4
PFBA	Perfluoro-n-butanoic acid	375-22-4	4.0	1	2	4
PFDS	Perfluoro-1-decanesulfonic acid	335-77-3	3.856	1	2	4
PFDA	Perfluoro-n-decanoic acid	335-76-2	4.0	1	2	4
PFDoA	Perfluoro-n-dodecanoic acid	307-55-1	4.0	1	2	4
PFHpS	Perfluoro-1-heptanesulfonic acid	375-92-8	3.808	1	2	4
PFHpA	Perfluoro-n-heptanoic acid	375-85-9	4.0	1	2	4
PFHxS	Perfluoro-1-hexanesulfonic acid	355-46-4	3.64	1	2	4
PFHxA	Perfluoro-n-hexanoic acid	307-24-4	4.0	1	2	4
PFNS	Perfluoro-1-nonanesulfonic acid	68259-12-1	3.84	2	4	8
PFNA	Perfluoro-n-nonanoic acid	375-95-1	4.0	1	2	4
PFOS	Perfluorooctanesulfonic acid	1763-23-1	3.712	1	2	4
PFOSA	Perfluoro-1-octanesulfonamide	754-91-6	4.0	2	4	8
PFOA	Perfluoro-n-octanoic acid	335-67-1	4.0	1	2	4
PFPeA	Perfluoro-n-pentanoic acid	2706-90-3	4.0	1	2	4
PFPeS	Perfluoro-1-pentansulfonic acid	2706-91-4	3.752	1	2	4
PFTeDA	Perfluoro-n-tetradecanoic acid	376-06-7	4.0	2	4	8
PFTrDA	Perfluoro-n-tridecanoic acid	72629-94-8	4.0	1	2	4
PFUdA	Perfluoro-n-undecanoic acid	2058-94-8	4.0	1	2	4
MeFOSA	N-methylperfluoro-1-octanesulfonamide	31506-32-8	4.0	4	8	16
EtFOSA	N-methylperfluoro-1-octanesulfonamide	4151-50-2	4.0	2	4	8
10:2FTS	1H,1H,2H,2H-perfluorododecane sulfonate	120226-60-0[2]	3.856	2	4	8
GenX	Tetrafluoro-2-(heptafluoropropoxy) propanoic acid	13252-13-6	8.0	1	2	8
ADONA	4,8-dioxa-3H-perfluorononanoic acid	919005-14-4	3.768	2	4	8
9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	756426-58-1	3.728	1	4	8
11Cl-PF3OUDS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	763051-92-9	3.768	1	4	8
MeFOSE	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	24448-09-7	4	2	4	8
EtFOSE	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	1691-99-2	4	1	4	8

[1]Spiking concentration used to determine DL.
[2]CAS Numbers are for the acid and not the salt.

TABLE 2B – REPORTING LIMITS (LOQ) – PFAS ISOTOPE DILUTION – SOLID MATRIX

Analyte Acronym	Analyte Name	CAS Number	Spiked Conc[1] (µg/kg)	DL (µg/kg)	LOD (µg/kg)	LOQ (µg/kg)
EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid	2991-50-6	1	0.2	0.5	1
8:2 FTS	Fluorotelomer sulfonate 8:2 [1H,1H,2H,2H-perfluorodecane sulfonate]	39108-34-4	0.958	0.3	0.6	2
4:2 FTS	Fluorotelomer sulfonate 4:2 [1H,1H,2H,2H-perfluorohexane sulfonate]	757124-72-4[2]	0.934	0.3	0.6	2
6:2 FTS	Fluorotelomer sulfonate 6:2 [1H,1H,2H,2H-perfluorooctane sulfonate]	27619-97-2	0.948	0.3	0.6	2
MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid	2355-31-9	1	0.2	0.5	1
PFBS	Perfluoro-1-butanesulfonic acid	375-73-5	0.884	0.1	0.5	1
PFBA	Perfluoro-n-butanoic acid	375-22-4	1	0.2	0.5	1
PFDS	Perfluoro-1-decanesulfonic acid	335-77-3	0.964	0.2	0.5	1
PFDA	Perfluoro-n-decanoic acid	335-76-2	1	0.2	0.5	1
PFDoA	Perfluoro-n-dodecanoic acid	307-55-1	1	0.2	0.5	1
PFHpS	Perfluoro-1-heptanesulfonic acid	375-92-8	0.952	0.2	0.5	1
PFHpA	Perfluoro-n-heptanoic acid	375-85-9	1	0.2	0.5	1
PFHxS	Perfluoro-1-hexanesulfonic acid	355-46-4	0.91	0.2	0.5	1
PFHxA	Perfluoro-n-hexanoic acid	307-24-4	1	0.2	0.5	1
PFNS	Perfluoro-1-nonanesulfonic acid	68259-12-1	0.96	0.2	0.5	1
PFNA	Perfluoro-n-nonanoic acid	375-95-1	1	0.2	0.5	1
PFOS	Perfluorooctanesulfonic acid	1763-23-1	0.928	0.15	0.5	1
PFOSA	Perfluoro-1-octanesulfonamide	754-91-6	1	0.3	0.5	1
PFOA	Perfluoro-n-octanoic acid	335-67-1	1	0.15	0.5	1
PFPeA	Perfluoro-n-pentanoic acid	2706-90-3	1	0.2	0.5	1
PFPeS	Perfluoro-1-pentanesulfonic acid	2706-91-4	0.938	0.2	0.5	1
PFTeDA	Perfluoro-n-tetradecanoic acid	376-06-7	1	0.2	0.5	1
PFTrDA	Perfluoro-n-tridecanoic acid	72629-94-8	1	0.2	0.5	1
PFUdA	Perfluoro-n-undecanoic acid	2058-94-8	1	0.2	0.5	1
MeFOSA	N-methylperfluoro-1-octanesulfonamide	31506-32-8	1	0.3	0.6	2
EtFOSA	N-ethylperfluoro-1-octanesulfonamide	4151-50-2	1	0.3	0.6	2
10:2FTS	1H,1H,2H,2H-perfluorododecane sulfonate	120226-60-0[2]	0.964	0.2	0.5	1
GenX	Tetrafluoro-2-(heptafluoropropoxy) propanoic acid	13252-13-6	2	0.5	1	4
ADONA	4,8-dioxa-3H-perfluorononanoic acid	919005-14-4	0.942	0.5	1	2
9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	756426-58-1	0.932	0.5	1	2
11Cl-PF3OUDS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	763051-92-9	0.942	0.5	1	2
MeFOSE	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	24448-09-7	1	0.5	1	2
EtFOSE	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	1691-99-2	1	0.5	1	2

[1]Spiking concentration used to determine DL.
[2]CAS Numbers are for the acid and not the salt.

TABLE 3 – LABELED STANDARD ASSOCIATIONS – PFAS ISOTOPE DILUTION – AQUEOUS AND SOLID MATRIX

Target Analyte	Associated Labeled Standard
4:2 FTS	13C2_4:2FTS_2
6:2 FTS	13C2_6:2FTS_2
8:2 FTS	13C2_8:2FTS_2
10:2FTS	13C2_8:2 FTS_2
EtFOSAA	d5-EtFOSAA
MeFOSAA	d3-MeFoSAA

PFBS	13C3_PFBS
PFBA	13C4_PFBA
PFDS	13C8_PFOS
PFDA	13C6_PFDA
PFDoA	13C2_PFDoA
PFHpS	13C3_PFHxS
PFHpA	13C4_PFHpA
PFHxS	13C3_PFHxS
PFHxA	13C5_PFHxA
PFNS	13C8_PFOS
PFNA	13C9_PFNA
PFOS	13C8_PFOS
PFOSA	13C8_PFOSA
PFOA	13C8_PFOA
PFPeA	13C5_PFPeA
PFPeS	13C3_PFBS
PFTeDA	13C2_PFTeDA
PFTrDA	13C2_PFDoA
PFUdA	13C7_PFUdA
MeFOSA	d3-MeFOSA
EtFOSA	d5-EtFOSA
GenX	13C3-GenX
ADONA	13C3_PFHxS
9Cl-PF3ONS	13C8_PFOS
11Cl-PF3OUDS	13C8_PFOS
MeFOSE	d7-MeFOSE
EtFOSE	d9-EtFOSE

NOTE: For method ID-AQ and ID-Solid, the labeled quantitation standards are contained in the SUR solution.

TABLE 4: ID INSTRUMENT CONDITIONS – AQUEOUS AND SOLID MATRIX

LC Program

Step	Total Time (min)	Flow Rate (uL/min)	A: 20mM Ammonium Acetate (%)	B: Methanol (%)
0	0.00	1200	95.0	5.0
1	0.10	1200	45.0	55.0
2	4.50	1000	1.0	99.0
3	6.00	1000	1.0	99.0
4	6.10	1000	95.0	5.0
5	8.10	1000	95.0	5.0

Built-in Diverter Valve Program

Step	Total Time (min)	Position
1	0.0	Waste
2	1.0	MS
3	5.8	Waste

Instrument Parameters

Parameter	Setting or Value
Syringe Size	100 µL
Injection Volume	10 µL
Draw Speed	50.0 µL/min
Eject Speed	50.0 µL/min
Needle Level	3.0 mm
Column Oven Temperature	40°C
MRM Scan Window	30 sec
Curtain Gas (CUR)	30.0
Collision Gas (CAD)	9
Ion Spray Voltage (IS)	-4500.0 V
Temperature (TEM)	450.0°C
Ion Source Gas 1 (GS1)	40.0
Ion Source Gas 2 (GS2)	60.0

MS/MS Conditions

ID	Q1 Mass (Da)	Q3 Mass (Da)	Time (min)	DP (volts)	EP (volts)	CE (volts)	CXP (volts)
4:2 FTS	327	307	2.42	-20	-4	-28	-8
4:2 FTS_2	327	81	2.42	-20	-4	-50	-8
6:2 FTS	427	407	3.23	-20	-4	-32	-8
6:2 FTS_2	427	81	3.23	-20	-4	-72	-8
8:2 FTS	527	507	4.02	-20	-4	-40	-8
8:2 FTS_2	527	81	4.02	-20	-4	-82	-8
9Cl-PF3ONS	531	351	3.88	-75	-10	-38	-10
10:2 FTS	627	607	4.66	-20	-8	-45	-8
10:2 FTS_2	627	80	4.66	-20	-8	-92	-8
11Cl-PF3OUDS	631	451	4.52	-90	-10	-41	-13
ADONA	377	251	2.95	-47	-8	-18	-8
ADONA_2	377	85	2.95	-47	-8	-68	-8
EtFOSA	526	169	4.71	-50	-10	-37	-8
EtFOSA_2	526	219	4.71	-50	-10	-37	-8
EtFOSE	630	59	4.65	-39	-4	-58	-8
GenX	285	119	2.58	-51	-10	-38	-8
GenX_2	285	185	2.58	-51	-10	-28	-8
MeFOSA	512	169	4.52	-50	-10	-37	-8
MeFOSA_2	512	219	4.52	-50	-10	-37	-8
MeFOSE	616	59	4.49	-50	-10	-58	-8
N-EtFOSAA	584	419	4.36	-50	-10	-28	-8
N-EtFOSAA_2	584	526	4.36	-50	-10	-28	-8
N-MeFOSAA	570	419	4.20	-50	-10	-28	-8
N-MeFOSAA_2	570	483	4.20	-50	-10	-22	-8
PFBA	212.9	168.9	1.71	-10	-8	-12	-8
PFBS	298.9	80	2.15	-20	-4	-56	-5.5
PFBS_2	298.9	99	2.15	-20	-4	-46	-9
PFDA	513	469	4.03	-10	-8	-17	-8
PFDA_2	513	169	4.03	-10	-8	-27	-8
PFDoA	613	569	4.66	-10	-8	-18	-8
PFDoA_2	613	169	4.66	-10	-8	-30	-8
PFDS	599	80	4.34	-20	-7	-118	-5.5
PFDS_2	599	99	4.34	-20	-7	-95	-9
PFHpA	363	319	2.85	-10	-8	-14	-8
PFHpA_2	363	169	2.85	-10	-8	-25	-8
PFHpS	449	80	3.27	-20	-4	-80	-5.5
PFHpS_2	449	99	3.27	-20	-4	-70	-9
PFHxA	313	269	2.46	-10	-8	-14	-8
PFHxA_2	313	119	2.46	-10	-8	-25	-8
PFHxDA	813	769	6	-10	-4	-24	-8
PFHxDA_2	813	169	6	-10	-4	-40	-8
PFHxS	399	80	2.87	-20	-4	-74	-5.5
PFHxS_2	399	99	2.87	-20	-4	-60	-9
PFNA	463	419	3.66	-10	-8	-16	-8
PFNA_2	463	169	3.66	-10	-8	-26	-8
PFNS	549	80	4.02	-20	-5.5	-115	-5.5
PFNS_2	549	99	4.02	-20	-5.5	-92	-5.5
PFOA	413	369	3.26	-10	-8	-14	-8
PFOA_2	413	169	3.26	-10	-8	-26	-8
PFODA	913	869	6.1	-10	-4	-26	-8
PFODA_2	913	169	6.1	-10	-4	-42	-8
PFOS	499	80	3.66	-20	-4	-95	-5.5

