Ms. Gail A. Dieter
Division of Environmental Remediation
New York State Department of Environmental Conservation – Region 9
625 Broadway, 12th Floor
Albany, New York 12233

Emerging Contaminants Sampling Workplan

Site #932163 – Niagara Highway Garage
7015 Lockport Road
Niagara Falls, New York

August 27, 2018

Emerging Contaminants Sampling Workplan

Site #932163
Niagara Highway Garage
7105 Lockport Road, Niagara Falls, New York

Prepared for:
Ms. Gail A. Dieter
Division of Environmental Remediation
New York State Department of Environmental Conservation
625 Broadway, 12th Floor
Albany, New York 12233-7017

Prepared by:
Groundwater & Environmental Services, Inc.
415 Lawrence Bell Drive, Suite 6
Williamsville, New York 14221
Tel: 800-278-7857
www.gesonline.com

GES Project:
0901749

Date:
August 27, 2018

Eric D. Popken, P.G.
Senior Project Manager

Table of Contents

Figure

Table

Appendix

Acronyms

GES	Groundwater & Environmental Services, Inc.
PFAS	Per-and Polyfluoroalkyl Substances
NYSDEC	New York State Department of Environmental Conservation
HDPE	High density polyethylene
PPE	Personal protective equipment
DUSR	Data Usability Summary Report
SIM	Selective ion monitoring
µg/L	micrograms per liter
MS	Matrix spike
MSD	Matrix spike duplicate
DI	deionized water

1 Introduction

Groundwater & Environmental Services, Inc. (GES) has prepared this workplan to describe the proposed groundwater sampling activities to be conducted at Site #932163 – Niagara Highway Garage (the Site). The purpose of this work is to analyze groundwater for the presence of emerging contaminants, including per- and polyfluoroalkyl substances (PFAS) and 1,4-dioxane. **Table 1** shows the list of the PFAS Target Analytes.

2 Site Background

The Site is a part of the New York State Department of Environmental Conservation (NYSDEC) State Superfund Program and referred to as Site #932163. The Site is located at 7105 Lockport Road, Niagara Falls, New York as shown in the Site Map (**Figure 1**).

The main site features consists of a material storage area for stone, pipe and other construction materials that are used by the Town of Niagara's Highway Department. The site sits at the rear of the property, behind the Highway Garage Building.

3 Emerging Contaminants

The NYSDEC has identified PFAS and 1,4-dioxane as emerging contaminants. PFAS are a group of chemicals used to make fluoropolymer coatings and products that resist heat, oil, stains, grease and water. Fluoropolymer coatings are blends of resins and lubricants used in products such as water-repellent clothing, furniture, adhesives, paint and varnish, food packaging, heat-resistant non-stick cooking surfaces and insulation of electric wires. 1,4-Dioxane is a synthetic industrial chemical that was most commonly used as a stabilizer for chlorinated solvents. Additionally, 1,4-dioxane has been identified as a by-product found in consumer products such as deodorants, shampoos, and cosmetics.

4 Proposed Groundwater Sampling Activities

4.1 Sampling Collection and Analysis

Prior to sampling, groundwater elevation data will be collected from monitoring wells GMW-1 through GMW-5.

Due to potential sources of cross-contamination by equipment, materials, and consumer products during sampling, a specific sampling method must be followed when sampling for PFAS and 1,4-dioxane.

Low flow sampling will be completed at monitoring wells GMW-1 through GMW-5. For each sample set, PFAS samples will be collected first to minimize contact with other sample containers and packing materials.

Each low flow sampling set-up will include a YSI 6920 MP Sonde (or equivalent) with Flow Cell attachment to monitor groundwater quality stability prior to sampling. To conduct low-flow

sampling, a Geotech Geopump Peristaltic Pump (or equivalent) will be set up at each monitoring well. High density polyethylene (HDPE) tubing will be inserted into the well to recover groundwater and silicon tubing will be utilized at the pump and YSI interface.

The sampling team will wear personal protective equipment (PPE), field clothing, and personal hygiene products that will not contaminate the samples. The sampling team will wear field clothing that are well-laundered and made of cotton. No cosmetics, moisturizers, hand cream, or related products will be applied to the sampling team the morning of the sampling. Additionally, no sun screen or insect repellent will be applied the day of the sampling event.

Nitrile gloves will be worn at all times during the sampling event and changed frequently. Alconox will be used to decontaminate equipment before and after sampling at each monitoring well. Further details are provided in GES Standard Operating Procedure for collection of PFAS samples (**Appendix A**). GES field forms are also provided in **Appendix A**.

Recovered groundwater will be sampled using laboratory supplied bottleware (HDPE without teflon) with a dedicated cooler for both PFAS and 1,4-dioxane samples. Upon completion of sampling activities, the coolers will be delivered to the TestAmerica Laboratory. PFAS samples will be sampled for analysis using the modified EPA method 537. Samples will also be analyzed for 1,4-Dioxane via method 8270D in selective ion monitoring (SIM) mode. TestAmerica will provide a full category B deliverable. TestAmerica's SOPs are provided in **Appendix A**.

4.2 Quality Assurance/Quality Control

Care will be taken during all aspects of the sample collection to ensure that high quality data is obtained. Equipment blanks (one sample), duplicate samples (one sample), and matrix spike and matrix spike duplicate (MS/MSD) samples (one sample) will be submitted for analysis for quality assurance of both the sample collection procedure and the laboratory method. All samples will be submitted via courier to the necessary laboratories for analysis under proper chain of custody.

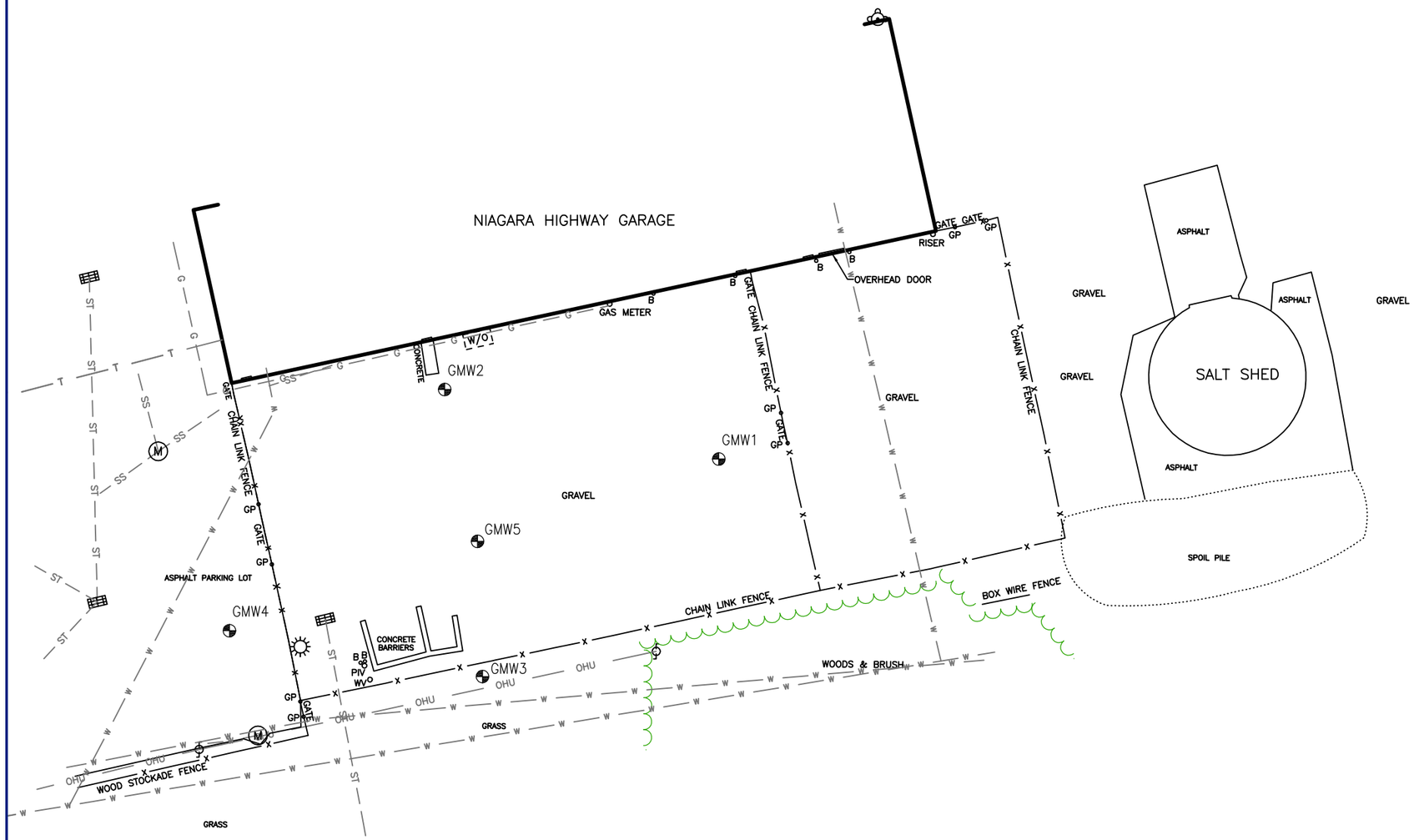
GES will subcontract a third party data validator to prepare a Data Usability Summary Report (DUSR) in accordance with NYSDEC Division of Environmental Remediation (DER-10) Guidance.

5 Reporting Activities

5.1 Summary Report

GES will prepare a summary report, outlining the sampling activities performed, as well as provide the field data collected and the laboratory analytical reports generated by the laboratory. In addition, GES will prepare and upload the electronic data deliverable (EDD) into NYSDEC's EQuIS Database. The uploaded EDD will include any qualifiers that are added by the third party data validator as part of the DUSR submittal.

Figure



LEGEND

- PROPERTY BOUNDARY
- W/O WASTE OIL TANK
- CATCH BASIN
- FIRE HYDRANT
- LIGHT POLE
- UTILITY POLE
- M UTILITY MANHOLE
- MONITORING WELL
- SS UNDERGROUND SANITARY SEWER LINE
- ST UNDERGROUND STORM SEWER LINE
- W UNDERGROUND WATER LINE
- G UNDERGROUND GAS LINE
- OHU OVERHEAD UTILITIES
- T UNDERGROUND TELEPHONE LINE

DRAFTED BY: W.G.S. (N.J.)	SITE MAP
CHECKED BY:	NYSDEC NIAGARA HIGHWAY GARAGE 7105 LOCKPORT ROAD NIAGARA FALLS, NEW YORK
REVIEWED BY:	Groundwater & Environmental Services, Inc. 495 AERO DRIVE, SUITE 3, CHEEKTOWAGA, NEW YORK 14225
NORTH	SCALE IN FEET: 0 APPROXIMATE 50 / DATE: 2-27-15 / FIGURE: 1

M:\Graphics\0900-Buffalo\NYSDEC\Niagara Falls (Highway Garage)\Niagara Falls (Highway Garage) SM.dwg, B-50, 2/27/2015 1:49:16 PM, WShea

Table

Table 1

Full PFAS Target Analyte List

Group	Chemical Name	Abbreviation	CAS Number
Perfluoroalkyl sulfonates	**Perfluorobutanesulfonic acid**	**PFBS**	**375-73-5**
	Perfluorohexanesulfonic acid	**PFHxS**	**355-46-4**
	Perfluoroheptanesulfonic acid	PFHpS	375-92-8
	Perfluorooctanesulfonic acid	**PFOS**	**1763-23-1**
	Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluoroalkyl carboxylates	Perfluorobutanoic acid	PFBA	375-22-4
	Perfluoropentanoic acid	PFPeA	2706-90-3
	Perfluorohexanoic acid	PFHxA	307-24-4
	Perfluoroheptanoic acid	**PFHpA**	**375-85-9**
	Perfluorooctanoic acid	**PFOA**	**335-67-1**
	Perfluorononanoic acid	**PFNA**	**375-95-1**
	Perfluorodecanoic acid	PFDA	335-76-2
	Perfluoroundecanoic acid	PFUA/PFUdA	2058-94-8
	Perfluorododecanoic acid	PFDoA	307-55-1
	Perfluorotridecanoic acid	PFTriA/PFTrDA	72629-94-8
	Perfluorotetradecanoic acid	PFTA/PFTeDA	376-06-7
Fluorinated telomer sulfonates	6:2 Fluorotelomer sulfonate	6:2 FTS	27619-97-2
	8:2 Fluorotelomer sulfonate	8:2 FTS	39108-34-4
Perfluorooctane-sulfonamides	Perfluroroctanesulfonamide	FOSA	754-91-6
Perfluorooctane-sulfonamidoacetic acids	N-methyl perfluorooctanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9
	N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6

Bold entries depict the six original UCMR3 chemicals.

Appendix A – Standard Operating Procedures

Standard Operating Procedure

Title: Media Sampling for Per- and Poly-Fluoroalkyl Substances (PFAS)

1. Purpose/Scope

The objective of this standard operating procedure is to provide additional direction and guidance for collection of samples (groundwater, drinking water, surface water, soil, sediment, soil gas, and vapors) for PFAS analysis. This information includes personal protective equipment (PPE) and sampling equipment and materials. PFAS analyses require extremely low detection limits (parts per trillion), and there are many potential sources of cross-contamination by common equipment, materials, and consumer products.

2. References

For additional information pertaining to groundwater sampling activities, the user of this manual may reference the following:

- Bartlett, Samuel A and Davis, Katherine L. Evaulating PFAS Cross Contamination Issues. Wiley Periodicals, Remediation. 2018;28:53-57.
- Department of Defense (DoD) Environment, Safety and Occupational Health Network and Information Exchange (DENIX) (2017): Bottle Selection and other Sampling Considerations When Sampling for Per- and Poly-Fluoroalkyl Substances (PFAS)
- GES SOP FM 4.1: Soil Boring Advancement
- GES SOP FM 4.5: Gas Probe Installation for Landfills
- GES SOP FM 5.6: Monitor Well Development
- GES SOP FM 8.3: Groundwater Sampling Acquisition
- GES SOP FM 8.5: Low-Flow Groundwater Sampling
- GES SOP FM 8.7: Well Purging Prior to Sample Collection
- GES SOP FM 8.12: Residential Well Sampling
- GES SOP FM 9.1: Soil Sampling for Analysis
- GES SOP FM 9.2: Standard Penetration Test (SPT) for Collecting Soil Samples Using a Split Spoon Sampler (SSS)
- GES SOP FM 9.4: Surficial Soil Sampling
- GES SOP FM 9.6: Soil Sampling in Test Pits and Trenches

- GES SOP FM 10.1: Surface Water and Sediment Sampling
- GES SOP FM 11.3: Soil Gas Sampling for Preliminary Site Characterization
- GES SOP FM 13.2: Sample Preservation and Handling
- GES SOP FM 13.3: Sample Identification and Labeling
- GES SOP FM 13.5: Sample Management, Packing, and Shipping
- GES SOP FM 14.1: Decontamination of Non-dedicated Sampling Equipment
- GES SOP FM 14.3: Field Personnel Decontamination
- GES SOP FM 20.1: Waste Sampling
- Government of Western Australia Department of Environmental Regulation (2016): Interim Guideline of the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS)
- ITRC (2018): Site Characterization Tools, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS) Fact Sheet
- Massachusetts Department of Environmental Protection (MassDEP) (2017): Draft Fact Sheet Guidance on Sampling and Analysis for PFAS at Disposal Sites Regulated Under the Massachusetts Contingency Plan
- Minnesota Pollution Control Agency (MPCA) Petroleum Remediation Program (2017): Groundwater Sample Collection and Analysis Procedures
- New Hampshire Department of Environmental Services (NHDES) (2016): Sampling for Per- and Polyfluoroalkyl Substances/Perfluorinated Chemicals (PFASs/PFCs) at Contaminated Sites

3. Equipment/Materials

Regarding PFAS, it critical that sampling equipment and materials do not contain materials that may themselves be manufactured in processes using PFAS (e.g., Teflon) or when PFAS may adsorb to the material (e.g., LDPE, glass). The table below identifies prohibited and acceptable materials for sampling when one or more PFAS are analyzed.

☒ Prohibited	☑ Acceptable
Field Equipment	
Teflon-containing materials (tubing, bailers, plumbing tape and paste)	HDPE-containing materials
LDPE materials including tubing	Acetate liners (direct push)

Standard Operating Procedure

☒ Prohibited	☑ Acceptable
Waterproof field books	Silicon tubing
Plastic clipboards, binders, spiral hard-cover notebooks	Aluminum or Masonite clipboards
Chemical (blue) ice packs	Ice
Decontamination	
Decon 90	Alconox and/or Liquinox
Sample Containers	
LDPE or glass containers	HDPE and polypropylene
Teflon-lined caps	Unlined polypropylene caps
PPE and Field Clothing	
New cotton clothing or synthetic water-resistant, waterproof, or stain-treated clothing	Well-laundered clothing made of natural fibers (cotton preferred)
Tyvek and clothing containing Gore-Tex	Cotton clothing
Clothing laundered using fabric softener	No fabric softener
Boots containing Gore-Tex	Boots made with polyurethane and PVC
Waterproof or resistant rain gear	Polyurethane or wax-coated materials
Personal Hygiene	
Apply NO cosmetics, moisturizers, hand cream, or other related products on the morning of sampling	Sunscreens : Alba Organics Natural Sunscreen, Yes To Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss my face, Baby sunscreens that are “free” or “natural” Insect Repellents: Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus Insect repellant, Herbal Armor, California Baby Natural Bug Spray, BabyGanics, Off! Deep Woods, Sawyer Permethrin Insect Repellent Treatment for Clothing, Gear, and Tents, Sunscreen/insect repellants: Avon Skin-So-Soft Bug Guard Plus – SPF 30 Lotion Clothing: InsectShield Pretreated Clothing
Avoid using paper towels if possible	Mechanical hand dryer (after washing hands), instant/waterless hand sanitizer (Purell is fluorinated chemical free)
Other Sampling Considerations	
Water from an on-site well	Potable water from municipal drinking water supply

☒ Prohibited	☑ Acceptable
Food and drink	Bottled water and hydration fluids only; deliver and consume in staging areas only
Post-It Notes, Sharpie and other markers	Ball point pens
Aluminum foil	
Vehicles with water/stain-proofing coatings (e.g., Scotch Guard)	

4. Additional Procedures

- Obtain bottle ware from the laboratory in a dedicated cooler containing only PFAS sampling containers if possible.
- Collect PFAS samples from each location prior to other analytes to minimize contact with other sample containers and packing materials. Keep the PFAS sampling containers (before and after collecting samples) separate (e.g., separate coolers).
- PFAS stratify in solution and accumulate at the air/water interface. Consider this stratification in selecting the sample depth of surface water bodies.
- When collecting surface water samples, triple rinse the sample container with PFAS-free water or the surface water to be sampled. If extension rods/handles are necessary to collect the sample, the extension rod/handle must be PFAS-free material and similarly triple-rinsed.
- When using bailers, use non-coated string/twine.
- Wear disposable nitrile gloves at all times.
- If field blanks are collected, collect them first to most accurately represent potential PFAS introduction to samples.
- Don new disposable nitrile gloves prior to the following activities at each sample location.
    - Decontamination of re-usable equipment
    - Prior to contact with sample bottles or water containers
    - Insertion of anything into the well (e.g., HDPE tubing, HydraSleeve bailer)
    - Insertion of silicon tubing into a peristaltic pump
    - Completion of well purging prior to sampling
    - Handling quality assurance/quality control samples, including field blanks and equipment blanks

  - After handling non-dedicated sampling equipment, contact with non-decontaminated surfaces, and when judged necessary by field personnel
- Do not place bottle ware caps on any surface during sampling collection and avoid contact with the inside of the bottle and cap.
- Label containers using pen after caps have been placed on each bottle.
- Place samples for PFAS in sealed plastic bags (e.g., Ziploc) to keep separate from other sample bottle ware, preferably in a dedicated PFAS sampling cooler.
- Use only PFAS-free water for decontamination and label containers storing decontamination water "PFAS-free." This includes sampling equipment and large equipment (e.g., drill rigs).
- Single-use (disposable) or dedicated sampling equipment is preferred to reuse of sampling equipment across multiple sampling locations.
- Confirm materials of construction of sampling equipment (e.g., sample pump o-rings/elastomers and bladders, tubing). Verify rather than assume materials of construction.
- Ensure tubing is HDPE (e.g., "poly" tubing may be HDPE or LDPE). Many types of tubing appear similar. Preferably, purchase/use tubing labeled by the manufacturer on the tubing. If new HDPE tubing is not labeled by the manufacturer, label the tubing and/or reel with "HDPE," the manufacturer name, vendor name, and part number.
- When sampling during precipitation events, field samples should wear appropriate clothing that does not pose a risk for cross-contamination.
- Consider using a gazebo-style tent that is only touched prior to and at the completion of sampling. Change gloves prior to collecting samples.
- If PPE such as personal floatation devices are necessary during surface water and sediment sampling, select PFAS-free PPE without waterproof coatings.
- Well-laundered clothing is that which has been washed at least three times and preferably six times prior to donning for PFAS sampling.
- New untreated leather boots may be worn with polypropylene, polyethane, or PVC boot covers. Well-worn leather boots may be worn.
- If 1,4-Dioxane is also an analyte, do not use Liquinox during decontamination.
- If visitors are present on-site, request that they remain outside of the sampling area. If necessary, stop work until the visitor has departed.

5. Unknown Materials of Construction

Materials that will come in direct contact with the media being sampled (e.g., groundwater, surface water, soil) must be evaluated in detail if the materials of construction are have not been evaluated for PFAS or are unknown. To be "known," the materials of construction/ingredients must be indicated as acceptable in this SOP or documented to be PFAS-free by the manufacturer. This also includes materials such as lubricants and fluids used during drilling. These materials must be evaluated by the project chemist.

Materials that will not come in direct contact with the media being sampled by could be reasonably expected to contain PFAS and may come in contact with sample containers, packing material, and sampling personnel must also be evaluated. These materials can be evaluated by the project manager using the safety data sheet (SDS) for the material. No PFAS-containing materials are permissible. Typical indicators of PFAS are "fluoro," "PTFE," "FEP," "TPE," "ETFE," and "PFA." If the SDS does not indicate PFAS, confirm acceptability with the project chemist.

6. Records

In addition to standard record keeping using the materials described herein, complete the Daily PFAS Sampling Procedure Checklist (Attachment A) to document compliance with this SOP.

Standard Operating Procedure

Attachments

Daily PFAS Sampling Checklist

DAILY PFAS SAMPLING CHECKLIST

Client Name: _____

Site Name: _____

Address: _____

GES PM: _____

Completed By: _____ **Date:** _____

THIS FORM IS TO BE COMPLETED DAILY DURING PFAS SAMPLING FOR ALL MEDIA

Field Equipment			
☐	No Teflon-containing materials on-site	☐	No chemical blue ice on-site
☐	No waterproof field books, plastic clipboards, binders, or spiral hard cover notebooks on-site	☐	All sample materials made from stainless steel, HDPE, acetate, silicon, or polypropylene
Decontamination			
☐	Alconox of Liquinox to be used	☐	PFAS-free water to be used
Sample Containers			
☐	All sample containers made of HDPE or polypropylene	☐	Caps are unlined and made of HDPE or polypropylene
PPE and Field Clothing			
☐	No waterproof or resistant rain gear or clothing or boots containing Gore-Tex or Tyvek	☐	Field crew has not used fabric softener on clothing
Personal Hygiene			
☐	Field crew has not used cosmetics, moisturizers, hand cream, or other related product this morning	☐	Field crew has not applied prohibited sunscreen or insect repellent
Other Sampling Considerations			
☐	No food or drink on-site exception for bottled water and hydration drinks in staging area	☐	No Post-It Notes on-site
☐	No aluminum foil on-site	☐	Using ball point pens; no markers

IF ANY APPLICABLE BOXES CANNOT BE CHECKED, THE FIELD LEAD SHALL DESCRIBE THE NONCOMPLIANCE ISSUES BELOW AND WORK WITH FIELD PERSONNEL TO ADDRESS NONCOMPLIANCE ISSUES PRIOR TO COMMENCEMENT OF THAT DAY'S WORK. CORRECTIVE ACTION SHALL INCLUDE REMOVAL OF NONCOMPLIANCE ITEMS FROM THE SITE OR REMOVAL OF WORKER OFFSITE UNTIL IN COMPLIANCE.

Describe the noncompliance issues (include personnel not in compliance) and action/outcome of noncompliance: _____

Field Lead Name: _____

Field Lead Signature: _____ **Time**: _____

Title: Per- and Polyfluorinated Substances (PFAS) in Water, Soils, Sediments and Tissue

[Method 537 (Modified), Method PFAS by LCMSMS Compliant with QSM 5.1 Table B-15]

Approvals (Signature/Date):

Robert Hrabak — Date 6/14/18
Technical Manager

Joe Schairer — Date 6/20/18
Health & Safety Manager / Coordinator

Lisa Stafford — Date 6/13/2018
Quality Assurance Manager

Crystal Pollock — Date 6.19.18
Laboratory Manager

1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of water, soil, sediment, and tissue samples for the following compounds using liquid chromatography / tandem mass spectrometry (LC/MS/MS).

Compound Name	Abbreviation	CAS #
Perfluoroalkylcarboxylic acids (PFCAs)		
Perfluoro-n-butanoic acid	PFBA	375-22-4
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3
Perfluoro-n-hexanoic acid	PFHxA	307-24-4
Perfluoro-n-heptanoic acid	PFHpA	375-85-9
Perfluoro-n-octanoic acid	PFOA	335-67-1
Perfluoro-n-nonanoic acid	PFNA	375-95-1
Perfluoro-n-decanoic acid	PFDA	335-76-2
Perfluoro-n-undecanoic acid	PFUdA (PFUnA)	2058-94-8
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8
Perfluoro-n-tetradecanoic acid	PFTeDA (PFTA)	376-06-7
Perfluoro-n-hexadecanoic acid (non-routine analyte)	PFHxDA	67905-19-5
Perfluoro-n-octadecanoic acid (non-routine analyte)	PFODA	16517-11-6
Perfluorinated sulfonic acids (PFSAs)		
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5
Perfluoro-1-pentanesulfonic acid	PFPeS	2706-91-1
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4
Perfluoro-1-heptanesulfonic acid	PFHpS	375-92-8
Perfluoro-1-octanesulfonic acid	PFOS	1763-23-1
Perfluoro-nonanesulfonic acid	PFNS	8789-57-2
Perfluoro-1-decanesulfonic acid	PFDS	335-77-3
Perfluorinated sulfonamides (FOSA)		
Perfluoro-1-octanesulfonamide	FOSA	754-91-6
Perfluorinated sulfonamidoacetic acids (FOSAA)		
N-ethylperfluoro-1-octanesulfonamidoacetic acid	EtFOSAA	2991-50-6
N-methylperfluoro-1-octanesulfonamidoacetic acid	MeFOSAA	2355-31-9
Fluorotelomer sulfonates (FTS)		
1H,1H,2H,2H-perfluorohexane sulfonate *(4:2)*	4:2 FTS	757124-72-4
1H,1H,2H,2H-perfluorooctane sulfonate *(6:2)*	6:2 FTS	27619-97-2
1H,1H,2H,2H-perfluorodecane sulfonate *(8:2)*	8:2 FTS	39108-34-4

Abbreviations in parenthesis are the abbreviations listed in Method 537, where they differ from the abbreviation used by the laboratory's LIMS.

1.2. Additional analytes supported by this method: The following analytes can be supported by this method under special request.

Compound Name	Abbreviation	CAS #
Fluorinated Replacement Chemicals		
Adona	Adona	958445-44-8
Perfluoro(2-propoxypropanoic) acid	HFPO-DA or GenX	13252-13-6
F53B (reported as the summation of the following)	F53B	NA
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonate	F53B major	73606-19-6
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonate	F5B minor	83329-89-9

1.3. The working range of the method is listed below. The linear range can be extended by diluting the extracts.

Matrix	Nominal Sample Size	Reporting Limit	Working Range
Water	250 mL	2.0 ng/L – 20 ng/L	2.0 ng/L - 400 ng/L
Soil/Sediment	5 g	0.2 ug/kg – 2.0 ug/kg	0.2 ug/kg - 40 ug/kg
Tissue	1 g	1.0 ug/kg – 10 ug/kg	1.0 ug/kg – 200 ug/kg

1.4. The procedure for the analysis of water samples via in line solid phase extraction (SPE) for a subset of the list in Section 1.1 using liquid chromatography / tandem mass spectrometry (LC/MS/MS) on a SCIEX 5500 is described in Attachment 1 of this SOP.

1.5. This procedure also includes direction for preparing and analyzing samples to determine “Total Oxidizable Precursors”, which may assist in improving understanding of potential PFAS environmental risk.

1.6. When undertaking projects for the Department of Defense (DoD) and/or the Department of Energy (DOE) the relevant criteria in QA Policy WS-PQA-021, “Federal Program Requirements” must be checked and incorporated.

2. SUMMARY OF METHOD

2.1. Water samples are extracted using a solid phase extraction (SPE) cartridge. PFAS are eluted from the cartridge with an ammonium hydroxide/methanol solution.

2.2. Soil/sediment/tissue samples are extracted with a KOH/methanol solution using an orbital shaker for 3 hours followed by sonication for 12 hours. The mixture is centrifuged and the solvent filtered.

2.3. The final 80:20 methanol:water extracts are analyzed by LC/MS/MS. PFAS are separated from other components on a C18 column with a solvent gradient program

using 20 mM ammonium acetate/water and methanol. The mass spectrometer detector is operated in the electrospray (ESI) negative ion mode for the analysis of PFAS.

2.4. An isotope dilution technique is employed with this method for the compounds of interest. The isotope dilution analytes (IDA) consist of carbon-13 labeled analogs, oxygen-18 labeled analogs, or deuterated analogs of the compounds of interest, and they are spiked into the samples at the time of extraction. This technique allows for the correction for analytical bias encountered when analyzing more chemically complex environmental samples. The isotopically labeled compounds are chemically similar to the compounds of concern and are therefore affected by sample-related interferences to the same extent as the compounds of concern. Compounds that do not have an identically labeled analog are quantitated by the IDA method using a closely related labeled analog.

2.5. Quantitation by the internal standard method is employed for the IDA analytes/recoveries. Peak response is measured as the area of the peak.

2.6. Samples for the "Total Oxidizable Precursor" assay (TOP) are analyzed in two phases – an aliquot is prepared and analyzed as a normal sample, and a second aliquot is subjected to oxidation with potassium persulfate and sodium hydroxide prior to solid phase extraction and analysis. The total perfluorocarboxylic acid value is determined for each aliquot, and the difference calculated.

3. DEFINITIONS

3.1. PFCAs: Perfluorocarboxylic acids

3.2. PFSAs: Perfluorinated sulfonic acids

3.3. FOSA: Perfluorinated sulfonamide

3.4. PFOA: Perfluorooctanoic acid

3.5. PFOS: Perfluorooctane sulfonic acid

3.6. MPFOA: Perfluoro-n-[1,2,3,4-13C4]octanoic acid. Carbon-13 labeled PFOA

3.7. MPFOS: Perfluoro-1-[1,2,3,4-13C4]octanesulfonic acid. Carbon-13 labeled PFOS

3.8. PTFE: Polytetrafluoroethylene (e.g., Teflon®)

3.9. SPE: Solid phase extraction

3.10. PP: Polypropylene

3.11. PE: Polyethylene

3.12. HDPE: High density polyethylene

3.13. AFFF: Aqueous Film Forming Foam

3.14. IDA: Isotope dilution analyte

3.15. Further definitions of terms used in this SOP may be found in the glossary of the Laboratory Quality Assurance Manual (QAM).

4. INTERFERENCES

4.1. PFAS have been used in a wide variety of manufacturing processes, and laboratory supplies should be considered potentially contaminated until they have been tested and shown to be otherwise. The materials and supplies used during the method validation process have been tested and shown to be clean. These items are listed below in Section 6.

4.2. To avoid contamination of samples, standards are prepared in a ventilation hood in an area separate from where samples are extracted.

4.3. PTFE products can be a source of PFOA contamination. The use of PTFE in the procedure should be avoided or at least thoroughly tested before use. Polypropylene (PP) or polyethylene (PE, HDPE) products may be used in place of PTFE products to minimize PFOA contamination.

4.3.1. Standards and samples are injected from polypropylene autosampler vials with polypropylene screw caps once. Multiple injections may be performed on Primers when conditioning the instrument for analysis.

4.3.2. Random evaporation losses have been observed with the polypropylene caps causing high IDA recovery after the vial was punctured and sample re-injected. For this reason, it is best to inject standards and samples once in the analytical sequence.

4.3.3. Teflon-lined screw caps have detected PFAS at low concentrations. Repeated injection from the same teflon-lined screw cap have detected PFNA at increasing concentration as each repeated injection was performed, therefore, it is best to use polypropylene screw caps.

4.4. Volumetric glassware and syringes are difficult to clean after being used for solutions containing high levels of PFOA. These items should be labeled for use only with similarly concentrated solutions or verified clean prior to re-use. To the extent possible, disposable labware is used.