MS/MS Conditions
Continued

ID	Q1 Mass (Da)	Q3 Mass (Da)	Time (min)	DP (volts)	EP (volts)	CE (volts)	CXP (volts)
PFOS_2	499	99	3.66	-20	-4	-87	-9
PFOSA	498	78	4.02	-20	-4	-85	-8
PFPeA	262.9	218.9	2.09	-10	-8	-13	-8
PFPeS	349	80	2.50	-20	-4	-70	-5.5
PFPeS_2	349	99	2.50	-20	-4	-60	-9
PFTeDA	713	669	5.15	-10	-4	-22	-8
PFTeDA_2	713	169	5.15	-10	-4	-38	-8
PFTrDA	663	619	4.92	-10	-4	-20	-8
PFTrDA_2	663	169	4.92	-10	-4	-36	-8
PFUdA	563	519	4.36	-10	-8	-18	-8
PFUdA_2	563	169	4.36	-10	-8	-28	-8
13C2-PFDA	515	470	4.03	-10	-8	-17	-8
13C2-PFDoA	615	570	4.66	-10	-4	-18	-8
13C2-PFHxA	315	270	2.46	-10	-8	-14	-8
13C2-PFHxDA	815	770	6	-10	-4	-24	-8
13C2-PFOA	415	370	3.26	-10	-8	-14	-8
13C2-PFTeDA	715	670	5.15	-10	-4	-22	-8
13C3-GenX	287	185	2.58	-55	-10	-24	-10
13C3-PFBA	216	172	1.71	-10	-8	-12	-8
13C3_PFBS	302	80	2.15	-20	-4	-56	-5.5
13C3_PFHxS	402	80	2.87	-20	-4	-74	-5.5
13C4_PFBA	217	172	1.71	-10	-8	-12	-8
13C4_PFHpA	367	322	2.85	-10	-8	-14	-8
13C4_PFOS	503	80	3.66	-20	-4	-95	-5.5
13C5_PFHxA	318	273	2.46	-10	-8	-14	-8
13C5_PFPeA	267.9	223	2.09	-10	-8	-13	-8
13C6_PFDA	519	474	4.03	-10	-8	-16	-8
13C7_PFUdA	570	525	4.36	-10	-8	-18	-8
13C8_PFOA	421	376	3.26	-10	-8	-14	-8
13C8_PFOS	507	80	3.66	-20	-4	-95	-5.5
13C8_PFOSA	506	78	4.02	-20	-4	-85	-8
13C9_PFNA	472	427	3.66	-10	-8	-16	-8
d3-MeFOSA	515	169	4.52	-50	-10	-37	-8
d3-MeFOSAA	573	419	4.20	-50	-10	-28	-8
d5-EtFOSA	531	169	4.71	-50	-10	-37	-8
d5-EtFOSAA	589	419	4.36	-50	-10	-28	-8
d7-MeFOSE	623	59	4.49	-50	-5.5	-58	-5.5
d9-EtFOSE	639	59	4.65	-60	-4	-60	-8
M2-4:2 FTS	329	309	2.42	-20	-4	-28	-8
13C2-4:2 FTS_2	329	81	2.42	-20	-4	-28	-8
M2-6:2FTS	429	409	3.23	-20	-4	-32	-8
13C2-6:2FTS_2	429	81	3.23	-20	-4	-32	-8
M2-8:2FTS	529	509	4.02	-20	-4	-40	-8
13C2-8:2FTS_2	529	81	4.02	-20	-4	-82	-8

NOTE: See Appendix E for the chemical derivation of the ion transitions.

TABLE 5: Calibration Levels (ng/L) – ID ICAL – AQUEOUS AND SOLID MATRIX

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8	Level 9	Level 10
	PFAS Full List Native PDS Mix, 1000X			PFAS Full List Native PDS Mix, 100X				PFAS Full List Native PDS Mix, 10X		
PFBA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFPeA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFBS	44	88	177	442	884	1768	4420	8840	13260	17680
PFHxA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFPeS	47	94	188	469	938	1876	4690	9380	14070	18760
PFHpA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFHxS	46	91	182	455	910	1820	4550	9100	13650	18200
PFOA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFHpS	48	95	190	476	952	1904	4760	9520	14280	19040
PFNA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFOS	46	93	186	464	928	1856	4640	9280	13920	18560
PFDA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFNS	48	96	192	480	960	1920	4800	9600	14400	19200
4:2FTS	47	93	187	467	934	1868	4670	9340	14010	18680
6:2FTS	47	95	190	474	948	1896	4740	9480	14220	18960
8:2 FTS	48	96	192	479	958	1916	4790	9580	14370	19160
PFOSA	50	100	200	500	1000	2000	5000	10000	15000	20000
MeFOSA	50	100	200	500	1000	2000	5000	10000	15000	20000
EtFOSA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFUDA	50	100	200	500	1000	2000	5000	10000	15000	20000
MeFOSAA	50	100	200	500	1000	2000	5000	10000	15000	20000
EtFOSAA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFDS	48	96	193	482	964	1928	4820	9640	14460	19280
PFDoA	50	100	200	500	1000	2000	5000	10000	15000	20000
10:2FTS	48	96	193	482	964	1928	4820	9640	14460	19280
PFTrDA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFTeDA	50	100	200	500	1000	2000	5000	10000	15000	20000
GenX	100	200	400	1000	2000	4000	10000	20000	30000	40000
ADONA	47	94	188	471	942	1884	4710	9420	14130	18840
9Cl-PF3ONS	47	93	186	466	932	1864	4660	9320	13980	18640
11Cl-PF3OUDS	47	94	188	471	942	1884	4710	9420	14130	18840
MeFOSE	50	100	200	500	1000	2000	5000	10000	15000	20000
EtFOSE	50	100	200	500	1000	2000	5000	10000	15000	20000
Surrogates (SUR)	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Internal Standards (IS)	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000

NOTE: See Table 1 for method specific target analytes.

NOTE: *The ID (Aqueous and Solid) SUR includes the following compounds:*

- Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-13C2] hexane sulfonate (M2-4:2FTS or 13C2-4:2FTS)
- Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-13C2] octane sulfonate (M2-6:2FTS or 13C2-6:2FTS)
- Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-13C2] decane sulfonate (M2-8:2FTS or 13C2-8:2FTS)
- Perfluoro-1-[13C8] octanesulfonamide (M8FOSA-I or 13C8FOSA)
- N-ethyl-d5-perfluoro-1-octanesulfonamide (d-N-EtFOSA-M)
- N-methyl-d3-perfluoro-1-octanesulfonamide (d-N-MeFOSA-M)
- N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid (d5-N-EtFOSAA)

- N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid (d3-N-MeFOSAA)
- Perfluoro-n-[13C4]butanoic acid (MPFBA or 13C4PFBA)
- Perfluoro-n-[13C5]pentanoic acid (M5PFPeA or 13C5PFPeA)
- Perfluoro-n-[1,2,3,4,6-13C5]hexanoic acid (M5PFHxA or 13C5PFHxA)
- Perfluoro-n-[1,2,3,4-13C4]heptanoic acid (M4PFHpA or 13C4PFHpA)
- Perfluoro-n-[13C8]octanoic acid (M8PFOA or 13C8PFOA)
- Perfluoro-n-[13C9]nonanoic acid (M9PFNA or 13C9PFNA)
- Perfluoro-n-[1,2,3,4,5,6-13C5]decanoicanoic acid (M6PFDA or 13C6PFDA)
- Sodium perfluoro-1-[2,3,4-13C3]butanesulfonate (M3PFBS or 13C3PFBS)
- Sodium perfluoro-1-[1,2,3-13C3]hexanesulfonate (M3PFHxS or 13C3PFHxS)
- Sodium perfluoro-1-[13C8]octanesulfonate (M8PFOS or 13C8PFOS)
- Perfluoro-n-[1,2,3,4,5,6,7-13C7]undecanoic acid (M7PFUdA or 13C7PFUdA)
- Perfluoro-n-[1,2-13C2]dodecanoic acid (MPFDoA or 13C2PFDoA)
- Perfluoro-n-[1,2-13C2]tetradecanoic acid (M2PFTeDA or 13C2PFTeDA)
- Tetrafluoro-2-(heptafluoropropoxy)-13C3 propanoic acid (13C3-GenX)
- 2-(N-methyl-d3-perfluoro-1-octanesulfonamido) ethan-4-ol (d7-MeFOSE)
- 2-(N-ethyl-d5-perfluoro-1-octanesulfonamido) ethan-4-ol (d9-EtFOSE)

NOTE: *The ID (Aqueous and Solid) IS includes the following compounds:*

- Perfluoro-n-[1,2-13C2]hexanoic acid (M2PFHxA or 13C2PFHxA)
- Perfluoro-n-[2,3,4-13C3]butanoic acid (M3PFBA or 13C3PFBA)
- Perfluoro-n-[1,2-13C2]octanoic acid (M2PFOA or 13C2PFOA)
- Perfluoro-n-[1,2-13C2]decanoic acid (MPFDA or 13C2PFDA)
- Sodium perfluoro-1-[1,2,3,4-13C4]octanesulfonate (MPFOS or 13C4PFOS)

Table 6A: DOD BATCH CONTROL LIMITS – AQUEOUS MATRIX

The limits outlined in this table shall be used when reporting data for DoD/DOE projects			
CAS	**Analyte Acronym**	**Lower Control Limit (%REC)**	**Upper Control Limit (%REC)**
2991-50-6	EtFOSAA	61	135
39108-34-4	8:2 FTS	67	138

757124-72-4	4:2 FTS	63	143
27619-97-2	6:2 FTS	64	140
2355-31-9	MeFOSAA	65	136
375-73-5	PFBS	72	130
375-22-4	PFBA	73	129
335-77-3	PFDS	53	142
335-76-2	PFDA	71	129
307-55-1	PFDoA	72	134
375-92-8	PFHpS	69	134
375-85-9	PFHpA	72	130
355-46-4	PFHxS	68	131
307-24-4	PFHxA	72	129
68259-12-1	PFNS	69	127
375-95-1	PFNA	69	130
1763-23-1	PFOS	65	140
754-91-6	PFOSA	67	137
335-67-1	PFOA	71	133
2706-90-3	PFPeA	72	129
2706-91-4	PFPeS	71	127
376-06-7	PFTeDA	71	132
72629-94-8	PFTrDA	65	144
2058-94-8	PFUdA	69	133
31506-32-8	MeFOSA	68	141
4151-50-2	EtFOSA	70	150
120226-60-0	10:2FTS	70	150
13252-13-6	GenX	70	150
919005-14-4	ADONA	70	150
756426-58-1	9Cl-PF3ONS	70	150
763051-92-9	11Cl-PF3OUDS	70	150
24448-09-7	MeFOSE	70	150
1691-99-2	EtFOSE	70	150

Table 6B: DOD BATCH CONTROL LIMITS – SOLID MATRIX

The limits outlined in this table shall be used when reporting data for DoD/DOE projects			
CAS	**Analyte Acronym**	**Lower Control Limit (%REC)**	**Upper Control Limit (%REC)**
2991-50-6	EtFOSAA	61	139
39108-34-4	8:2 FTS	65	137
757124-72-4	4:2 FTS	62	145
27619-97-2	6:2 FTS	64	140
2355-31-9	MeFOSAA	63	144
375-73-5	PFBS	72	128
375-22-4	PFBA	71	135
335-77-3	PFDS	59	134
335-76-2	PFDA	69	133
307-55-1	PFDoA	69	135
375-92-8	PFHpS	70	132
375-85-9	PFHpA	71	131
355-46-4	PFHxS	67	130
307-24-4	PFHxA	70	132
68259-12-1	PFNS	69	125
375-95-1	PFNA	72	129
1763-23-1	PFOS	68	136
754-91-6	PFOSA	67	137
335-67-1	PFOA	69	133
2706-90-3	PFPeA	69	132
2706-91-4	PFPeS	73	123
376-06-7	PFTeDA	69	133
72629-94-8	PFTrDA	66	139
2058-94-8	PFUdA	64	136
31506-32-8	MeFOSA	70	150
4151-50-2	EtFOSA	70	150
120226-60-0	10:2FTS	70	150
13252-13-6	GenX	70	150
919005-14-4	ADONA	70	150
756426-58-1	9Cl-PF3ONS	70	150
763051-92-9	11Cl-PF3OUDS	70	150
24448-09-7	MeFOSE	70	150
1691-99-2	EtFOSE	70	150

APPENDIX NJ. New Jersey (NJ) NELAP Secondary Accreditation Method Requirements

Sections found in this appendix replace and/or supplement the existing sections of this SOP. These requirements must be met when

analyzing samples for NJ compliance.

SCOPE AND APPLICATION

The main body of this SOP describes a Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) method for the determination of selected Per- and Polyfluorinated Alkyl Substances (PFAS) in aqueous and solid samples using isotope dilution (ID) quantitation; however, **only those procedures applicable to determination in non-potable water are valid for NJ compliance. Procedures covering determination in solid and chemical materials are not approved for NJ compliance.**

SUMMARY OF METHOD

PFAS Isotope Dilution method (aqueous; ID-AQ) - A 250-mL water sample is fortified with surrogates (SUR; isotope dilution standards) and passed through a solid phase extraction (SPE) cartridge (Phenomenex Strata-XL-AW or equivalent) to extract the method analytes and SUR. The compounds are eluted from the Strata-XL-AW cartridge with 4-mL of methanol and 4-mL of ammonia-methanol (0.3%). Samples are then filtered by SPE (Strata-GCB or equivalent), with a tube rinse of 2-mL of clean MeOH. With the SPE-Strata-GCB tube rinse, the final extract volume is approximately 10 mL. An aliquot of the extract is fortified with internal standards (IS). 10-µL of the fortified aliquot is injected on an LC equipped with a C18 column that is coupled to an MS/MS detector. The analytes are separated and identified by comparing the acquired mass spectra and retention times to the reference spectra and retention times for calibration standards acquired under identical LC/MS/MS conditions. The concentration of each analyte is determined by using the internal standard isotope dilution technique.

NOTE: Procedures covering determination in solid and chemical materials (sections 2.2 and 2.3 of existing SOP) are not approved for NJ compliance.

SAMPLE COLLECTION, PRESERVATION AND STORAGE

Aqueous samples must be collected in a 250mL HDPE bottle fitted with a polyethylene screw-cap. Samples collected from chlorinated sources must be preserved with Trizma (5.0 g/L), which is added to the sample bottle prior to collection.

NOTE: Trizma is not required if the sample source is known to be non-chlorinated. The laboratory may obtain documentation from the client in order to make this determination.

Aqueous samples should be extracted as soon as possible but must be extracted within 14 days. Extracts must be stored at room temperature and analyzed within 28 days after extraction.

QUALITY CONTROL

If samples are preserved with Trizma, all associated batch QC samples must also contain Trizma from the same lot and at the same concentration.

Continuing Calibration Verification (CCV) – CCV standards are analyzed at the beginning of each analysis batch, after every 10 field samples, and at the end of the analysis batch. The beginning CCV of each analysis batch must be at or below the LoQ (100 ppt and 200 ppt); the daily Instrument Sensitivity Check (ISC) will be used as the daily opening CCV. For NJ compliance, subsequent CCVs should alternate between a medium ICAL standard (1000 ppt) and a high ICAL standard (10,000 ppt). The calculated amount for each analyte and surrogate for medium and high level CCV/CCCs must be within ± 30% of the true value. The calculated amount for the lowest calibration point for each analyte must be within ± 50% and the surrogate must be within ± 30% of the true value.

Laboratory Control Sample (LCS) - The spiked concentration of the LCS must be rotated between low, medium, and high concentrations from batch to batch for NJ compliance. The low concentration LCS must be as near as practical to, but no more than two times, the MRL. Similarly, the high concentration LCS should be near the high end of the calibration range established during the initial calibration. Results of the low-level LCS analyses must be 50-150% of the true value. Results of the medium and high-level LCS analyses must be 70-130% of the true value.

Matrix Spike (MS) – For matrix spike samples, recoveries must range between 70-130% for NJ compliance.

Field Duplicate (FD) or Matrix Spike Duplicate (MSD) - Every effort is made to ensure that an MS/MSD or an FD is included in every batch. In the event that there is insufficient sample to analyze an MS/MSD pair or if no FD is available, a duplicate LCS (laboratory control sample duplicate (LCSD)) is included in the batch. In instances where an LCSD must be analyzed in a batch containing NJ compliance samples, an NCM must be generated to ensure this event is denoted in the final report.

CALIBRATION AND STANDARDIZATION

Calibration curves may not be produced using average response factor for NJ compliance sample analysis.

PROCEDURE

If a sample dilution requires addition of isotope dilution standard (surrogate) post-extraction, samples are no longer considered as analyzed by isotope dilution for NJ compliance. An NCM must be generated to ensure this event is denoted in the final report.

Target Analytes – NJ Compliance		
Analyte Name	**Analyte Acronym**	**CAS Number**
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5*
Perfluoro-n-decanoic acid	PFDA	335-76-2
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1
Perfluoro-n-heptanoic acid	PFHpA	375-85-9
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4*
Perfluoro-n-hexanoic acid	PFHxA	307-24-4
Perfluoro-n-nonanoic acid	PFNA	375-95-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1*
Perfluoro-n-octanoic acid	PFOA	335-67-1
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8
Perfluoro-n-undecanoic acid	PFUdA	2058-94-8
* CAS Numbers are for the acid and not the salt.		

APPENDIX B. PFAS ID – SOLID MATRIX

1. Standard Preparation

1.1 Internal standards for ID-Solid are the following five compounds: Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid ($^{13}C_2$-PFHxA), Perfluoro-n-[1,2-$^{13}C_2$] octanoic acid ($^{13}C_2$-PFOA) and Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate ($^{13}C_4$-PFOS), Perfluoro-n-[2,3,4-$^{13}C_3$] butanoic acid ($^{13}C_3$-PFBA) and Perfluoro-n-[1,2-$^{13}C_2$] decanoic acid ($^{13}C_2$-PFDA).

1.2 Internal Standard (IS) 50X Mix: dilute the stock standard with methanol/water in accordance to section 1.10 and the table below:

ID (Solid) IS 50X Mix

Standard Name	Conc. of Stock Std.	Aliquoted Volume	Dilution Volume	Final Conc.

	µg/mL	µL	mL	µg/mL
Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid (13C2-PFHxA)	50	200.0	10.0	1.0

1.3 20 ppb IS Mix: combine the IS 50X mix in section 1.2 and Wellington Labs standard part# MPFAC-C-IS and dilute with methanol/water in accordance to section 1.10 and the table below:

ID (Solid) 20 ppb IS Mix

Standard Name	Conc. of Stock Std.	Aliquoted Volume	Dilution Volume	Final Conc.
	µg/mL	**µL**	**mL**	**µg/mL**
MOD-ID IS 50X Mix	1	300.0	15.0	0.020
MPFAC-C-IS stock	2	150.0	15.0	0.020

1.4 SUR 50X Mix: Dilute the stock standards with methanol/water in accordance to section 1.10 and the table below:

ID (Solid) SUR 50X Mix

Standard Name	Conc. of Stock Std.	Aliquoted Volume	Dilution Volume	Final Conc.
	µg/mL	**µL**	**mL**	**µg/mL**
Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-$^{13}C_2$] hexane sulfonate (13C2-4:2FTS)	50	1000	10.0	5.0
Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-$^{13}C_2$] octane sulfonate (13C2-6:2FTS)	50	1000	10.0	5.0
Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-$^{13}C_2$] decane sulfonate (13C2-8:2FTS)	50	1000	10.0	5.0
Perfluoro-1-[$^{13}C_8$] octanesulfonamide (13C8-PFOSA)	50	200	10.0	1.0
N-ethyl-d5-perfluoro-1-octanesulfonamide (d5-EtFOSA)	50	200	10.0	1.0
N-methyl-d3-perfluoro-1-octanesulfonamide (d3-MeFOSA)	50	200	10.0	1.0
N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid (d5-EtFOSAA)	50	1000	10.0	5.0
N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid (d3-MeFOSAA)	50	1000	10.0	5.0
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-$^{13}C_3$-propanoic acid (13C3-GenX)	50	1000	10.0	5.0
2-(N-methyl-d3-perfluoro-1-octanesulfonamido) ethan-4-ol (d7-MeFOSE)	50	200	10.0	1.0
2-(N-ethyl-d5-perfluoro-1-octanesulfonamido) ethan-4-ol (d9-EtFOSE)	50	200	10.0	1.0

1.5 20 ppb SUR mix: combine the SUR 50X mix in section 1.4 and Wellington Labs standard part# MPFAC-C-ES and dilute with methanol/water in accordance to section 1.10 and the table below:

ID (Solid) 20 ppb SUR Mix

Standard Name	Conc. of Stock Std.	Aliquoted Volume	Dilution Volume	Final Conc.
	µg/mL	**µL**	**mL**	**µg/mL**
MOD ID SUR 50X mix	1	300.0	15.0	0.020
MPFAC-C-ES stock	2	150.0	15.0	0.020

1.6 100 ppb SUR mix: combine the SUR 50X mix in section 1.4 and Wellington Labs standard part# MPFAC-C-ES and dilute with methanol/water in accordance with section 1.10 and the table below:

ID (Solid) 100 ppb SUR Mix

Standard Name	Conc. of Stock Std.	Aliquoted Volume	Dilution Volume	Final Conc.
	µg/mL	µL	mL	µg/mL
MOD ID SUR 50X mix	1	1500	15.0	0.10
MPFAC-C-ES stock	2	750	15.0	0.10

NOTE: The compounds included in the ID (Aqueous and Solid) SUR Mix are listed under Table 5.

1.7 Solid Spiking Standard (SSS) – For ID-Solid, a separate solution of target analytes will be prepared and used to spike all QC samples (LCS, MS/MSD) prior to extraction. The concentration of all target analytes will be 1000 ng/mL, except GenX which will be 2000 ng/mL. The SSS is stable for 12 months when stored at 2-6°C. Prepare according to section 1.10 and the table below:

ID Solid Spiking Standard (SSS)

Standard Name	Conc. of Stock Std.	Aliquoted Volume	Dilution Volume	Final Conc.
	ng/mL	µL	mL	ng/mL
PFAC-24PAR	2000	1100	2.2	1000
MeFOSA	50000	44	2.2	1000
EtFOSA	50000	44	2.2	1000
10:2 FTS	50000	44	2.2	1000
GenX	50000	88	2.2	2000

1.8 Analyte Primary Dilution Standard (PDS) Solutions – For ID-Solid, a list of these solutions is provided below. The PDS standards are stable for two weeks when stored at room temperature, or 12 months when stored at 2-6°C. Wellington Laboratories item #s for the standards used to prepare the PDS solutions are as follows: PFAC-24PAR (24 compound mix of native PFAS); N-MeFOSA-M; N-EtFOSA-M; 10:2FTS; HFPO-DA (GenX); N-MeFOSE-M; N-EtFOSE-M; NaDONA; 9Cl-PF3ONS; 11Cl-PFOUdS

1.8.1 Stock (10X) Analyte PDS (containing all target analytes at 0.2 ug/mL, except GenX which is present at 0.4 ug/mL) - 1 mL of the primary lot of PFAC-24PAR standard mix, 40 uL of MeFOSA, EtFOSA, 10:2 FTS, MeFOSE, EtFOSE, NADONA, 9Cl-PF3ONS, and 11Cl-PF3OUDS primary standards, and 80 uL of GenX primary standard are diluted to 10 mL with 8.2 mL of methanol and 400 uL reagent water.