4.5. Both branched and linear PFAS isomers can potentially be found in the environment. Linear and branched isomers are known to exist for PFOS, PFOA, PFHxS, PFBS, EtFOSAA, and MeFOSAA based upon the scientific literature. If multiple isomers are present for one of these PFAS they might be adjacent peaks that completely resolve or not, but usually with a deflection point resolved during peak integration. The later of these peaks matches the retention time of its labeled linear analog. In general, earlier peaks are the branched isomers and are not the result of peak splitting.

As of this writing, only PFOS, PFOA, and PFHxS are commercially available as technical mixtures. These reference standards of the technical mixtures for these specific PFAS are used to ensure that all appropriate peaks are included during peak integration.

4.6. In an attempt to reduce PFOS bias, it is required that *m/z* 499>80 transition be used as the quantitation transition.

4.7. Per the Certificate of Analysis for labeled perfluorohexadecanoic acid ($13C_2$-PFHxDA) produced by Wellington Laboratories, the stock standard contains roughly 0.3% of native perfluorohexadecanoic acid. This equates to roughly 0.30 ng/L or 0.015 ug/kg of perfluorohexadecanoic acid expected in all samples and blanks.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Sacramento Supplement to the CSM, and this document. All work must be stopped in the event of a known or potential compromise to the health or safety of an associate. The situation must be reported **immediately** to a supervisor, the EH&S Staff, or a senior manager.

5.1. Specific Safety Concerns

5.1.1. Preliminary toxicity studies indicate that PFAS could have significant toxic effects. In the interest of keeping exposure levels as low as reasonably achievable, PFAS and PFAS samples must be handled in the laboratory as hazardous and toxic chemicals.

5.1.2. Exercise caution when using syringes with attached filter disc assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.

5.1.3. Laboratory procedures such as repetitive use of pipets, repetitive transferring of extracts and manipulation of filled separatory funnels and other glassware represent a significant potential for repetitive motion or other ergonomic injuries. Laboratory associates performing these procedures are in the best position to realize when they are at risk for these types of injuries. Whenever a situation is found in which an employee is performing the same repetitive motion, the employee shall immediately bring this to the attention

of their supervisor, manager, or the EH&S staff. The task will be analyzed to determine a better means of accomplishing it.

5.1.4. Eye protection that satisfies ANSI Z87.1 (as per the TestAmerica Corporate Safety Manual), laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.1.5. Perfluorocarboxylic acids are acids and are not compatible with strong bases.

5.1.6. The use of vacuum systems presents the risk of imploding glassware. All glassware used during vacuum operations must be thoroughly inspected prior to each use. Glass that is chipped, scratched, cracked, rubbed, or marred in any manner must not be used under vacuum. It must be removed from service and replaced.

5.1.7. Glass containers are not to be used for "tumbling" soil samples.

5.2. Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and Symptoms of Exposure
Acetic Acid (3-2-1)	Corrosive Poison Flammable	10 ppm-TWA 15 ppm-STEL	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
Ammonium Hydroxide (3-0-0)	Corrosive Poison	50 ppm-TWA	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage to the upper respiratory tract. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent damage, including blindness. Brief exposure to 5000 PPM can be fatal.

Material[1]	Hazards	Exposure Limit[2]	Signs and Symptoms of Exposure
Hexane (2-3-0)	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Hydrochloric Acid (3-0-1)	Corrosive Poison	5 ppm (Ceiling)	Can cause pain and severe burns upon inhalation, ingestion, eye or skin contact. Exposure to concentrated solutions may cause deep ulcerations to skin, permanent eye damage, circulatory failure and swallowing may be fatal.
Methanol (2-3-0)	Flammable Poison Irritant	200 ppm (TWA)	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Potassium Hydroxide (3-0-1)	Corrosive Poison		Severe irritant. Can cause severe burns upon inhalation, ingestion, eye or skin contact. Exposure to concentrated solutions may cause severe scarring of tissue, blindness, and may be fatal if swallowed.
Potassium Persulfate (2-0-1-OX)	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
Sodium Hydroxide (3-0-1)	Corrosive Poison	2 mg/cm^3 (Ceiling)	Severe irritant. Can cause severe burns upon inhalation, ingestion, eye or skin contact. Exposure to concentrated solutions may cause severe scarring of tissue, blindness, and may be fatal if swallowed.
(1) Always add acid to water to prevent violent reactions. (2) Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. 15 mL polypropylene test tubes with polypropylene screw caps.

6.2. 50 mL graduated plastic centrifuge tubes.

6.3. 125 mL HDPE bottles with HDPE screw caps.

6.4. 250 mL HDPE bottles with HDPE screw caps.

6.5. Analytical balance capable of accurately weighing to the nearest 0.0001g, and checked for accuracy each day it is used in accordance with WS-QA-0041.

6.6. Extract concentrator or nitrogen manifold with water bath heating to 50-55°C.

6.7. Syringe filter, Millipore Millex-HV 0.45 um, or equivalent. Do not use PTFE type filters.

6.8. 300 µL autosampler vials, polypropylene, with polypropylene screw caps, Waters PN 1860004112, or equivalent.

6.9. SPE columns

6.9.1. Phenomenex Strata SPE C18, 6 mL, 500 mg, part number 8B-S002-HCH, Waters SepPak C18, 1 to 10g, or equivalent.

6.9.2. Waters Oasis WAX 150 mg/6 cc (PN 186002493) for the cleanup of solids.

6.9.3. Waters Oasis WAX 500 mg/6 cc (PN 186004647) for extraction of PFAS from aqueous sample.

6.9.4. Phenomonex Gemini 3 µm C18 110Å, 50 X 2 mm, Part No. 00B-4439-B0.

6.9.5. Phenomonex Luna 5 µm C18(2) 100Å, 30 X 3 mm, Part No. 00A-4252-Y0.

6.10. Graphitized carbon (Envi-Carb™ or equivalent).

6.11. Vacuum manifold for Solid Phase Extraction (SPE).

6.12. Miscellaneous laboratory apparatus (beakers, test tubes, volumetric flasks, pipettes, etc.). These should be disposable where possible, or marked and segregated for high-level versus low-level use.

6.13. Water bath: Heated with concentric ring cover capable of temperature control (±5°C) up to 95°C. The bath must be used in a fume hood.

6.14. Plastic tub for an ice bath, AKRO-N.S.T. part No. 35-180 or equivalent.

6.15. pH indicator paper, wide range.

6.16. Bottle rotating apparatus for soil extractions.

6.17. Glass fiber filter, Whatman GF/F, catalog number 1825 090 or equivalent.

6.18. Liquid Chromatography/Tandem Mass Spectrometer (LC/MS/MS) – Either of the instruments described below, or equivalent, may be used for this method. Both HPLC are equipped with a refrigerated autosampler, an injection valve, and a pump capable of variable flow rate. The use of a column heater is required to maintain a stable

temperature throughout the analytical run. Data is processed using Chrom Peak Review, version 2.1 or equivalent.

6.18.1. Waters LC/MS/MS

This consists of a Waters Acquity UPLC system interfaced with a Waters Quattro Premier tandem mass spectrometer. The instrument control and data acquisition software is MassLynx version 4.1, or equivalent.

6.18.1.1. Analytical column: Waters Acquity UPLC BEH C18 1.7 um, 3.0 mm x 150 mm, Part No. 186004690,

6.18.1.2. PFAS Isolator column, Waters Acquity UPLC BEH Shield RP-18, 1.7 um, 2.1 mm x 50 mm, PN 186004476, or equivalent. This is plumbed between the UPLC pumps and autosampler valve to minimize PFAS background from the UPLC solvent lines and filters.

6.18.2. SCIEX LC/MS/MS

This system consists of a Shimadzu HPLC interfaced with a SCIEX 5500 Triple Quad MS. The instrument control and data acquisition software is SCIEX Analyst, version 1.6.3 or equivalent.

6.18.2.1. Shimadzu CTO-20AC HPLC equipped with 3 LC-20AD pumps and one DGU-20 degassing unit or equivalent.

6.18.2.2. Phenomenex Gemini C_{18} 3 um, 3.0 mm x 100 mm, Part No. 00D-4439-Y0, or equivalent.

6.18.2.3. PFAS Isolator column, Phenomenex Luna C_{18} 5 um, 50 mm x 4.6 mm, part no. 00B-4252-E0 or equivalent. This is plumbed between the UPLC pumps and autosampler valve to minimize PFAS background from the UPLC solvent lines and filters.

6.19. Preventive and routine maintenance is described in the table below

HPLC/MS/MS Preventative Maintenance	
As Needed: Change pump seals. Change in-line filters in autosampler (HPLC). Check/replace in-line frit if excessive pressure or poor performance. Replace column if no change following in-line frit change. Clean corona needle. Replace sample inlet tube in APCI (10.1 cm). Replace fused silica tube in ESI interface. Clean lenses. Clean skimmer. Ballast rough pump 30 minutes. Create all eluents in Reagent module, label eluent containers with TALS label and place 2nd label into maintenance log when put into use.	**Daily (When in use)** Check solvent reservoirs for sufficient level of solvent. Verify that pump is primed, operating pulse free. Check needle wash reservoir for sufficient solvent. Verify capillary heater temperature functioning. Verify vaporizer heater temperature. Verify rough pump oil levels. Verify turbo-pump functioning. Verify nitrogen pressure for auxiliary and sheath gasses. Verify that corona and multiplier are functioning.
Semi-Annually Replace rough-pump oil (4-6 months). Replace oil mist and odor elements. Replace activated alumina filter if applicable	**Annually** Vacuum system components including fans and fan covers. Clean/replace fan filters, if applicable.

7. REAGENTS AND STANDARDS

7.1. Reagent grade chemicals shall be used in all tests whenever available. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on the Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1.1. Acetic acid, glacial

7.1.2. Ammonium acetate (20 mM in water): Prepared by weighing 1.509g of ammonium acetate and dissolving in 1L of water. The resultant solution is filtered through a 0.22um filter before use. This solution has volatile components, thus it should be replaced every 7 days or sooner.

7.1.3. Ammonium hydroxide (NH4OH), 0.3% in methanol: Prepared by diluting 12mL of ammonium hydroxide into 4L of methanol.

7.1.4. Hexane

7.1.5. Hydrochloric acid (HCl), 2.0 M solution in water

7.1.6. Hydrochloric acid (HCl), concentrated, reagent grade

7.1.7. Methanol

7.1.8. Potassium hydroxide (KOH), 0.4% in methanol: Prepared by weighing 16g of potassium hydroxide and dissolving in 4L of methanol.

7.1.9. Potassium persulfate, reagent grade

7.1.10. Ottawa Sand

7.1.11. Sodium hydroxide (NaOH), 0.1N, in water: Prepared by diluting 400mL of 1N NaOH into 3.6L of water for a total volume of 4L.

7.1.12. Sodium hydroxide (NaOH), 10N, reagent grade

7.1.13. Water, Nanopure or Millipore, must be free of interference and target analytes

7.2. Standards

7.2.1. PFAS are purchased as high purity solids (96% or greater) or as certified solutions. Standard materials are verified compared to a second source material at the time of initial calibration. The solid stock material is stored at room temperature or as specified by the manufacturer or vendor.

7.2.1.1. Per the Certificate of Analysis for labeled perfluorohexadecanoic acid ($13C_2$-PFHxDA) produced by Wellington Laboratories, the stock standard contains roughly 0.3% of native perfluorohexadecanoic acid. This equates to roughly 0.30 ng/L or 0.015 ug/kg of perfluorohexadecanoic acid expected in all samples and blanks.

7.2.2. If solid material is used for preparing a standard, stock standard solutions are prepared from the solids and are stored at 4 ± 2°C. Stock standard solutions should be brought to room temperature before using. Standards are monitored for signs of degradation or evaporation. Standard solutions must be replaced at least annually from the date of preparation.

7.2.3. PFBS, PFHxS, PFHpS, PFOS, PFDS, MPFOS, and many other PFAS are not available in the acid form, but rather as their corresponding salts, such as sodium or potassium. The standards are prepared and corrected for their salt content according to the equation below.

$Mass_{acid}$ = Measured $Mass_{salt}$ × MW_{acid} / MW_{salt}

Where: MW_{acid} is the molecular weight of PFAA

MW_{salt} is the molecular weight of the purchased salt.

7.2.4. For example, the molecular weight of PFOS is 500.1295 and the molecular weight of NaPFOS is 523.1193. Therefore, the amount of NaPFOS used must be adjusted by a factor of 0.956.

7.3. Calibration Standards

The calibration stock solution is prepared by diluting the appropriate amounts of PFCA and PFSA stock solutions in 80% methanol/water. The calibration stock solution is diluted with methanol to produce initial calibration standards. These are the normal calibration levels used. A different range can be used if needed to achieve lower reporting limits or a higher linear range.

7.4. Initial Calibration (ICAL) Levels (ng/mL)

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
Perfluoroalkylcarboxylic acids (PFCAs)							
PFBA	0.5	1.0	5.0	20	50	200	400
PFPeA	0.5	1.0	5.0	20	50	200	400
PFHxA	0.5	1.0	5.0	20	50	200	400
PFHpA	0.5	1.0	5.0	20	50	200	400
PFOA	0.5	1.0	5.0	20	50	200	400
PFNA	0.5	1.0	5.0	20	50	200	400
PFDA	0.5	1.0	5.0	20	50	200	400
PFUdA	0.5	1.0	5.0	20	50	200	400
PFDoA	0.5	1.0	5.0	20	50	200	400
PFTrDA	0.5	1.0	5.0	20	50	200	400
PFTeDA	0.5	1.0	5.0	20	50	200	400
PFHxDA	0.5	1.0	5.0	20	50	200	400
PFODA	0.5	1.0	5.0	20	50	200	400
Perfluorinated sulfonic acids (PFSAs)							
PFBS	0.5	1.0	5.0	20	50	200	400
PFPeS	0.5	1.0	5.0	20	50	200	400
PFHxS *	0.5	1.0	5.0	20	50	200	400
PFHpS	0.5	1.0	5.0	20	50	200	400
PFOS *	0.5	1.0	5.0	20	50	200	400
PFNS	0.5	1.0	5.0	20	50	200	400
PFDS	0.5	1.0	5.0	20	50	200	400
Perfluorinated sulfonamides (FOSA)							
FOSA	0.5	1.0	5.0	20	50	200	400

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
Perfluorinated sulfonamidoacetic acids (FOSAA)							
EtFOSAA	0.5	1.0	5.0	20	50	200	400
MeFOSAA	0.5	1.0	5.0	20	50	200	400
Fluorotelomer sulfonates (FTS)							
4:2 FTS	0.5	1.0	2.0	20	50	200	400
6:2 FTS	0.5	1.0	5.0	20	50	200	400
8:2 FTS	0.5	1.0	5.0	20	50	200	400
Labeled Isotope Dilution Analytes (IDA)							
13C4-PFBA	50	50	50	50	50	50	50
13C5-PFPeA	50	50	50	50	50	50	50
13C2-PFHxA	50	50	50	50	50	50	50
13C4-PFHpA	50	50	50	50	50	50	50
13C4-PFOA	50	50	50	50	50	50	50
13C5-PFNA	50	50	50	50	50	50	50
13C2-PFDA	50	50	50	50	50	50	50
13C2-PFUdA	50	50	50	50	50	50	50
13C2-PFDoA	50	50	50	50	50	50	50
18O2-PFHxS	50	50	50	50	50	50	50
13C4-PFOS	50	50	50	50	50	50	50
13C3-PFBS	50	50	50	50	50	50	50
13C2-PFTeDA	50	50	50	50	50	50	50
13C2-PFHxDA	50	50	50	50	50	50	50
13C8-FOSA	50	50	50	50	50	50	50
d5-EtFOSAA	50	50	50	50	50	50	50
d3-MeFOSAA	50	50	50	50	50	50	50
M2-4:2FTS ǂ	50	50	50	50	50	50	50
M2-6:2FTS	50	50	50	50	50	50	50
M2-8:2FTS	50	50	50	50	50	50	50
Internal Standard (IS)							
13C2-PFOA	50	50	50	50	50	50	50

* Both branched and linear isomers are used.

ǂ - This compound is used as a reverse surrogate for the TOP analysis.

Note: Sample extracts are in 80% MeOH/H_2O.

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
Fluorinated Replacement Chemicals							
HFPO-DA	0.5	1.0	5.0	20	50	200	400
9Cl-PF3ONS (F53B major)	0.5	1.0	5.0	20	50	200	400
11Cl-PF3OUdS (F53B minor)	0.5	1.0	5.0	20	50	200	400

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
Fluorinated Replacement Chemicals							
Adona	0.5	1.0	5.0	20	50	200	400
Labeled Isotope Dilution Analytes							
13C3-HFPO-DA	0.5	1.0	5.0	20	50	200	400

Note: Sample extracts are in 80% MeOH/H_2O.

***Note**: The above calibration limits are provided only as an example. The actual ICAL level used for each analytical batch will depend upon the LOQ requirements of the program. The concentration of the calibration solutions for non-concentrated extracts is 1/20th the levels indicated above.*

7.4.1. A technical (qualitative) grade PFOA standard which contains both linear and branched isomers is used as a retention time (RT) marker. This is used to integrate the total response for both linear and branched isomers of PFOA in environmental samples while relying on the initial calibration with the linear isomer quantitative standard This technical (qualitative) grade PFOA standard is analyzed initially, after an initial calibration when a new column is installed or when significant changes are made to the HPLC parameters.

7.5. Initial Calibration Verification Standard (ICV)

A second source solution for PFAS is purchased from the same vendor; the PFC-MXB contains most of the target analytes in this mixture and is used as an ICV. A few compounds are not available in this mixture, may not be available as another lot, and are not available from another vendor. For these analytes only, a second analyst may prepare a second source standard from the same source as the ICAL to produce an ICV. The recommended concentration of the ICV standard should be in the mid-range of the calibration curve. The concentration may be adjusted if the initial calibration levels are changed or altered. The IDA and IS are added at a fixed concentration of 50 ng/mL.

7.6. LCS/Matrix PFC Spike Solution, 20 ng/mL

The PFC spike solution is prepared by diluting all PFAS to produce a solution containing each PFAS at a concentration of 20 ng/mL in methanol.

7.7. PFC Isotope Dilution Analyte Solution, 50 ng/mL

The PFC-IDA solution is prepared by diluting all labeled PFAS to produce a solution containing each compound at a concentration of 50 ng/mL in methanol.

7.8. Reverse Surrogate Solution, 1000 ng/mL

The reverse surrogate solution is prepared by diluting M2-4:2 FTS to produce a solution containing this compound at a concentration of 1000 ng/mL in methanol. This is added to all samples for the TOP assay to monitor the efficiency of the oxidation process.

7.9. Internal Standard Solution, 250 ng/mL

The internal standard solution is prepared by diluting 13C2-PFOA to produce a solution containing this compound at a concentration of 250 ng/mL in methanol. This is added to all extracts prior to analysis. The internal standard solution used for the non-concentrated extracts is at a concentration of 50 ng/mL.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Water samples are collected in pre-cleaned 250 mL HDPE containers. Soil samples are collected in pre-cleaned 8 oz. HDPE containers. Other containers may also be suitable. Samples are chilled to 0 - 6°C for shipment to the laboratory.

8.1.1. Water samples collected from a known chlorinated source should be preserved with Trizma.

8.2. Samples are logged in following normal laboratory procedures and are stored under refrigeration at 0 - 6°C. Water samples must be extracted within 14 days of collection. Soil samples must also be extracted within 14 days of collection. Tissue samples must be extracted within 1 year of collection if stored at -20°C. Extracts must be refrigerated at 0 - 6°C, and analyzed within 40 days from extraction.

***Note**: As of this writing, Method 537 provides for a 14 day holding time for water samples preserved with Trizma buffer. The scientific literature indicates that perfluorinated substances are highly persistent in the environment. TestAmerica Sacramento has conducted time stability studies that support a 14 day holding time for aqueous samples with and without Trizma preservation. TestAmerica Denver has conducted stability studies indicating that medium- and low-level solutions of PFOA are stable for at least three months in polystyrene and polypropylene plastics at 0-6°C. The 14/40 day holding times given above are based on the stability study and general EPA convention for the holding time of extractable organic compounds in water and soil.*

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability (IDOC)

The initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.

9.2. Batches are defined at the sample preparation step. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the QC program document (WS-PQA-003) for further details of the batch definition.

9.2.1. The quality control batch is a set of up to 20 samples of the same matrix processed using the same procedure and reagents within the same time period. The quality control batch must contain a matrix spike/matrix spike

duplicate (MS/MSD), a laboratory control sample (LCS) and a method blank. Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count toward the maximum 20 samples in a batch. Field QC samples are included in the batch count. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. If insufficient sample is available for an MS/MSD, an LCSD may be substituted if batch precision is required by the program or client. In the event that multiple MS/MSDs are run with a batch due to client requirements, the additional MS/MSDs do not count toward the maximum 20 samples in a batch.

9.3. One method blank (MB, laboratory reagent blank) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. For aqueous samples, the method blank is an aliquot of laboratory reagent water. For solid samples, the method blank is an aliquot of Ottawa sand. The method blank is processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, and then implemented when target analytes are detected in the method blank above the reporting limit or when IDA recoveries are outside of the control limits. Re-extraction of the blank, other batch QC and the affected samples are required when the method blank is deemed unacceptable. See policy WS-PQA-003 for specific acceptance criteria.

9.3.1. If the MB produces a peak within the retention time window of any of the analytes, determine the source of the contamination and eliminate the interference before processing samples.

9.3.2. The method blank must not contain any analyte at or above the reporting limit, or at or above 10% of the measured concentration of that analyte in the associated samples, whichever is higher.

9.3.3. If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.3.4. Re-extraction and reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

9.3.5. Refer to WS-PQA-003 for further details of the corrective actions.

9.3.6. Projects performed under the auspices of the DOD/DOE must meet QSM specific criteria for method blanks. Results are acceptable if the blank contamination is less than ½ of the reporting limit/LOQ for each analyte, or less than 1/10 of the regulatory limit, or less than 1/10 of the sample result for the same analyte, whichever is greater. If the method blank does not

meet the acceptance criteria, the source of contamination must be investigated and measures taken to correct, minimize or eliminate the problem. Reprepare and reanalyze all field and QC samples associated with the contaminated method blank.

9.4. A laboratory control sample (LCS) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The LCS is an aliquot of laboratory matrix (e.g. water for aqueous samples and Ottawa sand for solids) spiked with analytes of known identity and concentration. The LCS must be processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside of the control limits. Re-extraction of the blank, other batch QC, and all associated samples are required if the LCS is deemed unacceptable. See WS-PQA-0003 for specific acceptance criteria. The control limits for the LCS are stored in TALS.

9.5. A matrix spike/matrix spike duplicate (MS/MSD or MS/SD) pair must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. An MS/MSD pair is aliquots of a selected field sample spiked with analytes of known identity and concentration. The MS/MSD pair must be processed in the same manner and at the same time as the associated samples. Spiked analytes with recoveries or precision outside of the control limits must be within the control limits in the LCS. Corrective actions must be documented on a nonconformance memo, and then implemented when recoveries of any spiked analyte are outside of the control limits provided by TALS or by the client.

9.6. A duplicate control sample (LCSD or DCS) may be added when insufficient sample volume is provided to process an MS/MSD pair, or is requested by the client. The LCSD is evaluated in the same manner as the LCS. See WS-PQA-003 for specific acceptance criteria.

9.7. Initial calibration verification (ICV) –A second source standard is analyzed with the initial calibration curve. The concentration should be at the mid range of the curve.

Corrective actions for the ICV include:

- Rerun the ICV.
- Remake or acquire a new ICV.
- Evaluate the instrument conditions.
- Evaluate the initial calibration standards.
- Rerun the initial calibration.

9.8. Isotope Dilution Analytes

9.8.1. The IDA solution is added to each field and QC sample at the time of

extraction, as described in Section 11. As described in Section 7, this solution consists of isotopically labeled analogs of the analytes of interest.

9.8.2. IDA recoveries are flagged if they are outside of the acceptance limits (25–150%). Quantitation by isotope dilution generally precludes any adverse effect on data quality due to IDA recoveries being outside of the acceptance limits as long as the signal-to-nose ratio is greater than 10:1.

9.8.2.1. Evaluate data quality for usability, flag and submit a non-conformance memo for any analytes outside of the recovery criteria, and report if data is deemed not adversely effected.

9.8.2.2. Re-extraction of samples should be performed if the signal-to-noise for any IDA is less than 10:1 or if the IDA recoveries fall below 10%.

9.8.2.2.1. Re-extraction may be necessary under other circumstances when data quality has been determined to be adversely affected.

9.8.2.3. Projects performed under the auspices of the DoD/DOE must meet QSM 5.1 specific criteria for IDA recoveries which are 50-150%. If QC or field samples do not meet these criteria then re-extraction is required.

9.9. Internal Standard

9.9.1. The Internal Standard (IS) is added to each field and QC samples prior to analysis. The CCV IS response (peak area) must not deviate by more than 50% from the average response (peak area) of the initial calibration.

9.9.2. Sample IS response (peak area) must be within ±50% of the response (peak area) in the most recent CCV.

9.9.3. If the IS does not meet criteria, re-analyze the extract. If the IS meets criteria in the second analysis, report that analysis. If the IS does not meet criteria in the second analysis, report the first analysis with narration.

10. CALIBRATION

10.1. For details of the calculations used to generate the regression equations, and how to use the factors generated by these equations, refer to SOP CA-Q-P-003 “Calibration Curves and Selection of Calibration Points”.

10.2. Routine instrument operating conditions are listed in the table in Section 11.18.

10.3. Instrument Tuning

Instrument tuning is done initially when the method is first developed and thereafter as needed to maintain the sensitivity and selectivity of the method. Tuning is done by infusing each individual compound (native and IDA) into the mobile phase using a tee fitting at a point just before the entrance to the electrospray probe. The responses for the parent and daughter ions for each compound are observed and optimized for sensitivity and resolution. Mass assignments are reviewed and calibrated if necessary. The mass assignments must be within ± 0.5 amu of the values shown in the table in Section 11.18.

10.3.1. Once the optimal mass assignments (within ±0.5 amu of true) are made immediately following the initial tune, the lowest level standard from the initial calibration curve is assessed to ensure that a signal to noise ratio greater than 10 to 1 (S/N > 10:1) is achieved for each PFAS analyte. The first level standard from the initial calibration curve is used to evaluate the tune stability on an ongoing basis. The instrument mass windows are set initially at ± 0.5 amu of the true value; therefore, continued detection of the analyte transition with S/N > 10:1 serves as verification that the assigned mass remains within ± 0.5 amu of the true value, which meets the DoD/DOE QSM tune criterion. For QSM work, the instrument sensitivity check (section 10.12.4) is also evaluated to ensure that the signal to noise criteria is met.

10.4. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include, but are not limited to, new columns or pump seals. A new calibration is not required after minor maintenance.

10.5. With the exception of the circumstances delineated in policy CA-Q-P-003, it is not acceptable to remove points from a calibration curve. In any event, at least five points must be included in the calibration curve. Average Response Factor and linear fit calibrations require five points, whereas Quadratic (second order) calibrations require six points.

10.6. A fixed injection volume is used for quantitation purposes and is to be the same for both the sample and standards.

10.7. All units used in the calculations must be consistently uniform, such as concentration in ng/mL.

10.8. Initial Calibration

10.8.1. A number of analytical standards of different analyte concentrations are used to generate the curve. Each standard is injected once to obtain the peak

response for each analyte at each concentration. These standards define the working range of the analysis.

10.8.1.1. A minimum of five analytical standards is used when using average response factor and/or linear calibration fits.

10.8.1.2. A minimum of six analytical standards is used when a quadratic fit is used to generate the curve.

10.8.2. Calibration is by average response factor, linear fit, or by quadratic fit. Quadratic fit is used for the analyte if the response is non-linear.

10.8.2.1. For average response factor (RFa), the relative standard deviation (RSD) for all compounds quantitated against an identically labeled analog must be < 35% for the curve to be valid.

10.8.2.2. For average response factor (RFa), the relative standard deviation (RSD) for all compounds quantitated against a closely related labeled analog IDA must be < 50% for the curve to be valid.

10.8.2.3. For linear fit, the intercept of the line must be less than ½ the reporting limit, and the coefficient of determination (r2) must be greater than or equal to 0.990 for the curve to be considered valid (or the correlation coefficient (r) > 0.995).

10.8.2.4. The Internal Standard (IS) response (peak area) must not deviate by more than 50% from the average response (peak area) of the initial calibration.

10.8.2.5. Projects performed under the auspices of the DoD/DOE must meet QSM 5.1 specific criteria for initial calibration: The %RSD of the RFS for all analytes must be <20%. Linear or non-linear calibrations must have r^2>0.99 for each analyte. Analytes must be within 70-130% of their true value for each calibration standard.

10.9. Calibration Curve Fits

10.9.1. Linear regression or quadratic curves may be used to fit the data to a calibration function. Detailed descriptions and formulas for each fitting type can be found in SOP CA-Q-P-003, “Calibration Curves and Selection of Calibration Points”.

10.9.2. The linear curve uses the following function:

Equation 1

$$y = bx + c$$

Where:

$$y = \frac{\text{Area (analyte)}}{\text{Area (IS)}} \times \text{Concentration (IS)}$$

x = concentration
b = slope
c = intercept

10.9.3. The quadratic curve uses the following function:

Equation 2

$$y = ax^2 + bx + c$$

Where y, x, b, and c are the same as above, and a = curvature.

10.9.4. Evaluation of Calibration Curves

The following requirements must be met for any calibration to be used:

- Response must increase with increasing concentration.
- The absolute value of the intercept of a regression line (linear or non-linear) at zero response must be less than the reporting limit.
- There should be no carryover at or above 1/2 MRL after a high CAL standard.

If these criteria are not met, instrument conditions and standards will be checked, and the ICAL successfully repeated before continuing.

10.9.5. Weighting of Calibration Points

In linear and quadratic calibration fits, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. Because accuracy at the low end of the curve is very important for this analysis, it is preferable to increase the weighting of the lower concentration points. 1/concentration or 1/x weighting is encouraged. Visual inspection of the line fitted to the data is important in selecting the best fit.

10.10. Initial Calibration Blank (ICB)

10.10.1. Immediately following the ICAL, a calibration blank is analyzed that consists of an injection of 80:20 methanol:water blank containing both IDA and IS.

10.10.2. The result for the calibration blank must be less than the reporting limit.

10.10.3. If the ICB is greater than the reporting limit then the source of contamination

must be identified and any necessary cleaning completed, and then the instrument should be recalibrated.

10.10.4. Projects performed under the auspices of the DoD/DOE must meet QSM 5.1 specific criteria for instrument blanks. One is required immediately following the highest standard analyzed and *daily prior to sample analysis*. The instrument blank must be < ½ the LOQ.

10.11. Initial Calibration Verification (ICV)

10.11.1. Following the ICAL and the ICB, an ICV standard obtained from a different source or vendor than the ICAL standards is analyzed. This ICV standard is a mid-range standard.

10.11.2. The recovery for the ICV must meet the appropriate following criteria:

10.11.2.1. The native analyte must be within or equal to 60-140% for all native analytes quantitated against an identically labeled analog IDA.

10.11.2.2. The native analyte must be within or equal to 50-150% for all native analytes quantitated against a closely related labeled analog IDA.

10.11.2.3. The IDA must be within or equal to 50-150%.

10.11.3. Projects performed under the auspices of the DoD/DOE must meet QSM 5.1 specific criteria for the ICV. Analyte concentrations must be within ±30% of their true values for all analytes, IDA and target.

10.11.4. See Section 9.7 for corrective actions in the event that the ICV does not meet the criteria above.

10.12. Continuing Calibration Verification (CCV)

Analyze a CCV at the beginning of a run, the end of a run, and after every 10 samples to determine if the calibration is still valid. The exception is after an acceptable curve and ICV are run 10 samples can be analyzed before a CCV is required. The CCVs are usually at the mid-level range of the curve and should vary throughout the run from low level (LOQ/RL) to mid level. The curve and ICV do not need to be run every day. To start an analytical run a CCV can be analyzed and if it meets acceptance criteria a run can be started. In addition, the low standard in the curve must be analyzed and must be within ± 50% of the expected value.

10.12.1. The recovery for the CCV standards must be equal to or within 60-140% for all natives quantitated against an identically labeled analog and equal to or

within 50% to 150% for all natives quantitated against a closely related labeled analog. The recovery for the IDA must be within or equal to 50-150%.

10.12.2. The Internal Standard (IS) response (peak area) must be within ± 50% from the response (peak area) from the midpoint of the initial calibration.

10.12.2.1. Sample IS response (peak area) must be within ± 50% of the response (peak area) in the most recent CCV.

10.12.3. If this is not achieved, the instrument has drifted outside the calibration limits. The instrument must be recalibrated.

10.12.4. Projects performed under the auspices of the DoD/DOE must meet QSM 5.1 specific criteria for CCV. All analyte concentrations must be within ± 30% of their true value. Additionally, prior to analysis and at least once every 12 hours an instrument sensitivity check (ISC/CCVL) must be analyzed. The analyte concentrations must be at LOQ and the concentrations must be within ± 30% of their true value. This can be used as a CCV.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of a supervisor to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an Non-Conformance Memo (NCM). The NCM process is described in more detail in SOP WS-QA-0023. The NCM shall be filed in the project file and addressed in the case narrative.

Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

11.2. Water Sample Preparation

11.2.1. Visually inspect samples for the presence of settled and/or suspended sediment/particulates. If present or if the sample is biphasic add IDA prior to any sample decanting or centrifugation. If the sample requires decanting or centrifugation contact the client for guidance prior to such action. Decanting or filtering of the sample can lead to a low bias.

11.2.2. If authorized by the client to filter the sample, filter the water sample through a glass fiber filter (Whatman GF/F Cat No 1825 090 or equivalent). Gravity or vacuum can be used to pass the sample through the filter. Prepare a filtration blank with any samples requiring filtration. File an NCM noting the need for filtration.

Warning: The use of a vacuum system creates the risk of glassware implosion. Inspect all glassware prior to use. Glassware with chips, scratches, rub marks or cracks must not be used.

11.2.3. Weigh the sample container prior to extraction and then weigh the sample container after extraction to determine the initial volume. Unless otherwise directed by client, use the entire sample volume.

11.2.4. Prepare additional aliquots of a field sample for the MS/MSD, if requested.

11.2.5. Prepare two 250 mL aliquots of HPLC-grade water for the method blank and LCS.

11.2.6. Spike the LCS and MS/MSD (if requested) with 0.5 mL of the LCS/Matrix PFC Spike solution (Section 7.6). This will result in a sample concentration of 40 ng/L.

11.2.7. Add 0.5 mL of the IDA PFC solution (Section 7.7) into each sample and QC sample, for a fixed concentration of 50 ng/mL in the final sample vial.

11.3. Solid Phase Extraction (SPE) of Aqueous Samples

The automated Zymark Auto-Trace Workstation can be used as long as the program follows these conditions and passes the background check.

11.3.1. Condition the SPE cartridges (Waters WAX, 500 mg/6 cc) by passing the following without drying the column.

Note: *The cartridges should not be allowed to go dry until the final elution step with methanol. At all of the other transition steps, the solvent/sample level should be stopped at the top of the column before the next liquid is added.*

WARNING: The use of a vacuum system creates the risk of glassware implosion. Inspect all glassware prior to use. Glassware with chips, scratches, rub marks or cracks must not be used.

11.3.2. Wash with 5.0 mL of 0.3% NH_4OH/methanol.

11.3.3. Wash with 5.0 mL of 0.1N NaOH/water. Close valve when ~ 200 uL remains on top to keep column wet. After this step, the columns cannot go dry until the completion of loading and rinsing samples.

11.3.4. Appropriately label the columns and add the reservoir to the column.

11.3.5. Add samples to the columns and with vacuum, pull the entire 250 mL aliquot of the sample through the cartridge at a rate of approximately 2 to 5 drops per second.

11.3.6. After the final loading of the sample but before completely passed through the column, rinse the SPE column with 1 mL of water.

11.3.7. After the sample and water rinse have completely passed through the cartridge, allow the column to dry well with vacuum for 15 minutes.

11.4. SPE Column Wash of Aqueous Samples with Hexane

11.4.1. Load the first 5 mL of hexane to soak for five minutes and then elute to waste.

11.4.2. Load the second 5 mL of hexane and elute to waste (without a soaking period).

11.4.3. Allow the column to dry with vacuum for 5 to 10 minutes. Columns must be dried before continuing.

11.5. SPE Elution of Aqueous Samples – using 15 mL polypropylene test tubes as receiving tubes in the SPE manifold.

11.5.1. Rinse sample bottles with 5 mL of 0.3% NH_4OH/methanol and transfer to the column reservoir onto the cartridge. Allow the solution to soak for 5 minutes and then elute into the 15 mL collection tube.

11.5.2. Repeat sample bottle to column reservoir rinse and cartridge elution with a second 5 mL aliquot of 0.3% NH_4OH/methanol. The total collection should be approximately 10 mL.

11.5.3. **Note: If the extracts will not be concentrated elute extract with a total of 8 mL of 0.3% NH_4OH/methanol.**

11.5.4. Proceed to Section 11.15.2 (Graphitized Carbon Cleanup) as needed. This required for all DoD/DOE extracts.

11.6. Extract Concentration for Aqueous Extracts (Note, if the extract will not be concentrated, proceed to Section 11.7.)

11.6.1. Prior to concentrating each sample, add 100 uL of water.

11.6.2. Concentrate each sample under a gentle stream of nitrogen until the methanol is evaporated and the 100 uL of water remains.

11.6.2.1. This blow down must take a minimum of 3.5 hours.

11.6.2.2. Extracts can not remain in the water bath longer than 5 minutes once concentrated.

11.6.3. Add 300 uL of methanol and mix the contents well using a vortex mixer.

11.6.4. Add 100 uL of Internal Standard (IS) 250 ng/mL concentration solution to each extract and vortex to mix.

11.6.5. This will create an extract with a final solvent composition of 80:20 methanol:water.

11.6.6. Transfer a portion of the extract to a 300 uL polypropylene autosampler vial (7 drop-wise or approximately ½ filled is sufficient). Archive the rest of the extracts for re-injection and dilution.

11.6.7. Seal the vial with a polypropylene screw cap. Note: Teflon lined caps can not be used due to detection of low level concentration of PFAS.

11.7. Final volume for non-concentrated extract

11.7.1. If the extract does not undergo concentration add 0.5 mL of IS 50 ng/mL concentration and 2 mL of water to the extract. This will create an extract with a final solvent composition of 80:20 methanol:water.

11.7.1.1. Seal the test tube tightly. Invert container several times and then vortex. Allow extract to settle for 10 minutes prior to moving to the next step.

11.7.2. Transfer a portion of the extract to a 300 uL polypropylene autosampler vial (7 drop-wise or approximately ½ filled is sufficient). Archive the rest of the extracts for re-injection and dilution.

11.7.3. Seal the vial with a polypropylene screw cap. Note: Teflon lined caps cannot be used due to detection of low level concentration of PFAS.

11.8. Soil, Sediment and Tissue Sample Preparation and Extraction

11.8.1. Visually inspect soil samples for homogeneity.

11.8.1.1. Projects performed under the auspices of the DoD/DOE must have the entire sample homogenized prior to subsampling in accordance with QSM 5.1 criteria (see SOP WS-QA-0018).

11.8.2. Weigh a representative 5 g aliquot of soil, sediment or 1 g of tissue sample into a 50 mL HDPE wide-mouth bottle. Weigh additional sample amounts for the matrix spike and matrix spike duplicate analyses if they are requested.

11.8.3. For the method blank and LCS matrix, use 5 g each of Ottawa sand or 0.1 g

of oil.

11.8.4. Spike the LCS and MS/MSD (if requested) with 1.0 mL of the LCS/Matrix PFC Spike solution (Section 7.6). This will result in a sample concentration of 4.0 ng/g.

11.8.4.1. Spike non-concentrated samples at 0.5 mL of LCS/Matrix PFC Spike Solution.

11.8.5. Add 1.0 mL of the IDA PFC solution (Section 7.7) into each sample and QC sample, for a fixed concentration of 50 ng/mL in the final sample vial.

11.8.5.1. Spike non-concentrated samples at 0.5 mL of IDA PFC Solution.

11.8.6. Cap the bottles and allow the spike to settle into the sample matrix. Gently shake the bottles to mix the spike into the matrix.

11.8.7. Add 20 mL of 0.4% KOH/methanol to each sample.

11.8.8. Shake each sample on an orbital shaker at room temperature for 3 hours.

11.8.9. Following the shaking, extract the samples in an ultrasonic water bath for an additional 12 hours.

11.8.10. After the completion of extraction, centrifuge each sample at 3500 rpm for 15 minutes.

11.8.11. Collect and decant the KOH/methanol extract to a new 50 mL centrifuge tube.

11.8.12. Add another 2 mL of 0.4% KOH/methanol solution to the residue, briefly shake to mix and centrifuge at 3500 rpm for 15 minutes.

11.8.13. Combine the rinsate to the first corresponding tubes.

11.8.14. To the final KOH/methanol extract, add 2 mL of water to each.

11.8.15. Concentrate the KOH/methanol/water extract under nitrogen to less than 2 mL, and dilute with water to 15 mL final volume.

11.8.16. Acidify with 80 uL of glacial acetic acid, and mix the contents well with vortex mixer. Check the pH to ensure pH is between 6 to 8.

11.8.17. Centrifuge at 3500 rpm for 15 minutes.

11.9. Solid Extract Cleanup by SPE

Set up WAX 150 mg/6 cc SPE columns for sample cleanup using vacuum manifold.

11.9.1. Condition the SPE cartridges by passing the following without drying the column.

Note: *The cartridges should not be allowed to go dry until the final elution step with methanol. At all of the other transition steps, the solvent/sample level should be stopped at the top of the column before the next liquid is added.*

WARNING: The use of a vacuum system creates the risk of glassware implosion. Inspect all glassware prior to use. Glassware with chips, scratches, rub marks or cracks must not be used.

11.9.2. Wash with 5.0 mL of 0.3% NH_4OH/methanol.

11.9.3. Wash with 10 mL of 0.1N NaOH/water. Close valve when ~ 500uL remains on top of column to keep column wet. *After this step, the columns cannot go dry until the completion of loading and rinsing samples.*

11.9.4. Add extracts to the columns and with vacuum, pull the entire extracts through the cartridge at rate of approximately 3 to 5 drops per second.

11.9.5. Rinse the sample tube with 5 mL of water and add to the SPE column.

11.9.6. Dry the columns with vacuum for 15 minutes.

11.10. SPE Column Wash of Solid Extracts with Hexane

11.10.1. Load the first 5 mL of hexane to soak for five minutes, and elute to waste.

11.10.2. Load the second 5 mL of hexane and elute to waste (without a soaking period).

11.10.3. Allow the column to dry with vacuum for 10 minutes. Columns must be dried before continuing.

11.11. SPE Elution of Solid Extracts – using 15 mL polypropylene test tube as receiving tube in the SPE manifold.

11.11.1. Rinse extraction bottles with 5 mL of 0.3% NH_4OH/methanol and transfer to the column reservoir onto the cartridge. Allow the solution to soak for 5 minutes and then elute into the 15 mL collection tube.

11.11.2. Repeat extract bottle to column reservoir rinse and cartridge elution with a second 5 mL aliquot of 0.3% NH_4OH/methanol. The total collection should be approximately 10 mL.

11.11.3. **Note: If the extracts will not be concentrated elute extract with a total of 8 mL of 0.3% NH_4OH/methanol.**

11.11.4. Proceed to Section 11.15.2 (Graphitized Carbon Cleanup) as needed. This is required for all DoD/DOE extracts.

11.12. Extract Concentration for Solid Samples (Note, if the extract will not be concentrated, proceed to Section 11.7)

11.12.1. Prior to concentrating each sample, add 200 uL of water.

11.12.2. Concentrate each sample under a gentle stream of nitrogen until the methanol is evaporated and the 200 uL of water remains.

11.12.2.1. This blow down must take a minimum of 3.5 hours.

11.12.2.2. Extracts can not remain in the water bath longer than 5 minutes once concentrated.

11.12.2.3. Add 600 uL of methanol and mix the contents well using a vortex mixer.

11.12.2.4. Add 200 uL of Internal Standard (IS) 250 ng/mL concentration solution to each extract and vortex to mix.

11.12.3. Transfer a portion of the extract to a 300 uL polypropylene autosampler vial (7 drop-wise or approximately ½ filled is sufficient). Archive the rest of the extracts for re-injection and dilution.

11.12.4. Seal the vial with a polypropylene screw cap. *Note: Teflon lined caps can not be used due to detection of low level concentration of PFAS.*

11.13. Product/Dispersion Samples

11.13.1. Check the solubility of the material in both methanol and water

11.13.1.1. If the material is soluble in water, dilute 0.5 mL of sample into 250 mL of DI water and proceed to Section 11.3 (follow water extraction procedures). Fortify sample appropriately with IDA or PFC spike solution, see Section 11.2.

11.13.1.2. If the material is soluble in methanol, dilute 1 g (if solid) or 1 mL (if liquid) of material into 10 mL of methanol (MeOH).

11.13.1.2.1. If the material does not completely dissolve, contact your immediate supervisor.

11.13.2. Take 100 uL of the 10 mL solution and dilute it to 10 mL in MeOH.

11.13.3. Take a 1 mL aliquot of this solution (effective dilution of 1000x (1 mg for solid or 0.001 mL for liquid)) and fortify with 0.5 mL of labeled IDA solution (Section 7.7).

11.13.4. DO NOT PASS EXTRACT THROUGH SPE CARTIRIDGE (omit steps 11.9 – 11.11).

11.13.5. Proceed to Section 11.6 of this SOP for extract concentration.

11.14. TOP (Total Oxidizable Precursor) Assay for Aqueous Samples

11.14.1. Prepare 3-250 mL HDPE containers with HPLC grade water to create the needed QC Samples (MB, LCS/LCSD).

11.14.2. Prepare enough 125 mL HDPE containers as needed for all “Pre” and “Post” samples, including QC. Label each appropriately.

11.14.3. Spike the “Pre” and “Post” MB 125 mL containers with 25 uL of the reverse surrogate solution of M2-4:2 FTS (Section 7.8).

11.14.4. Spike the “Pre” and “Post” LCS/LCSD 125 mL containers with 0.5 mL of the LCS Spike solution (Section 7.6), both regular and “add-on”, and 25 uL of the reverse surrogate solution (Section 7.8).

11.14.5. Remove the methanol solvent from all Post QC sample 125 mL containers (MB and LCS/LCSD) by using N2 evaporation.

11.14.6. Add 2g of potassium persulfate and 1.9 mL of 10 M NaOH to each “Post” sample container.

11.14.7. Subsample 100 mL aliquots of water from each field sample and QC from the 250 mL containers into each of the corresponding 125 mL containers for both the “Pre” and “Post” samples. Spike all “Pre” and “Post” samples with 25uL of the reverse surrogate solution (Section 7.8).

11.14.8. Set aside all “Pre” sample containers.

11.14.9. Cap each “Post” sample container, invert 2-3 times prior to placing container into water bath.

11.14.10. Add 2g of potassium persulfate and 1.9 mL of 10N NaOH to each “Post” sample container.

11.14.11. Heat each “Post” sample container in a water bath (KD) at 85°C for 6 hours.

11.14.12. After digestion for 6 hours, place the “Post” sample containers in an ice bath for 30 minutes.

11.14.13. Adjust the pH of “Post” samples and associated QC aliquots to 7 with concentrated HCl. Use pH paper to determine the pH.

11.14.14. Spike both “Pre” and “Post” samples and their associated QC samples with 0.5 mL of PFC IDA solution (Section 7.7), both regular and add-on.

11.14.15. Use the following SPE procedure for both “Pre” and “Post” samples:

11.14.15.1. Set up WAX 150 mg/6 cc SPE columns for sample extraction using a vacuum manifold.

11.14.15.2. Establish a sample loading flow rate of 1 mL/minute for each port of the vacuum manifold, for as many ports as will be used simultaneously during sample loading.

11.14.15.3. Wash/condition the SPE column with 5 mL of 0.3% NH_4OH/Methanol, then 5 mL water.

11.14.15.4. Load 100 mL of sample onto the SPE cartridge at a flow rate of 1 mL/minute.

11.14.15.5. Add 5 mL rinse water

11.14.15.6. After the sample and water rinse have completely passed through the column, allow it to dry well using vacuum with a flow rate of 1 mL/minute for 15 minutes.

11.14.15.7. Wash the SPE column with 10 mL hexane rinse eluting all to waste.

11.14.15.8. Allow the column to dry well using vacuum with a flow rate of 1 mL/minute for 5 minutes. Columns must be dry before continuing.

11.14.15.9. Elute the samples into 15 mL polypropylene test tubes in the SPE manifold by rinsing each 125 mL sample container with 5 mL of 0.3% NH_4OH/methanol, and add to the SPE cartridge as eluent.

11.14.15.10. Repeat with another 5 mL of 0.3% NH_4OH/methanol.

11.14.15.11. Collect the 10 mL of eluent and concentrate per Section 11.6.

11.15. TOP (Total Oxidizable Precursor) Assay for Soil Samples

11.15.1. Weigh representative 2 g aliquots of soil for each “Pre” and “Post” sample into a 50 mL centrifuge tube.

11.15.2. For the method blank and LCS matrix, use 2 g each of Ottawa sand for each “Pre” and “Post” QC sample.

11.15.3. Add 20 mL of 0.4% KOH/methanol to each sample.

11.15.4. Shake each sample on an orbital shaker at room temperature for 3 hours.

11.15.5. Following the shaking, extract the samples in an ultrasonic water bath for an additional 12 hours.

11.15.6. After the completion of extraction, centrifuge each sample at 3500 rpm for 15 minutes.

11.15.7. Collect and decant the KOH/methanol extract to a new 50 mL centrifuge tube.

11.15.8. Add another 2 mL of 0.4% KOH/methanol solution to the residue, briefly shake to mix and centrifuge at 3500 rpm for 15 minutes.

11.15.9. Combine the rinsate to the first corresponding tubes.

11.15.10. Proceed to Section 11.16.2 (Envi-carb clean up)

11.15.11. To the final KOH/methanol extract, add 0.5 mL of water to each.

11.15.12. Concentrate the KOH/methanol/water extract under nitrogen to less than 0.25 mL.

11.15.13. Dilute extract up to 50 mL with water in the centrifuge tube and vortex.

11.15.14. Prepare enough 125 mL HDPE containers as needed for all “Pre” and “Post” samples, including QC. Label each appropriately.

11.15.15. Spike the “Pre” and “Post” MB 125 mL containers with 25 uL of the reverse surrogate solution of M2-4:2 FTS (Section 7.8).

11.15.16. Spike the “Pre” and “Post” LCS/LCSD 125 mL containers with 0.5 mL of the LCS Spike solution and 25 uL of the reverse surrogate solution (Section 7.8).

11.15.17. Remove the methanol solvent from all “Post” QC sample 125 mL containers (MB and LCS/LCSD) by using N2 evaporation.

11.15.18. Add 2g of potassium persulfate and 1.9 mL of 10N NaOH to each “Post” sample container.

11.15.19. Transfer extract from the centrifuge tube to the appropriate 125 mL container.

11.15.20. Rinse the centrifuge container with an additional 50 mL of water and transfer to the appropriate 125 mL container.

11.15.21. Set aside all “Pre” sample containers.

11.15.22. Cap each “Post” sample container, invert 2-3 times prior to placing container into water bath.

11.15.23. Heat each “Post” sample container in a water bath (KD) at 85°C for 6 hours.

11.15.24. After digestion for 6 hours, place the “Post” sample containers in an ice bath for 30 minutes.

11.15.25. Adjust the pH of “Post” samples and associated QC aliquots to 7 with concentrated HCl. Use pH paper to determine the pH.

11.15.26. Spike both “Pre” and “Post” samples and their associated QC samples with 0.5 mL of PFC IDA solution (Section 7.7).

11.15.27. Use the following SPE procedure for both “Pre” and “Post” samples:

11.15.27.1. Set up WAX 150 mg/6 cc SPE columns for sample extraction using a vacuum manifold.

11.15.27.2. Establish a sample loading flow rate of 1 mL/minute for each port of the vacuum manifold, for as many ports as will be used simultaneously during sample loading.

11.15.27.3. Wash/condition the SPE column with 5 mL of 0.3% NH_4OH/Methanol, then 5 mL water.

11.15.27.4. Load 100 mL of sample onto the SPE cartridge at a flow rate of 1 mL/minute.

11.15.27.5. Add 5 mL rinse water

11.15.27.6. After the sample and water rinse have completely passed through the column, allow it to dry well using vacuum with a flow rate of 1 mL/minute for 15 minutes.

11.15.27.7. Wash the SPE column with 10 mL hexane rinse eluting all to waste.

11.15.27.8. Allow the column to dry well using vacuum with a flow rate of 1 mL/minute for 5 minutes. Columns must be dry before continuing.

11.15.27.9. Elute the samples into 15 mL polypropylene test tubes in the SPE manifold by rinsing each 125 mL sample container with 5 mL of 0.3% NH_4OH/methanol, and add to the SPE cartridge as eluent.

11.15.27.10. Repeat with another 5 mL of 0.3% NH_4OH/methanol.

11.15.27.11. Collect the 10 mL of eluent and concentrate per Section 11.6.

11.15.27.12. Note: If the extracts will not be concentrated elute extract with a total of 8 mL (2 4 mL rinses) of 0.3% NH_4OH/methanol.

11.16. Other Types of Sample Cleanup

11.16.1. Freezing technique to remove lipids.

If samples contain lipids then freeze the methanolic extract and QC extracts at -20^{o}C for at least 1 hour. Collect the solvent layer.

11.16.2. Cleanup with graphitized carbon will be applied to all samples as needed but is required for all DoD/DOE extracts.

11.16.2.1. Add 100 mg of graphitized carbon to each sample extract and QC extracts.

11.16.2.2. Shake vigorously and then let sit for 10 minutes.

11.16.2.3. Centrifuge each sample for 2 minutes at 1000 rpm.

11.16.2.4. Decant the solvent layer

11.16.2.5. Proceed to Section 11.6, 11.7 or 11.12 as applicable.

11.17. AFFF Sample Preparation

11.17.1. QC for AFFF samples consists of a method blank, a laboratory control sample and a sample or matrix duplicate only. No matrix spike or matrix spike duplicate is needed.

11.17.2. Perform a 1,000,000 X serial dilution of the AFFF sample. Dilute 1 mL of AFFF sample to 1L with laboratory supplied water. Then dilute 1mL of this dilution to 1L with laboratory supplied water.

11.17.2.1. Be sure to retain all dilutions should the initial analysis warrant re-analysis at higher concentration.

11.17.3. Subsample 2.0 mL of this dilution and fortify with 0.5 mL IDA solution and 0.5mL of IS (50 ng/mL) solution: then add 7.0 mL of methanol.

11.17.4. Transfer a portion of the sample to a 300 uL polypropylene autosampler vial (7 drop-wise or approximately ½ filled is sufficient). Archive the rest of the sample for re-injection or dilution.

11.18. Instrument Analysis

Suggested operating conditions are listed in Tables 1-7 for the Waters and SCIEX LCMS systems:

Table 1 - Recommended Instrument Operating Conditions

HPLC Conditions (Waters Acquity UPLC)					
Column (Column temp = 50°C)	Waters Acquity BEH 1.7µm C18, 3.0 x 150 mm				
Mobile Phase Composition	A = 20 mM Ammonium Acetate in Water B = Methanol				
Gradient Program	**Time**	**%A**	**%B**	**Curve**	**Flow Rate - mL/min.**
	0	98	2	6	0.30
	1	98	2	6	0.30
	2	50	50	6	0.30
	12	10	90	6	0.30
	12.5	0	100	6	0.30
	16	0	100	6	0.30
	16.2	98	2	6	0.30
	Maximum pressure limit = 15,000 psi				
Injection Size	10 µL (fixed amount throughout the sequence)				
Run Time	~20 minutes				
Mass Spectrometer Interface Settings (Quattro Premier XE)					
MS Interface Mode	ESI Negative Ion. Minimum of 10 scans/peak.				
Capillary (kV)	2.8				
Cone (V)	Varies from 8.0 to 65				
Extractor (V)	3				
Source Temp	135ºC				
Desolvation Temp	350ºC				
Cone Gas (nitrogen) Flow	25 L/hour				
Desolvation Gas (nitrogen) Flow	1100 L/hour				

Table 2 - Recommended Instrument Operating Conditions						
Mass Spectrometer Scan Settings (Quattro Premier XE)						
Compound	Comments	Reaction (MRM)	Dwell (sec)	Cone Volt.	Col. Energy	Function Number
PFBA	Native analyte	213 > 169	0.02	8	10	1
13C4-PFBA	IDA	217 > 172	0.02	12	10	1
PFPeA	Native analyte	263 > 219	0.02	10	10	2
13C5-PFPeA	IDA	268 > 223	0.02	11	9	2
PFBS	Native analyte	299 > 80	0.02	45	35	2
PFBS_2	Native analyte	299 > 99	0.02	45	35	2
13C3-PFBS	IDA	302 > 83	0.02	45	35	2
PFHxA	Native analyte	313 > 269	0.02	10	10	3
PFHxA_2	Native analyte	313 > 119	0.02	10	10	3
13C2-PFHxA	IDA	315 > 270	0.02	12	9	3
PFHpA	Native analyte	363 > 319	0.02	10	10	4
PFHpA_2	Native analyte	363 > 169	0.02	10	10	4
13C4-PFHpA	IDA	367 > 322	0.02	12	10	4
PFHxS	Native analyte	399 > 80	0.02	55	35	4
PFHxS_2	Native analyte	339 > 99	0.02	55	35	4
18O2-PFHxS	IDA	403 > 84	0.02	50	40	4
PFOA	Native analyte	413 > 369	0.02	12	10	5
PFOA_2	Native analyte	413 > 169	0.02	12	10	5
13C2-PFOA	IS	415 > 370	0.02	12	12	5
13C4-PFOA	IDA	417 > 372	0.02	12	12	5
PFHpS	Native analyte	449 > 80	0.02	60	38	5
PFHpS_2	Native analyte	449 > 99	0.02	60	38	5
PFNA	Native analyte	463 > 419	0.02	16	10	7
PFNA_2	Native analyte	463 > 169	0.02	16	10	7
13C5-PFNA	IDA	468 > 423	0.02	12	12	7
PFOS	Native analyte	499 > 80	0.02	60	40	6
PFOS_2	Native analyte	499 > 99	0.02	60	40	6
PFNS	Native analyte	549 > 80	0.02	60	40	6
PFNS_2	Native analyte	549 > 99	0.02	60	40	6
13C4-PFOS	IDA	503 > 80	0.02	35	48	6
PFDA	Native analyte	513 > 469	0.02	16	12	8
PFDA_2	Native analyte	513 > 169	0.02	16	12	8
13C2-PFDA	IDA	515 > 470	0.02	14	12	8
PFUdA	Native analyte	563 > 519	0.02	15	12	10
PFUdA_2	Native analyte	563 > 169	0.02	15	12	10
13C2-PFUdA	IDA	565 > 520	0.02	14	12	10
PFDS	Native analyte	599 > 80	0.02	74	48	10
PFDS_2	Native analyte	559 > 99	0.02	74	48	10
FOSA	Native analyte	498 > 78	0.02	40	32	9

Table 2 - Recommended Instrument Operating Conditions						
Mass Spectrometer Scan Settings (Quattro Premier XE)						
Compound	Comments	Reaction (MRM)	Dwell (sec)	Cone Volt.	Col. Energy	Function Number
13C8-FOSA	IDA	506 > 78	0.02	48	32	9
PFDoA	Native analyte	613 > 569	0.02	15	14	11
PFDoA_2	Native analyte	613 > 169	0.02	15	14	11
13C2-PFDoA	IDA	615 > 570	0.02	16	12	11
PFTrDA	Native analyte	663 > 619	0.02	12	12	11
PFTrDA_2	Native analyte	663 > 169	0.02	12	12	11
PFTeDA	Native analyte	713 > 169	0.02	12	18	11
PFTeDA_2	Native analyte	713 > 219	0.02	12	18	11
13C2-PFTeDA	IDA	715 > 670	0.02	15	15	11
PFHxDA	Native analyte	813 > 769	0.02	18	15	12
PFHxDA_2	Native analyte	813 > 169	0.02	18	15	12
PFODA	Native analyte	913 > 869	0.02	20	16	12
PFODA_2	Native analyte	913 > 169	0.02	20	16	12
13C2-PFHxDA	IDA	815 > 770	0.02	18	15	12
EtFOSAA	Native analyte	584 > 419	0.02	35	20	9
d5-EtFOSAA	IDA	589 > 419	0.02	30	25	9
MeFOSAA	Native analyte	570 > 419	0.02	30	28	9
d3-MeFOSAA	IDA	573 > 419	0.02	30	25	9
4:2FTS	Native analyte	327 > 307	0.02	40	30	5
M2-4:2FTS	Reverse Surrogate	329 > 81	0.02	40	30	5
6:2FTS	Native analyte	427 > 407	0.02	40	30	5
M2-6:2FTS	IDA	429 > 81	0.02	40	28	5
8:2FTS	Native analyte	527 > 507	0.02	40	28	8
M2-8:2FTS	IDA	529 > 81	0.02	40	28	8

Table 3 - Recommended Instrument Operating Conditions				
Retention Times & Quantitation (Quattro Premier XE)				
Native Compounds	**Typical Native RT (minutes)**	**IS analog**	**Typical IDA RT (minutes)**	**Quantitation Method**
PFBA	4.77	13C4-PFBA	4.79	Isotope Dilution
PFPeA	5.90	13C5-PFPeA	5.92	Isotope Dilution
PFBS	6.01	13C3-PFBS	6.01	Isotope Dilution
PFHxA	7.22	13C2-PFHxA	7.25	Isotope Dilution
PFPeS	7.20	18O2-PFHxS	8.64	Isotope Dilution
PFHpA	8.57	13C4-PFHpA	8.59	Isotope Dilution
PFHxS	8.60	18O2-PFHxS	8.64	Isotope Dilution
PFOA	9.80	13C4-PFOA	9.83	Isotope Dilution
PFHpS	9.80	13C4-PFOS	10.90	Isotope Dilution
PFNA	10.88	13C5-PFNA	10.92	Isotope Dilution
PFOS	10.87	13C4-PFOS	10.90	Isotope Dilution
PFNS	11.70	13C4-PFOS	10.90	Isotope Dilution
PFDA	11.82	13C2-PFDA	11.86	Isotope Dilution
FOSA	12.41	13C8-FOSA	12.46	Isotope Dilution
PFDS	12.57	13C4-PFOS	10.90	Isotope Dilution
PFUdA	12.62	13C2-PFUdA	12.66	Isotope Dilution
PFDoA	13.32	13C2-PFDoA	13.34	Isotope Dilution
PFTrDA	13.91	13C2-PFDoA	13.34	Isotope Dilution
PFTeDA	14.39	13C2-PFTeDA	14.39	Isotope Dilution
PFHxDA	15.16	13C2-PFHxDA	15.16	Isotope Dilution
PFODA	15.57	13C2-PFHxDA	15.16	Isotope Dilution
EtFOSAA	12.63	d5-EtFOSAA	12.62	Isotope Dilution
MeFOSAA	12.3	d3-MeFOSAA	12.28	Isotope Dilution
4:2FTS	7.02	13C3-PFBS	6.01	Isotope Dilution
6:2FTS	10.08	M2-6:2FTS	10.08	Isotope Dilution
8:2FTS	11.95	M2-8:2FTS	11.95	Isotope Dilution

Table 4 - Recommended Instrument Operating Conditions				
HPLC Conditions (Shimadzu HPLC)				
Column (Column temp = 45°C)	Phenomenex Gemini 3 µm C18 110Å, 50 X 2 mm			
Mobile Phase Composition	A = 20 mM Ammonium Acetate in Water B = Methanol			
Gradient Program	**Time**	**%A**	**%B**	**Flow Rate - mL/min**
	0	90	10	0.60
	0.1	45	55	0.60
	4.5	1	99	0.60
	4.95	1	99	0.60
	5	90	10	0.60
	Maximum pressure limit = 5,000 psi			

Table 4 - Recommended Instrument Operating Conditions	
HPLC Conditions (Shimadzu HPLC)	
Injection Size	2 µL (fixed amount throughout the sequence). If non-concentrated extract then use 20 uL.
Run Time	~6.6 minutes
Mass Spectrometer Interface Settings (SCIEX 5500)	
MS Interface Mode	ESI Negative Ion. Minimum of 10 scans/peak.
Ion Spray Voltage (kV)	4.5
Entrance Potential (V)	5
Declustering Potential (V)	25
Desolvation Temp	600ºC
Curtain Gas	35 psi
Collision Gas	8 psi

Table 5 - Recommended Instrument Operating Conditions

Mass Spectrometer Scan Settings (SCIEX 5500)

Compound	Comments	Reaction (MRM)	Dwell (sec)	Ent. Pot. (V)	Col. Energy (V)	Declu. Pot. (V)	Cell Exit Pot. (V)	Typ RT (Min)
PFBA	Native analyte	212.9 > 169	0.011	-5	-12	-25	-31	1.74
13C4-PFBA	IDA	217 > 172	0.011	-5	-12	-25	-31	1.74
PFBS	Native analyte	298.9 > 80	0.011	-6	-58	-55	-37	1.76
PFBS_2	Native analyte	298.9 > 99	0.011	-5	-40	-55	-12	1.76
13C3-PFBS	IDA	301.9 > 83	0.011	-5	-40	-55	-12	1.76
PFPeA	Native analyte	262.9 > 219	0.011	-7	-12	-20	-34	1.99
13C5-PFPeA	IDA	267.9 > 223	0.011	-7	-12	-20	-35	1.99
4:2 FTS	Native analyte	327 > 307	0.011	-7	-32	-50	-10	2.06
M2-4:2FTS	Reverse Surrogate	329 > 81	0.011	-7	-32	-50	-10	2.06
PFHxA	Native analyte	313 > 269	0.011	-5	-12	-25	-37	2.25
PFHxA_2	Native analyte	313 > 119	0.011	-5	-12	-25	-37	2.25
13C2-PFHxA	IDA	315 > 270	0.011	-5	-12	-25	-38	2.25
PFHpA	Native analyte	363 > 319	0.011	-6	-12	-25	-41	2.57
PFHpA_2	Native analyte	363 > 169	0.011	-6	-12	-25	-41	2.57
13C4-PFHpA	IDA	367 > 322	0.011	-6	-12	-25	-41	2.57
PFPeS	Native analyte	349 > 80	0.011	-9	-66	-57	-40	2.15
PFPeS_2	Native analyte	349 > 99	0.011	-9	-40	-57	-12	2.15
PFHxS	Native analyte	399 > 80	0.011	-12	-74	-60	-43	2.59
PFHxS_2	Native analyte	399 > 99	0.011	-12	-74	-60	-43	2.59
18O2-PFHxS	IDA	403 > 84	0.011	-12	-74	-60	-43	2.59
6:2 FTS	Native analyte	427 > 407	0.011	-7	-32	-50	-10	2.91
M2-6:2FTS	IDA	429 > 81	0.011	-7	-32	-50	-10	2.91
PFOA	Native analyte	413 > 369	0.011	-6	-14	-25	-44	2.93
PFOA_2	Native analyte	413 > 169	0.011	-5	-22	-25	-12	2.93
13C4-PFOA	IDA	417 > 372	0.011	-6	-14	-25	-44	2.93