1.8.2 100X Analyte PDS (containing all target analytes at 20 ng/mL; GenX at 40 ng/mL) – 1 mL of Stock (10X) Analyte PDS is diluted to 10 mL with 9 mL of 96% MeOH

1.8.3 1000X Analyte PDS (containing all target analytes at 2.0 ng/mL; GenX at 4.0 ng/mL) – 1 mL of 100X Analyte PDS is diluted to 10 mL with 9 mL of 96% MeOH

1.9 Initial Calibration Standards (ICAL) – Using the standards in sections 1.3, 1.5, and 1.8 and according to the table below prepare calibration standards at the following concentrations in pg/mL (ng/L): 50, 100, 200, 500, 1000, 2000, 5000, 10000, and 20000, except GenX which will be at double these concentrations. The ICAL standards are stable for two weeks when stored at room temperature, or 12 months when stored at 2-6°C. The final compositions of the above solutions contain 96:4% (vol/vol) methanol: water. See Table 5 for a list of analytes and exact concentrations.

ID-Solid ICAL Preparation

PFAS Conc. (pg/mL)	SUR Conc. (pg/mL)	IS Conc. (pg/mL)	PFAS FL PDS 10X	PFAS FL PDS 100X	PFAS FL PDS 1000X	20 ppb SUR	20 ppb IS	Final Volume
			mL	mL	mL	mL	mL	mL
50	1000	1000	-	-	0.125	0.25	0.25	5.00
100	1000	1000	-	-	0.250	0.25	0.25	5.00
200	1000	1000	-	-	0.500	0.25	0.25	5.00
500	1000	1000	-	0.125	-	0.25	0.25	5.00

1000	1000	1000	-	0.250	-	0.25	0.25	5.00
2000	1000	1000	-	0.500	-	0.25	0.25	5.00
5000	1000	1000	0.125	-	-	0.25	0.25	5.00
10000	1000	1000	0.25	-	-	0.25	0.25	5.00
15000	1000	1000	0.375	-	-	0.25	0.25	5.00
20000	1000	1000	0.50	-	-	0.25	0.25	5.00

1.10 The final composition for all the standards in sections 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8 and 1.9 contains 96:4% (v/v) methanol/water.

1.11 Initial Calibration Verification (ICV) – Prepare the ICV according to the sections and the table below. The final composition of the solutions below contains 96:4% (vol/vol) methanol:water.

1.11.1 100X ICV Mix (second source standard containing required target analytes at 0.02 ug/mL or 20ppb) – 100 uL of the secondary lot (different than the lot used to prepare the PDS solutions) of PFAC-24PAR standard mix and 20 uL of GenX secondary standard is diluted to 10 mL with 9.88 mL of methanol. The PFAC-24PAR standard includes all analytes listed in Table 5 except the following: MeFOSA, EtFOSA, 10:2FTS, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUDS, MeFOSE, and EtFOSE.

1.11.2 ICV Sample Solution (500ppt; GenX at 2500ppt) – combine the solutions in sections 1.3, 1.5 and 1.11.1 according to the table below. The final solvent composition of this solution should be 96:4% MeOH: water.

ID-Solid ICV Preparation				
Compound	**Conc. of Stock Std.**	**Aliquoted Volume**	**Dilution Volume**	**Final Conc.**
	pg/mL	µL	mL	pg/mL
PFAS ICV 100X Mix	20000	25	1.0	500
Full List SUR mix, 20ppb	20000	50	1.0	1000
Full List IS mix, 20ppb	20000	50	1.0	1000

1.12 Isomer check – For target compounds which have multiple chromatographic peaks due to branched and linear isomers, but for which quantitative standards are not available, a qualitative check is analyzed with each calibration event to demonstrate the peak shape and retention time of the branched isomers. See Sec. 12.5 for integration information.

1.12.1 Isomer Check 50X Mix – 20 µL each of TPFOA, br-MeFOSAA, and br-EtFOSAA standards (Wellington Laboratories item #s T-PFOA, br-MeFOSAA, and br-EtFOSAA) are diluted to 1 mL with 900 µL of MeOH and 40 µL of reagent water. Final solvent composition is 96:4% MeOH:water. This solution is used to create the actual isomer check standard to be analyzed with each ICAL.

1.12.2 Isomer Check Standard - 10 µL of the Isomer Check 50X Mix plus 50 µL each of the 20 ppb IS and 20 ppb SUR are diluted to 1 mL with 890 µL of 96% MeOH. The concentrations of the isomer components should be approximately 10000 ppt. Final solvent composition is 96:4% MeOH:water. This sample will be analyzed with each calibration event to demonstrate peak shape and retention time of the additional branched isomers of the included compounds.

1.13 Instrument Blank (IBLK) – The instrument blank is prepared by spiking 180 µL 96% MeOH with 10 µL of 20 ppb IS Mix and 10 µL of 20 ppb SUR Mix in an autosampler vial. Cap and vortex to mix. Alternatively, spike 900 µL of 96% MeOH with 50 µL of IS 20ppb mix and 50 µL of SUR 20ppb; cap and vortex to mix, then aliquot into auto-sampler vial.

1.14 Method Blank (MB) – Weigh 1.0g of Ottawa sand into a pre-tared 15mL Falcon tube and spike with 110µL of 100ppb SUR mix. Extract as normal alongside client samples.

1.15 Continuing Calibration Verification/Instrument Sensitivity Check (CCV/ISC) - The CCV and the ISC are prepared in

the same manner. The daily Instrument Sensitivity Check (ISC; DOD required) will be used as the daily opening CCV, and will be analyzed at both the 100ppt and 200ppt levels using prepared ICAL standards. The prepared ICAL standard at the 1000ppt level will be used as the CCV to be analyzed every ten samples and at the conclusion of the analytical run, as closing CCV. Analyte concentrations must be within +/-30% of their true values.

1.16 Laboratory Control Sample (LCS) – The LCS is prepared by spiking approximately 1g of Ottawa sand with 55 µL of Solid Spiking Standard (1000 ng/mL), for a concentration of 55 µg/kg (55000 pg/g; 55000 ng/kg; 55 ng/g). The LCS is also spiked with 110 µL of Full List SUR mix (100 ppb) and extracted as normal alongside client samples.

1.17 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – Client samples are spiked in the same manner as an LCS. 1g of sample is spiked with 55 µL of Solid Spiking Standard (1000 ng/mL) for a concentration of 55µg/kg plus 110µL of Full List SUR mix (100ppb) and extracted as normal alongside other client samples.

1.18 Method Detection Limit (MDL) – MDL sample preparation and analysis will be performed over three separate days. Each MDL sample will be extracted with an equal number of MB samples. The MDL is prepared by spiking approximately 1g of Ottawa sand with 50 µL of 100X PDS mix for a concentration of 1000 pg/g (1000 ng/kg; 1 µg/kg), plus 110µL of Full List SUR mix (100ppb) and extracted as normal. An equal number of MB (see section 1.14 above) will be extracted and analyzed with MDL samples.

1.19 Initial (and Continuing) Demonstration of Capability (IDOC/CDOC) – The IDOC/CDOC is prepared by spiking approximately 1g of Ottawa sand with 55 µL of Solid Spiking Standard (SSS) plus 110µL of Full List SUR mix (100ppb) and extracted as normal. IDOC/CDOC sample final concentration equals 55µg/kg. Four replicates should be prepared and analyzed.

2.1.1 Ammonia-Methanol (Amm-MeOH, 0.3%) – In a 1000 mL graduated cylinder, add 13.52 mL NH4OH (Ammonium Hydroxide) and fill to volume with methanol (986.48 mL reagent MeOH). Invert to mix.

2. Sample Preparation

2.1 Allow samples time to come to room temperature.

2.2 Mix sample with a tongue depressor and/or vigorously shake sample container to ensure sample homogeneity.

2.3 Weigh approximately 1.0 g of sample into a pre-tared 15 mL Falcon tube, record sample weight.

2.4 Spike sample aliquot with 110 µL 100ppb SUR mix; spike QC samples appropriately (LCS, MS/MSD spiked with 55 µL of SSS)

2.5 Add 4 mL MeOH and 4 mL 0.3% Amm-MeOH to sample tube and cap tightly.

2.6 Place sample tubes on orbital shaker table for 30-35mins, on level 9.

2.7 Place samples in a tray and place the tray in a sonic bath at room temperature, sonicate for 30-35mins.

2.8 Remove rack from sonic bath and dry individual sample tubes before placing in a centrifuge and centrifuge at 3000RPM for 5 mins.

2.9 If centrifugation of sample does not fully separate solids from the extraction fluids, the resultant supernatant can be decanted from original sample tube into a clean centrifuge tube by pouring or using a plastic pipette. Decanting the supernatant from poorly separated extracts may help speed up the filtration process.

2.10 Place Strata-GCB SPE tubes, labelled for each sample, into individual active luer ports in the vacuum manifold top.

2.11 Wet rim of manifold body and place manifold top on manifold body. Start the vacuum pump and ensure that a proper seal is formed between the manifold top and body, and vacuum is at a proper level (approximately 5in. Hg).

2.12 Condition the Strata-GCB tubes by passing 3mL MeOH in a slow drop-wise fashion through the tube, discard eluent. Do not dry tubes; if a tube goes dry, restart the conditioning.

2.13 Release vacuum and remove manifold top. Place a rack containing clean, labelled 15mL Falcon tubes in the manifold body and replace the top. Ensure that the correct luer is inserted into the corresponding falcon tube in the manifold body.

2.14 Start vacuum and ensure proper seal and vacuum are achieved.

2.15 Load decanted extracts into corresponding labelled Strata-GCB filtration tubes and begin passing the extracts through the tube in a drop-wise fashion; collect in the previously positioned clean, labelled 15mL Falcon tubes. Not all of the extract will fit at once in the tube, so be ready to load the remainder.

2.16 When the entire extract has eluted through the tube, close the stopcock to keep the tube from drying during the following step.

2.17 Rinse each tube with 2mL of MeOH and collect the eluent in a slow drop-wise fashion.

2.18 Release vacuum, remove manifold top from body, and remove collection tubes. Cap tubes until ready to prepare autosampler vials for injection.

2.19 Add 8µL of reagent water, 10µL of IS mix, and 182µL of extract to a clean, labelled polypropylene autosampler vial. Cap and vortex thoroughly to mix. Ensure there is not an air bubble trapped at the bottom of the insert. This vial is ready for analysis.

2.20 Correction Factors – Correction Factors (CF) will be multiplied by the calculated concentration (Sec. 12.2 of main SOP body) measured by the instrument in order to calculate the actual concentration in the original sample. CF is based on total sample weight extracted, fraction of dry solids in sample, and final extract volume. Dividing by 1000 adjusts the CF so that the actual concentration calculated in the original sample has the unit µg/kg instead of pg/g. The percent solids will be determined as described in SOP ME0013F-03. The CF for solid samples will be calculated as follows:

$$CF = ((V_E/(M \times S)) \times DF)/1000$$

Where:

V_E is the final extract volume (mL)
M is the mass of sample extracted (g)
S is the percent solids of the sample (as a decimal)
DF is the dilution factor. For undiluted analysis, DF = 1/0.91

APPENDIX C. AQUEOUS SERIAL DILUTION

1 Standard Preparation

1.1 IS, SUR, and ICV standard solutions prepared for ID-AQ are used for samples analyzed by serial dilution instead of SPE. See Section 7 in the main body of the SOP for more information on preparation and contents of these solutions.

1.2 Dilutions of individual analyte stock standards are used for fortifying post-spike samples. Typically, these diluted stocks are prepared by a two-step serial dilution for a nominal concentration of 5ppb (some analytes have different concentrations due to differing stock concentrations). These diluted stocks are prepared by diluting 10uL of stock solution with 950uL of MeOH and 40uL of reagent water (FV=1mL), then further diluting 10uL of this initial 100X solution with 990uL of 96% MeOH, for a final dilution of 10,000X. The 10,000X DIL stock solution will typically be used for fortifying post-spike samples.

1.3 ICALs, ICAL standards, and instrument QC (CCVs, IBLKs) are the same as for ID-AQ and all acceptance criteria used for ID-AQ applies.

1.4 Samples analyzed by serial dilution do not require an LCS or MB to be prepared alongside the samples, as no extraction is performed. Daily IBLKs take the place of MBs.

2 Sample Preparation –

Samples of known high PFAS concentrations can be prepared by serial dilution instead of SPE, with documented project approval.

2.1 All solutions prepared for instrumental analysis in this section and Section 3 shall have a solvent composition of 96:4% MeOH:water.

2.2 An initial dilution of the sample is made up with no IS or SUR added, to be used as the base dilution for successive serial dilutions. This initial dilution is typically prepared at 100X.

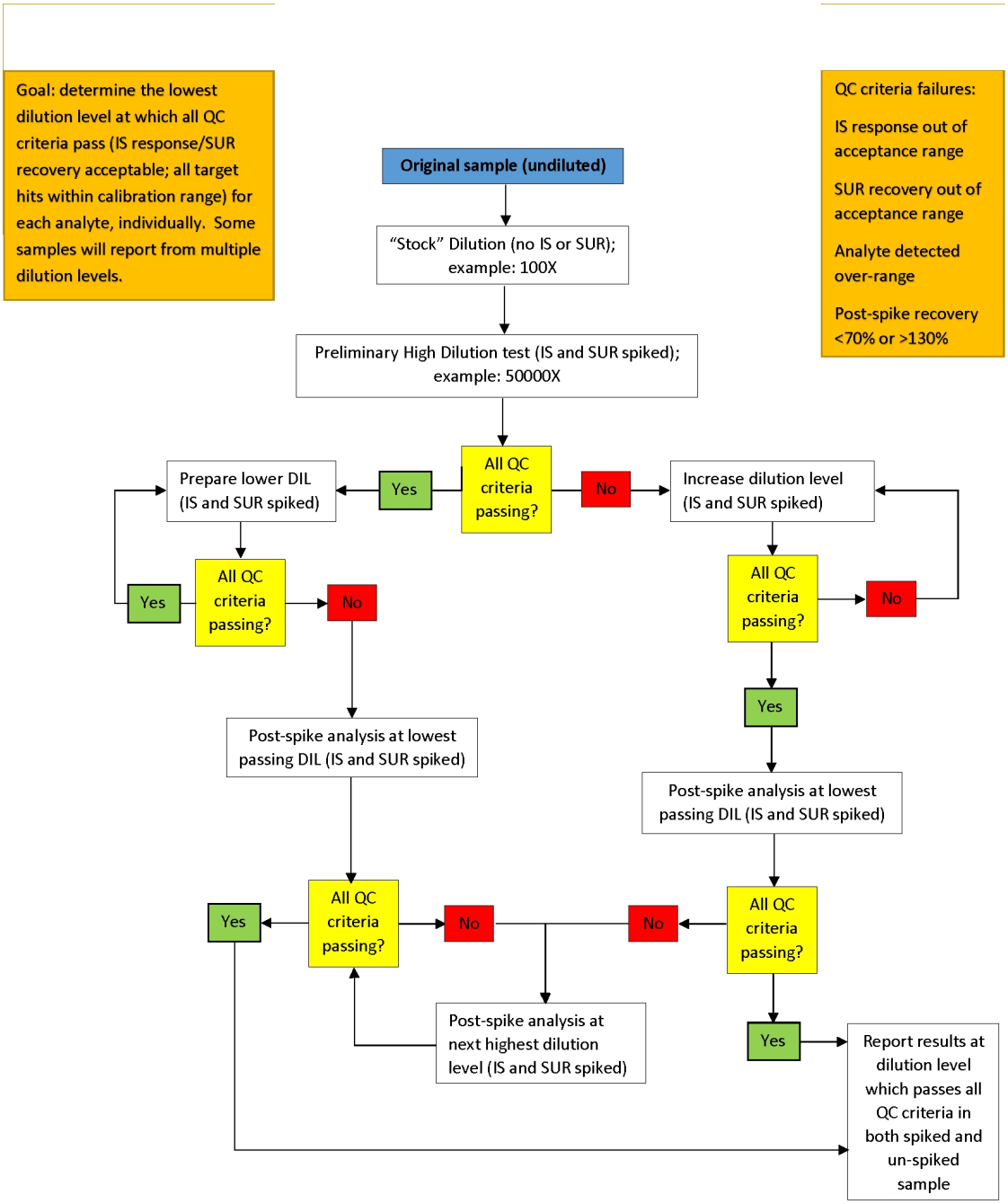
2.3 Using the initial sample dilution, prepare a high dilution (e.g. 50,000X) and analyze it to determine the approximate concentration of target analytes in the samples. Use the information obtained from this analysis to determine the next serial dilution to be prepared. Be sure to include IS and SUR standards at the appropriate concentration in each analyzed serial dilution. IS/SUR compounds should typically be present at a concentration of 1000pg/mL (1ppb).

2.4 Prepare successively lower dilutions of each serial dilution sample until all target analytes fail for over-range detection, IS response being out of acceptance, and/or SUR recovery being out of acceptance. Use the Non-Extracted Method PFAS Serial Dilution Prep Log and Post-spike Log (ME002DR) to record dilution and post-spike preparations. Be sure to include IS and SUR standards at the appropriate concentration in each analyzed serial dilution. No serial dilution samples will be analyzed at a dilution below 25X, in order to maintain proper solvent composition in the analyzed sample.

NOTE: Each target analyte should be evaluated individually in each serial dilution preparation. Associated IS/SUR compounds must pass acceptance criteria for an individual analyte to be reported. If the associated SUR and/or IS for one compound fails in a dilution sample, but *any* others pass, further dilution analysis will be necessary. Once a dilution level is reached in which all targets fail for one of the above-stated reasons, analysis will begin on the post-spiked samples.

2.5 For each target analyte, determine the dilution level at which the sample fails for one of the reasons stated in Section 2.4. The corresponding post-spike sample should be prepared at the next highest dilution level; in other words, determine the lowest dilution level at which a target analyte and its corresponding IS/SUR pass and prepare post-spike samples beginning at that dilution level.

Serial Dilution Decision Tree



3 Post-spike sample preparation – Post-spike samples must be prepared for all serial dilution samples which are ND for any target analyte at the reported dilution level. Non-detected target analytes will be individually spiked into post-spike dilution preparations at an expected on-column concentration equal to the stated LOQ in order to validate the stated LOQ in the sample matrix. If an analyte is detected in a reportable dilution, no post-spiking of that analyte is required; the LOQ will equal the stated LOQ times the dilution factor of the reported analysis.

3.1 Post-spike samples must be prepared at the same dilution level as the reported sample results, and spiked at a concentration equivalent to the LOQ in the diluted sample. Post-spike analysis shall be prepared and evaluated for EACH non-detected analyte in EACH sample.

3.2 Calculate the appropriate amount of 10000X DIL stock solution necessary for the post-spike preparation by using the

following equation:

$$\text{Spike Volume (mL)} = \frac{\text{LOQ(pg/mL)} * \text{final volume(mL)}}{\text{DIL stock(pg/mL)}}$$

3.3 Calculate the appropriate amount of 20ppb SUR and 20ppb IS necessary for the post-spike preparation by using the following equation:

$$\text{Spike Volume(mL)} = \frac{\text{1000(pg/mL)} * \text{final volume(mL)}}{\text{20000(pg/mL)}}$$

3.4 Prepare post-spikes at the reported dilution level for all ND analytes and record all post-spike preparation information using ME002DR. Use this logbook to ensure final volumes are correct and that all post-spike samples have solvent concentrations of 96% MeOH.

3.4.1 The analyte post-spiked into the dilution preparation must recover within 70-130% in order to be acceptable/reportable. All other QC criteria must be met as well (IS, SUR passing; opening/closing CCVs passing; acceptable IBLK).

3.4.2 Only the target analyte(s) being spiked and its corresponding IS/SUR must pass for each individual post-spike sample to be acceptable.

3.4.3 If a spiked analyte does not meet the 70-130% recovery limit, re-prepare the post-spike sample at successively higher dilutions using the steps above until recovery is within acceptance limits and corresponding IS/SUR compounds pass.

3.5 When a post-spike sample passes recovery and other QC criteria for the specific analyte(s) spiked, post-spiking analysis is complete for that sample/analyte combination.

3.6 The dilution reported for any individual analyte shall be the same dilution at which the post-spike sample passes for that analyte. If the initial post-spike sample fails when prepared at the expected reportable sample dilution, the LOQ has not been validated for this dilution level. Therefore, the reported dilution for that analyte/sample will be elevated to match the lowest passing dilution level of the post-spike analysis.

3.7 Report analyte results from the lowest dilution level which passes for all sample and post-spike QC criteria. The LOQ for ND analytes will equal the stated LOQ times the reported dilution factor.

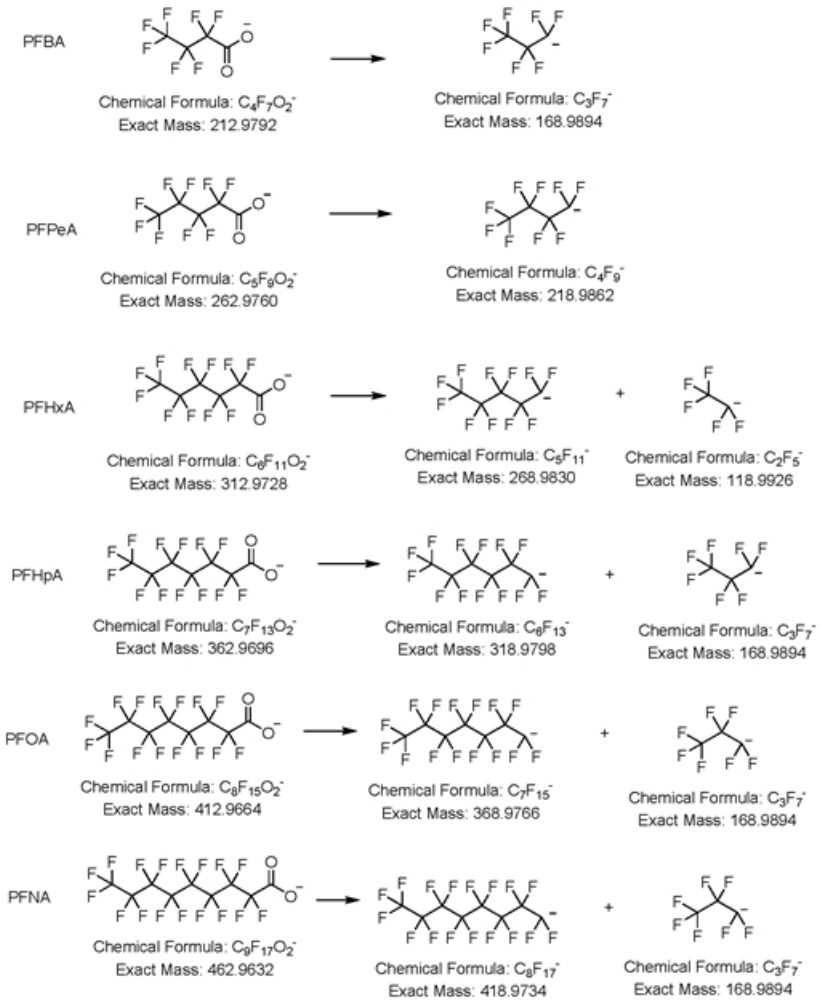
Appendix D. EXTRACT DILUTION PREPARATIONS