Table 5 - Recommended Instrument Operating Conditions								
Mass Spectrometer Scan Settings (SCIEX 5500)								
Compound	Comments	Reaction (MRM)	Dwell (sec)	Ent. Pot. (V)	Col. Energy (V)	Declu. Pot. (V)	Cell Exit Pot. (V)	Typ RT (Min)
13C2-PFOA	IS	415 > 370	0.011	-6	-14	-25	-44	2.93
PFHpS	Native analyte	449 > 80	0.011	-11	-88	-65	-46	2.94
PFHpS_2	Native analyte	449 > 99	0.011	-11	-88	-65	-46	2.94
PFNA	Native analyte	463 > 419	0.011	-6	-14	-25	-47	3.29
PFNA_2	Native analyte	463 > 169	0.011	-6	-14	-25	-47	3.29
13C5-PFNA	IDA	468 > 423	0.011	-6	-14	-25	-48	3.29
PFOS	Native analyte	499 > 80	0.011	-9	-108	-65	-50	3.29
PFOS_2	Native analyte	499 > 99	0.011	-5	-58	-65	-12	3.29
PFNS	Native analyte	549 > 80	0.011	-10	-113	-75	-52	3.40
PFNS_2	Native analyte	549 > 99	0.011	-8	-71	-75	-12	3.40
13C4-PFOS	IDA	503 > 80	0.011	-9	-108	-65	-50	3.29
PFDA	Native analyte	513 > 469	0.011	-6	-16	-25	-51	3.65
PFDA_2	Native analyte	513 > 169	0.011	-6	-16	-25	-51	3.65
13C2-PFDA	IDA	515 > 470	0.011	-6	-16	-25	-51	3.65
8:2 FTS	Native analyte	527 > 507	0.011	-7	-40	-50	-15	3.65
M2-8:2FTS	IDA	529 > 81	0.011	-7	-40	-50	-15	3.65
PFOSA	Native analyte	498 > 78	0.011	-8	-85	-60	-50	3.7
13C8-PFOSA	IDA	506 > 78	0.011	-8	-85	-60	-50	3.7
N-MeFOSAA	Native analyte	570 > 419	0.011	-7	-36	-40	-15	3.82
d3-MeFOSAA	IDA	573 > 419	0.011	-7	-36	-40	-15	3.82
PFDS	Native analyte	599 > 80	0.011	-11	-118	-85	-54	3.96
PFDS_2	Native analyte	599 > 99	0.011	-11	-118	-85	-54	3.96
PFUdA	Native analyte	563 > 519	0.011	-7	-18	-25	-54	3.97
PFUdA_2	Native analyte	563 > 169	0.011	-7	-18	-25	-54	3.97
13C2-PFUdA	IDA	565 > 520	0.011	-7	-18	-25	-54	3.97
N-EtFOSAA	Native analyte	584 > 419	0.011	-7	-36	-50	-15	3.99
d5-EtFOSAA	IDA	589 > 419	0.011	-7	-36	-50	-15	3.99
PFDoA	Native analyte	613 > 569	0.011	-5	-18	-25	-54	4.3
PFDoA_2	Native analyte	613 > 169	0.011	-5	-18	-25	-54	4.3
13C2-PFDoA	IDA	615 > 570	0.011	-5	-18	-25	-54	4.3
PFTrDA	Native analyte	663 > 619	0.011	-7	-20	-25	-54	4.56
PFTrDA_2	Native analyte	663 > 169	0.011	-7	-20	-25	-54	4.56
PFTeDA	Native analyte	713 > 169	0.011	-2	-22	-25	-10	4.79
PFTeDA_2	Native analyte	713 > 219	0.011	-7	-36	-25	-30	4.79
13C2-PFTeDA	IDA	715 > 670	0.011	-2	-22	-25	-10	4.79
PFHxDA	Native analyte	813 > 769	0.011	-7	-24	-25	-54	5.25
PFHxDA_2	Native analyte	813 > 169	0.011	-7	-24	-25	-54	5.25
13C2-PFHxDA	IDA	815 > 770	0.011	-7	-24	-25	-54	5.25
PFODA	Native analyte	913 > 869	0.011	-7	-26	-25	-54	5.55
PFODA_2	Native analyte	913 > 169	0.011	-7	-26	-25	-54	5.55

Table 6 - Recommended Instrument Operating Conditions Mass Spectrometer Scan Settings (SCIEX 5500) for Fluorinated Replacement Chemicals								
Compound	Comments	Reaction (MRM)	Dwell (sec)	Ent. Pot. (V)	Col. Energy (V)	Declu. Pot. (V)	Cell Exit Pot. (V)	Typ RT (Min)
HFPO-DA	Native analyte	329.1 > 285	0.011	-10	-6	-48	-17	2.06
13C3-HFPO-DA	IDA	332.1 > 287	0.011	-10	-10	-40	-17	2.06
9Cl-PF3ONS (F53B major)	Native analyte	531 > 351	0.011	-10	-30	-120	-17	3.23
11Cl-PF3OUdS (F53B minor)	Native analyte	631 > 451	0.011	-10	-40	-160	-17	3.84
Adona	Native analyte	377 > 251	0.011	-10	-16	-55	-17	2.33
Adona_2	Native analyte	377 > 85	0.011	-10	-35	-55	-17	2.33

Table 7 - Retention Times & Quantitation (SCIEX 5500)				
Native Compounds	**Typical Native RT (minutes)**	**IS analog**	**Typical IDA RT (minutes)**	**Quantitation Method**
PFBA	1.54	13C4-PFBA	1.54	Isotope Dilution
PFPeA	1.56	13C5-PFPeA	1.56	Isotope Dilution
PFBS	1.78	13C3-PFBS	1.78	Isotope Dilution
PFHxA	2.03	13C2-PFHxA	2.03	Isotope Dilution
PFPeS	2.06	13C3-PFBS	1.78	Isotope Dilution
PFHpA	2.36	13C4-PFHpA	2.36	Isotope Dilution
PFHxS	2.37	18O2-PFHxS	2.37	Isotope Dilution
PFOA	2.71	13C4-PFOA	2.71	Isotope Dilution
PFHpS	2.72	13C4-PFOS	3.09	Isotope Dilution
PFNA	3.09	13C5-PFNA	3.09	Isotope Dilution
PFOS	3.09	13C4-PFOS	3.09	Isotope Dilution
PFNS	3.40	13C4-PFOS	3.09	Isotope Dilution
PFDA	3.45	13C2-PFDA	3.45	Isotope Dilution
FOSA	3.43	13C8-FOSA	3.43	Isotope Dilution
PFDS	3.77	13C4-PFOS	3.09	Isotope Dilution
PFUdA	3.78	13C2-PFUdA	3.78	Isotope Dilution
PFDoA	4.07	13C2-PFDoA	4.07	Isotope Dilution
PFTrDA	4.34	13C2-PFDoA	4.07	Isotope Dilution
PFTeDA	4.58	13C2-PFTeDA	4.58	Isotope Dilution
PFHxDA	4.99	13C2-PFHxDA	4.99	Isotope Dilution
PFODA	5.34	13C2-PFHxDA	4.99	Isotope Dilution
EtFOSAA	3.78	d5-EtFOSAA	3.78	Isotope Dilution
MeFOSAA	3.61	d3-MeFOSAA	3.60	Isotope Dilution
4:2 FTS	1.98	13C3-PFBS	1.78	Isotope Dilution
6:2FTS	2.69	M2-6:2FTS	2.69	Isotope Dilution
8:2FTS	3.44	M2-8:2FTS	3.44	Isotope Dilution

Table 7 - Retention Times & Quantitation (SCIEX 5500)				
Native Compounds	**Typical Native RT (minutes)**	**IS analog**	**Typical IDA RT (minutes)**	**Quantitation Method**
HFPO-DA	2.06	13C3-HFPO-DA	2.06	Isotope Dilution
9Cl-PF3ONS (F53B major)	3.23	13C4-PFOS	3.09	Isotope Dilution
11Cl-PF3OUdS (F53B minor)	3.84	13C4-PFOS	3.09	Isotope Dilution
Adona	2.33	13C4-PFOS	3.09	Isotope Dilution

11.18.1. Post Spike Sample Analysis for AFFF samples

11.18.1.1. This section only applies to aqueous samples prepared by serial dilution instead of SPE that have reported value of <LOQ (RL) for any analyte.

11.18.1.2. Spike aliquots of the sample at the final dilution reported for the sample with all analytes that have reported of <LOQ in the final dilution. The spike must be at the LOQ concentration to be reported with the sample (the < LOQ value).

11.18.1.3. When analyte concentrations are calculated as <LOQ, the spike must recover within 70-130% of its true value.

11.18.1.4. It the recovery does not meet this criteria, the sample, sample duplicate and post spike sample must be reanalyzed at consecutively higher dilutions until the criteria is met.

11.18.2. Tune and calibrate the instrument as described in Section 10.

11.18.3. A typical run sequence is as follows:

- Rinse Blank (RB, not linked to anything)
- Start ICAL with CCVL but called IC in TALS (starts the 12 hour clock or time 0:00)
- Rest of ICAL
- ICB: link to midpoint of ICAL and samples
- ICV: link to midpoint of ICAL and samples (If ICAL good)
- CCB: link to midpoint of ICAL and samples
- PFOA RT marker (as needed)
- Rinse Blank (RB, not linked to anything)
- 10 samples: link to midpoint of ICAL
- CCV: link to midpoint of ICAL
- 10 more samples: link to midpoint of ICAL

- CCV: link to midpoint of ICAL
- Etc.
- CCVL (within 12 hours from CCVL in ICAL, can be the ending CCV and starts 12 hours all over again): if this occurs link to the midpoint of the ICAL/toggle it as opening/closing CCV.
- CCV: link to midpoint of ICAL
- 10 samples: link to midpoint of ICAL
- CCV: link to midpoint of ICAL
- If no ICAL run that day
- CCB: link to CCVIS
- CCVL (starts 12 hour clock): link to CCVIS
- CCVIS: link to midpoint of ICAL
- 10 samples: link to CCVIS
- CCV: link to CCVIS
- 10 samples: link to CCVIS
- CCV: link to CCVIS
- Etc.
- If going over 12 hours in the sequence : CCVL (within 12 hours from CCVL at item 2 above, can be the ending CCV and starts 12 hours all over again): if this occurs link to the CCVIS /toggle as opening and closing CCV.
- CCV: link to CCVIS
- 10 samples: link to CCVIS
- CCV: link to CCVIS

12. CALCULATIONS

12.1. If the concentration of the analyte ions exceeds the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. It may be necessary to dilute samples due to matrix.

12.2. Qualitative Identification

12.2.1. The retention times of PFAS with labeled standards should be the same as that of the labeled IDA's to within 0.05 min. For PFAS with no labeled standards, the RT must be within ± 0.3 minutes of the ICV and CCV standards. *Note: The IDA RT and native RT may be offset by 0.02 to 0.04 minutes.*

12.3. The ICAL established in Section 10 is used to calculate concentrations for the extracts.

12.4. Extract concentrations are calculated as below. The first equation applies to the linear fit, the second to the quadratic line fit.

Equation 3

$$\text{Concentration, ng/mL} = \frac{y - c}{b}$$

Equation 4

$$\text{Concentration, ng/mL} = \frac{-b + \sqrt{b^2 - 4a(c - y)}}{2a}$$

Where:

y = $\frac{\text{Area (analyte)}}{\text{Area (IS)}} \times \text{Concentration (IS)}$

x = concentration
a = curvature
b = slope
c = intercept

12.5. Water Sample Result Calculation:

Equation 5

$$\text{Concentration, ng/L} = \frac{C_{ex} V_t}{V_o}$$

Where:

C_{ex} = Concentration measured in sample extract (ng/mL)
V_t = Volume of total extract (mL)
V_o = Volume of water extracted (L)

12.6. Soil Sample Result Calculation:

Equation 6

$$\text{Concentration, } ng/g = \frac{C_{ex} V_t}{W_s D}$$

Where ng/g = µg/kg and:

C_{ex} = Concentration measured in sample extract (ng/mL)
V_t = Volume of total extract (mL)
W_s = Weight of sample extracted (g)
D = Fraction of dry solids, which is calculated as follows:

$\frac{100 - \%\text{ moisture in sample}}{100}$ (for dry weight result)

12.7. IDA Recovery Calculation:

Equation 7

$$\%\,\mathrm{Recovery} = \frac{A_t Q_{is}}{A_{is} Q_t RRF_{IDA}} X 100$$

Where ng/g = µg/kg and:

RF_{IDA}	=	Response Factor for IDA compound
A_t	=	Area response for IDA compound
A_{IS}	=	Area Response for IS compound
Q_{IS}	=	Amount of IS added
Q_t	=	Amount of IDA added

12.8. Raw data, calibration summaries, QC data, and sample results are reviewed by the analyst. These must also be reviewed thoroughly by a second qualified person. See the Data Review Policy (WS-PQA-0012). These reviews are documented on the Data Review Checklist.

13. METHOD PERFORMANCE

13.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required expertise.

13.2. Method Detection Limit

The laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in SOP WS-QA-0006 and policy WS-PQA-003. MDLs are available in the Quality Assurance Department.

13.3. Initial Demonstration of Capability (IDOC)

Each analyst performing this procedure must successfully analyze four LCS QC samples using current laboratory LCS control limits. IDOCs are approved by the Quality Assurance Manager and the Technical Director. IDOC records are maintained by the QA staff in the central training files.

13.4. The laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in WS-QA-0006 and policy WS-PQA-003.

14. POLLUTION PREVENTION

14.1. All waste will be disposed of in accordance with Federal, State and Local regulations.

14.2. Solid phase extraction used for water samples greatly reduces the amount of solvent used compared to liquid-liquid extraction.

14.3. Standards and reagents are purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.4. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.5. Do not allow waste solvent to vent into the hoods. All solvent waste is stored in capped containers unless waste is being transferred.

14.6. Transfer waste solvent from collection cups (tri-pour and similar containers) to jugs and/or carboys as quickly as possible to minimize evaporation.

15. WASTE MANAGEMENT

The following waste streams are produced when this method is carried out:

15.1. Assorted test tubes, autovials, syringes, filter discs and cartridges. Dump the solid waste into a yellow contaminated lab trash bucket. When the bucket is full or after no more than one year, tie the plastic bag liner shut and put the lab trash into the hazardous waste – landfill steel collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.2. Extracted soil samples, used sodium sulfate, paper funnel filters, glass wool, thimbles, and extracted solids saturated with solvents. Dump these materials into an orange contaminated lab trash bucket. When the bucket is full or after no more than one year, tie the plastic bag liner shut and put the lab trash into the incineration steel collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.3. Waste Methanol. Collect the waste solvents in tripours during use. Empty the tripours into a 1-liter to 4-liter carboy at the fume hood. When the carboy is full, or at the end of your shift, whichever comes first, empty the carboy into the steel flammable solvent drum in the H3 closet. When full to no less than six inches of the top, or after no more than 75 days, move the steel flammable solvent drum to the waste collection area for shipment.

15.4. Mixed water/methanol waste from soil extraction. Collect the waste in the HPLC waste carboy. When full, or after no more than one year, dump into the blue plastic HPLC collection drum in the H3 closet. When the drum is full, to no less than six inches of the top, or after no more than 75 days, move it to the waste collection area for shipment.

15.5. Aqueous acidic waste from the LCMS instrument contaminated with methanol. This is collected in a 1-gallon carboy at the instrument. When the carboy is full, or after no more than one year, it is emptied into the blue plastic HPLC collection drum in the H3 closet. When the drum is full to between two and six inches of the top, or after no more than 75 days, move it to the waste collection area for shipment.

15.6. Autovials contaminated with methanol. As the autovials are removed from the instrument after analysis, they are collected in open containers at the instrument. After all autovials are removed, the open container must be dumped into a closed satellite collection container in a fume hood, as the punctured septa in the autovial can allow methanol and other contaminants to evaporate into the atmosphere. The satellite collection containers are transferred to the waste disposal area when full or after no more than one year, where they are disposed through the vial eater.

16. REFERENCES

16.1. Cheryl Moody, Wai Chi Kwan, Johnathan W. Martin, Derek C. G. Muir, Scott A. Mabury, “Determination of Perfluorinated Surfactants in Surface Water Samples by Two Independent Analytical Techniques: Liquid Chromatography/Tandem Mass Spectrometry and 19FNMR,” Analytical Chemistry 2001, 73, 2200-2206.

16.2. John Giesy et al., “Accumulation of Perfluorooctane Sulfonate in Marine Mammals”, Environmental Science & Technology, 2001 Vol. 35, No. 8, pages 1593-1598.

16.3. U.S. EPA, “Residue Chemistry Test Guidelines, OPPTS 860.1340, Residue Analytical Method”, EPA 712-C-95-174, August 1995.

16.4. STL Denver White Paper DEN-W-LC-002, “Method Validation Study for Analysis of Ammonium Perfluorooctanate in Soil Matrices by High Performance Liquid Chromatography/Mass Spectrometry (HPLC/MS/MS)”, Mark Dymerski, September 5, 2003.

16.5. STL Denver White Paper DEN-W-LC-003, “Addendum A to Method Validation Study for Analysis of Ammonium Perfluorooctanate in Soil Matrices by High Performance Liquid Chromatography/Mass Spectrometry (HPLC/MS/MS)”, Mark Dymerski, August 6, 2003.

16.6. STL Denver White Paper DEN-W-LC-004, “Method Validation Study for Analysis of Perfluorooctanoic Acid in Waters by High Performance Liquid Chromatography/Tandem Mass Spectrometry (HPLC/MS/MS)”, Mark Dymerski, January 26, 2005.

16.7. Waters application note; “Acquity UPLC System for Quantifying Trace Levels of Perfluorinated Compounds with an Acquity PFC Analysis Kit”, Peter J. Lee, Evan T.

Bernier, Gordon T. Fujimoto, Jeremy Shia, Michael S. Young, and Alice J. Di Gloia, Waters Corporation, Milford, MA. USA.

16.8. US EPA, "Method 537 - Determination of Selected Perfluorinated alkyl acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometery (LC/MS/MS)", Version 1.1, September 2009, J.A. Shoemaker, P.E. Grimmett, B.K. Boutin, EPA Document #: EPA/600/R-08/092

16.9. Erika F. Houtz and David L. Sedlak, "Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff," Environmental Science and Technology 46, no. 17 (2012): 9342-49.

17. METHOD MODIFICATIONS

17.1. Modifications from Method 537 are detailed below:

17.1.1. Water sample containers are not preserved with Trizma.

17.1.2. The method has been modified to address soil/solid matrices. The extraction holding time is set at 14 days.

17.1.3. The analyte list has been expanded. The number of labeled analytes has been expanded as well to improve quantitation.

17.1.4. The reporting limits differ as they are all set at one consistent value.

17.1.5. Calibration levels differ from the referenced method.

17.1.6. More labeled analytes are fortified into the samples prior to the extraction process. Most target analytes are quantitated against a labeled analyte.

17.1.7. There is no symmetry requirement.

17.1.8. Calibration, both initial and continuing, has different acceptance criteria due to the longer list of analytes, and the use of isotope dilution quantitation.

17.1.9. The eluents and HPLC configuration differs. As a result the final extract is in 80:20 methanol:water.

17.1.10. The LCS and MS/MSD are spiked at one concentration and do not rotate between a low to high levels.

17.1.11. Samples are not checked for residual chlorine or pH.

17.1.12. A different SPE cartridge (Waters OASIS WAX) is used for the extraction

process. As a result solvents and elution procedures are different.

18. ATTACHMENTS

18.1. Attachment 1 - Analysis of Perfluorinated Compounds (PFAS) in Water via In Line Solid Phase Extraction (SPE).

19. REVISION HISTORY

Revisions to Attachment 1 are documented in the attachment.

Revisions prior to 05/01/2017 have been removed and are available in previous versions of this SOP.

19.1. WS-LC-0025, Revision 3.1, Effective 06/21/2018

19.1.1. Section 11.2.1 revised to, “Visually inspect samples for the presence of settled and/or suspended sediment/particulates. If present or if the sample is biphasic add IDA prior to any sample decanting or centrifugation. If the sample requires decanting or centrifugation contact the client for guidance prior to such action. Decanting or filtering of the sample can lead to a low bias.”

19.1.2. Editorial changes.

19.2. WS-LC-0025, Revision 3.0, Effective 04/13/2018

19.2.1. Section 1.1 updated table with PFPeS and PFNS analytes.

19.2.2. Added Section 2.2, which details the analytes that can be covered by the method under special request.

19.2.3. Added Section 3.13, “AFFF: Aqueous Film Forming Foam”.

19.2.4. Section 6.19 added, “Create all eluents in Reagent module, label eluent containers with TALS label and place 2nd label into maintenance log when put into use” to table.

19.2.5. Section 7.1.2 added, “Prepared by weighing 1.509g of ammonium acetate and dissolving in 1L of water. The resultant solution is filtered through a 0.22um filter before use. This solution has volatile components, thus it should be replaced every 7 days or sooner.”

19.2.6. Section 7.1.3 added, “Prepared by diluting 12mL of ammonium hydroxide into 4L of methanol.”

19.2.7. Section 7.1.8 added, “Prepared by weighing 16g of potassium hydroxide and

dissolving in 4L of methanol."

19.2.8. Section 7.1.11 added, "Prepared by diluting 400mL of 1N NaOH into 3.6L of water for a total volume of 4L."

19.2.9. Section 7.4 updated table with PFPeS and PFNS analytes.

19.2.10. Section 7.4, added table to detail ICAL for Fluorinated Replacement Compounds.

19.2.11. Added Section 8.1.1, "Water samples collected from a known chlorinated source should be preserved with Trizma."

19.2.12. Added Section 9.9.3, "If the IS does not meet criteria, re-analyze the extract. If the IS meets criteria in the second analysis, report that analysis. If the IS does not meet criteria in the second analysis, report the first analysis with narration."

19.2.13. Added Section 11.14.6, "Add 2g of potassium persulfate and 1.9 mL of 10N NaOH to each "Post" sample container."

19.2.14. Removed Section 11.14.8, "Add 2g of potassium persulfate and 1.9 mL of 10N NaOH to each "Post" sample container."

19.2.15. Added Section 11.14.9, "Cap each "Post" sample container, invert 2-3 times prior to placing container into water bath."

19.2.16. Added Section 11.5 and associated subsections, which detail the "TOPS (Total Oxidizable Precursor) Assay for Soil Sample".

19.2.17. Section 11.8 updated Table labeling, added PFPeS and PFNS analytes throughout Tables where applicable, and updated Table 7 to reflect current retention times and quantitation.

19.2.18. Section 11.8 added Table 6, "Recommended Instrument Operating Conditions Mass Spectrometer Scan Settings (SCIEX 5500) for Fluorinated Replacement Chemicals"

19.2.19. Section 11.18.3 removed outdated run sequence and replaced with current run sequence.

19.2.20. Editorial changes.

19.3. WS-LC-0025, Revision 2.9, Effective 11/22/2017

19.3.1. Section 1.2, table updated to reflect ranges after removing MeFOSA and

EtFOSA from the SOP in the previous revision.

19.3.2. Section 9.3.6, last sentence changed to read, “Reprepare and reanalyze all field and QC samples associated with the contaminated method blank.”

19.3.3. Section 9.7, first sentence changed to read, “Initial calibration verification (ICV) – A second source standard is analyzed with the initial calibration curve.

19.3.4. Section 1.3.1 revised to read, “Once the optimal mass assignments (within ±0.5 amu of true) are made immediately following the initial tune, the lowest level standard from the initial calibration curve is assessed to ensure that a signal to noise ratio greater than 10 to 1 (S/N > 10:1) is achieved for each PFAS analyte. The first level standard from the initial calibration curve is used to evaluate the tune stability on an ongoing basis. The instrument mass windows are set initially at ± 0.5 amu of the true value; therefore, continued detection of the analyte transition with S/N > 10:1 serves as verification that the assigned mass remains within ± 0.5 amu of the true value, which meets the DoD/DOE QSM tune criterion. For QSM work, the instrument sensitivity check (section 10.12.4) is also evaluated to ensure that the signal to noise criteria is met.”

19.3.5. Editorial changes.

19.4. WS-LC-0025, Revision 2.8, Effective 11/06/2017

19.4.1. Revised Section 4.5 to “Both branched and linear PFAS isomers can potentially be found in the environment. Linear and branched isomers are known to exist for PFOS, PFOA, PFHxS, PFBS, EtFOSAA, and MeFOSAA based upon the literature. If multiple isomers are present for one of these PFAS they might be adjacent peaks that completely resolved or not, but usually with a deflection point resolved during peak integration. The later of these peaks match the retention time of its labeled linear analog. In general, earlier peaks are the branched isomers and are not the result of peak splitting.

At this time only PFOS, PFOA and PFHxS are commercially available as technical mixtures. These reference standards of the technical mixtures for these specific PFAS are used to ensure that all appropriate peaks are included during peak integration.”

19.4.2. Sections 4.8 and 7.2.1.1, corrected the in-sample contributions to 0.30 ng/L and 0.015 ug/kg.

19.4.3. Removed Section 7.1.14, “Methanol-Water, 78:22 vol./vol., prepared by

mixing 780 mL methanol and 220 mL reagent water. Stored in polypropylene bottle and sealed with polypropylene screw cap." Reagent was added incorrectly.

19.4.4. Section 7.2.4, corrected the factor to 0.956 from 1.046.

19.4.5. Added Section 7.4.1, "A technical (qualitative) grade PFOA standard which contains both linear and branched isomers is used as a retention time (RT) marker. This is used to integrate the total response for both linear and branched isomers of PFOA in environmental samples while relying on the initial calibration with the linear isomer quantitative standard This technical (qualitative) grade PFOA standard is analyzed initially, after an initial calibration when a new column is installed or when significant changes are made to the HPLC parameters."

19.4.6. Section 9.7, added "Rerun the initial calibration" as the last bullet item.

19.4.7. Added Section 10.3.1, "The first level standard from the initial calibration curve is used to evaluate the tune criteria. The instrument mass windows are set at ±0.5 amu; therefore, detection of the analyte serves as verification that the assigned mass is within ±0.5 amu of the true value, which meets the DoD/DOE QSM tune criterion.

19.4.8. Section 10.10.1, appended "containing both IDA and IS" to the end of the paragraph.

19.4.9. Sections 11.6.3 and 11.12.2.3, changed "78:22 methanol:water" to "methanol".

19.4.10. Sections 1.1 and 7.4, removed EtFOSA and MeFOSA from tables due to low volume of requests for those analytes.

19.4.11. Removed Section 2.2.1, "Optional cleanups may include sample freezing and/or cleanup by SPE cartridge, unless EtFOSA and MeFOSA are requested."

19.4.12. Removed EtFOSA/MeFOSA specific comments in various sections throughout the document.

19.4.13. Section 7.4 Note added, "The concentration of the calibration solutions for non-concentrated extracts is 1/20th the levels indicated above."

19.4.14. Section 7.9, changed 1000 ng/mL to 250 ng/mL and replaced final sentence with "The internal standard solution used for the non-concentrated extracts is at a concentration of 50 ng/mL."

19.4.15. Removed Section 11.2.8, “If EtFOSA and/or MeFOSA are requested, add 100uL of IS and then adjust the final volume (FV) of these aliquots to 5.0 mL with MeOH. QC samples, LCS, MS, and MSD will require concentration via nitrogen to adjust the FV to 5.0 mL. Vortex each sample. Then, transfer a portion of the extract to a 300 uL polypropylene autosampler vial (7 drop-wise or approximately ½ filled is sufficient). Archive the rest of the extracts for re-injection and dilution.”

19.4.16. Added Section 11.5.4, “Proceed to Section 11.15.2 (Graphitized Carbon Cleanup) as needed. This is required for all DoD/DOE extracts.”

19.4.17. Added Section 11.7.1.1, “Seal the test tube tightly. Invert container several times and then vortex. Allow extract to settle for 10 minutes prior to moving to the next step.”

19.4.18. Inserted Section 11.8.1.1, “Projects performed under the auspices of the DoD/DOE must have the entire sample homogenized prior to subsampling in accordance with QSM 5.1 criteria.”

19.4.19. Section 11.11.4, added “(Graphitized Carbon Cleanup) as needed. This is required for all DoD/DOE extracts.”

19.4.20. Section 11.14.6, added “Spike all “Pre” and “Post” samples with 25uL of the reverse surrogate solution (Section 7.8).”

19.4.21. Section 11.15.2, revised to read, “Cleanup with graphitized carbon will be applied to all samples as needed but is required for all DoD/DOE extracts.”

19.4.22. Added Section 11.15.2.5, “Proceed to Section 11.6, 11.7, or 11.12 as applicable.”

19.4.23. Removed Sections 11.15.3 through 11.15.6.

19.4.24. Added Section 11.16, “AFFF Sample Preparation”.

19.4.25. Section 11.17, removed EtFOSA, MeFOSA, d5-EtFOSA, and d3MeFOSA from all tables.

19.4.26. Section 11.17, changed masses for M2-4:2FTS, M2-6:2FTS, and M2-8:2FTS. Initially assigned daughter masses were bleeding through from the native analog.

19.4.27. Section 11.17, all tables on MS Interface Mode Line, added “Minimum of 10 scans/peak.”

19.4.28. Added Section 11.17.1, “Post Spike Sample Analysis for AFFF Samples”.

19.4.29. Added Section 11.8.4.1 “Spike non-concentrated samples at 0.5 mL of LCS/Matrix Spike Solution.”

19.4.30. Added Section 11.8.5.1, “Spike non-concentrated samples at 0.5 mL of IDA PFC Solution.”

19.4.31. Editorial changes.

19.5. WS-LC-0025, Revision 2.7, Effective 09/20/2017

19.5.1. Section 1.1 table, added 1H,1H,2H,2H-perfluorohexane sulfonate *(4:2).*

19.5.2. Section 1.1, removed “Sample results for PFOA may also be reported as APFO, at the request of the client. (See Section 12.7).”

19.5.3. Section 1.2 and 11.8.2, updated tissue extracted mass and RL.

19.5.4. Section 2.5, removed “and assumes a proportional relationship between the initial calibration and the analyte in the extract. The ratio of the peak response to mass or concentration injected is used to prepare a calibration curve.”

19.5.5. Added Section 6.6, “Extract concentrator or nitrogen manifold with water bath heating to 50-55°C”.

19.5.6. Added Section 7.1.14, “Methanol-Water, 78:22 vol./vol., prepared by mixing 780 mL methanol and 220 mL reagent water. Stored in polypropylene bottle and sealed with polypropylene screw cap.”

19.5.7. Section 7.2.1.1, revised “roughly 0.15 pg/L” to “roughly 0.15 ng/L”.

19.5.8. Section 7.4 table, added:

4:2 FTS	0.5	1.0	2.0	20	50	200	400

19.5.9. Section 7.4 table, revised Labeled Isotope Dilution Analytes (IDA) Section.

19.5.10. Section 7.4 table, added:

Internal Standard (IS)							
13C2-PFOA	50	50	50	50	50	50	50

19.5.11. Section 7.4, removed “FOSAA may be added to the mix and are added at the same concentration as FOSA.”

19.5.12. Added Section 7.9, “Internal Standard Solution, 1000 ng/mL. The internal standard solution is prepared by diluting 13C2-PFOA to produce a solution containing this compound at a concentration of 1000 ng/mL in methanol. This is added to all extracts prior to analysis. Non-concentrated extracts are fortified with a 5X dilution of this solution.”

19.5.13. Section 8.1, changed “250 mL” to “8 oz.”

19.5.14. Added Sections 9.3.6, 9.8.2.3, 10.10.4, 10.8.2.5, 10.11.3, and 10.12.4 to address DOD QSM 5.1 Table B-15 criteria.

19.5.15. Added Section 9.9, “Internal Standard.”

19.5.16. Updated all tables to indicate target analyte quantitation via isotope dilution. Internal standard quantitation is only used to quantitate the IDA recoveries.

19.5.17. Added Section 10.8.2.4, 10.12.2, and 10.12.2.1 to incorporate IS criteria into calibrations.

19.5.18. Section 11.2.1, “Evaluate if the sample can be decanted or centrifuged; if not, contact the client for guidance. Filtering the sample can lead to a low bias.”