Extract Dilution Preparations

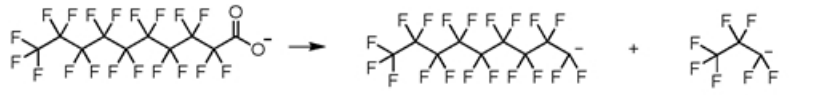
537	1X	5X	10X	20X	50X	100X	200X	500X	1000X	2000X
EXTRACT (uL)	950	200	100	50	20	10	20	8	4	2
IS (uL)	50	40	45	47.5	49	49.5	199	199.6	199.8	199.9
96% MeOH (uL)	-	760	855	902.5	931	940.5	3781	3792.4	3796.2	3798.1
TOTAL (uL)	1000	1000	1000	1000	1000	1000	4000	4000	4000	4000
CF calc	1/Vol	1/(Vol*0.2)	1/(Vol*0.1)	1/(Vol*0.05)	1/(Vol*0.02)	1/(Vol*0.01)	1/(Vol*0.005)	1/(Vol*0.002)	1/(Vol*0.001)	1/(Vol*0.0005)
ID Aq	**1X**	**5X**	**10X**	**20X**	**50X**	**100X**	**200X**	**500X**	**1000X**	**2000X**
EXTRACT (uL)	182	200	100	50	20	10	20	8	4	2
IS (uL)	10	50	50	50	50	50	200	200	200	200
SUR (uL)	0	40	45	47.5	49	49.5	199	199.6	199.8	199.9
MeOH (uL)	0	674	769	816.5	845	854.5	3437	3448	3452	3454
WATER (uL)	8	36	36	36	36	36	144	144	144	144
TOTAL (uL)	200	1000	1000	1000	1000	1000	4000	3999.6	3999.8	3999.9
CF calc	(1/0.91)* (FV/V_o)	5* (FV/V_o)	10* (FV/V_o)	20* (FV/V_o)	50* (FV/V_o)	100* (FV/V_o)	200* (FV/V_o)	500* (FV/V_o)	1000* (FV/V_o)	2000* (FV/V_o)
DAI	**1X**	**5X**	**10X**	**20X**	**50X**	**100X**	**200X**	**500X**	**1000X**	**2000X**
SAMPLE (uL)	700	140	70	35	14	7	14	5.6	2.8	1.4
SUR (uL)	25	25	25	25	25	25	100	100	100	100
MeOH (uL)	275	275	275	275	275	275	1100	1100	1100	1100
Water (uL)	0	560	630	665	686	693	2786	2794.4	2797.2	2798.6
TOTAL (uL)	1000	1000	1000	1000	1000	1000	4000	4000	4000	4000
CF calc	1/.7	1/.14	1/.07	1/.035	1/.014	1/.007	4/.014	4/.0056	4/.0028	4/.0014
ID Solid	**1X**	**5X**	**10X**	**20X**	**50X**	**100X**	**200X**	**500X**	**1000X**	**2000X**
EXTRACT (uL)	182	200	100	50	20	10	20	8	4	2
IS (uL)	10	50	50	50	50	50	200	200	200	200
SUR (uL)	0	40	45	47.5	49	49.5	199	199.6	199.8	199.9
MeOH (uL)	0	674	769	816.5	845	854.5	3437	3448	3452	3454
WATER (uL)	8	36	36	36	36	36	144	144	144	144
TOTAL (uL)	200	1000	1000	1000	1000	1000	4000	3999.6	3999.8	3999.9
CF calc	((V_E/(M*S))/ 0.91)/1000	((V_E/(M*S))/ 0.2)/1000	((V_E/(M*S))/ 0.1)/1000	((V_E/(M*S))/ 0.05)/1000	((V_E/(M*S))/ 0.02)/1000	((V_E/(M*S))/ 0.01)/1000	((V_E/(M*S))/ 0.005)/1000	((V_E/ (M*S))/ 0.002)/1000	((V_E/ (M*S))/ 0.001)/1000	((V_E/ (M*S))/ 0.0005)/1000

NOTE: Dilutions of 100x or below will be prepped in 1-mL FV; dilutions higher than 100x and will be prepped in 4-mL FV.

Appendix E. CHEMICAL DERIVATION OF ION TRANSITIONS



PFDA



Chemical Formula: $C_{10}F_{19}O_2^-$
Exact Mass: 512.9600

Chemical Formula: $C_9F_{19}^-$
Exact Mass: 468.9702

Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894

PFUnA

Chemical Formula: $C_{11}F_{21}O_2^-$
Exact Mass: 562.9568

Chemical Formula: $C_{10}F_{21}^-$
Exact Mass: 518.9670

Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894

PFDoA

Chemical Formula: $C_{12}F_{23}O_2^-$
Exact Mass: 612.9537

Chemical Formula: $C_{11}F_{23}^-$
Exact Mass: 568.9638

Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894

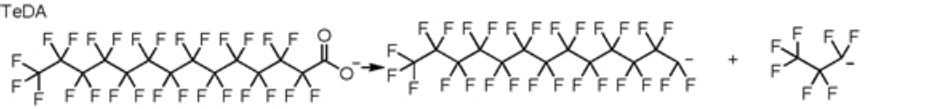
PFTrA

Chemical Formula: $C_{13}F_{25}O_2^-$
Exact Mass: 662.9505

Chemical Formula: $C_{12}F_{25}^-$
Exact Mass: 618.9606

Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894

PFTeDA

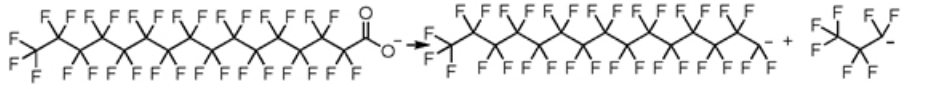


Chemical Formula: $C_{14}F_{27}O_2^-$
Exact Mass: 712.9473

Chemical Formula: $C_{13}F_{27}^-$
Exact Mass: 668.9574

Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894

PFHxDA



Chemical Formula: $C_{16}F_{31}O_2^-$
Exact Mass: 812.9409

Chemical Formula: $C_{15}F_{31}^-$
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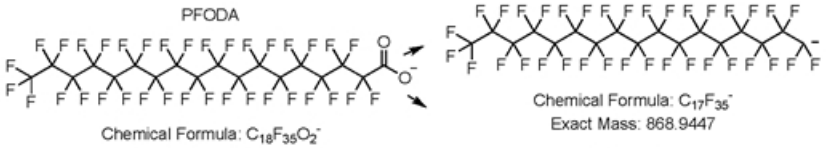
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894

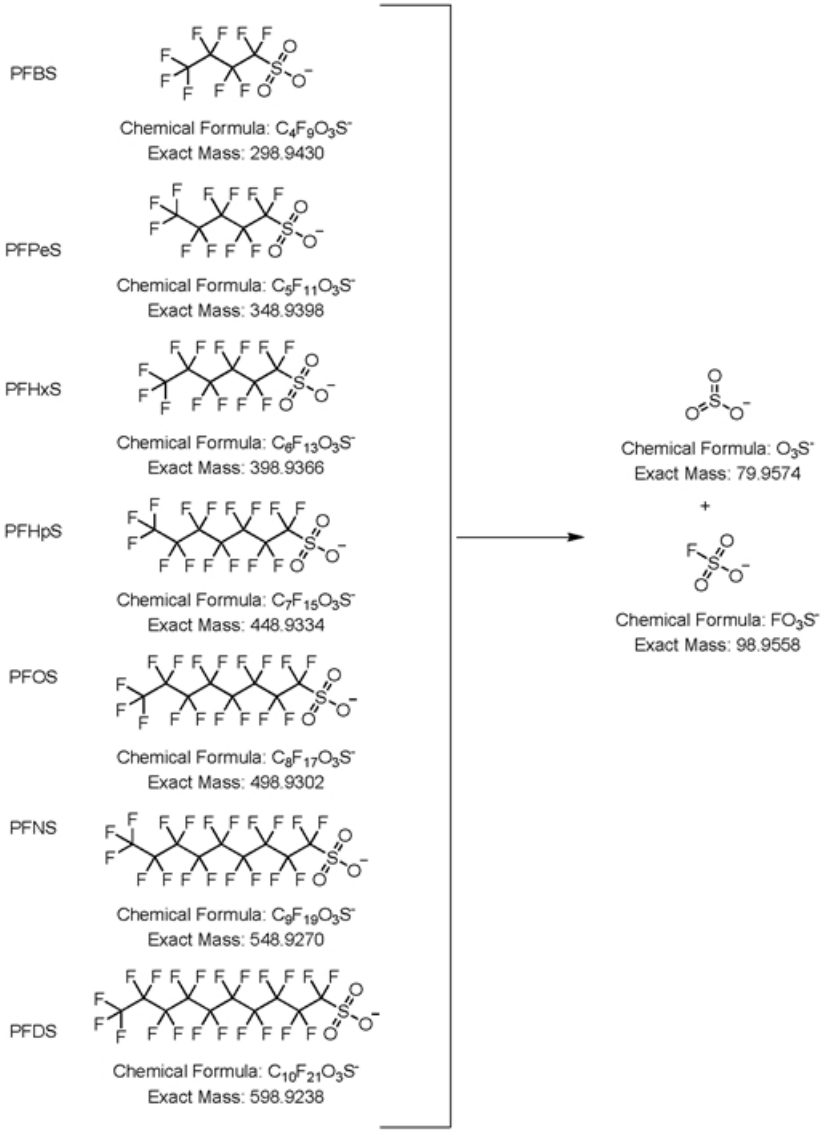
PFODA



Chemical Formula: $C_{18}F_{35}O_2^-$
Exact Mass: 912.9345

Chemical Formula: $C_{17}F_{35}^-$
Exact Mass: 868.9447

Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894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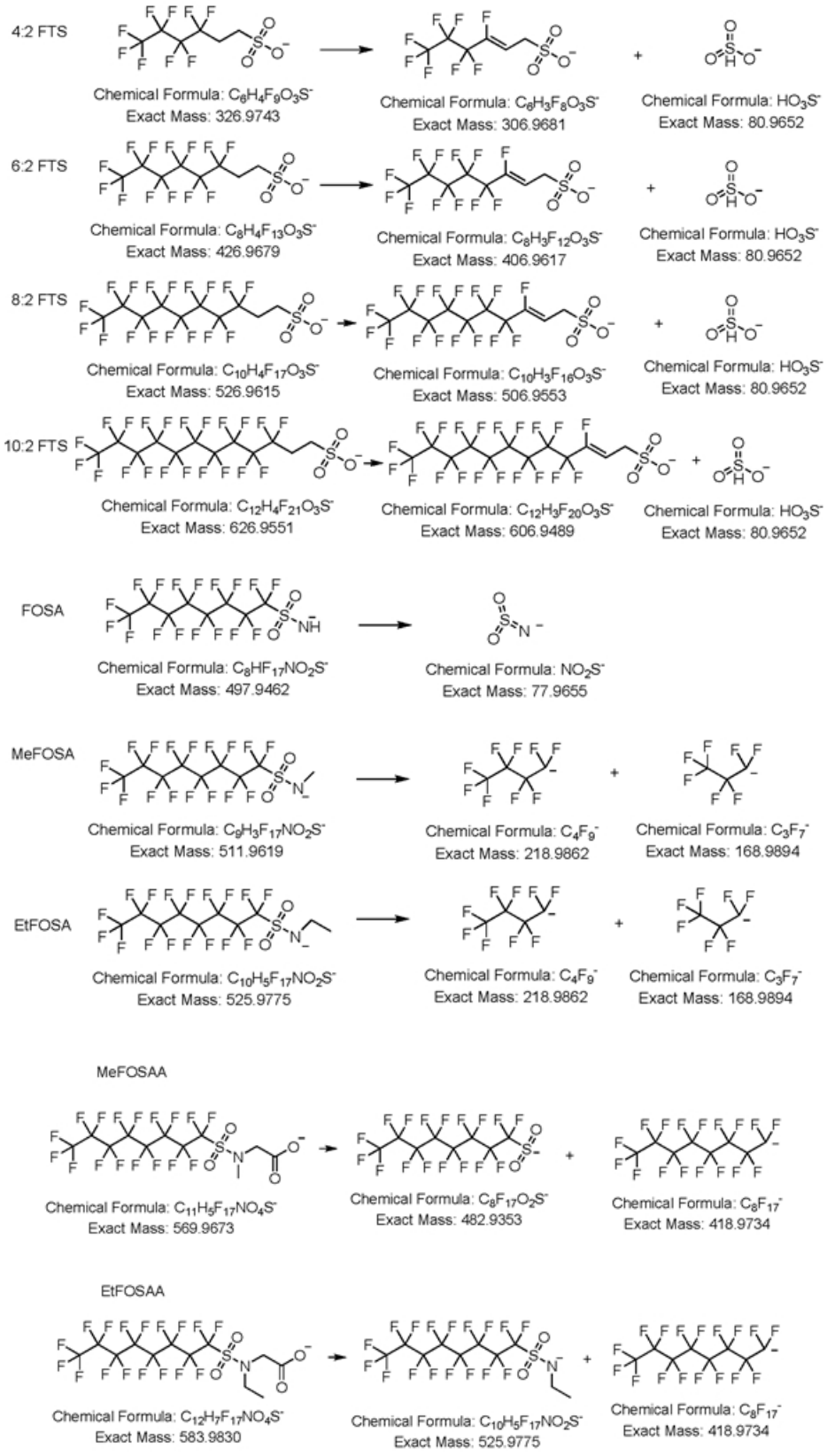
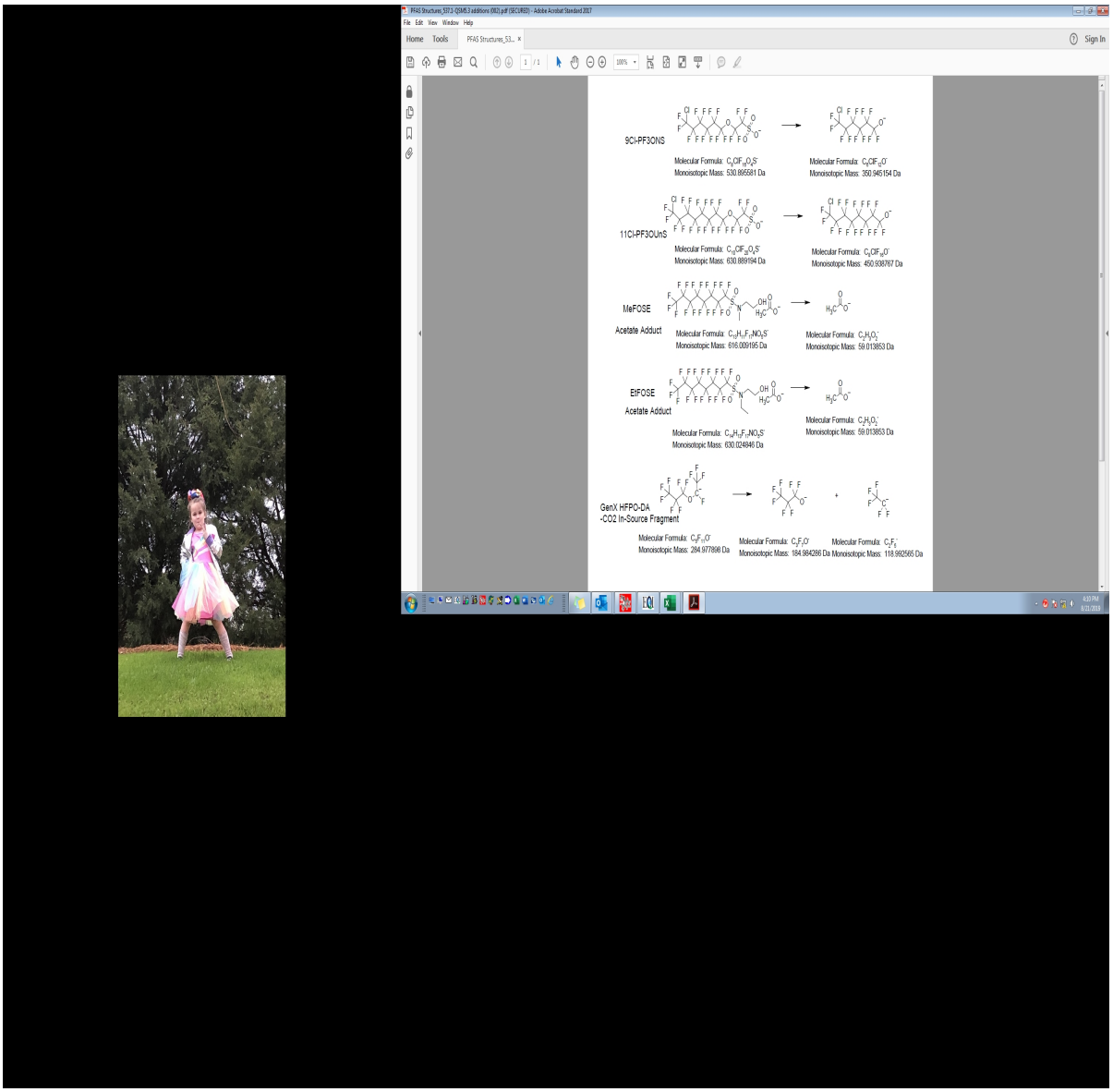
Chemical Formula: $C_4F_9O_3S^-$
Exact Mass: 298.9430
PFPeS
Chemical Formula: $C_5F_{11}O_3S^-$
Exact Mass: 348.9398
PFHxS
Chemical Formula: $C_6F_{13}O_3S^-$
Exact Mass: 398.9366
PFHpS
Chemical Formula: $C_7F_{15}O_3S^-$
Exact Mass: 448.9334
PFOS
Chemical Formula: $C_8F_{17}O_3S^-$
Exact Mass: 498.9302
PFNS
Chemical Formula: $C_9F_{19}O_3S^-$
Exact Mass: 548.9270
PFDS
Chemical Formula: $C_{10}F_{21}O_3S^-$
Exact Mass: 598.9238
Chemical Formula: O_3S^-
Exact Mass: 79.9574
+
Chemical Formula: FO_3S^-
Exact Mass: 98.9558


4:2 FTS
Chemical Formula: $C_6H_4F_9O_3S^-$
Exact Mass: 326.9743
Chemical Formula: $C_6H_3F_8O_3S^-$
Exact Mass: 306.9681
Chemical Formula: HO_3S^-
Exact Mass: 80.9652
6:2 FTS
Chemical Formula: $C_8H_4F_{13}O_3S^-$
Exact Mass: 426.9679
Chemical Formula: $C_8H_3F_{12}O_3S^-$
Exact Mass: 406.9617
Chemical Formula: HO_3S^-
Exact Mass: 80.9652
8:2 FTS
Chemical Formula: $C_{10}H_4F_{17}O_3S^-$
Exact Mass: 526.9615
Chemical Formula: $C_{10}H_3F_{16}O_3S^-$
Exact Mass: 506.9553
Chemical Formula: HO_3S^-
Exact Mass: 80.9652
10:2 FTS
Chemical Formula: $C_{12}H_4F_{21}O_3S^-$
Exact Mass: 626.9551
Chemical Formula: $C_{12}H_3F_{20}O_3S^-$
Exact Mass: 606.9489
Chemical Formula: HO_3S^-
Exact Mass: 80.9652
FOSA
Chemical Formula: $C_8HF_{17}NO_2S^-$
Exact Mass: 497.9462
Chemical Formula: NO_2S^-
Exact Mass: 77.9655
MeFOSA
Chemical Formula: $C_9H_3F_{17}NO_2S^-$
Exact Mass: 511.9619
Chemical Formula: $C_4F_9^-$
Exact Mass: 218.9862
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
EtFOSA
Chemical Formula: $C_{10}H_5F_{17}NO_2S^-$
Exact Mass: 525.9775
Chemical Formula: $C_4F_9^-$
Exact Mass: 218.9862
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
MeFOSAA
Chemical Formula: $C_{11}H_5F_{17}NO_4S^-$
Exact Mass: 569.9673
Chemical Formula: $C_8F_{17}O_2S^-$
Exact Mass: 482.9353
Chemical Formula: $C_8F_{17}^-$
Exact Mass: 418.9734
EtFOSAA
Chemical Formula: $C_{12}H_7F_{17}NO_4S^-$
Exact Mass: 583.9830
Chemical Formula: $C_{10}H_5F_{17}NO_2S^-$
Exact Mass: 525.9775
Chemical Formula: $C_8F_{17}^-$
Exact Mass: 418.9734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Monoisotopic Mass: 530.895581 Da
Molecular Formula: C8ClF16O-
Monoisotopic Mass: 360.945154 Da
11Cl-PF3OUnS
Molecular Formula: C10ClF20O4S-
Monoisotopic Mass: 630.889194 Da
Molecular Formula: C9ClF18O-
Monoisotopic Mass: 450.938767 Da
MeFOSE
Acetate Adduct
Molecular Formula: C23H17F17NO6S-
Monoisotopic Mass: 616.009195 Da
Molecular Formula: C2H3O2-
Monoisotopic Mass: 59.013853 Da
EtFOSE
Acetate Adduct
Molecular Formula: C24H19F17NO6S-
Monoisotopic Mass: 630.024846 Da
Molecular Formula: C2H3O2-
Monoisotopic Mass: 59.013853 Da
GenX HFPO-DA
-CO2 In-Source Fragment
Molecular Formula: C5F11O-
Monoisotopic Mass: 284.977898 Da
Molecular Formula: C5F9O-
Monoisotopic Mass: 184.984286 Da
Molecular Formula: C3F7-
Monoisotopic Mass: 118.992565 Da

Appendix DOD. DOD/DOE QSM REQUIREMENTS

Sections found in this appendix replace and/or supplement the existing sections of the SOP. These requirements must be met when analyzing samples for the Department of Defense, as stipulated in the DOD Quality System Manual.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Aqueous Sample Preparation	Each sample and associated batch QC samples.	Solid Phase Extraction (SPE) must be used unless samples are known to contain high PFAS concentrations (e.g., Aqueous Film Forming Foam (AFFF) formulations). Inline SPE is acceptable. Entire sample plus bottle rinsate must be extracted using SPE. Known high PFAS concentration samples require serial dilution be performed in duplicate. Documented project approval is needed for samples prepared by serial dilution as opposed to SPE.	NA.	NA.	Samples with > 1% solids may require centrifugation prior to SPE extraction. Pre-screening of separate aliquots of aqueous samples is recommended.
Solid Sample Preparation	Each sample and associated batch QC samples.	Entire sample received by the laboratory must be homogenized prior to subsampling.	NA.	NA.	NA.
Biota Sample Preparation	Each sample and associated batch QC samples.	Sample prepared as defined by the project (e.g., whole fish versus filleted fish).	NA.	NA.	NA.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
AFFF and AFFF Mixture Samples Preparation	Each sample and associated batch QC samples.	Each field sample must be prepared in duplicate (equivalent to matrix duplicate). Serial dilutions must be performed to achieve the lowest LOQ possible for each analyte.	NA.	NA.	Adsorption onto bottle is negligible compared to sample concentration so subsampling is allowed. Multiple dilutions will most likely have to be reported in order to achieve the lowest LOQ possible for each analyte.
Sample Cleanup Procedure	Each sample and associated batch QC samples. Not applicable to AFFF and AFFF Mixture Samples.	ENVI-Carb™ or equivalent must be used on each sample and batch QC sample.	NA.	Flagging is not appropriate.	Cleanup should reduce bias from matrix interferences.
Mass Calibration	Instrument must have a valid mass calibration prior to any sample analysis. Mass calibration is verified after each mass calibration, prior to initial calibration (ICAL).	Calibrate the mass scale of the MS with calibration compounds and procedures described by the manufacturer. Mass calibration range must bracket the ion masses of interest. The most recent mass calibration must be used for every acquisition in an analytical run. Mass calibration must be verified to be ±0.5 amu of the true value, by acquiring a full scan continuum mass spectrum of a PFAS stock standard.	If the mass calibration fails, then recalibrate. If it fails again, consult manufacturer instructions on corrective maintenance.	Flagging is not appropriate.	Problem must be corrected. No samples may be analyzed under a failing mass calibration. The mass calibration is updated on an as-needed basis (e.g., QC failures, ion masses fall outside of the ±0.5 amu of the true value, major instrument maintenance is performed, or the instrument is moved).