19.5.19. Added Section 11.2.3.1, “Alternatively, weigh the sample container prior to extraction and then weigh the sample container after extraction to determine the initial volume.”

19.5.20. Added Section 11.5.3, “Note: If the extracts will not be concentrated elute extract with a total of 8 mL of 0.3% NH_4OH/methanol.”

19.5.21. Added Section 11.6.2.3, “Add 300 uL of the 78:22 methanol:water solution and mix the contents well using a vortex mixer.”

19.5.22. Added Section 11.6.2.4, “Add 100 uL of Internal Standard (IS) solution to each extract and vortex to mix.”

19.5.23. Added Section 11.7, “Final volume for non-concentrated extract”.

19.5.24. Revised Section 11.11, “SPE Elution of Solid Extracts”.

19.5.25. Revised Section 11.12, “Extract Concentration for Solid Samples”.

19.5.26. Removed Section 12.8, “If results are to be reported as ammonium perfluorooctanoate (APFO), instead of PFOA, apply a multiplier of 1.0406 to the sample results to correct for the molecular weight differences between

PFOA and APFO or this adjustment can be made during the preparation of the standards used for calibration. (Use one, not both.)"

19.5.27. Removed Section 13.4 – it was a copy of Section 13.2.

19.5.28. Various revisions to fulfill requirements based on DOD/DOE QSM 5.1.

19.5.29. Editorial changes.

19.6. WS-LC-0025, Revision 2.6, Effective 08/15/2017

19.6.1. Section 7.4, added MPFBS, MPFTeDA, and MPFHxDA to the table.

19.6.2. Section 11.15, added 13C-PFBS to the Recommended Instrument Operating Conditions table for SCIEX 5500.

19.6.3. Section 11.15 Recommended Instrument Operating Conditions table, changed the mass transitions for native PFTeDA from 713 > 669 (quant) and 713 > 169 (qualifier) to 713 > 169 (quant) and 713 > 219 (qualifier).

19.6.4. Editorial changes.

19.7. WS-LC-0025, Revision 2.5, Effective 07/10/2017

19.7.1. Revised Section 11.6.1 to read "Prior to concentrating each sample, add 100 uL of water."

19.7.2. Revised Section 11.6.2 to read "Concentrate each sample under a gentle stream of nitrogen until the methanol is evaporated and the 100 uL of water remains.

11.6.2.1 This blow down must take a minimum of 3.5 hours.

11.6.2.2 Extracts can not remain in the water bath longer than 5 minutes once concentrated."

19.7.3. Revised Section 11.6.3 to read "Add 400 uL of methanol to each extract, soak, and vortex to mix well. This will create an extract with a final solvent composition of 80:20 methanol:water."

19.7.4. Revised Section 11.11.1 to read "Prior to concentrating each sample, add 200 uL of water."

19.7.5. Revised Section 11.11.2 to read "Concentrate each sample under a gentle stream of nitrogen until the methanol is evaporated and the 200 uL of water remains."

11.11.2.1 This blow down must take a minimum of 3.5 hours.

11.11.2.2 Extracts can not remain in the water bath longer than 5 minutes once concentrated."

19.7.6. Revised Section 11.11.3 to read "Add 800 uL of methanol to each extract, soak, and vortex to mix well. This will create an extract with a final solvent composition of 80:20 methanol:water."

1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of water samples via in line solid phase extraction (SPE) for the following compounds using liquid chromatography / tandem mass spectrometry (LC/MS/MS) on a SCIEX 5500.

Compound Name	Abbreviation	CAS #
Perfluoroalkylcarboxylic acids (PFCAs)		
Perfluoro-n-heptanoic acid	PFHpA	375-85-9
Perfluoro-n-octanoic acid	PFOA	335-67-1
Perfluoro-n-nonanoic acid	PFNA	375-95-1
Perfluorinated sulfonic acids (PFSAs)		
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4
Perfluoro-1-octanesulfonic acid	PFOS	1763-23-1

1.2. The working range of the method is listed below. The linear range can be extended by diluting the extracts.

Matrix	Nominal Sample Size	Reporting Limit	Working Range
Water	1.0 mL	2.0 ng/L	2 to 200 ng/L

2. SUMMARY OF METHOD

2.1. A 1 mL aliquot of sample is diluted to a 40:60 methanol:water extract and analyzed by LC/MS/MS. PFAS are separated from other components on a C18 column with a solvent gradient program using 20mM ammonium acetate/water and methanol.

3. DEFINITIONS

Refer to Section 3 of the main body of this SOP for a summary of definitions.

4. INTERFERENCES

Refer to Section 4 of the main body of this SOP for interferences.

5. SAFETY

Refer to Section 5 of the main body of this SOP for safety information.

6. EQUIPMENT AND SUPPLIES

Refer to Section 6 of the main body of this SOP for supplies, other than those listed below specific to the in line SPE analysis.

6.1. 2 mL auto sampler vials, clear glass, Thermo Scientific Nation surestop vial, part no. C5000-1, or equivalent**.**

6.2. Vial caps, Thermo Scientific National AVCS blue cap, pre slit TEF/STL septa, part no. C5000-55B or equivalent.

6.3. Eppendorf 1000 uL epTIPS, part no. 022491954 or equivalent.

6.4. Eppendorf 200 uL epTIPS, part no. 022491938 or equivalent.

6.5. 50 mL graduated plastic centrifuge tubes, SCP Science DigiTUBES part no. 010-500-263 or equivalent

6.6. 1000 uL Pipette: Eppendorf Research Plus

6.7. 100 uL Pipette: Rainin EDP3-Plus

6.8. 250 mL HDPE bottles with PPE screw caps, ESS part no. 0250-1902-QC or equivalent.

6.9. Analytical columns

6.9.1. Phenomenex Gemini C18 3 um, 3.0 mm x 100 mm, Part No. 00D-4439-Y0, or equivalent.

6.9.2. PFAS Isolator column, Phenomenex Luna C18 5 um, 50 mm x 4.6 mm, part no. 00B-4252-E 0 or equivalent.

6.10. SCIEX 5500 Triple Quad MS. The system utilizes Chrom Peak Review, version 2.1 or equivalent.

6.11. Shimadzu CTO-20AC HPLC equipped with 3 LC-20AD pumps and one DGU-20 degassing unit or equivalent.

7. REAGENTS AND STANDARDS

Refer to Section 7 of the main body of this SOP for reagents and standards, other than those listed below specific to the in line SPE analysis.

7.1. Reagent grade chemicals shall be used in all tests whenever available. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on the Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1.1. Ammonium acetate, Fisher Optima LCMS grade (20 mM in water), part no. A114-50, or equivalent.

7.1.2. Methanol, Baker HPLC grade, part no. 9093-03.

7.1.3. Water, Nanopure or Millipore or Fisher Optima LCMS grade, part no. W6-4, must be free of interference and target analytes.

7.2. Calibration Standards

The calibration stock solution is prepared by diluting the appropriate amounts of the stock solutions (Section 7.2 of the main body of this SOP) in 40:60 methanol:water. The calibration stock solution is diluted with methanol to produce initial calibration standards. These are the normal calibration levels used. A different range can be used if needed to achieve lower reporting limits or a higher linear range.

7.3. Initial Calibration (ICAL) Levels (ng/L)

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7	CS-8
Perfluoroalkylcarboxylic acids (PFCAs)								
PFHpA	1.0	2.0	5.0	10	20	50	100	200
PFOA	1.0	2.0	5.0	10	20	50	100	200
PFNA	1.0	2.0	5.0	10	20	50	100	200
Perfluorinated sulfonic acids (PFSAs)								
PFBS	1.0	2.0	5.0	10	20	50	100	200
PFHxS	1.0	2.0	5.0	10	20	50	100	200
PFOS	1.0	2.0	5.0	10	20	50	100	200
Labeled Isotope Dilution Analytes (IDA)								
13C4-PFHpA	50	50	50	50	50	50	50	50
13C4-PFOA	50	50	50	50	50	50	50	50
13C5-PFNA	50	50	50	50	50	50	50	50
18O2-PFHxS	50	50	50	50	50	50	50	50
13C4-PFOS	50	50	50	50	50	50	50	50

Note- The above calibration levels are provided only as an example. The actual ICAL level used for each analytical batch will depend upon the LOQ requirements of the program.

7.4. LCS/Matrix PFC Spike Solution, 100 ng/mL.

The PFC spike solution is prepared by diluting all PFAS to produce a solution containing each PFAS at 100 ng/mL in methanol.

7.5. PFC Isotope Dilution Analyte (IDA) Spike Solution, 1 ng/mL.

The PFC-IDA solution is prepared by diluting all labeled PFAS to produce a solution containing each at 1 ng/mL in methanol.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Water samples are collected in pre-cleaned 250 mL HDPE containers. Other containers may also be suitable. Samples are chilled to 0 - 6 °C for shipment to the laboratory.

8.2. Samples are logged in following normal laboratory procedures and are stored under refrigeration at 0 - 6 °C. Water samples must be analyzed within 28 days of collection.

9. QUALITY CONTROL

Refer to Section 9 of the main body of this SOP for Quality Control information.

9.1. If potable water samples from the state of New York (NY) are analyzed via this method the control limits for LCS and IDA for PFOS and PFOA recoveries are 70-130%. If these limits are not met, refer to Section 9 of the main body of this SOP for corrective action.

9.2. If POST (treatment) samples have positive detections, review the associated PRE and MID (treatment) samples for similar detections. Re-preparation and re-analysis may be needed.

9.3. If PFBS is detected in the method blank greater than the RL, evaluate data for impact. PFBS is a known laboratory artifact. Re-preparation and re-analysis may be needed.

10. CALIBRATION

Refer to Section 10 of the main body of the SOP for calibration information.

11. PROCEDURE

Refer to Section 11 of the main body of this SOP for procedures, other than those listed below specific to the in line SPE analysis.

11.1. Water Sample Preparation

11.1.1. Visually inspect samples for the presence of settled and or suspended sediment/particulate. Evaluate if the sample can be decanted or centrifuged; if not, contact the client for guidance. Filtering the sample can lead to a low bias.

If authorized by the client to filter the sample, filter the water sample through a glass fiber filter (Whatman GF/F Cat No 1825 090 or equivalent). Gravity of vacuum can be used to pass the sample through the filter. Prepare a filtration blank with any samples requiring filtration. File an NCM noting the need for filtration.

Warning: The use of a vacuum system creates the risk of glassware implosion. Inspect all glassware prior to use. Glassware with chips, scratches, rub marks or cracks must not be used.

11.1.2. Prepare an LCS and method blank by adding 250 mL of HPLC grade water into a 250 mL HDPE bottle.

11.1.3. If requested, find the client assigned sample for MS/MSD.

11.1.4. Spike directly into the sample bottles for the LCS and MS/MSD (if requested) with 0.050 mL (50 uL) of the LCS/Matrix PFC Spike solution (Section 7.4). This will result in a sample concentration of 20 ng/L. Shake well to disperse spike.

11.1.5. Measure 1 mL of each sample using an Eppendorf pipette and pour into a labeled 2.0 mL injection vial. This includes the LCS and method blank samples as well.

11.1.6. Be sure to "prepare" the pipette by collecting two 1 mL aliquots and disposing of them, and then collect the aliquot for testing.

11.1.7. Add 83 uL of surrogate solution (PFC IDA Spike Solution, Section 7.5) into each vial for each sample and QC sample. This will result in an extract concentration of 50 ng/L for the surrogate.

11.1.8. Add 577 uL of methanol to each sample for a final solvent composition of 40:60 methanol:water.

11.1.9. Seal the vial with a polypropylene screw cap. Note: Teflon lined caps can not be used due to detection of low level concentration of PFAS.

11.1.10. Vortex to mix the mixture well.

11.2. Instrument Analysis

11.2.1. Suggested operation conditions are listed in Tables 1A-1C below:

Table 1A - Routine Instrument Operating Conditions

HPLC Conditions (Shimadzu HPLC)					
Column (Column temp = 35°C)	Phenomenex Gemini C18 3 um, 3.0 mm x 100 mm				
Mobile Phase Composition	A = 20 mM Ammonium Acetate in Water B = Methanol				
Gradient Program	**Time (min)**	**%A**	**%B**	**Curve**	**Flow Rate (mL/min)**
	0	90	10	6	0.60
	1	90	10	6	0.60

Table 1A - Routine Instrument Operating Conditions					
HPLC Conditions (Shimadzu HPLC)					
	1.5	35	65	6	0.60
	8	5	95	6	0.60
	8.1	1	99	6	0.60
	12	1	99	6	0.60
	12.5	90	10	6	0.60
	Maximum Pressure limit = 5,000 psi				
Injection Size	950 uL (fixed amount throughout the sequence)				
Run Time	17.1 minutes				
MS Interface Mode	ESI Negative Ion. Minimum of 10 scans/peak.				
Ion Spray Voltage (kV)	4.5				
Entrance Potential (V)	5				
Declustering Potential (V)	25				
Desolvation Temp	550 ºC				
Curtain Gas (nitrogen) Flow	35 psi				
Collision Gas (nitrogen) Flow	8 psi				

Table 1B - Routine Instrument Operating Conditions						
Mass Spectrometer Scan Settings (SCIEX 5500)						
Compound	**Comments**	**Reaction (MRM)**	**Dwell (sec)**	**Ent. Pot. (V)**	**Col. Energy (V)**	**Declu. Pot. (V)**
PFBS	Perfluorobutanesulfonate	299 > 80	0.02	6	58	55
18O2-PFHxS	IDA	403 > 84	0.02	12	74	60
PFHpA	Perfluoroheptanoic acid	363 > 319	0.02	6	12	25
13C4-PFHpA	IDA	367 > 322	0.02	6	12	25
PFHxS	Perfluorohexanesulfonate	399 > 80	0.02	12	74	60
18O2-PFHxS	IDA	403 > 84	0.02	12	74	60
PFOA	Perfluorooctanoic acid	413 > 369	0.02	6	14	25
13C4PFOA	IDA	417 > 372	0.02	6	14	25
PFNA	Perfluorononanoic acid	463 > 419	0.02	6	14	25
13C5-PFNA	IDA	468 > 423	0.02	6	14	25
PFOS	Perfluorooctanesulfonate	499 > 80	0.02	9	108	65
13C4-PFOS	IDA	503 > 80	0.02	9	108	65

Table 1C				
Native Compounds	**Typical Native RT (minutes)**	**IS analog**	**Typical IDA RT (minutes)**	**Quantitation Method**
PFBS	6.68	18O2-PFHxS	7.76	Isotope Dilution
PFHpA	7.77	13C4-PFHpA	7.77	Isotope Dilution

Table 1C				
Native Compounds	**Typical Native RT (minutes)**	**IS analog**	**Typical IDA RT (minutes)**	**Quantitation Method**
PFHxS	7.76	18O2-PFHxS	7.76	Isotope Dilution
PFOA	8.44	13C4-PFOA	8.44	Isotope Dilution
PFNA	9.10	13C5-PFNA	9.10	Isotope Dilution
PFOS	9.06	13C4-PFOS	9.06	Isotope Dilution

11.2.2. Tune and calibrate the instrument as described in Section 10.

11.2.3. A typical run sequence is as follows:

- Primer (A number of primers are injected for conditioning of the instrument before analysis, especially when the instrument was idled or changed from a different analysis).
- Blank
- Calibration Curve
- ICB
- ICV
- PFOA RT marker (as needed)
- Rinse Blank (RB, not linked to anything)
- MB
- LCS
- LCSD (if applicable)
- Sample 1
- Sample 1 MS (if applicable)
- Sample 1 MSD (if applicable)
- Sample 2 (up to sample 10 before next CCV)
- CCV
- Up to 10 samples.
- End sequence with CCV

12. CALCULATIONS

Refer to Section 12 of the main body of this SOP for calculation information.

13. METHOD PERFORMANCE

Refer to Section 13 of the main body of this SOP for method performance information.

14. POLLUTION PREVENTION

Refer to Section 14 of the main body of this SOP for pollution prevention information.

15. WASTE MANAGEMENT

Refer to Section 15 of the main body of this SOP for waste management information.

16. REFERENCES

Refer to Section 16 of the main body of this SOP for reference information.

17. METHOD MODIFICATIONS

17.1. Refer to Section 17 of the main body of this SOP for modifications from Method 537, except as detailed below:

17.1.1. Water samples are prepared at 1.0 mL, not 250 mL.

17.1.2. Water sample containers are not preserved with Trizma. Holding time has been changed to 28 days for analysis.

17.1.3. The eluents and HPLC configuration differs. As a result the final extract is in 40:60 methanol:water.

18. ATTACHMENTS

There are no attachments to this Appendix.

19. REVISION HISTORY

Revisions prior to 04/10/2017 have been removed and are available in previous versions of this SOP.

19.1. WS-LC-0025, Attachment 1, Revision 3.0, Effective 04/13/2018

19.1.1. Updated labeling and formatting of Tables 1A-1C.

19.1.2. Added section 11.2.3, detailing a typical run sequence.

19.2. WS-LC-0025, Attachment 1, Revision 2.9, Effective 11/27/2017

19.2.1. No changes to the attachment with this revision.

19.3. WS-LC-0025, Attachment 1, Revision 2.8, Effective 11/06/2017

19.3.1. Section 11.2.1, Routine Instrument Operating Conditions table (SCIEX 5500), added “Minimum of 10 scans/peak”.

19.4. WS-LC-0025, Attachment 1, Revision 2.7, Effective 09/22/2017

19.4.1. Section 6.5, removed “The 5 items above are to be maintained in the drawer labeled “Segregated Supplies for in line SPE Analysis” in the LC/MS instrument room.”

19.4.2. Added Sections 9.1 – 9.3.

19.4.3. Updated Section 11.1.

19.4.4. Editorial changes.

19.5. WS-LC-0025 Attachment 1, Revision 2.6, Effective 08/11/2017

19.5.1. No revisions to this attachment.

19.6. WS-LC-0025 Attachment 1, Revision 2.5, Effective 07/10/2017

19.6.1. No revisions to this attachment.

19.7. WS-LC-0025 Attachment 1, Revision 2.4, Effective 04/25/2017

19.7.1. No revisions to this attachment.

19.8. WS-LC-0025 Attachment 1, Revision 2.3, Effective 04/10/2017

19.8.1. Changed all mentions of “direct aqueous injection (DAI)” to “in line solid phase extraction (SPE).”

19.8.2. Inserted Section 17.1, and changed formatting of the modifications to Method 537 to Section 17.2 and subheadings.

Title: Analytical Methods for GC/MS Semivolatile Samples by SW846 8270D, MCP, RCP and SIM

Once printed, this document is considered an uncontrolled document.

Approvals (Signature/Date):

Michelle Page Department Manager	12/15/17 Date
Kenneth Kasperek Laboratory Director	12/15/17 Date
Michael Mosscrop Quality Assurance Manager	12/18/17 Date
Gary Rudz Organic Ops Manager	12/15/17 Date

Facility Distribution No. _____ **Distributed To:_____**

1.0 Scope and Application

This SOP contains the procedures for the determination of extractable semi-volatile organic compounds (SVOC) by gas chromatography/mass spectrometry (GC/MS).

Procedures for analyzing via Large Volume Injection (LVI), Low Level analysis and Selective Ion Monitoring (SIM) are also included in this SOP.

Technical acceptance criteria and corrective actions for MCP and RCP analysis are also included in this SOP.

The routine matrices performed by this procedure are waters and soils. Other matrices which may be performed include wipes, leachates, and wastes.

A complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

2.0 Summary of Method

A measured volume or weight of sample is extracted using separatory funnels (3510C, 3510C_LVI), sonication (3550C) or microwave (3546) extraction procedures. The extract is then analyzed by GC/MS. Qualitative identification of the target compounds in the extract is based on the retention time and the relative abundance of the characteristic masses as compared to component reference spectra determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis of the target compounds is performed by the internal standard technique using a single characteristic ion. Quantitative analysis of the SIM method is performed by Isotopic Dilution.

3.0 Definitions

MCP – Massachusetts Contingency Plan
RCP – Connecticut Reasonable Confidence Protocols
SIM – Selective Ion Monitoring
Additional definitions can be found in the TAL Buffalo Laboratory Quality Manual (QAM)

4.0 Interferences

Some of the possible interferences that arise during GCMS Semivolatile analysis include, but are not limited to:

1. Glassware contamination
2. Matrix interference
3. Aldol condensation
4. System air leaks
5. Injection port/liner contamination
6. Warped filament, and/or dirty source

Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

Phthalate contamination is commonly observed in the LVI and Low Level analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with TestAmerica Buffalo SOP BF-GP-003, current revision, to ensure it is free from contaminants and does not contribute artifacts.

High purity reagents and solvents are used to help minimize interference problems. Acetone and methylene chloride must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program (SOP CA-Q-S-001, current revision) and TestAmerica Buffalo SOP BF-OP-013, current revision.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Chemicals that have been classified as carcinogens or potential carcinogens in association with this method, defined by OSHA include: Acrylamide, Benzo(a)anthracene, Benzidine, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Dibenz(a,h)acridine, Dibenz(a,h)anthracene, Dibenzo(a,e)pyrene, 1,4-Dichlorobenzene, 3,3'-Dichlorobenzidine, 1,4-Dioxane, Hexachlorobenzene, Hexachloroethane, Kepone, Methyl Methanesulfonate, Methylene Chloride, Naphthalene, 1-Naphthylamine, 2-Naphthylamine Nitrobenzene, n-Nitrosodimethylamine, n-Nitrosodiethylamine, n-Nitrosodi-n-butylamine, n-Nitrosodi-n-propylamine, n-Nitrosopiperidine, n-Nitrosopyrrolidine, Safrole, o-Toluidine and 2,4,6-Trichlorophenol. This list can be obtained from the TestAmerica Corporate Safety Manual CW-E-M-001, Appendix XII (current revision). Primary standards should be purchased in solution. If neat materials must be obtained, they shall be handled in a hood.

Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers should be kept closed unless transfers are being made.

Analysts are expected to use caution and common sense while working in a laboratory environment. Each employee is required to read the TestAmerica Corporate Safety Manual. All of the samples to be analyzed have the potential to contain hazardous substances. Most standards also contain hazardous chemicals and many do contain known carcinogens. Employees must use protective equipment when handling standards, samples and extracts including gloves, lab coats and safety glasses. It is the analyst's responsibility to read and familiarize themselves with the SDS of each chemical and/or reagent involved in this method.

Samples, standards and/or extracts should never be opened or transferred outside of a fume hood.

Liquid waste disposal is all C waste with the exception of some acids used in the cleaning of equipment which is disposed of in AN waste.

Spills should be cleaned up promptly and waste should be disposed of as per the Chemical Hygiene Plan.

There is also the danger of burns while doing repair or maintenance on a gas chromatograph. One must use caution while working on or near the injection port or transfer line.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety data Sheets (SDS) for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Chart 1

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Micro syringes 10, 25, 50, 100, 500, 1000 microliter.

6.2 2mL amber and clear glass vials and caps.

6.3 Disposable pipets and pipet bulbs.

6.4 Volumetric flasks.

6.5 Instrumentation
Gas Chromatograph/Mass Spectrometer (GC/MS) System

6.5.1 Gas Chromatograph -
- Hewlett Packard 6890
- Carrier gas Helium UPC grade or equivalent

6.5.2 Gas Chromatography Column
- Analysis: Restek 5Sil MS with or without Integra-Guard cat# 13623 (without guard) 13623-127 (with guard) or equivalent

6.5.3 Mass Spectrometer
- HP5973 and HP5973 inert
- Tuning compound PFTBA
- Scan Range 35-500 AMU

6.5.4 Data System
- HP Chemstation
- Chrom chromatography analysis system
- TALS data analysis system

7.0 Reagents and Standards

7.1 Methylene Chloride – high purity

7.2 Stock Standards

7.2.1 Corporate approved Primary and Second Source Restek mixtures:

8270 List1/Std #1 MegaMix	8270 List2/Std #1	8270 List2/Std #5
8270 List1/Std #9	8270 List2/Std #2	8270 List2/Std #7
8270 List1/Std #10	8270 List2/Std #3	8270 Internal Standard
8270 List1/Std #11	8270 List2/Std #4	8270 Surrogate Standard

7.2.2 Equivalent vendor mixtures:

Semi-Volatile GC/MS Tuning Standard (Ultra Scientific)
Custom List 3 Mix (Supelco)
Custom ADD#3 Mix (Absolute Standards, Inc.)
Dicyclohexylamine (Absolute Standards, Inc.)
Tributyl Phosphate (Absolute Standards, Inc.)
TetraEthyl Lead (Absolute Standards, Inc.)
1,4-Dioxane Stock for SIM (Restek)
1,4-Dioxane-d8 labeled analog for SIM (Restek)

All Certificates of Analysis received from the manufacturer are maintained in the laboratory's LIMS system.

7.3 Working Standards

7.3.1 Surrogate Standard Spiking Solution

Surrogate Standard spiking solution is prepared by the extractions department that contains nitrobenzene-d5, p-terphenyl1-d14, 2-fluorobiphenyl, phenol-d5, 2,4,6-tribromophenol and 2-fluorophenol at a concentration of 40µg/mL for the 3510C, 3550C and 3546 extractions and 8ug/mL for the 3510C_LVI and low level extractions. Surrogate standards are added to all QC and client samples. Additional surrogates may be added at the laboratory's discretion.

The isotopically labeled analog 1,4-Dioxane-d8 used in the SIM analysis is prepared by the extractions department at a concentration of 10 ug/mL. This is added to all QC and client samples.

7.3.2 Laboratory Control Sample and Matrix Spiking Solution

Laboratory Control Sample and Matrix spiking solution is prepared by the extractions department that contains each of the base-neutral compounds and acid compounds at 50ug/mL for the 3510C, 3550C and 3546 extractions and 8ug/mL for the 3510C_LVI and low level extractions. SIM spiking solution is prepared that contains 1,4-Dioxane at a concentration of 1ug/mL.

7.3.3 Instrument Performance Check Solution (DFTPP)

A solution of Decafluorotriphenylphosphine (DFTPP) is prepared at a concentration of 50ug/mL in methylene chloride for soil analysis, as well as 1Liter water extractions.

For LVI, Low Level analysis and SIM, the concentration of this solution is prepared at 10ug/mL.

The instrument performance check solution contains 50ug/mL and 10ug/mL respectively of Benzidine, Pentachlorophenol and 4,4'-DDT for use in evaluating chromatographic performance.

Chart 2 – DFTPP Check Solution

DFTPP Working reagent (MB_DFTPP_WRK)	Solvent	Stock Conc. (ug/mL)	Initial Volume (uL)	Final Volume (mL)	Final Conc. (ug/mL)
1L Water/Soil	$MeCL_2$	1000	500	10	50
LVI/LL Water/SIM	$MeCL_2$	1000	100	10	10

7.3.4 Initial and Continuing Calibration Standards

Calibration standards are prepared at a minimum of five concentration levels from a working intermediate mix. For the main list of compounds, List 1, each calibration standard shall contain each compound of interest and each surrogate. A six and seventh level may be added for 2nd order quadratic curves.

Chart 3 – 8270 List 1 Working Intermediate Mix

8270 Working Intermediate Calibration Mix (MB_List1_INT)	Solvent	Stock Conc. (µg/ml)	Initial Vol. (uL)	Final Vol. (mL)	Final Conc. (µg/mL)
8270 List 1/Std #1 Mega mix	$MeCl_2$	1000	2000	10	200
8270 List 1/Std #9	$MeCl_2$	2000	1000	10	200
8270 List 1/Std #10	$MeCl_2$	2000	3000	10	600
8270 List1/Std #11	$MeCl_2$	2000	1000	10	200
8270 Surrogate Standard	$MeCl_2$	5000	400	10	200

Chart 4 - 1 Liter Water/Soil Calibration Levels

Calibration Level (ppm) (MB_LIST1_WRK)	Reagent Added	Solvent	Stock Conc. (µg/mL)	Initial Vol. (µL)	Final Vol. (mL)	Final Conc. (µg/mL)
5	MB_LIST1_INT	$MeCl_2$	200	250	5	5.00
	Internal Standard		2000	100		40.0
20	MB_LIST1_INT	MeCl2	200	100	1	20.0
	Internal Standard		2000	20		40.0
50	MB_LIST1_INT	MeCl2	200	1250	5	50.0
	Internal Standard		2000	100		40.0
80	MB_LIST1_INT	MeCl2	200	400	1	80.0
	Internal Standard		2000	20		40.0
100	MB_LIST1_INT	MeCl2	200	500	1	100.0
	Internal Standard		2000	20		40.0
120	MB_LIST1_INT	MeCl2	200	600	1	120.0
	Internal Standard		2000	20		40.0

Chart 5 - LVI/Low Level Water Calibration Levels

Calibration Level (ppm) (MB_L1LVI_WRK)	Reagent Added	Solvent	Stock Conc. (µg/mL)	Initial Vol. (µL)	Final Vol. (mL)	Final Conc. (µg/mL)
0.25	MB_LIST1_INT	$MeCl_2$	200	12.5	10	0.25
	Internal Standard		2000	20		4.0
1.0	MB_LIST1_INT	MeCl2	200	50	10	1.0
	Internal Standard		2000	20		4.0
2.0	MB_LIST1_INT	MeCl2	200	100	10	2.0
	Internal Standard		2000	20		4.0
4.0	MB_LIST1_INT	MeCl2	200	200	10	4.0
	Internal Standard		2000	20		4.0
8.0	MB_LIST1_INT	MeCl2	200	400	10	8.0
	Internal Standard		2000	20		4.0
10	MB_LIST1_INT	MeCl2	200	500	10	10.0
	Internal Standard		2000	20		4.0
12	MB_LIST1_INT	MeCl2	200	600	10	12.0
	Internal Standard		2000	20		4.0

An additional calibration level is added, when required, for Low Level PAH analysis for 1L

water/soil samples and LVI/Low Level water samples. For 1L/soil analysis, a 0.5ug/mL standard is prepared with 12.5uL of MB_List1_INT and 100uL of Internal Standard into 5mL of $MeCl_2$. For LVI/Low Level water samples, a 0.125ug/mL standard is prepared with 6.25uL of MB_List1_INT and 20uL of Internal Standard into 10mL of $MeCl_2$.

Additional calibration standards may be analyzed to include compounds not in the main list (List 1). Surrogate analytes are not added to additional calibration mixes and are only calibrated from List 1. Additional routine calibrations are List 2 and List 3 and are prepared using Charts 6 through 11.

Chart 6 - 8270 List 2 Working Intermediate Mix

8270 Working Intermediate Calibration Mix (MB_List2_INT)	Solvent	Stock Conc. (µg/ml)	Initial Vol. (µL)	Final Vol. (mL)	Final Conc. (µg/mL)
8270 List 2/Std #1	$MeCl_2$	1000	2000	10	200
8270 List 2/Std #2	$MeCl_2$	1000	2000	10	200
8270 List 2/Std #3	$MeCl_2$	2000	1000	10	200
8270 List2/Std #4	$MeCl_2$	1000	2000	10	200
8270 List2/Std #5	$MeCl_2$	2000	1000	10	200

Chart 7 - 1 Liter Water/Soil Calibration Levels
List 2

Calibration Level (ppm) (MB_LIST1_WRK)	Reagent Added	Solvent	Stock Conc. (µg/mL)	Initial Vol. (µL)	Final Vol. (mL)	Final Conc. (µg/mL)
5	MB_LIST2_INT	$MeCl_2$	200	125	5	5.00
	Internal Standard		2000	100		40.0
20	MB_LIST2_INT	MeCl2	200	100	1	20.0
	Internal Standard		2000	20		40.0
50	MB_LIST2_INT	MeCl2	200	1250	5	50.0
	Internal Standard		2000	100		40.0
80	MB_LIST2_INT	MeCl2	200	400	1	80.0
	Internal Standard		2000	20		40.0
100	MB_LIST2_INT	MeCl2	200	500	1	100.0

	Internal Standard		2000	20		40.0
120	MB_LIST2_INT	MeCl2	200	600	1	120.0
	Internal Standard		2000	20		40.0

Chart 8 - LVI/Low Level Water Calibration Levels
List 2

Calibration Level (ppm) (MB_L1LVI_WRK)	Reagent Added	Solvent	Stock Conc. (µg/mL)	Initial Vol. (µL)	Final Vol. (mL)	Final Conc. (µg/mL)
0.25	MB_LIST2_INT	$MeCl_2$	200	12.5	10	0.25
	Internal Standard		2000	20		4.0
1.0	MB_LIST2_INT	MeCl2	200	50	10	1.0
	Internal Standard		2000	20		4.0
2.0	MB_LIST2_INT	MeCl2	200	100	10	2.0
	Internal Standard		2000	20		4.0
4.0	MB_LIST2_INT	MeCl2	200	200	10	4.0
	Internal Standard		2000	20		4.0
8.0	MB_LIST2_INT	MeCl2	200	400	10	8.0
	Internal Standard		2000	20		4.0
10	MB_LIST2_INT	MeCl2	200	500	10	10.0
	Internal Standard		2000	20		4.0
12	MB_LIST2_INT	MeCl2	200	600	10	12.0
	Internal Standard		2000	20		4.0

Chart 9 - 8270 List 3 Working Intermediate Mix

8270 Working Intermediate Calibration Mix (MB_List3_INT)	Solvent	Stock Conc. (µg/ml)	Initial Vol. (µL)	Final Vol. (mL)	Final Conc. (µg/mL)
MB_ADD#3_STK	$MeCl_2$	2000	1000	10	200
MB_DICYCL_STD	$MeCl_2$	1000	2000	10	200
MB_List3_STK	$MeCl_2$	2000	1000	10	200
MB_TBP_STK	$MeCl_2$	1000	2000	10	200
MB_TEL_STK	$MeCl_2$	1000	2000	10	200

Chart 10 - 1 Liter Water/Soil Calibration Levels
List 3

Calibration Level (ppm) (MB_LIST1_WRK)	Reagent Added	Solvent	Stock Conc. (µg/mL)	Initial Vol. (µL)	Final Vol. (mL)	Final Conc. (µg/mL)
5	MB_LIST3_INT	$MeCl_2$	200	125	5	5.00
	Internal Standard		2000	100		40.0
20	MB_LIST3_INT	MeCl2	200	100	1	20.0
	Internal Standard		2000	20		40.0
50	MB_LIST3_INT	MeCl2	200	1250	5	50.0
	Internal Standard		2000	100		40.0
80	MB_LIST3_INT	MeCl2	200	400	1	80.0
	Internal Standard		2000	20		40.0
100	MB_LIST3_INT	MeCl2	200	500	1	100.0
	Internal Standard		2000	20		40.0
120	MB_LIST3_INT	MeCl2	200	600	1	120.0
	Internal Standard		2000	20		40.0

Chart 11 - LVI/Low Level Water Calibration Levels
List 3

Calibration Level (ppm) (MB_L1LVI_WRK)	Reagent Added	Solvent	Stock Conc. (µg/mL)	Initial Vol. (µL)	Final Vol. (mL)	Final Conc. (µg/mL)
0.25	MB_LIST3_INT	$MeCl_2$	200	12.5	10	0.25
	Internal Standard		2000	20		4.0
1.0	MB_LIST3_INT	MeCl2	200	50	10	1.0
	Internal Standard		2000	20		4.0
2.0	MB_LIST3_INT	MeCl2	200	100	10	2.0
	Internal Standard		2000	20		4.0
4.0	MB_LIST3_INT	MeCl2	200	200	10	4.0
	Internal Standard		2000	20		4.0
8.0	MB_LIST3_INT	MeCl2	200	400	10	8.0
	Internal Standard		2000	20		4.0
10	MB_LIST3_INT	MeCl2	200	500	10	10.0
	Internal Standard		2000	20		4.0
12	MB_LIST3_INT	MeCl2	200	600	10	12.0
	Internal Standard		2000	20		4.0

SIM calibrations are prepared using Charts 12 and 13.