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Mass Spectral Acquisition Rate	Each analyte, Extracted Internal Standard (EIS) Analyte.	A minimum of 10 spectra scans are acquired across each chromatographic peak.	NA.	Flagging is not appropriate.	NA.
Calibration, Calibration Verification, and Spiking Standards	All analytes.	Standards containing both branched and linear isomers must be used when commercially available. PFAS method analytes may consist of both branched and linear isomers, but quantitative standards that contain the linear and branched isomers do not exist for all method analytes. For PFAS that do not have a quantitative branched and linear standard, identify the branched isomers by analyzing a qualitative standard that includes both linear and branched isomers and determine retention times, transitions and transition ion ratios. Quantitate samples by integrating the total response (i.e., accounting for peaks that are identified as linear and branched isomers) and relying on the initial calibration that uses the linear isomer quantitative standard.	NA.	Flagging is not appropriate.	Standards containing both branched and linear isomers are to be used during method validation and when reestablishing retention times, to ensure the total response is quantitated for that analyte. Technical grade standards cannot be used for quantitative analysis.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Sample PFAS Identification	All analytes detected in a sample.	The chemical derivation of the ion transitions must be documented. A minimum of two ion transitions (Precursor → quant ion and precursor → confirmation ion) and the ion transitions ratio per analyte are required for confirmation. Exception is made for analytes where two transitions do not exist (PFBA and PFPeA). Documentation of the primary and confirmation transitions and the ion ratio is required. In-house acceptance criteria for evaluation of ion ratios must be used and must not exceed 50-150%. Signal to Noise Ratio (S/N) must be ≥ 10 for all ions used for quantification and must be ≥ 3 for all ions used for confirmation. Quant ion and confirmation ion must be present and must maximize simultaneously (±2 seconds).	NA.	PFAS identified with Ion ratios that fail acceptance criteria must be flagged. Any quantitation ion peak that does not meet the maximization criteria shall be included in the summed integration and the resulting data flagged as “estimated, biased high”.	For example: Ion Ratio = (quant ion abundance/ confirm ion abundance) Calculate the average ratio (A) and standard deviation (SD) using the ICAL standards. An acceptance range of ratio could be within A ±3SD for confirmation of detection.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Ion Transitions (Precursor-> Product)	Every field sample, standard, blank, and QC sample.	In order to avoid biasing results high due to known interferences for some transitions, the following transitions must be used for the quantification of the following analytes: PFOA: 413 → 369 PFOS: 499 → 80 PFHxS: 399 → 80 PFBS: 299 → 80 4:2 FTS: 327 → 307 6:2 FTS: 427 → 407 8:2 FTS: 527 → 507 NEtFOSAA: 584 → 419 NMeFOSAA: 570 → 419 If these transitions are not used, the reason must be technically justified and documented (e.g., alternate transition was used due to observed interferences).	NA.	Flagging is not appropriate	NA.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Initial Calibration (ICAL)	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	The isotopically labeled analog of an analyte (Extracted Internal Standard Analyte) must be used for quantitation if commercially available (Isotope Dilution Quantitation). Commercial PFAS standards available as salts are acceptable providing the measured mass is corrected to the neutral acid concentration. Results shall be reported as the neutral acid with appropriate CAS number. If a labeled analog is not commercially available, the Extracted Internal Standard Analyte with the closest retention time or chemical similarity to the analyte must be used for quantitation. (Internal Standard Quantitation) Analytes must be within 70-130% of their true value for each calibration standard. *(continued next page)*	Correct problem, then repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until ICAL has passed. External Calibration is not allowed for any analyte. Calibration can be linear (minimum of 5 standards) or quadratic (minimum of 6 standards); weighting is allowed.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Initial Calibration (ICAL) *(Continued)*		ICAL must meet one of the two options below: Option 1: The RSD of the RFs for all analytes must be ≤ 20%. Option 2: Linear or non-linear calibrations must have $r_2 \geq 0.99$ for each analyte.			
Retention Time window position establishment	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	Calculated for each analyte and EIS.
Retention Time (RT) window width	Every field sample, standard, blank, and QC sample.	RT of each analyte and EIS analyte must fall within 0.4 minutes of the predicted retention times from the daily calibration verification or, on days when ICAL is performed, from the midpoint standard of the ICAL. Analytes must elute within 0.1 minutes of the associated EIS. This criterion applies only to analyte and labeled analog pairs.	Correct problem and reanalyze samples.	NA.	Calculated for each analyte and EIS.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Instrument Sensitivity Check (ISC)	Prior to analysis and at least once every 12 hours.	Analyte concentrations must be at LOQ; concentrations must be within ±30% of their true values.	Correct problem, rerun ISC. If problem persists, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until ISC has met acceptance criteria. ISC can serve as the initial daily CCV.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	Analyte concentrations must be within ±30% of their true value.	Correct problem, rerun ICV. If problem persists, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified.
Continuing Calibration Verification (CCV)	Prior to sample analysis, after every 10 field samples, and at the end of the analytical sequence.	Concentration of analytes must range from the LOQ to the mid-level calibration concentration. Analyte concentrations must be within ±30% of their true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since last successful CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Results may not be reported without valid CCVs. Instrument Sensitivity Check (ISC) can serve as a bracketing CCV.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Instrument Blanks	Immediately following the highest standard analyzed and daily prior to sample analysis.	Concentration of each analyte must be ≤ ½ the LOQ. Instrument Blank must contain EIS to enable quantitation of contamination.	If acceptance criteria are not met after the highest calibration standard, calibration must be performed using a lower concentration for the highest standard until acceptance criteria is met. If sample concentrations exceed the highest allowed standard and the sample(s) following exceed this acceptance criteria (>1/2 LOQ), they must be reanalyzed.	Flagging is only appropriate in cases when the sample cannot be reanalyzed and when there is no more sample left.	No samples shall be analyzed until instrument blank has met acceptance criteria. Note: Successful analysis following the highest standard analyzed determines the highest concentration that carryover does not occur. When the highest standard analyzed is not part of the calibration curve, it cannot be used to extend out the calibration range, it is used only to document a higher concentration at which carryover still does not occur.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Extracted Internal Standard (EIS) Analytes	Every field sample, standard, blank, and QC sample.	Added to solid sample prior to extraction. Added to aqueous samples, into the original container, prior to extraction. For aqueous samples prepared by serial dilution instead of SPE, added to final dilution of samples prior to analysis. Extracted Internal Standard Analyte recoveries must be within 50% to 150% of ICAL midpoint standard area or area measured in the initial CCV on days when an ICAL is not performed.	Correct problem. If required, re-extract and reanalyze associated field and QC samples. If recoveries are acceptable for QC samples, but not field samples, the field samples must be re-extracted and analyzed (greater dilution may be needed). Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure.	Apply Q-flag and discuss in the Case Narrative only if reanalysis confirms failures in exactly the same manner.	Failing analytes shall be thoroughly documented in the Case Narrative. EIS should be 96% (or greater) purity. When the impurity consists of the unlabeled analyte, the EIS can result in a background artifact in every sample, standard and blank, if the EIS is fortified at excessive concentrations.
Method Blank (MB)	One per preparatory batch.	No analytes detected >½ LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater.	Correct problem. If required, re-extract and reanalyze MB and all QC samples and field samples processed with the contaminated blank. Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure. Examine the project-specific requirements. Contact the client as to additional measures to be taken.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid MB. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Laboratory Control Sample (LCS)	One per preparatory batch.	Blank spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then re-extract and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure. Examine the project-specific requirements. Contact the client as to additional measures to be taken.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch. Not required for aqueous samples prepared by serial dilution instead of SPE.	Sample spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference (i.e., matrix effect or analytical error).

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**

Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	For MSD: One per preparatory batch. For MD: Each aqueous sample prepared by serial dilution instead of SPE.	For MSD: Sample spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. RPD ≤ 30% (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is ≥ LOQ. The MD is a second aliquot of the field sample that has been prepared by serial dilution.
Post Spike Sample	Only applies to aqueous samples prepared by serial dilution instead of SPE that have reported value of < LOQ for analyte(s).	Spike all analytes reported as < LOQ into the dilution that the result for that analyte is reported from. The spike must be at the LOQ concentration to be reported for this sample as < LOQ. When analyte concentrations are calculated as < LOQ, the post spike for that analyte must recover within 70-130% of its true value.	When analyte concentrations are calculated as < LOQ, and the spike recovery does not meet the acceptance criteria, the sample, sample duplicate, and post spike sample must be reanalyzed at consecutively higher dilutions until the criteria is met.	Flagging is not appropriate.	When analyte concentrations are calculated as < LOQ, results may not be reported without acceptable post spike recoveries.

REVISION HISTORY

Revision #	Revision Date	Section Modified	Modification	Reason for Modification
-10	10/23/2018	7.14	MDL concentration and preparation procedure updated	Preparation procedure updated to account for concentration update; concentration updated to reflect current LoQ
		7.15	IDOC spike volumes updated from 99 µL to 110µL IDOC spike mix updated from ICV to PDS	Update to account for increase in final volume IDOC not required to be spiked with 2° source
		10	Added reference to Quality Assurance Management Plan and Equipment and Instrumentation SOP	Reference to support equipment standardization/calibration requirements
		10.2.3.1	Entire section regarding IS/SUR suppression was removed	Suppression conditions were not being monitored or reviewed. Removed per client request.
		10.2.4.1	Entire section added	Acceptance criteria not in previous revision
		11.2.1	Spike volume changed from 99µL to 110µL	Update to account for increase in final volume
		11.2.9	Added equated load time	Clarity
		11.2.11	Added requirement to round all sample volumes to the nearest 1.0mL	Clarity
		Table1 Table 2A Table 2B	Updated the following analytes from sulfonate to sulfonicacid: PFBS; PFDS; PFHpS; PFHxS; PFNS; PFOS; PFPeS	Previous references incorrect
		Table1 Table 2A Table 2B	Updated CAS # for the following analytes: PFDS; PFNS	Reflect acids not salts
		Table 3	IS for PFHpS updated from 13C3-PFOS to 13C3-PFHxS; IS for GenX updated from 13C3-GenX to 13C5-PFHxA	Previous references incorrect
		AppB, Section 1.7	SSS expiration date extended from 6mo. to 12 mo.	Based on stock solution expiration date and stability verified during analysis
		AppB, Section 1.8	PDS solution expiration date extended from 6 mo. to 12 mo.	Based on stock solution expiration date and stability verified during analysis
		AppB, Section 1.9	ICAL standard expiration dates extended from 6 mo. to 12 mo.	Based on stock solution expiration date and stability verified during analysis

Revision #	Revision Date	Section Modified	Modification	Reason for Modification
-11	03/13/2019	7.2.2	Added MeFOSE and EtFOSE to table	Scope expansion
		7.5	Added isomer check standards	Method update
		Table 2A&2B	Added ADONA, 9Cl-PF3ONS, 11Cl-PF3OUDS, MeFOSE, and EtFOSE	Scope expansion
		DoD/DoE App.	Replaced Table B-15	QAM update
-12	07/10/2019	Title Page Entire doc.	QSM reference updated to reflect 5.3	Standard update
-13	08/21/2019	App. E	Added structures of ion transitions for GenX, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUDS, MeFOSE,and EtFOSE	Not included in previous revision
-014	11/21/2019	Entire Document	General formatting and editorial updates	Clarity
		6.8	Removed reference to SDVB cartridge	Not used in ID procedure due to failure of analyte recovery
		10.4.1	Added statement "at a concentration at or below the LoQ"	Clarity; define LoQ concentrations of 100ppt and 200ppt
		9.1	Added reference to the Demonstration of Capability SOP; all existing DOC procedures were removed	Maintain reference to currently approved DOC procedures; reduce risk of reference to obsolete procedures
		13	Added reference to the QAMP and Method Validation Policy	Maintain reference to currently approved method validation and performance procedures; reduce risk of reference to obsolete procedures
		1, 2, 7, 8, 9, 10	Added reference to appendices	Reference to location of state and/or program specific method criteria
		3	Definitions removed for the following terms: CCV, LoD, LoQ, LCS, MS, MSD, MB, MDL, ICV, trip blank	Terms defined in QAMP
		App. NJ	Entire appendix added	Inclusion of NJ compliance requirements; refer to initial accreditation correspondences
		6	Removed reference to data software	Reference to software included in major operational equipment list; reduce risk of referencing obsolete information
		10.2	Added requirement for 6 ICAL standards for quadratic regressions	
		Table 6A, 6B	Added note regarding use of limits for DoD/DOE projects	Clarity
		Appendix D	Replaced Table with updated form [ME003JZ]	Reference to form to allow for easier updates if needed.