Chart 12 – SIM Working Intermediate Mix

SIM Working Intermediate Calibration Mix (MB_1,4SIM_INT)	Solvent	Stock Conc.	Initial Vol.	Final Vol.	Final Conc.
1,4-Dioxane Stock	MeCl2	2000µg/ml	100 uL	10 mLs	20µg/mL
1,4-Dioxane-d8 Stock	MeCl2	2000µg/ml	1000 uL	10 mLs	200ug/mL

Chart 13 – SIM Calibration Levels

Calibration Level (ppm) (MB_LIST1_WRK)	Reagent Added	Solvent	Stock Conc. (µg/mL)	Initial Vol. (µL)	Final Vol. (mL)	Final Conc. (µg/mL)
0.2	MB_1,4SIM_INT	$MeCl_2$	20/200	10	1.0	0.2/2.0
	Internal Standard		50	20		1.0
0.4	MB_1,4SIM_INT	MeCl2	20/200	20	1.0	0.4/4.0
	Internal Standard		50	20		1.0
0.6	MB_1,4SIM_INT	MeCl2	20/200	30	1.0	0.6/6.0
	Internal Standard		50	20		1.0
0.8	MB_1,4SIM_INT	MeCl2	20/200	40	1.0	0.8/8.0
	Internal Standard		50	20		1.0
1.0	MB_1,4SIM_INT	MeCl2	20/200	50	1.0	1.0/10.0
	Internal Standard		50	20		1.0
1.2	MB_1,4SIM_INT	MeCl2	20/200	60	1.0	1.2/12.0
	Internal Standard		50	20		1.0

7.3.5 Internal Standard Solution

Internal standard used in the analysis of 1L/soil samples is from the stock standard, which contains the following compounds at a concentration of 2000ug/mL: 1,4-Dichlorobenzene-d4, Acenaphthalene-d10, Chrysene-d12, Naphthalene-d8, Perylene-d12 and Phenanthrene-d10.

Internal standard used in the analysis of LVI/LL samples is from a working standard and is prepared in accordance with Chart 14. The working standard contains the following compounds at a concentration of 200ug/mL: 1,4-Dichlorobenzene-d4, Acenaphthalene-d10, Chrysene-d12, Naphthalene-d8, Perylene-d12 and Phenanthrene-d10.

Chart 14 - LVI/Low Level Water Internal Standard Working Solution

8270 Working Internal Standard Mix (MB_LLIS_WRK)	Solvent	Stock Conc. (ug/mL)	Initial Vol. (uL)	Final Vol. (mL)	Final Conc. (ug/mL)
8270 SV Internal Standard Mix (MB_INTSTD_STK)	$MeCl_2$	2000	1000	10	200

Internal standard used in the analysis of SIM samples is from a working standard and is prepared in accordance with Chart 15. The working standard contains the following compounds at a concentration of 50ug/mL: 1,4-Dichlorobenzene-d4, Acenaphthalene-d10, Chrysene-d12, Naphthalene-d8, Perylene-d12 and Phenanthrene-d10.

Chart 15 – SIM Internal Standard Working Solution

SIM Working Internal Standard Mix (MB_SIMIS_WRK)	Solvent	Stock Conc. (ug/mL)	Initial Vol. (uL)	Final Vol. (mL)	Final Conc. (ug/mL)
8270 SV Internal Standard Mix (MB_INTSTD_STK)	$MeCl_2$	2000	250	10	50

7.4 Storage of Standards

Stock, intermediates and working standards are stored at 4ºC ± 2ºC or less in Teflon-lined crimp-cap amber bottles or vials. Standards are stored separately from sample extracts.

Preparation of standards is done in accordance with the TestAmerica Buffalo SOP BF-GP-019. Stock and working calibration standards are prepared every twelve months or sooner, if the expiration date of any parent precedes 1 year.

The daily continuing calibration mix (CCV), DFTPP tuning mix, Reporting Limit check mix and all Internal Standard working reagents are prepared every 6 months or sooner, if the expiration date of any parent precedes 6 months.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and preservation requirements.

Water samples may be collected in 1L or 250 mL amber glass containers with Teflon lined, screw-caps.

Soil/Sediment Samples may be collected in glass containers fitted with Teflon-lined screw-caps or closed end tubes.

All samples are stored at 4ºC±2ºC from the time of collection until extraction.

Aqueous samples must be extracted within 7 days of collection and analyzed within 40 days of extraction.

Soil samples must be extracted within 14 days of collection and analyzed within 40 days of extraction.

Sample extracts are stored at 4ºC±2ºC in the SVOA sample extract refrigerator prior to analysis.

9.0 Quality Control

9.1 Batch QC - The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 in 20 or fewer samples	<ReportingLimit (RL)
Laboratory Control Sample (LCS)[1]	1 in 20 or fewer samples	Statistical Limits [4]
Matrix Spike (MS)[2]	1 in 20 or fewer samples	Statistical Limits [4]
MS Duplicate (MSD)[2]	1 in 20 or fewer samples	Statistical Limits [4]
Surrogates	every sample[3]	Statistical Limits [4]

[1] LCS Duplicate (LCSD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.
[2] The sample selection for MS/MSD is randomly selected by the extractions group, unless specifically requested by a client.
[3] Analytical and QC samples (MB, LCS, MS/MSD)
[4] Statistical control limits are updated annually and are updated into LIMS.

Technical requirements and acceptance of batch QC for 8270D, MCP, RCP and SIM is detailed below and summarized in Table 11 in section 18.

9.1.1 Method Blanks

A method blank is a volume of a clean reference matrix (reagent water for water samples, or purified sodium sulfate/clean sand for soil/sediment samples) that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the preparation and analysis of samples.

A method blank must be prepared once for the following, whichever is more frequent:

Each prep batch.
Each 20 Samples in a batch, in addition to matrix spikes/matrix spike duplicates that are of a similar matrix.
Whenever samples are extracted by the same procedure.

9.1.1.1 Preparation of the Method Blank

For semivolatile analysis, a method blank for samples consists of the following volumes/weights and spikes:

1L water analysis: 1L of reagent water is spiked with 1.0mL of the surrogate spiking solution and concentrated to 1mL.

LVI water analysis: 250mL of reagent water is spiked with 1.0mL of the LVI surrogate solution and concentrated to a final volume of 1mL.

Low Level water analysis: 1L of reagent water is spiked with 1.0mL of the LVI surrogate solution and concentrated to a final of 1mL.

SIM analysis: 1L of reagent water is spiked with 1.0mL of the SIM isotopically labeled analog solution and concentrated to a final of 1mL.

Soil/sediment samples: 30g of sodium sulfate/clean sand is spiked with 1.0mL of the surrogate spiking solution.

9.1.1.2 Technical Acceptance Criteria for Method Blank Analysis

All technical acceptance criteria for retention time, surrogate and IS recovery must be met for blank analysis. In addition, the following acceptance criterion applies.

For all target analytes, the method blank must contain less than the reporting limit (RL) of any single target compound.

If any single target compound is detected in the method blank with a concentration above the RL, samples that contain detections below the RL or samples containing detections that are 10X greater than the detection found in the blank will be flagged, noted the job narrative and reported. Final concentrations in the LIMS system are to be utilized when making this determination.

9.1.1.3 Corrective Actions for Method Blank Analyses

If the acceptance criteria for method blank analysis are not met, the analytical system may be assumed to be out of control.

Any contamination in the method must be investigated. Samples associated with the contaminated blank must be re-extracted and re-analyzed.

If surrogate recoveries in the method blank do not meet the acceptance criteria, first reanalyze the method blank. If the surrogate recoveries do not meet the acceptance criteria after reanalysis, re-extract and re-analyze the blank and all associated samples OR the samples may be reported as estimated, and noted in the case narrative.

If the method blank does not meet internal standard response requirements, check calculations, the internal standard spiking solutions, and the instrument operation. If the calculations were incorrect, correct the calculations and verify that the internal standard responses meet their acceptance criteria. If the internal standard compound spiking solution was improperly prepared, concentrated, or degraded, re-prepare solutions and re-extract/reanalyze samples. If the instrument malfunctioned, correct the instrument problem and reanalyze the method blank. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the blank

9.1.2 Laboratory Control Sample/Matrix Spike/Matrix Spike Duplicate

A Laboratory Control Sample (LCS), matrix spike (MS) and matrix spike duplicate (MSD) are analyzed to evaluate the analytical system and the effects of sample matrix on the methods used for semivolatile analysis.

The LCS, matrix spike, and matrix spike duplicate are spiked with the compounds listed in table 2 (at concentrations noted in section 7.3.2).

A LCS, matrix spike and matrix spike duplicate are extracted and analyzed for every batch of 20 samples of a similar matrix. Matrix spike and matrix spike duplicates are not performed for field QC samples such as rinsates, or field/trip blanks.

If insufficient sample amount is received to perform matrix spike and matrix spike duplicate analysis, or is requested by the client, a Laboratory Control Sample Duplicate (LCSD) may be analyzed.

A LCSD is always performed for MCP analysis. A LCSD is required for RCP analysis when a site specific MS/MSD is not provided. A MS/MSD may be performed in addition for MCP when requested.

9.1.2.1 Preparation of LCS/MS/MSD Samples

For semivolatile analysis, the laboratory control sample, matrix spike and matrix spike duplicates consists of the following volumes/weights and spikes:

1L water analysis: 1L of reagent water is spiked with 1.0mL of the surrogate spiking solution and 1.0mL of the spiking solution and concentrated to 1mL.

LVI water analysis: 250mL of reagent water is spiked with 1.0mL of the LVI surrogate solution 1.0mL of the LVI spiking solution and concentrated to a final volume of 1mL.

Low Level water analysis: 1L of reagent water is spiked with 1.0mL of the LVI surrogate solution and 1.0mL of the LVI spiking solution and concentrated to a final of 1mL.

SIM analysis: 1L of reagent water is spiked with 1.0mL of the SIM isotopically labeled analog solution and 1.0mL of the SIM spiking solution and concentrated to a final of 1mL.

Soil/sediment samples: 30g of sodium sulfate/clean sand is spiked with 1.0mL of the surrogate spiking solution and 1.0mL of the spiking solution and concentrated to a final of 1mL.

9.1.2.2 Dilutions

Dilutions of MS/MSD samples are performed only if the unspiked parent sample requires a dilution in order to maintain any target compound concentration in the upper half of the calibration. Any sample diluted 20x or greater will be deemed to have too low a recovery and shall be qualified accordingly.

Preparation of dilutions are described in equation 11 in section 11.2 and Table 10 in the attachments of Section 18.

9.1.2.3 Calculations for MS/MSD

The concentrations of the spiked compounds are determined using equations 12, 13 and 14 in section 11.4.1. After determining the compound concentrations, the percent recovery is calculated using Equation 1.

Equation 1

$$\text{Matrix Spike Recovery} = \frac{\text{SSR - SR}}{\text{SA}} x100$$

Where,

SSR= Spike Sample Result

SR = Sample Result

SA = Spike Added

The relative percent difference between the matrix spike and matrix spike duplicate is calculated using Equation 2.

Equation 2

$$\text{RPD} = \frac{[\text{MSR - MSDR}]}{1/2\,(\text{MSR} + \text{MSDR})} \text{ X } 100$$

Where,

RPD = Relative Percent Difference

MSR = Matrix Spike Recovery

MSDR = Matrix Spike Duplicate Recovery

The vertical bars in the formula above indicate the absolute value of the difference; hence RPD is always expressed as a positive value.

9.1.2.4 Calculation for LCS/LCSD

The concentrations of the spiked compounds are determined using equations 12, 13 and 14 in section 11.4.1. After determining the compound concentrations, the percent recovery is calculated using Equation 3.

Equation 3

$$\text{LCS} = \frac{\text{SSR}}{\text{SA}} x100$$

Where,

SSR = Spiked Sample Result

SA = Spike Added

The relative percent difference between the laboratory control sample and the laboratory control sample duplicate is calculated using Equation 2, where the MSR and MSDR are equivalent to the LCS recovery and the LCSD recovery respectively.

9.1.2.5 Technical Acceptance Criteria for MS/MSD

The acceptance criteria for retention time and IS recovery must be met for matrix spike and matrix spike duplicate analysis.

The matrix spike recovery and RPD limits for 8270D are based on historical data and are updated annually.

MS limits for MCP and RCP are 40-140% for base-neutral compounds and 30-130% for acid compounds. RPD limits are ≤20% for waters and ≤30% for soils.

SIM limits are 40-140%. RPD limit is ≤20%.

The matrix spike recovery limits are advisory. If the recovery limits are not met, no further corrective action will be necessary. However, frequent occurrences of this nature should be investigated.

Re-extraction and re-analysis of the matrix spike and matrix spike duplicate may be necessary if, in the technical judgment of the analyst and/or supervisors, an error was made during the extraction procedure.

Exceedances of 150% or less than 10% and/or RPD of >50% should be narrated for potential matrix interference, especially when an associated LCS meets acceptance criteria.

9.1.2.6 Technical Acceptance Criteria for LCS

The acceptance criteria for retention time, surrogate and IS recovery must be met for the LCS analysis. Any failures in the LCS are flagged automatically in the laboratories TALS LIMS system.

The Laboratory Control Sample recovery and RPD limits for 8270D are based on historical data and are updated annually.

The laboratory defines several compounds for 8270D as poor performers in association to this analytical method. These analytes are identified as such through current and historical performance and are listed in Table 6. Recoveries of poor performers in the laboratory control sample (and/or duplicate) that are below the lower control limit are allowed, provided that the recovery is greater than or equal to 10%, with the exception of Benzidine, which must meet 5%. Any poor performer that meets this condition described will be noted in the job narrative.

Recovery limits for MCP and RCP are 40-140% for base-neutral compounds and 30-130% for acid compounds. RPD limits are ≤20% for waters and ≤30% for soils.

MCP allows the following “difficult” analytes to be outside of criteria, provided the recovery is within 15-140%: 4-Chloroaniline, 4-Nitrophenol, Phenol and 2,4-Dinitrophenol.

For MCP, ≤10% of the target analytes may be outside acceptance limits, provided the recovery is ≥10%.

For RCP, ≤20% of the target analytes may be outside acceptance limits, provided the recovery is ≥10%.

Recovery limits for SIM are 40-140%. RPD limits are ≤20%.

Any single target compound that recovers above the upper control limit for 8270D, MCP, RCP or SIM is to be considered high bias in all samples associated to that LCS (and/or LCSD). If the detection of that analyte in associated samples is either not detected or detected at a concentration below the reporting limit (RL), the deficiency will be noted in the job narrative and the sample(s) will be reported.

If a surrogate exceeds the upper control limit, associated samples may be reported if all target compounds associated to that surrogate class are not detected or detected at a concentration below the reporting limit (RL). The deficiency will be noted in the job narrative and the sample(s) will be reported.

9.1.2.7 Corrective Actions for Laboratory Control Sample Analysis

If the acceptance criteria for laboratory control sample/laboratory control sample duplicate analysis are not met, the analytical system may be assumed to be out of control. The following corrective actions may be taken:

If the recovery of any target analyte is above the upper control limit and associated samples contain detections for this analyte greater than the reporting limit, re-extraction and re-analysis must be performed for those samples.

If the recovery of any target analyte is below the lower control limit and is not a poor performer, or if a poor performer recovers below 10% (Benzidine less than 5%), re-analyze the laboratory control sample and/or laboratory control sample duplicate to ensure an issue with the injection did not occur. If the LCS/LCSD fails in the re-analysis, all samples associated to the LCS/LCSD that require the non-compliant compound must be re-extracted.

If surrogate recoveries in the LCS/LCSD do not meet the acceptance criteria, first reanalyze the LCS/LCSD. If the surrogate recoveries do not meet the acceptance criteria after reanalysis, re-extract and re-analyze the LCS/LCSD and all associated samples OR the samples may be reported as estimated, and noted in the job narrative.

If the LCS/LCSD does not meet internal standard response requirements, check the calculations, the internal standard spiking solutions, and the instrument operation. If the calculations were incorrect, correct the calculations and verify that the internal standard responses meet their acceptance criteria. If the internal standard spiking solution was improperly prepared, concentrated, or degraded, re-prepare solutions and re-extract/re-analyze the LCS and associated samples. If the instrument malfunctions affected the calibration, recalibrate the instrument before reanalyzing the LCS.

An exception to corrective action for LCSD-only failures may be allowed on a case by case basis, depending on client requirements.

9.2 Surrogate Recoveries

The surrogate compound concentrations are determined using equations 12, 13 and 14 in section 11.4.1. The recoveries are then determined using Equation 4.

Equation 4

$$\%\ Recovery = \frac{Concentration\ (\vee\ amount)\ found}{Concentration\ (\vee\ amount)\ spiked} \text{ X } 100$$

9.2.1 Technical Acceptance Criteria for Surrogate Recovery

Surrogate recovery limits for 8270D are based on historical data and are updated annually.

Limits for MCP and RCP are 30-130% in a soil matrix, 30-130% for base-neutral compounds in a water matrix and 15-110% for acid compounds in a water matrix.

Up to one acid and/or one base/neutral surrogate can be outside the acceptance limits in sample analysis, provided the recovery is greater than or equal to 10%.

Multiple surrogates of the same class (acid and/or base/neutral) may recover above the upper control limit as long as sample detections are below the reporting limit or are not detected for any compound associated to that surrogate class.

Multiple surrogates of the same class may recover below the lower control limit provided the requested target analyte list does not contain any compounds in that failing surrogate class.

Surrogates failing to meet acceptance criteria related to significant and obvious matrix interference may be reported, or a dilution may be performed to reduce the amount of interference.

Surrogate recoveries in samples diluted by a factor of 20X or greater are to be considered estimated as they are below the lowest calibration level.

Any surrogate recovery outside acceptance limits will be qualified and noted in the job narrative.

9.2.2 Corrective Actions for Surrogate Recovery

Calculations, injection volumes and preparation volumes are checked to ensure an error was not made. If all calculations, volumes, etc., were correct the analyst will proceed to the next step in the corrective action process.

The sample is re-injected to verify an error was not made during the original analysis. If after re-injection, surrogate recoveries are outside of the acceptance criteria, the analysis will proceed to the next step in the corrective action process.

The sample is re-extracted. Exceptions for this are either in the case where MS/SD and parent surrogate recoveries all agree, there is significant matrix identified at the retention time of the surrogate or insufficient volume of the sample remains. In either case, the situation will be documented in the job narrative.

After re-extraction, the sample is re-injected. If after re-analysis surrogate recoveries are within criteria limits, this extract is considered the first because the original problem may have been due to a laboratory error during extraction. If, after re-analysis surrogate recoveries are not within criteria limits, a matrix effect may be assumed. If this should occur, the original analysis may be reported. The instance will be documented in the job narrative.

9.3 Internal Standard Recoveries

Internal standards are added to all initial calibration standards, initial calibration verification (ICV) and continuing calibration verification (CCV) standards, batch QC (MB/LCS/MS/MSD) and client samples. For the ICV and CCV, the internal standard responses are compared to the mid-level calibration standard. For batch QC and samples, internal standards are compared to the daily CCV. The recoveries are determined using Equation 5.

Equation 5

$$\%\text{Recovery} = \frac{\text{Area of IS in Sample}}{\text{Area of IS in Standard}} \text{ X } 100$$

9.3.1 Technical Acceptance Criteria for Internal Standard Recoveries

Internal standard recovery for instrument QC must be within 50-200% of the mid-range calibration level.

Internal standard recovery for batch QC and samples must be within 50-200% of the daily continuing calibration verification (CCV).

Retention time shifts for each Internal Standard must be within ±0.5 min between the continuing calibration verification and the mid-level standard of the most recent initial calibration.

Retention time shifts for each Internal Standard must be within ±0.5 min between the sample and the most recent continuing calibration verification.

9.3.2 Corrective Actions for Internal Standard Recoveries

Calculations, internal standard solution volumes and injected volumes are checked to ensure that an error was not made. If all calculation and volumes were correct, the analyst will proceed to the next step in the corrective action process.

The sample is re-injected to ensure that the instrument was working properly. If after re-analysis, the internal standard recoveries are within criteria limits, the second analysis will be reported. If after re-analysis the internal standard recoveries are outside of criteria limits, the following steps will be taken:

If an instrument QC standard fails internal standard recovery, the electron multipler (EM) voltage can be adjusted accordingly and the DFTPP and standards must be reanalyzed. Failure again and the reagent will be re-prepared and reanalyzed. Repeat IS failures requires initial calibration and/or instrument maintenance.

If a batch QC sample fails internal standard recovery, the entire batch will be re-extracted and re-analyzed.

If a client sample fails internal standard recovery, the sample will be re-extracted and re-analyzed.

Exception: If internal standard recoveries of a sample, MS/MSD agree (i.e., recoveries are outside of criteria limits for all three samples), it may be assumed that a matrix effect is involved and no corrective action is necessary. The instance will be documented in the job narrative.

9.4 Labeled Analog Recoveries for SIM

The isotopically labeled analog 1,4-Dioxane-d8 is added to all samples during extraction. This analyte is used for the quantitation of 1,4-Dioxane.

9.4.1 Technical Acceptance Criteria for Labeled Analog Recoveries

Recovery limits for SIM are based on historical data and are updated annually.

1,4-Dioxane-d8 may recover above the upper limit, provided the recovery of 1,4-Dioxane is below the reporting limit and/or not-detected.

Recovery failing to meet acceptance criteria due to significant and obvious matrix interference may be reported, or a dilution may be performed to reduce the amount of interference.

Recovery of 1,4-Dioxane-d8 in samples diluted below the lowest calibration level can be determined to be acceptable if the signal to noise ratio of the quantitation ion is 10:1 and the qualifier ion is 3:1.

If dilutions do not recover 1,4-Dioxane-d8, then recovery of 1,4-Dioxane cannot be calculated. In this case, lower dilutions with results over the upper calibration level may be reported for 1,4-Dioxane, with proper flagging and notation in the job narrative.

9.4.2 Corrective Actions for Labeled Analog Recovery

Calculations, injection volumes and preparation volumes are checked to ensure an error was not made. If all calculations, volumes, etc., were correct the analyst will proceed to the next step in the corrective action process.

The sample is re-injected to verify an error was not made during the original analysis. If after re-injection, analog recoveries are outside of the acceptance criteria, the analysis will proceed to the next step in the corrective action process.

The sample is re-extracted. Exceptions for this are either in the case where MS/SD and parent analog recoveries all agree, there is significant matrix identified at the retention time of the analog or insufficient volume of the sample remains. In either case, the situation will be documented in the job narrative.

After re-extraction, the sample is re-injected. If after re-analysis analog recoveries are within criteria limits, this extract is considered the first because the original problem may have been due to a laboratory error during extraction. If, after re-analysis analog recoveries are not within criteria limits, a matrix effect may be assumed. If this should occur, the original analysis may be reported. The instance will be documented in the job narrative.

10.0 Procedure

Technical requirements and acceptance of instrument QC for 8270D, MCP, RCP and SIM is detailed below and summarized in Table 11 in section 18.

10.1 Sample preparation

For complete procedure on sample preparation, see the following TestAmerica Buffalo SOPs:

3510C:	BF-OP-003, current revision
3510C_LVI:	BF-OP-019, current revision
3550C:	BF-OP-016, current revision
3546:	BF-OP-018, current revision

10.2 Instrument QC

Typical Instrument Operating Conditions are presented below. These may be modified as necessary to accommodate large volume injection (LVI) techniques which may utilize up to a 5uL injection.

DFTPP analyzed for SIM is through full scan and should use the LVI Suggested Parameters.

OVEN
LVI Suggested Parameters
Initial temp: 45 °C (On) Maximum temp: 340 °C
Initial time: 3.00 min Equilibration time: 0.20 min
Ramps:

#	Rate	Final temp	Final time
1	30.00	280	0.00
2	9.00	325	4.00
3	0.0(Off)		

Post temp: 70 °C
Post time: 0.00 min
Run time: 19.83 min

Note, the run time must be extended so that the instrument acquires at least 1 min after the last compound elutes off the column.

1L Suggested Parameters

Initial temp: 55 °C (On) Maximum temp: 340 °C
Initial time: 2.75 min Equilibration time: 0.20 min
Ramps:

#	Rate	Final temp	Final time
1	23.00	70	0.00
2	20.00	195	0.00
3	30.0	330	5.00
4	0.00 (off)		

Post temp: 70 °C
Post time: 0.00 min
Run time: 19.15 min

Note, the run time must be extended so that the instrument acquires at least 1 min after the last compound elutes off the column. For the analysis of Dibenzo(a,e)pyrene, the Final Time for rate #3 should be adjusted by several minutes to allow this compound to properly elute off the column.

SIM Suggested Parameters

Initial temp: 45 °C (On) Maximum temp: 340 °C
Initial time: 3.00 min Equilibration time: 0.20 min
Ramps:

#	Rate	Final temp	Final time
1	30.00	325	4.00
2	0.00 (off)		

Post temp: 45 °C
Post time: 0.00 min
Run time: 16.33 min

FRONT INLET (SPLIT/SPLITLESS)
LVI Suggested Parameters

Mode: Pulsed Splitless
Initial temp: 280 °C (On)
Pressure: 14.90 psi (On)
Pulse pressure: 30.0psi
Pulse time: 0.55 min
Purge flow: 50.0 mL/min
Purge time: 0.50 min
Total flow: 54.7 mL/min
Gas saver: On
Saver flow: 20.0 mL/min
Saver time: 2.00 min
Gas type: Helium

1L Suggested Parameters
Mode: Splitless
Initial temp: 280 °C (On)
Pressure: 7.00 psi (On)
Purge Flow: 30.0 mL/min
Purge Time: 0.40 min
Total flow: 33.9 mL/min
Gas saver: On
Saver flow: 20.0 mL/min
Saver time: 3.00 min
Gas type: Helium

SIM Suggested Parameters
Mode: Pulsed Splitless
Initial temp: 280 °C (On)
Pressure: 13.44 psi (On)
Pulse pressure: 30.0psi
Pulse time: 0.55 min
Purge flow: 50.0 mL/min
Purge time: 0.50 min
Total flow: 54.0 mL/min
Gas saver: On
Saver flow: 20.0 mL/min
Saver time: 2.00 min
Gas type: Helium

COLUMN 1
LVI Suggested Parameters
Capillary Column
Model Number: Phenomenex ZB-Semivolatile GUARDIAN
Max temperature: 330 °C
Nominal length: 30.0 m (with integral 10m guard column)
Note, this may be removed or a column without a guard column may be installed.
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Note, a film thickness of 0.5 um may be utilized.
Mode: constant flow
Initial flow: 2.2 mL/min
Nominal initial pressure: 14.91 psi
Average velocity: 59 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

1L Suggested Parameters
Capillary Column
Model Number: Phenomenex ZB-Semivolatile GUARDIAN
Max temperature: 330 °C
Nominal length: 30.0 m (with integral 10m guard column)

Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Note, a film thickness of 0.5 um may be utilized.
Mode: ramped pressure
Initial pressure: 7.00 psi
Initial time: 0.00 min

#	Rate	Final pres	Final time
1	90.00	30.00	0.10
2	99.00	12.00	2.60
3	2.40	35.00	0.00

Post pressure: 0.00 psi
Nominal initial flow: 0.7 mL/min
Average velocity: 26 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

SIM Suggested Parameters
Capillary Column
Model Number: Phenomenex ZB-Semivolatile GUARDIAN
Max temperature: 330 °C
Nominal length: 30.0 m (with integral 10m guard column)
Note, this may be removed or a column without a guard column may be installed.
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Note, a film thickness of 0.5 um may be utilized.
Mode: constant flow
Initial flow: 1.4 mL/min
Nominal initial pressure: 13.45 psi
Average velocity: 40 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

FRONT DETECTOR (NO DET)
LVI, 1L and SIM Suggested Parameters

SIGNAL 1	SIGNAL 2
Data rate: 20 Hz	Data rate: 20 Hz
Type: test plot	Type: test plot
Save Data: Off	Save Data: Off
Zero: 0.0 (Off)	Zero: 0.0 (Off)
Range: 0	Range: 0
Fast Peaks: Off	Fast Peaks: Off
Attenuation: 0	Attenuation: 0

COLUMN COMP 1
(No Detectors Installed)

THERMAL AUX 2

LVI and SIM Suggested Parameters
Use: MSD Transfer Line Heater
Description: MSD Transfer Line
Initial temp: 325 °C (On)
Initial time: 0.00 min
Rate Final temp Final time
1 0.0(Off)
Post Run
Post Time: 0.00 min

1L Suggested Parameters
Use: MSD Transfer Line Heater
Description: MSD Transfer Line
Initial temp: 310 °C (On)
Initial time: 0.00 min
Rate Final temp Final time
1 0.0(Off)
Post Run
Post Time: 0.00 min

GC INJECTOR
LVI and SIM Suggested Parameters
Front Injector:

Sample Washes	2
Sample Pumps	4
Injection Volume	2.00 microliters
Syringe Size	10.0 microliters
PreInj Solvent A Washes	0
PreInj Solvent B Washes	0
PostInj Solvent A Washes	4
PostInj Solvent B Washes	2
Viscosity Delay	0 seconds
Plunger Speed	Fast
PreInjection Dwell	0.00 minutes
PostInjection Dwell	0.00 minutes

1L Suggested Parameters
Front Injector:

Sample Washes	1
Sample Pumps	4
Injection Volume	1.00 microliters
Syringe Size	10.0 microliters
PreInj Solvent A Washes	0
PreInj Solvent B Washes	0
PostInj Solvent A Washes	2
PostInj Solvent B Washes	2
Viscosity Delay	0 seconds
Plunger Speed	Fast
PreInjection Dwell	0.00 minutes
PostInjection Dwell	0.00 minutes

MS ACQUISITION PARAMETERS
LVI and 1L Suggested Parameters
General Information
Tune File : dftpp.u
Acquisition Mode : Scan

MS Information
Solvent Delay : 2.60 min
Note, this will vary depending on the age of the column.
EM Offset : 0
Resulting EM Voltage : 976.5
Note, this will vary depending on the age of the Electron Multiplier. Once the EM Voltage is ~ 2300-2600, it may need to be replaced. 3000 is the maximum voltage of an EM.

[Scan Parameters]

Low Mass : 35.0
High Mass : 500.0
Threshold : 100
Sample # : 2
A/D Samples : 4

[MSZones]
MS Quad : 150 °C maximum 200 °C
MS Source : 230 °C maximum 250 °C

SIM Suggested Parameters
General Information
Tune File : dftpp.u
Acquisition Mode : SIM

MS Information
Solvent Delay : 1.50 min
Note, this will vary depending on the age of the column.
EM Voltage : False
EM Offset : 47
Resulting EM Voltage : 1705.9
Note, this will vary depending on the age of the Electron Multiplier. Once the EM Voltage is ~ 2300-2600, it may need to be replaced. 3000 is the maximum voltage of an EM.

[SIM Parameters]

Group 1
Group ID : 1
Resolution : Low
Plot 1 Ion : 88.0
Plot 2 Ion : 88.0

Ions / Dwell In Group	(Mass, Dwell)	(Mass, Dwell)	(Mass, Dwell)
	(43.0, 100)	(58.0, 100)	(64.0, 100)
	(88.0, 100)	(96.0, 100)	(115.0, 100)
	(152.0, 100)		

[MSZones]
MS Quad : 150 °C maximum 200 °C
MS Source : 230 °C maximum 250 °C

10.3 Instrument Performance Check

The GC/MS system is tuned using Perfluorotributylamine (PFTBA) such that an injection of 50ng (for 1L/Soils) or 10ng (for LVI/Low Level/SIM) of DFTPP will meet the abundance criteria listed in Table 3.

Prior to the analysis of standards or samples, the mass calibration and resolution of the GC/MS system is verified by the analysis of DFTPP. This analysis will verify the proper tuning of the system for 12 hours. After 12 hours, the instrument performance must be verified before standard and sample analysis may continue.

The average of the apex of the DFTPP peak, the scan before and scan after the apex is used to assess ion abundances. If the criteria is not met, a single scan of the apex may be evaluated. This is performed automatically in the Chrom system.

The mass spectrum of DFTPP may be background subtracted to eliminate column bleed or instrument background ions. The background spectrum is selected as one scan before the start of the integrated DFTPP peak.

Breakdown of 4,4'-DDT into 4,4'-DDD and 4,4'-DDE may be used to assess GC column performance and injection port inertness and must be less than 20%.

The compounds Benzidine and Pentachlorophenol should be present and at their normal responses for this concentration. Peak tailing should not be visible (PCP tailing factor ≤2 and Benzidine ≤2). If responses are poor and excessive peak tailing is present, corrective actions for the GC/MS instrument performance check solution may be required. Benzidine and Pentachlorophenol tailing may also be verified in the CCV.

Breakdown and tailing is not evaluated for SIM analysis.

All subsequent standards and samples must be acquired under the same GC/MS tuning conditions that were used for the analysis of the instrument performance check solution.

10.3.1 Technical Acceptance Criteria for the GC/MS Instrument Performance Check

DFTPP criteria is listed in Table 3.

Tailing of Pentachlorophenol and Benzidine must be ≤2.

Breakdown of 4,4’-DDT into 4,4’-DDD and 4,4’-DDE must be ≤20%.

All tune acceptance criteria applies to MCP and RCP analysis.

10.3.2 Corrective Actions for the GC/MS Instrument Performance Check

If any of the acceptance criteria are not met, the DFTPP should be re-injected to ensure that the injection made was not a cause for failure. If, after reinjection, acceptance criteria has not been met, one or more of the following corrective actions may be taken:

1. Replace the injection port liner
2. Replace the septum in the injector
3. Cut the column at the injector end
4. Re-prepare the DFTPP working standard and re-analyze
5. Clean injection port with $MeCl_2$
6. Change injection port seal
7. Retune the GC/MS
8. Replace the column
9. Clean the source; replace parts, etc.
10. An instrument service call may be placed.

10.4 Initial Calibration

After the instrument performance check criteria has been met and prior to the analysis of samples, the GC/MS system is calibrated at a minimum of five concentration levels in order to establish instrument sensitivity and linearity.

The initial calibration shall be performed when major instrument maintenance has been performed or if continuing calibration criteria cannot be met.

Major instrument maintenance may consist of source cleaning, column changing, injection port replacement or quadrupole rod adjustment. Preventative maintenance such as septum changes, injector liner changes or column cutting may not require an initial calibration to be performed.

10.4.1 Procedure for Initial Calibration

Calibration standards for common target semivolatile compounds are prepared to contain all target, internal standard and surrogate compounds. Additional calibration mixes may be prepared that contains an extra list of target compounds and internal standards only. Surrogates should not be added to additional mixes. Refer to section 7.3.4 for preparation of calibration mixes and section 7.3.5 for preparation of Internal Standard working mix.

The relative response factors (RRF) for each target and surrogate compound is determined using equation 6. The characteristic ions for a given compound are listed in Tables 5. Internal standard assignments are listed in Table 4.

Equation 6

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

Where,
A_x = Area of the quantitation ion for the compound to be measured (see Table 5)
A_{is} = Area of the quantitation ion for specific internal standard (see Table 5)
C_{is} = Amount of the internal standard injected (ng)
C_x = Amount of the compound to be measured injected (ng)

The mean relative response factor (RRF) must be calculated for all compounds. Calculate the % Relative Standard Deviation (%RSD) of the RRF values for the initial calibration using the following equation:

Equation 7

$$\%RDS = \frac{Standard\ \ Deviation}{Mean}\ x\ 100$$

Where,

$$Standard\ \ Deviation = \sqrt{\frac{\sum_{i+1}^{n} (X_i - \overline{X})^2}{(n-1)}}$$

x_i = each individual value used to calculate the mean
x = the mean of n values
n = the total number of values

For the SIM analysis, the RRF of the analog compound (1,4-Dioxane-d8) is calculated by Equation 6 using the Internal Standard 1,4-Dichlorobenzene-d4. For the analyte 1,4-Dioxane, the RRF is calculated by Equation 6 using the analog 1,4-Dioxane-d8 as the Internal Standard.

10.4.2 Technical Acceptance Criteria for Initial Calibration

The relative standard deviation (RSD) should be less than or equal to 20% for each target analyte for 8270D, MCP, RCP and SIM. If the relative standard deviation is greater than 20%, a linear calibration fit may be used. The criterion for this is a correlation coefficient (r^2) value greater than or equal to 0.990.

If less than 10% of the calibrated compounds fail to meet the above criteria for 8270D, analysis may proceed, given the following conditions:

A standard with a concentration at or below the reporting limit for compounds failing to meet the RSD or correlation coefficient must be analyzed with each analytical sequence, preceding the analysis of samples. Acceptance criterion for this is detection only.

Any non-detection in sample analysis associated to compounds failing to meet RSD or correlation coefficient criteria may be reported without flagging,

only with the successful detection of the analyte in the reporting limit standard.

Any detection associated to compounds failing to meet RSD or correlation coefficient criteria must be must be flagged as estimated. Every effort should be made to reanalyze the sample on an instrument with a passing calibration.

If less than 10% of the compounds for MCP fail to meet the above criteria, analysis may proceed, given the following conditions:

The %RSD is <40% or the r^2 value is >0.98

If less than 20% of the compounds for RCP fail to meet the above criteria, analysis may continue.

The relative response factors (RRF) for the most common target analytes are compared to the minimum relative response factor criteria required by 8270D, listed in Table 7.

If a compound fails to meet the minimum response factor defined in Table 7, a standard with a concentration at or below the reporting limit (RL) must be analyzed in each analytical batch, preceding sample analysis. Acceptance criterion for this is detection only.

Samples containing non-detections for these compounds may be reported without flagging only with a passing RL check.

Samples with positive detections must be flagged as estimated. Every effort should be made to reanalyze the sample on an instrument with passing minimum response factors in the initial calibration.

The relative response factors for MCP must meet the minimum response factors listed in Table 7 for the lowest concentration standard and for the average RF. All other compounds must recover a response of 0.05 or greater on the lowest calibration standard and average RF.

If the minimum response factor is not met, the non-conformity will be narrated.

For RCP analysis, all compounds must meet a minimum response factor of 0.05.

Non-conforming compounds will be narrated.

Analytes fitted with a linear calibration model must have a readback concentration of 30% of the true value at the low level of the calibration, for 8270D and MCP. Linear-fitted analytes for RCP and SIM should meet 30% readback as well. For 8270D, any non-detection in samples associated to a compound that fails to meet this criterion in the calibration may be reported without flagging. Detections must be flagged as estimated and noted in the job narrative.

Any compound that fails to meet the criterion for MCP must be reported as estimated in the narrative.

Identification of analytes in all calibration levels can be made only if there are 5-10 scans of the quantitation ion across the peak. All minor ions, where the expected abundance set from the mid-level standard is greater than 10%, must also be present.

For SIM, the signal to noise ratio for each level should be 10:1 for the quantitation ion and 3:1 for the qualifying ion(s) for both the analyte and isotopically labeled analog.

Internal Standard responses of each calibration level should be within 50%-200% of the mid-level standard.

Relative retention times of Internal Standards, surrogates and compounds must be within ±0.06 mins of the RT set in the mid-level point of the calibration.

Additional Initial Calibration requirements are described in TestAmerica Buffalo SOP BF-GP-012 (current revision), beginning with section 5.5: Initial Calibration Review.

10.4.3 Corrective Actions for Initial Calibration

If any of the acceptance criteria for initial calibration are not met, it may be necessary to reanalyze one or more of the calibration standards. This must be completed within the same 12 hour tune as the other calibration levels and before sample analysis. If after reanalysis, the acceptance criteria have not been met, it may be necessary to take further corrective actions.

The following corrective actions may be taken if the acceptance criteria for initial calibration cannot be met.

1. Replace the septum on the injector
2. Replace the injector liner
3. Cut column at the injector end
4. Prepare fresh standards and reanalyze the initial calibration
5. Re-tune the GC/MS system and reanalyze the instrument performance check
6. Replace the analytical column
7. Clean the source
8. An instrument service call may be placed

The acceptance criteria must be met before sample analysis may proceed.

10.4.4 Initial Calibration Verification

To verify the accuracy of the initial calibration, a standard is obtained from a source different from the calibration standards. Alternatively, if a different source is not available, a differing lot number of the standards used in the initial calibration may substitute as the second source.

Immediately following analysis of an acceptable initial calibration curve, an aliquot of the second source standard with a concentration approximating the mid point of the curve of is injected.

10.4.5 Technical Acceptance Criteria for Initial Calibration Verification

For 8270D, recoveries of all compounds shall fall within the required 70-130% acceptance limit with the exception of the "Poor performers", whose criteria are listed Table 6.

Relative response factors (RRF) must meet the minimum response factor criteria listed in Table 7 for the most common semivolatile target analytes.

If any analyte recovery exceeds the upper control limit, data analysis may continue. Non-detections in sample analysis associated to a failing analyte may be reported without flagging. Any detection in sample analysis must be flagged as estimated. Every effort should be made to re-analysis samples with detections on an instrument which has a passing initial calibration and initial calibration verification.

If any analyte recovery exceeds the lower control limit, including limits set for poor performing compounds, the calibration is deemed to be out of control and corrective action must be taken prior to sample analysis.

For MCP, recoveries of all compounds shall fall within the required 70-130% acceptance limit with the exception of the "difficult" analytes, listed below, whose recovery must be within 40-160%. 10% of the total compounds may fail the criteria. If any analyte is outside acceptance limits, report the non-conforming compound in the narrative.

> MCP list of "difficult" analytes includes 4-Chloroaniline, 4-Nitrophenol, Phenol and 2,4-Dinitrophenol.

For RCP, recoveries of all compounds shall fall within 80-120%. 20% of the total compounds may fail the criteria, as long as recovery is within 65-135%. If any analyte is outside acceptance limits, report the non-conforming compound in the narrative.

Internal Standard retention times and responses are evaluated after acquisition of the initial calibration verification. If the retention time of any internal standard shifts by more than 30 seconds from that in the mid-point standard level of the initial calibration or the response of any internal standard is outside of the 50% to 200% range compared to the mid-point standard level of the initial calibration, the system shall be inspected and corrected as needed. The ICV will be reanalyzed after inspection. If the problem is not resolved, a new initial calibration must be performed.

10.4.6 Corrective Actions for Initial Calibration Verification

If the Technical Acceptance Criteria for Initial Calibration Verification is not met, the following corrective action steps should be taken.

Re-inject the ICV to verify there was not an error made during the original analysis.

Re-prepare the ICV to verify an error was not made during the original preparation.

Perform instrument maintenance and re-calibrate.

Re-prepare initial calibration standards and re-calibrate.

Prepare the ICV and/or initial calibration reagents from different lot numbers to verify degradation hasn't occurred.

Re-order either initial calibration or ICV reagents.

10.4.7 Continuing Calibration

If there is no time left in the 12-hour time period after initial calibration, the instrument performance is verified by the injection of a mid level standard.

The continuing calibration check must be analyzed once every 12-hour time period of operation. This check must be analyzed prior to the analysis of samples for a given 12-hour time period.

10.4.8 Procedure for Continuing Calibration

A mid-level calibration standard is used for the continuing calibration verification (CCV). The relative response factor is calculated using Equation 6 in section 10.4.1. The relative response factor is compared to the minimum relative response factors required by 8270D, listed in Table 7.

If quantitation is performed using average response factor, calculate the percent difference between the mean relative response factor from the most recent initial calibration and the continuing calibration relative response factor for each semivolatile target and surrogate compound using Equation 8.

Equation 8

$$\%\ Difference_{RRF} = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} x\ 100$$

Where,

$\overline{RRF_i}$ = Mean relative response factor from the most recent initial calibration meeting technical acceptance criteria
RRF_c = Relative response factor from continuing calibration standard

If quantitation is performed using a linear regression or a non-linear model, calculate the concentration using equations 12, 13 and 14 in section 11.4.1 of this SOP. Calculate the percent drift using Equation 9.

Equation 9:

$$\%\text{Drift} = \frac{\text{Conc}_E - \text{Conc}_A}{\text{Conc}_E} x100$$

Where:

Conc_E = Expected Concentration
Conc_A = Actual Concentration

10.4.9 Acceptance Criteria for Continuing Calibration

The relative response factor (RRF) for the most common semivolatile compounds must be greater than or equal to the minimum response factors listed in Table 7 for 8270D and MCP.

RCP and compounds excluded from Table 7 for MCP must have a minimum response factor greater or equal to 0.05.

The percent difference or percent drift (%D) should be less than or equal to ±20% for all compounds, for 8270D, MCP, RCP and SIM.

For 8270D, 10% of the total calibrated analyte list is allowed to have %D limits outside ±20%, provided that the limit is set to a maximum of ±50%. These analytes are defined as poor perfomers by the laboratory. Poor performers and their limits are listed in Table 6.

For 8270D, up to 20% of the total compounds analyzed between CCVs in a batch are allowed to be outside of the ±20%D criterion, or outside of the limits set for poor performing compounds. The total number allowed to fail based on the CCVs analyzed in any given batch, are listed in Table 9. Note: this is based on the laboratory's main list of calibrated analytes. Additional analytes/CCVs may be analyzed and the total number may be adjusted accordingly.

For 8270D, if a compound fails to meet the %D criteria or minimum response factor criteria, a standard at or below the reporting limit must be analyzed following the CCV and prior to sample analysis. Acceptance criteria for this is detection only.

Any non-detection for analytes failing to meet the %D or minimum response factor criteria in samples and only with a passing reporting limit check may be reported with notation in the job narrative only.

Any detection for analytes failing to meet the %D or minimum response factor criteria in samples must be flagged as estimated. Every effort should be made to reanalyze the sample on an instrument with a passing CCV.

For MCP, 20% of the total compound list is allowed to exceed criteria, as long as the %D is <40%.

If %D and/or minimum response factors are not met, the non-conformance will be narrated.

For RCP, 10% of the total compound list is allowed to exceed criteria. Any failures will be narrated.

Internal Standard retention times and responses are evaluated after acquisition of the continuing calibration check. If the retention time of any internal standard shifts by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration or the response of any internal standard is outside of the 50% to 200% range compared to the mid-point standard level of the most recent initial calibration, the system shall be inspected and corrected as needed. The CCV will be reanalyzed after inspection. If the problem is not resolved, a new initial calibration must be performed.

10.4.10 Corrective Actions for Continuing Calibration

If any of the technical acceptance criteria for continuing calibration are not met, it may be necessary to reanalyze the continuing calibration standard. If after reanalysis the acceptance criteria cannot be met, further corrective actions may be required.

The following corrective actions may be taken if the acceptance criteria for continuing calibration cannot be met.

1. Replace the septum on the injector
2. Replace the injector liner
3. Replace injection port seal
4. Cut the column at the injector end
5. Retune the GC/MS system and reanalyze the instrument performance check
6. Prepare fresh standards
7. Reanalyze the initial calibration

11.0 Sample Analysis

11.1 Procedure

Sample extracts shall be analyzed only after the GC/MS system has met the instrument performance check, initial calibration, second source calibration verification and continuing calibration requirements. The same instrument conditions must be employed for the analysis of samples as were used for calibration.

Internal standard solution is added to each sample extract. 20µL of internal standard solution is added to each accurately measured 1.0mL of sample extract so that the expected concentration for 1L and soil samples is 40 ng/uL, 4 ng/uL for LVI and LL samples and 1 ng/uL for SIM. The amount of internal standard needs to be adjusted according to how much extract volume was present in the extract vial. The exact volume of extract is measured using a syringe. The amount of Internal Standard solution to be added is then adjusted accordingly. The calculation to determine the amount of IS to add is provided below:

Equation 10

$$\frac{\text{Vol. Extract (ul) X 20 uL}}{1000} = \text{FV of IS (uL)}$$

Necessary dilutions are made prior to adding internal standard solution.

11.2 Dilutions

Dilutions of sample extracts are required if any target compound exceeds the initial calibration range.

The dilution chosen should keep the response of the largest target compound within the upper portion calibration range.

Dilutions of sample extracts may be performed due to the matrix of the sample. Any coating of the vial by the sample will be diluted appropriately to the level of viscosity observed.

Dilutions are prepared according to equation 11:

Equation 11:

$$\text{Dilution Factor} = \frac{\text{Final Volume}}{\text{Sample extract volume added}}$$

Dilutions are performed by adding a volume of sample extract and bringing to a final volume of 1mL with $MeCl_2$. Internal standards are added after and are not included in the calculation for final volume.

The final volume may be adjusted accordingly for cases where the sample extract volume received after extraction is not enough to perform a dilution to reach a 1mL final volume.

Dilutions that are greater than 100X must be performed by serial dilution.

For routine dilutions, see Table 10 for volumes utilized in performing these dilutions.

Dilutions above 20x will be deemed to have to low a surrogate recovery and shall be qualified accordingly.

For dilutions associated with SIM analysis, Internal Standard 1,4-Dichlorobenzene should be added accordingly. Analog 1,4-Dioxane-d8 should not be added to the dilution.

11.3 Qualitative Identification

11.3.1 Target Compounds

Target compound identification is done by comparing the sample mass spectrum to that of the standard. The following criteria must be satisfied in order to verify identifications.

Elution of the sample analyte within GC relative retention time unit window established from the 12-hour calibration standard.

To establish correspondence of the GC relative retention time (RRT), the sample component RRT must compare with ±0.06 RRT units of the mid level calibration. If samples are analyzed within the same 12-hour period as the initial calibration, the 50ng standard is used to verify relative retention times.

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

To establish correspondence of the sample component mass spectra to that of the standard, the following criteria must be met:

All ions present in the standard mass spectrum at a relative intensity greater than 10.0 percent (most abundant ion in the spectrum equals 100.0 percent) must be present in the sample spectrum.

The relative intensities of ions specified in the paragraph above must agree within ±20.0 percent between the standard and sample spectrum. (Example: For an ion with an abundance of 50.0 percent in the standard spectrum, the corresponding sample ion abundance must be between 30.0 and 70.0 percent).

Ions greater than 10.0 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. When target compounds are above the method detection limit (MDL) but are below the reporting limit (RL) but the spectrum meets the identification criteria, report the concentration with a "J".

If a compound does not meet all of the above criteria, but in the technical judgment of the mass spectral interpretation specialist the identification is correct, the compound will be identified

For SIM, the quantitation ions of 88 for 1,4-Dioxane and 96 for 1,4-Dioxane-d8 must demonstrate a signal to noise ratio of at least 10:1. For the qualifying ions of 58 (1,4-Dioxane) and 64 (1,4-Dioxane-d8), the signal to noise ratio must be at least than 3:1.

11.3.2 Non-Target Compounds

A library search may be executed for non-target sample components for the purpose of tentative identification. For this purpose, the NIST/EPA/NIH mass spectral library is used to identify non-target compounds of greatest apparent concentration by a forward search of the library. A background subtraction method may be employed to better match a peak's spectrum to the library. TIC processing is performed only on client requested samples and the Method Blank (MB) associated to those samples. The following compounds will not be identified by a library search routine:

Internal standard compounds
Surrogate compounds
Methylene Chloride

11.3.3 Guidelines for Making Tentative Identifications

After samples have been processed for Target compounds, any unidentified peak in a sample which has an area count of 10% or greater of the closest Internal Standard will be eligible for TIC identification.

A start and end retention time should be set to 0, which allows the entire chromatogram to be searched.

Note, if the solvent delay is not set appropriately during sample acquisition, the solvent may be collected. This should not be reported as a TIC.

Major ions in the reference spectrum (ions greater than 10 percent of the most abundant ion) should be present in the sample spectrum.

The relative intensities of the major ions should agree within ±20 percent. Molecular ions present in reference spectrum should be present in sample spectrum.

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.

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 compounds.

Sample spectra are compared to the NIST/EPA/NIH library for tentative identification. A criterion of 85% or greater confidence is used in determining IDs.

These settings are entered into the data processing software (Chrom). For routine work, these settings perform the bulk of TIC identification. Manual review of all TIC matches are not part of the standard review, except in the following situations:

CO_2 should be removed as a TIC.

Methylene Chloride should be removed as a TIC.

Internal Standards/surrogates not required by the client should be removed as a TIC.

Any aldol condensation product should be reported as “Aldol Condensation Products”. These include the following compounds: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one and 5,5-dimethyl-2(5H)-furanone.

Siloxanes should be reported as “Column Bleed”.

Multiple peaks may result in the same ID from the library. In this case, every effort should be made to identify the peak with the greatest confidence for that ID. The other shall be re-identified with the next ID listed, or re-identified as unknown.

If, in the technical judgment of the mass spectral interpretation specialist, no tentative identification can be made the compound will be reported as unknown. Further identification may be possible, such as molecular weights or classifications (i.e., unknown hydrocarbon, unknown acid, etc.)

Further information on TICs is documented in TestAmerica Corporate Quality Policy Memorandum No. CA-Q-QM-001.

TIC processing is not performed on SIM analysis.

10.3.4 Targeted TICs

Targeted Tentatively Identified Compounds may be requested and reported on occasion. Unlike TICS, Targeted TICs are searched and reported even if they are not detected.

These are included in the client requested compound list, but are not calibrated.

Identification is made using the NIST/EPA/NIH spectral library to compare all peaks in a chromatogram that are not identified as part of the client target analyte list.

An Internal Standard is a pre-determined based on the proximity of a detected peak to the closest internal standard.

A match threshold of 50% is used for identification of the sample spectrum versus the reference spectrum assigned for that compound.

A response factor of 1 is assumed for quantitation.

Any detection of a Targeted TIC is flagged as estimated in the data system (TALS).

11.4 Quantitative Identification

11.4.1 Target Compounds

Target compounds identified shall be quantitated by the internal standard method. The internal standard used shall be the one assigned to that analyte for quantitation (see Table 4). The EICP area of primary characteristic ions of analytes listed in Tables 5 are used for quantitation.

The calculation of analyte on-column (raw) concentration is based on the equations 12, 13 and 14. In each equation, the concentration is designated as “x”.

Average calibration fit:

Equation 12:

$$x = \frac{A_c \times C_I}{A_I \times RF}$$

Where:

Ac = Area of the compound
C_I = Expected concentration of the Internal Standard
A_I = Area of the Internal Standard
RF = Response Factor from the initial calibration

Linear calibration fit:

Equation 13:

$$y = mx + b$$

Where:

m = slope of the line
b = y-intercept
y = response factor as determined from equation 14.

Equation 14:

$$y = \frac{A_c \times C_I}{A_I}$$

Where:

A_c, C_I and A_I are given above.

The quantification of 1,4-Dioxane-d8 in the SIM analysis is based off the area and expected concentration of Internal Standard 1,4-Dichlorobenzene. The quantification of 1,4-Dioxane is based off the area and expected concentration of analog 1,4-Dioxane-d8.

In instances where manual integration is necessary due to co-elution, baseline noise or matrix interferences, all instances will be initialed and dated by the analyst. The quantitation report is documented as such by a "m" next to the compound that has been edited. In all instances of manual integration, a hardcopy of the EICP for that compound will be supplied with the raw data. This applies to all target compounds, internal standards and surrogate compounds. Manual Integrations are completed in accordance with TestAmerica Buffalo SOP BF-GP-013.

11.4.2 Water Samples

The following Equation (Eq. 15) is used to determine the final concentration of target compounds identified in water samples:

Equation 15

$$Concentration\ \mu g/L = \frac{(A_x)(I_s)(V_c)(Df)}{(A_{is})(RRFi)(V_o)(V_i)}$$

Where,

A_x = Area of the characteristic ion for the compound to be measured
A_{is} = Area of the characteristic ion for the internal standard
I_s = Amount of internal standard injected in nanograms (ng)
V_o = Volume of water extracted in milliliters (mL)
V_i = Volume of extract injected in microliters (µL)
Note: A value of 1uL should be assumed. LVI injections of 2uL or greater are accounted for in the initial calibration and are consistent through the calculation of the on-column (raw) concentrations.
V_c = Volume of the concentrated extract in microliters (µL)
RRFi= Relative response factor determined from the initial calibration
Df = Dilution factor. The dilution factor for analysis of water samples for semivolatiles by this method is defined in equation 11.

If no dilution is performed, Df = 1.0

11.4.3 Soil/Sediment Samples

The following Equation (Eq. 16) is used to determine the concentration of target compounds in soil/sediment samples:

Equation 16

$$Concentration\ \mu g/Kg\ (Dry\ weight\ basis) = \frac{(A_x)(I_s)(V_c)(Df)}{(A_{is})(RRF_i)(V_i)(W_s)(D)}$$

Where,

A_x, I_s, A_{is} are as given for water, above.
V_c = Volume of the concentrated extract in microliters (µL)
V_i = Volume of the extract injected in microliters (µL)
D = $\frac{100 - \%\ moisture}{100}$
W_s = Weight of sample extracted in grams (g)
RRFi= Relative response factor determined from the initial calibration.
Df = Dilution factor. The dilution factor for analysis of soil/sediment samples for semivolatile by this method is defined in equation 11.

11.4.4 Tentatively Identified Compounds

Non-Target Compounds
An estimated concentration for non-target tentatively identified compounds is quantitated by the internal standard method. For quantitation, the nearest internal standard free of interferences is to be used. The equations for calculating concentrations are the same as equations 15 and 16. Total area counts from the total ion chromatograms are used for both the compounds to be measured and the internal standard. A relative response factor (RRF) of one (1) is assumed. The resulting concentration is to be qualified as “J” (estimated, due to lack of a compound specific response factor), and “N” (Presumptive evidence of presence), indicating the quantitative and qualitative uncertainties is calculated for all tentatively identified compounds as well as those identified as unknowns.

11.5 Technical Acceptance Criteria For Sample Analysis

The samples must be analyzed on a GC/MS system meeting the DFTPP, initial calibration and continuing calibration criteria.

The sample must be extracted and analyzed within specified holding times.

The sample must have an associated method blank meeting the technical acceptance criteria for a MB, defined in section 9.1.1.2.

The sample must have an associated laboratory control sample meeting the technical acceptance criteria for a LCS, defined in section 9.1.2.6.

A matrix spike/matrix spike duplicate should be prepared with samples. If insufficient volume for a MS/SD, a laboratory control sample duplicate must be analyzed and meet the technical acceptance criteria for a LCS, defined in section 9.1.2.6.

All surrogates must meet the technical acceptance criteria for Surrogate Recoveries, defined in section 9.2.1.

The relative retention time of each compound must be within ±0.06 RRT units of its relative retention time in the continuing calibration standard.

The instrumental response (EICP area) for each of the internal standards must meet the technical acceptance criteria for Internal Standard recoveries, defined in section 9.3.1.

Excluding those ions in the solvent front, no ion may saturate the detector. No target compound concentration may exceed the upper limit of the initial calibration range unless a more dilute aliquot of the sample extract is also analyzed.

11.5 Corrective Actions for Sample Analysis

The technical acceptance criteria must be met before data are reported. If any of the criteria listed above are not met, either re-analyze the sample on an instrument meeting all technical criteria, refer to corrective actions defined throughout sections 9.0 and 10.0, or re-extract and re-analyze the sample.

If the technical acceptance criteria for the relative retention times of the internal standard, surrogate or target compounds are not met, the following corrective actions are taken in the given order:

Carrier gas, zone temperatures and instrument temperature programs are checked to ensure that an error was not made or that the gas tank was not dry or clogged. If no errors are found the analyst will proceed to the next step in the corrective action process.

The sample is re-analyzed to ensure that an error was not made during the first injection. If, after reanalysis, the relative retention times are not within the technical acceptance criteria, it may be assumed that a matrix effect was involved. Both analyses will be reported and the instance will be documented

in the job narrative. If, after re-analysis, the relative retention times are within the technical acceptance criteria, the second analysis will be reported only.

Exception: If the relative retention times of a sample, MS/MSD agree (i.e., relative retention times are outside of criteria limits for the sample, MS and MSD), it may be assumed that a matrix effect was involved and further corrective action is not necessary.

12.0 Documentation

12.1 Instrument Logbook

A logbook must be maintained to track major maintenance as well as daily maintenance to an instrument. The logbook must contain the date of the maintenance, the initials of the analyst performing the work, the reason why maintenance was performed and the maintenance completed. If any parts are replaced, catalog and lot numbers must be recorded. If maintenance either resolves the issue or further maintenance is required, this should be notated as well.

12.2 Reagents

All standards must be entered into LIMS. Each ampule will receive a LIMS ID# for traceability.

The certificate of analysis (COA) for each standard is initialized, dated and given the corresponding LIMS ID#. It is then scanned and attached to the reagent in LIMS.

When intermediates or working mixes are created, they are to be logged into LIMS and will be assigned an unique LIMS reference number.

12.3 Sample Logbook

Prior to the start of the analysis, QC and samples are logged into an unique LIMS worklist which serves as an electronic run log. This is accomplished with either a barcode scanner or the prep batch import function in Chrom, which uses the unique sample ID supplied directly from TALS via the prep batch.

Run Logs must contain the following information:

- Date, time, and analyst initials
- File number, sample ID, vial #, and job #
- Injection volume, final volume, initial volume and dilution factor
- References for the standards, tune mix, IS mix

All samples injected must be added to a LIMS worklist. If injections are not used, they are labelled accordingly in the worklist. Files must not remain in the Missing Samples list in Chrom and must not be deleted from this list. These must be entered into the worklist, properly linked and processed.

12.4 Checklists

Calibration checklist CA-Q-WI-046 (current revision) is to be completed by first and second level review. This is scanned and attached to the batch in LIMS.

Data Review checklist CA-Q-WI-045 (current revision) is to be completed by first and second level review. This is scanned and attached to the batch in LIMS.

An electronic checklist for an initial calibration as well as sample batch is also completed by first and second level review in LIMS.

Reagent Review Checklists for Unopened, Opened and Intermediate reagents (current revisions) are used for first and second level review of all LIMs reagents. These are scanned and attached with the COA to the reagent in LIMs.

13.0 Data Review

Technical data review of initial calibrations, instrument/batch QC and client data criteria is listed in TestAmerica Buffalo SOP BF-GP-012 (current revision).

13.4 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in the Corporate QA Manual. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

13.5 Demonstration of Capabilities

Initial Demonstration of Capability (IDOC): The initial demonstration with each sample preparation technique and analytical method combination utilized must be performed by generating data of acceptable accuracy and precision for target analytes in a clean matrix. This is also done for new staff or when significant changes in instrumentation are made. Demonstration of Capability (DOC) will be performed annually for those analysts whom have passing IDOCs.

14.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to section 13 of the Corporate Safety Manual. The following waste streams are produced when this method is carried out.

There are two types of aqueous waste generated in the lab:

A-Waste: All non-nitric acid and alkaline aqueous waste.

AN-Waste: All aqueous waste containing nitric acid.

These types of waste are to be disposed of into appropriately marked plastic containers.

The following lists other types of non-aqueous lab waste and where to dispose of:

C-Waste: all solvent waste gets dumped into appropriately marked metal cans. These cans need to be grounded whenever they are emptied to reduce explosion hazards. Discarded standards (except PCBs) will also be dumped into C-waste cans.

Solid Waste: all contaminated paper, solid sample waste, sodium sulfate and all other non-glass material that has been contaminated is to be wrapped in foil and gathered to be dumped into 55 gallon drums.

Glass: contaminated glass needs to be rinsed off with methylene chloride and disposed of with all other glass in glass specific containers with special extra thick polypropylene liners. These containers are for glass only.

Extract Vials: extract vials are to be archived for 6 months after they have been analyzed. After the archival period, vials are to be crushed into a 55 gallon drum.

16.0 References / Cross-References

16.1 US EPA Methods for Evaluating Solid Waste; SW-846, Third Edition, Update IV, Method 8270D, 07/14.

16.2 US EPA Methods for Evaluating Solid Waste; SW-846, Third Edition, Update IV, Method 8000D, 7/14.

16.3 MassDEP MCP WSC-CAM, section II-B, revision 1, 7/10.

16.4 Connecticut DEP RCP, version 2.0, 7/06.

17.0 Method Modifications

TestAmerica Corporate Quality Policy Memorandum NO. CA-Q-QM-009

18.0 Attachments

18.1 Table 1: Semi-volatile Target Compound List and Reporting Limits
18.2 Table 2: LCS/MS/MSD Spike Analytes
18.3 Table 3: DFTPP Ion Abundance Criteria
18.4 Table 4: Internal Standards, Surrogates and Corresponding Target Compounds Assigned for Quantitation
18.5 Table 5: Characteristic Ions for Target Compounds, Surrogates and Internal Standards
18.6 Table 6: Poor Performing Compounds
18.7 Table 7: Update 4 Minimum Response Factors for selected compounds
18.8 Table 8: Surrogate Recovery Limits
18.9 Table 9: Allowable CCV Failures
18.10 Table 10: Sample Dilutions

18.11 Table 11: 8270D/MCP/RCP/SIM QC Requirements and Acceptance Criterion Summary

19.0 Revision History

- Revision 4, Dated 18 December 2017
  - Updated QA Manager, signatures added
  - Added SIM, MCP and RCP to the scope and application section. Removed tissue from matrices performed.
  - Added definitions of MCP, RCP and SIM to section 3.0
  - Updated OSHA's list of known carcinogens in section 5.1
  - Added SIM reagents to section 7.2
  - Added preparation of SIM extraction reagents to section 7.3
  - Added preparation information for List2 and 3 calibration levels in charts 6 through 11.
  - Added SIM calibration preparation information in charts 12, 13 and 15.
  - Added SIM, MCP and RCP QC requirements throughout section 9.0.
  - Included SIM instrument parameters in section 10.2.
  - Section 10.3 – added how the DFTPP spectrum is evaluated.
  - Section 10.4 – added initial calibration, initial calibration verification and continuing calibration verification requirements for SIM, MCP and RCP.
  - Section 11.2 – added SIM dilution information.
  - Section 11.3.1 – included Signal to Noise requirement for SIM.
  - Section 11.3.2 – added Methylene Chloride as a compound to be removed as a reportable TIC.
  - Added reagent review checklists to section 12.4.
  - Section 16 – added references to 8000D, MADEP CAM and Connecticut DEP RCP.
  - Updated Tables 1,4,5 and 8 to include SIM compound information.
  - Updated limits in Table 8 to match current LIMS limits.
  - Added Table 11 – Acceptance criterion summary for 8270D, SIM, MCP and RCP.

- Revision 3, Dated 23 September 2016
  - Updated Department Manager, Laboratory Director, QA Manager, signatures added.
  - Added Organic Ops Manager, signature added
  - Added 8270D_LL method techniques and requirements to multiple sections.
  - Reformatted multiple sections, primarily section titles and numbers.
  - Renumbered charts, equations and tables.
  - Added SOP and Corporate Policy numbers when applicable.
  - Replaced all references to MSDS with SDS.
  - Updated Reagents to include Corporate approved Restek Standards.
  - Included preparation tables of working calibration standards in Charts 3, 4 and 5.
  - Added Internal Standard preparation table for LVI/LL in Chart 6.
  - Section 9.1.2: Added preparation, calculation information for LCS/MS/MSD samples. Added criteria to Technical Acceptance and Corrective actions sections.
  - Section 9.1.2: Removed Marginal Exceedance

  - Section 9.2.1/9.2.2: Added Technical Acceptance Criteria and Corrective Actions for Surrogates
  - Added section 9.3: Calculation, Technical Acceptance Criteria and Corrective Actions for Internal Standards
  - Added preparation SOP numbers to section 10.1
  - Section 10.2: Updated parameters to match current LVI instrument parameters. Added parameters for 1L acquisition parameters.
  - Updated Initial Calibration and Continuing Calibration Verification Technical Acceptance Criteria to follow Corporate Quality Policy Memorandum CA-Q-QM-009.
  - Added Technical Acceptance Criteria and Corrective Actions for Initial Calibration Verification.
  - Section 11.4.1: Added equations for calculating concentrations based on an average and linear calibration model.
  - Removed references to GPC.
  - Replaced contract required quantitation limits (CRQL) with reporting limits (RL).
  - Updated TIC qualification procedures in accordance with Corporate Quality Policy Memorandum CA-Q-QM-001.
  - Added Targeted TIC procedures.
  - Section 11.2: Added dilution calculation equation.
  - Added section 12 to include Instrument, Reagent and Sample Logbooks.
  - Section 13: Replaced Method Performance with Data Review.
  - Updated Table 1 to include all routinely calibrated compounds and RLs.
  - Added Table 2 – LCS/MS/MSD Spike Analytes
  - Table 3: Updated mass 441 to be compared to mass 442; previously 443.
  - Updated Table 4 to include all routinely calibrated compounds and current IS assignments.
  - Updated Table 5 to include all routinely calibrated compounds and current quantitation/qualifying ions.
  - Table 6: Updated the poor performer list of analytes. Added alternative %D criteria for ICV and CCV recoveries.
  - Reformatted Table 7.
  - Added Table 8: Surrogate Recoveries
  - Added Table 9: Allowable CCV Failures
  - Added Table 10: Sample Dilutions
  - Removed Attachment A: SOP Procedure Summary

- Revision 2, Dated 11 March 2015
  - Added LVI into sampling and preparation sections
  - Added 8270 % drift requirements
  - Updated instrument operation parameters
  - Changed Department Manager, signature added
  - Changed Lab Director, signature added
- Revision 1, Dated 11 March 2011
  - QA Manager updated, signature added

18.1 TABLE 1
Semivolatiles Target Compound List and Reporting Limits

CAS #	Analytes	Water Limits (1L/LVI) ug/L	Soil Limits (3550C/3546) ug/kg	Water Limits (LL) ug/L	Water Limits (LL_PAH) ug/L	Soil Limits (LL_PAH) ug/kg	SIM Limits ug/L
92-52-4	1,1'-Biphenyl	5	170	5			
95-94-3	1,2,4,5-Tetrachlorobenzene	5	170	5			
120-82-1	1,2,4-Trichlorobenzene	10	330	0.5			
95-50-1	1,2-Dichlorobenzene	10	330	0.5			
122-66-7	1,2-Diphenylhydrazine	10	330	5			
99-35-4	1,3,5-Trinitrobenzene	10	330				
541-73-1	1,3-Dichlorobenzene	10	330				
99-65-0	1,3-Dinitrobenzene	20	330				
106-46-7	1,4-Dichlorobenzene	10	330	0.5			
81-64-1	1,4-Dihydroxyanthraquinone	40	660				
100-25-4	1,4-Dinitrobenzene	10	330				
123-91-1	1,4-Dioxane	10	200				0.2
130-15-4	1,4-Naphthoquinone	10	330				
90-13-1	1-Chloronaphthalene	10	330	0.5			
129-43-1	1-Hydroxyanthraquinone	20	660				
90-12-0	1-Methylnaphthalene	5	330	5			
134-32-7	1-Naphthylamine	10	330				
108-60-1	2,2'-oxybis[1-chloropropane]	5	170	5			
58-90-2	2,3,4,6-Tetrachlorophenol	5	170	5			
935-95-5	2,3,5,6-Tetrachlorophenol	20	660				
95-95-4	2,4,5-Trichlorophenol	5	170	5			
88-06-2	2,4,6-Trichlorophenol	5	170	5			
120-83-2	2,4-Dichlorophenol	5	170	0.5			
105-67-9	2,4-Dimethylphenol	5	170	1			
51-28-5	2,4-Dinitrophenol	10	1660	5			
121-14-2	2,4-Dinitrotoluene	5	170	5			
87-65-0	2,6-Dichlorophenol	10	330				
606-20-2	2,6-Dinitrotoluene	5	170	5			
53-96-3	2-Acetylaminofluorene	10	330	0.5			
95-51-2	2-Chloroaniline	10	330				
91-58-7	2-Chloronaphthalene	5	170	0.5			
95-57-8	2-Chlorophenol	5	170	5			
91-57-6	2-Methylnaphthalene	5	170	0.5	0.5	17	
95-48-7	2-Methylphenol	5	170	1			
91-59-8	2-Naphthylamine	10	330				
88-74-4	2-Nitroaniline	10	330	5			
88-75-5	2-Nitrophenol	5	170	5			

109-06-8	2-Picoline	80	330				
95-53-4	2-Toluidine	10	330				
15831-10-4	3 & 4 Methylphenol	10	330	1			
91-94-1	3,3'-Dichlorobenzidine	5	330	5			
119-93-7	3,3'-Dimethylbenzidine	40	660				
56-49-5	3-Methylcholanthrene	10	330				
99-09-2	3-Nitroaniline	10	330				
101-14-4	4,4'-Methylene bis(2-chloroaniline)	10	330				
534-52-1	4,6-Dinitro-2-methylphenol	10	330	5			
92-67-1	4-Aminobiphenyl	10	330				
101-55-3	4-Bromophenyl phenyl ether	5	170	5			
59-50-7	4-Chloro-3-methylphenol	5	170	5			
106-47-8	4-Chloroaniline	5	170	5			
7005-72-3	4-Chlorophenyl phenyl ether	5	170	5			
106-49-0	4-Methylbenzenamine	10	330				
106-44-5	4-Methylphenol	10	330	1			
100-01-6	4-Nitroaniline	10	330	5			
100-02-7	4-Nitrophenol	10	330	5			
56-57-5	4-Nitroquinoline-1-oxide	10	660				
1705-85-7	6-Methylchrysene	10	330	0.5			
57-97-6	7,12-Dimethylbenz(a)anthracene	10	330				
301-02-0	9-Octadecenamide	100	3300				
83-32-9	Acenaphthene	5	170	0.5	0.5	17	
208-96-8	Acenaphthylene	5	170	0.3	0.5	17	
98-86-2	Acetophenone	5	170	5			
79-06-1	Acrylamide	5	330				
15972-60-8	Alachlor	10	330	1.5			
122-09-8	alpha,alpha-Dimethyl phenethylamine	100	330				
98-55-5	Alpha-Terpineol	10	330				
62-53-3	Aniline	10	330	0.5			
120-12-7	Anthracene	5	170	0.5	0.5	17	
84-65-1	Anthraquinone	10	330				
140-57-8	Aramite, Total	20	330				
1912-24-9	Atrazine	5	170	2			
103-33-3	Azobenzene	10	330	0.5			
100-52-7	Benzaldehyde	5	170	5			
92-87-5	Benzidine	80	5000	5			
56-55-3	Benzo[a]anthracene	5	170	0.3	0.5	17	
50-32-8	Benzo[a]pyrene	5	170	0.18	0.5	17	
205-99-2	Benzo[b]fluoranthene	5	170	0.3	0.5	17	
191-24-2	Benzo[g,h,i]perylene	5	170	0.5	0.5	17	

207-08-9	Benzo[k]fluoranthene	5	170	0.3	0.5	17	
65-85-0	Benzoic acid	150	4800	5			
100-51-6	Benzyl alcohol	20	330	5			
111-91-1	Bis(2-chloroethoxy)methane	5	170	5			
111-44-4	Bis(2-chloroethyl)ether	5	170	5			
117-81-7	Bis(2-ethylhexyl) phthalate	5	170	5			
85-68-7	Butyl benzyl phthalate	5	170	3			
105-60-2	Caprolactam	5	170	5			
86-74-8	Carbazole	5	170	5			
510-15-6	Chlorobenzilate	20	330	0.5			
218-01-9	Chrysene	5	170	0.5			
2303-16-4	Diallate	10	330				
53-70-3	Dibenz(a,h)anthracene	5	170	0.5	0.5	17	
226-36-8	Dibenz[a,h]acridine	10	330	0.5			
192-65-4	Dibenzo[a,e]pyrene	10	330				
132-64-9	Dibenzofuran	10	170	5	0.5	17	
101-83-7	Dicyclohexylamine	10	3000				
84-66-2	Diethyl phthalate	5	170	0.5			
60-51-5	Dimethoate	10	330				
131-11-3	Dimethyl phthalate	5	170	0.5			
84-74-2	Di-n-butyl phthalate	5	170	2			
117-84-0	Di-n-octyl phthalate	5	170	5			
88-85-7	Dinoseb	10	330				
122-39-4	Diphenylamine	10	330	5			
298-04-4	Disulfoton	10	330				
62-50-0	Ethyl methanesulfonate	10	330				
56-38-2	Ethyl Parathion	10	330	1			
52-85-7	Famphur	40	660				
206-44-0	Fluoranthene	5	170	0.5	0.5	17	
86-73-7	Fluorene	5	170	0.5	0.5	17	
118-74-1	Hexachlorobenzene	5	170	0.5			
87-68-3	Hexachlorobutadiene	5	170	1.0			
77-47-4	Hexachlorocyclopentadiene	5	170	1			
67-72-1	Hexachloroethane	5	170	5			
70-30-4	Hexachlorophene	310	5000				
1888-71-7	Hexachloropropene	10	330				
544-76-3	Hexadecane	10	330	0.5			
95-13-6	Indene	60	3000	5			
193-39-5	Indeno[1,2,3-cd]pyrene	5	170	0.5	0.5	17	
465-73-6	Isodrin	10	330				
78-59-1	Isophorone	5	170				

120-58-1	Isosafrole	10	330	0.5			
143-50-0	Kepone	50	660				
91-80-5	Methapyrilene	50	1500				
66-27-3	Methyl methanesulfonate	10	330				
298-00-0	Methyl parathion	10	330				
91-20-3	Naphthalene	5	170	1	0.5	17	
124-18-5	n-Decane	5	330				
98-95-3	Nitrobenzene	5	170	0.5			
99-55-8	N-Nitro-o-toluidine	10	330				
55-18-5	N-Nitrosodiethylamine	10	330				
62-75-9	N-Nitrosodimethylamine	10	330	5			
924-16-3	N-Nitrosodi-n-butylamine	10	330				
621-64-7	N-Nitrosodi-n-propylamine	5	170	5			
86-30-6	N-Nitrosodiphenylamine	5	170	5			
10595-95-6	N-Nitrosomethylethylamine	10	330				
59-89-2	N-Nitrosomorpholine	10	330				
100-75-4	N-Nitrosopiperidine	10	330				
930-55-2	N-Nitrosopyrrolidine	10	330				
593-45-3	n-Octadecane	5	330				
126-68-1	o,o',o''-Triethylphosphorothioate	10	330				
60-11-7	p-Dimethylamino azobenzene	10	330				
608-93-5	Pentachlorobenzene	10	330				
76-01-7	Pentachloroethane	10	330				
82-68-8	Pentachloronitrobenzene	10	330				
87-86-5	Pentachlorophenol	10	330	1			
62-44-2	Phenacetin	10	330				
85-01-8	Phenanthrene	5	170	0.2	0.5	17	
108-95-2	Phenol	5	170	1			
298-02-2	Phorate	10	330				
85-44-9	Phthalic anhydride	500	10000				
106-50-3	p-Phenylene diamine	800	800				
23950-58-5	Pronamide	10	330				
129-00-0	Pyrene	5	170	0.5	0.5	17	
110-86-1	Pyridine	25	330				
91-22-5	Quinoline	10	330				
94-59-7	Safrole, Total	10	330				
122-34-9	Simazine	10	330	0.5			
3689-24-5	Sulfotepp	10	330				
78-00-2	Tetraethyl lead	10	1000				
297-97-2	Thionazin	10	330				
126-73-8	Tributyl phosphate	10	330				

Note, the most current reporting limits are maintained in the laboratory's LIMS system. These may be updated in LIMS as MDL studies are performed.

18.2 TABLE 2
LCS/MS/MSD Spike Analytes

1,1'-Biphenyl	4-Bromophenyl phenyl ether	Chrysene
1,2,4,5-Tetrachlorobenzene	4-Chloro-3-methylphenol	Dibenz(a,h)anthracene
1,2,4-Trichlorobenzene	4-Chloroaniline	Dibenzofuran
1,2-Dichlorobenzene	4-Chlorophenyl phenyl ether	Diethyl phthalate
1,2-Diphenylhydrazine	4-Methylphenol	Dimethyl phthalate
1,3-Dichlorobenzene	4-Nitroaniline	Di-n-butyl phthalate
1,4-Dichlorobenzene	4-Nitrophenol	Di-n-octyl phthalate
1,4-Dioxane	Acenaphthene	Diphenylamine
1-Methylnaphthalene	Acenaphthylene	Fluoranthene
2,2'-oxybis[1-chloropropane]	Acetophenone	Fluorene
2,3,4,6-Tetrachlorophenol	Aniline	Hexachlorobenzene
2,3-Dimethylphenol	Anthracene	Hexachlorobutadiene
2,4,5-Trichlorophenol	Atrazine	Hexachlorocyclopentadiene
2,4,6-Trichlorophenol	Azobenzene	Hexachloroethane
2,4-Dichlorophenol	Benzaldehyde	Hexadecane
2,4-Dimethylphenol	Benzidine	Indene
2,4-Dinitrophenol	Benzo[a]anthracene	Indeno[1,2,3-cd]pyrene
2,4-Dinitrotoluene	Benzo[a]pyrene	Isophorone
2,6-Dinitrotoluene	Benzo[b]fluoranthene	Naphthalene
2-Chloronaphthalene	Benzo[g,h,i]perylene	Nitrobenzene
2-Chlorophenol	Benzo[k]fluoranthene	N-Nitrosodimethylamine
2-Methylnaphthalene	Benzoic acid	N-Nitrosodi-n-propylamine
2-Methylphenol	Benzyl alcohol	N-Nitrosodiphenylamine
2-Nitroaniline	Bis(2-chloroethoxy)methane	Pentachlorophenol
2-Nitrophenol	Bis(2-chloroethyl)ether	Phenanthrene
3,3'-Dichlorobenzidine	Bis(2-ethylhexyl) phthalate	Phenol
3-Methylphenol	Butyl benzyl phthalate	Pyrene
3-Nitroaniline	Caprolactam	Pyridine
4,6-Dinitro-2-methylphenol	Carbazole	

18.3 TABLE 3
DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	10.0 – 80.0 percent of mass 198
68	Less than 2.0 percent of mass 69
69	0-100 percent of mass 198

70	Less than 2.0 percent of mass 69
127	10.0 – 80.0 percent of mass 198
197	Less than 2.0 percent of mass 198
198	Base peak, or greater than 50 percent of mass 442
199	5.0-9.0 percent of mass 198
275	10.0-60.0 percent of mass 198
365	Greater than 1.0 percent of mass 198
441	Present but less than 24 percent of mass 442
442	Base Peak, or greater than50 percent of mass 198
443	15.0 – 24.0 percent of mass 442

18.4 TABLE 4
Semivolatile Internal Standards with Corresponding Target Compounds and Surrogates Assigned for Quantitation

1,4-Dichlorobenzene-d4	**Naphthalene-d8**	**Acenaphthene-d10**	**Phenanthrene-d10**	**Chrysene-d12**	**Perylene-d12**
1,2,3,4-Tetrachlorobenzene	1,2,4-Trichlorobenzene	1,1'-Biphenyl	1,2-Diphenylhydrazine	2-Methylanthracene	3-Methylcholanthrene
1,2-Dichlorobenzene	1,3-Dinitrobenzene	1,2,4,5-Tetrachlorobenzene	1,4-Dihydroxyanthraquinone	3,3'-Dichlorobenzidine	Benzo[a]pyrene
1,3,5-Trichlorobenzene	1,4-Dinitrobenzene	1,3,5-Trinitrobenzene	1-Hydroxyanthraquinone	4,4'-Methylene bis(2-chloroaniline)	Benzo[b]fluoranthene
1,3-Dichlorobenzene	1-Methylnaphthalene	1,4-Naphthoquinone	2,3,5,6-Tetrachlorophenol	6-Methylchrysene	Benzo[g,h,i]perylene
1,4-Dichlorobenzene	2,4-Dichlorophenol	1-Chloronapthalene	2,4,6-Tribromophenol (surr)	7,12-Dimethylbenz(a)anthracene	Benzo[k]fluoranthene
1,4-Dioxane	2,4-Dimethylphenol	1-Naphthylamine	2-Acetylaminofluorene	Benzidine	Dibenz[a,h]acridine
2,2'-oxybis-(1-Chloropropane)	2,6-Dichlorophenol	2,3,4,6-Tetrachlorophenol	3.3'-Dimethylbenzidine	Benzo[a]anthracene	Dibenzo(a,h)anthracene
2-chloroaniline	2-Methylnaphthalene	2,4,5-Trichlorophenol	4,6-Dinitro-2-methylphenol	bis(2-ethylhexyl) phthalate	Dibenzo[a,e]pyrene
2-Chlorophenol	2-Nitrophenol	2,4,6-Trichlorophenol	4-Aminobiphenyl	Butyl benzyl phthalate	Indeno[1,2,3-cd]pyrene
2-Fluorophenol(surr)	4-Chloro-3-methylphenol	2,4-Dinitrophenol	4-Bromophenyl phenyl ether	Chrysene	
2-Methylphenol	4-Chloroaniline	2,4-Dinitrotoluene	4-Nitroquinoline-1-oxide	Di-n-octyl phthalate	
2-Picoline	alpha,alpha-Dimethyl phenethylamine	2,6-Dinitrotoluene	9-Octadecenamide	Hexachlorophene	
2-Toluidine	Alpha-Terpineol	2-Chloroaphthalene	Alachlor	p-Dimethylamino azobenzene	
4-Methylbenzenamine	Benzoic acid	2-Fluorobiphenyl (surr)	Anthracene	Pyrene	

4-Methylphenol	bis(2-Chloroethoxy)methane	2-Naphthylamine	Anthraquinone	p-Terphenyl-d14 (surr)	
Acetophenone	Caprolactam	2-Nitroaniline	Aramite, Total		
Acrylamide	Hexachlorobutadiene	3-Nitroaniline	Atrazine		
Aniline	Hexachloropropene	4-Chlorophenyl phenyl ether	Azobenzene		
Benzaldehyde	Isophorone	4-Nitroaniline	Carbazole		
Benzyl Alcohol	Naphthalene	4-Nitrophenol	Chlorobenzilate		
bis(2-Chloroethyl)ether	Nitrobenzene	Acenaphthene	Di-n-butyl phthalate		
Ethyl methanesulfonate	Nitrobenzene-d5 (surr)	Acenaphthylene	Dinoseb		
Hexachloroethane	N-Nitrosodi-n-butylamine	Diallate	Diphenylamine		
Indene	N-Nitrosopiperidine	Dibenzofuran	Disulfoton		
Methyl methanesulfonate	Phthalic Anhydride	Dicyclohexylamine	Ethyl parathion		
n-Decane	Quinoline	Diethyl phthalate	Famphur		
N-nitrosodiethylamine	Safrole, Total	Dimethoate	Fluoranthene		
N-nitrosodimethylamine	TetraEthyl Lead	Dimethyl phthalate	Hexachlorobenzene		
N-Nitrosodi-n-propylamine		Fluorene	Isodrin		
N-Nitrosomethylethylamine		Hexachlorocyclopentadiene	Kepone		
N-Nitrosomorpholine		Hexadecane	Methyapyrilene		
N-nitrosopyrrolidine		Isosafrole	Methyl parathion		
o,o',o"-Triethylphosphorothioate		N-Nitro-o-toluidine	N-nitrosodiphenylamine		
Pentachloroethane		Pentachlorobenzene	n-Octadecane		
Phenol		Phorate	Pentachloronitrobenzene		
Phenol-d5 (surr)		Simazine	Pentachlorophenol		
p-Phenylene diamine		Sulfotepp	Phenacetin		
Pyridine		Thionazin	Phenanthrene		
1,4-Dioxane-d8 (analog)		Tributyl phosphate	Pronamide		

Note: Internal Standard assignments are by suggestion only. Assignments may vary slightly between instrument methods.

18.5 Table 5
Characteristic Ions for Semivolatile
Target Compounds, Surrogates and Internal Standards

Parameters	Primary Quantitation Ion	Secondary Ion(s)	Parameters	Primary Quantitation Ion	Secondary Ion(s)	Parameters	Primary Quantitation Ion	Secondary Ion(s)
1,1'-Biphenyl	154	153, 152	4-Methylphenol	108	107	Famphur	218	125, 93
1,2,4,5-Tetrachlorobenzene	216	214, 179	4-Nitroaniline	138	92, 108	Fluoranthene	202	101, 203
1,2,4-Trichlorobenzene	180	182, 145	4-Nitrophenol	109	139, 64	Fluorene	166	165, 167
1,2-Dichlorobenzene	146	111, 75	4-Nitroquinoline-1-oxide	190	160, 89	Hexachlorobenzene	284	142, 249
1,2-Diphenylhydrazine	77	182, 51	6-Methylchrysene	242	239, 119	Hexachlorobutadiene	225	223, 227
1,3,5-Trichlorobenzene	180	182, 184	7,12-Dimethylbenz(a)anthracene	256	241, 239	Hexachlorocyclopentadiene	237	235, 272
1,3,5-Trinitrobenzene	213	75, 74	9-Otadecenamide	59	72, 55	Hexachloroethane	117	201, 199
1,3-Dichlorobenzene	146	111, 75	a.a.-Dimethyl phenethylamine	58	91, 134	Hexachlorophene	196	198, 209
1,3-Dinitrobenzene	168	50, 76	Acenaphthene	153	152, 154	Hexachloropropene	213	215, 117
1,4-Dichlorobenzene	146	111, 75	Acenaphthylene	152	151, 153	Hexadecane	57	43, 71
1,4-Dihydroxyanthraquinone	240	239, 128	Acetophenone	105	77, 51	Indene	115	116, 89
1,4-Dinitrobenzene	168	75, 50	Acrylamide	71	55, 44	Indeno(1,2,3-cd)pyrene	276	138, 277
1,4-Dioxane	88	58	Alachlor	160	188, 146	Isodrin	193	195, 66
1,4-Naphthoquinone	158	102, 130	Aniline	93	66, 39	Isophorone	82	95, 138
1-Chloronaphthalene	162	127, 164	Anthracene	178	179, 176	Isosafrole	162	104, 131
1-Hydroxyanthraquinone	224	139, 168	Anthraquinone	180	208, 152	Kepone	272	237, 357
1-Methylnaphthalene	142	141, 115	Aramite, Total	185	63, 135	Methapyrilene	58	97, 191
1-Naphthylamine	143	115, 116	A-Terpineol	59	93, 121	Methyl parathion	109	125, 263
2,2'-oxybis[1-chloropropane]	45	77, 79	Atrazine	200	215, 202	Naphthalene	128	129, 127
2,3,4,6-Tetrachlorophenol	232	230, 131	Azobenzene	77	182, 51	n-Decane	57	43, 41

2,3,5,6-Tetrachlorophenol	232	230, 234	Benzaldehyde	77	105, 106	Nitrobenzene	77	123, 65
2,4,5-Trichlorophenol	196	198, 200	Benzidine	184	92, 156	N-Nitro-o-toluidine	152	106, 77
2,4,6-Trichlorophenol	196	198, 200	Benzo[a]anthracene	228	229, 226	N-Nitrosodiethylamine	102	42, 44
2,4-Dichlorophenol	162	164, 98	Benzo[a]pyrene	252	253, 125	N-Nitrosodimethylamine	42	74, 43
2,4-Dimethylphenol	107	121, 122	Benzo[b]fluoranthene	252	253, 125	N-Nitrosodi-n-butylamine	84	57, 116
2,4-Dinitrophenol	184	63, 154	Benzo[g,h,i]perylene	276	138,277	N-Nitrosodi-n-propylamine	70	42, 130
2,4-Dinitrotoluene	165	63, 182	Benzo[k]fluoranthene	252	253, 125	N-Nitrosodiphenylamine	169	168, 167
2,6-Dichlorophenol	162	164, 166	Benzoic Acid	105	122, 77	N-Nitrosomethylethylamine	88	42, 43
2,6-Dinitrotoluene	165	89, 121	Benzyl Alcohol	108	79, 77	N-Nitrosomorpholine	56	86, 116
2-Acetylaminofluorene	181	180, 223	bis(2-Chloroethoxy) methane	93	95, 123	N-Nitrosopiperidine	114	55, 42
2-Chloroaniline	127	129, 65	bis(2-Chloroethyl)ether	93	63, 95	N-Nitrosopyrrolidine	100	41, 42
2-Chloronaphthalene	162	164, 127	bis(2-Ethylhexyl) phthalate	149	167, 279	n-Octadecane	57	43, 71
2-Chlorophenol	128	64, 130	Butyl benzyl phthalate	149	91, 206	o,o'o"-Triethylphosphorothioate	198	121, 97
2-Methylanthracene	192	191, 193	Caprolactam	113	85, 84	p-Dimethylamino azobenzene	120	225, 77
2-Methylnaphthalene	142	141, 115	Carbazole	167	139, 166	Pentachlorobenzene	250	252, 254
2-Methylphenol	108	107, 77	Chlorobenzilate	251	139, 111	Pentachloroethane	167	165, 169
2-Naphthylamine	143	115, 116	Chrysene	228	226, 229	Pentachloronitrobenzene	237	214, 295
2-Nitroaniline	65	92, 138	Diallate	43	234, 236	Pentachlorophenol	266	264, 268
2-Nitrophenol	139	65, 109	Dibenz[a,h]acridine	279	139, 125	Phenacetin	108	179, 137
2-Picoline	93	66, 39	Dibenzo(a,h)anthracene	278	139, 279	Phenanthrene	178	179, 176
2-Toluidine	106	107, 77	Dibenzo[a,e]pyrene	302	151, 150	Phenol	94	65, 66

3,3'-Dichlorobenzidine	252	254, 154	Dibenzofuran	168	139, 169	Phorate	75	121, 97
3,3'-Dimethylbenzidine	212	106, 196	Dicyclohexylamine	138	56, 55	Phthalic Anhydride	104	76, 148
3-Methylcholanthrene	268	252, 126	Diethyl phthalate	149	177, 150	p-Phenylene diamine	108	107, 80
3-Nitroaniline	138	92, 65	Dimethoate	87	125, 93	Pronamide	173	175, 177
4,4'-Methylene bis(2-chloroaniline	231	266, 268	Dimethyl phthalate	163	194, 164	Pyrene	202	101, 100
4,6-Dinitro-2-methylphenol	198	121, 105	Di-n-butylphthalate	149	150, 104	Pyridine	52	79, 51
4-Aminobiphenyl	169	168, 170	Di-n-octyl phthalate	149	150, 167	Quinoline	129	128, 102
4-Bromophenyl-phenylether	248	250, 141	Dinoseb	211	163, 147	Safrole, Total	162	131, 104
4-Chloro-3-methylphenol	107	144, 142	Diphenylamine	169	168, 167	Simazine	201	186, 173
4-Chloroaniline	127	129, 65	Disulfoton	88	97, 61	Sulfotepp	322	202, 97
4-Chlorophenyl phenyl ether	204	206, 141	Ethyl methanesulfonate	79	109, 97	TetraEthyl Lead	237	295, 208
4-Methylbenzenamine	106	107, 77	Ethyl parathion	97	109, 291	Thionazin	97	107, 143
SURROGATES			**INTERNAL STANDARDS**			Tributyl phosphate	99	155, 211
Phenol-d5	99	42, 71	1,4-Dichlorobenzene-d4	152	115, 150	1,4-Dioxane-d8 (analog)	96	64
2-Fluorophenol	112	64, 92	Naphthalene-d8	136	68, 108			
2,4,6-Tribormophenol	330	332, 141	Acenaphthene-d10	164	162, 160			
Nitrobenzene-d5	82	128, 54	Phenanthrene-d10	188	94, 80			
2-Fluorobiphenyl	172	171, 170	Chrysene-d12	240	120, 236			
Terphenyl-d14	244	122, 212	Perylene-d12	264	260, 265			

Note: Quantitation and/or secondary qualifying ions are by suggestion only. Assignments may vary slightly between instrument methods.

18.6 Table 6
Poor Performing Compounds

Poor Performers	ICV %D Limit	CCV %D Limit	LCS %R Limit
3,3'-Dichlorobenzidine	± 50%	± 50%	10
9-Octadecenamide	± 50%	± 50%	10
a,a-Dimethyl phenethylamine	± 50%	± 50%	10
Acrylamide	± 50%	± 50%	10
Benzaldehyde	± 50%	± 50%	10
Benzidine	± 50%	± 50%	5
Benzoic Acid	± 50%	± 50%	10
Caprolactam	± 50%	± 50%	10
Isosafrole	± 50%	± 50%	10
Kepone	± 50%	± 50%	10
Methapyrilene	± 50%	± 50%	10
n-Nitrosodimethylamine	± 50%	± 50%	10
p-Phenylene diamine	± 50%	± 50%	10
Phthalic Anhydride	± 50%	± 50%	10
Pyridine	± 50%	± 50%	10
Safrole, Total	± 50%	± 50%	10

The laboratory's GC/MS semi-volatiles group identified this list of compounds based on current and historical performance. The recovery performance was reviewed against full spike recovery data as well as calibration data to validate each compound as a "poor performer".

18.7 Table 7
Minimum Response Factors for common target compounds

Semivolatile Compounds	Minimum Response Factor (RF)	Semivolatile Compounds	Minimum Response Factor (RF)
1,2,4-Trichlorobenzene	0.010	bis(2-Chloroethoxy)methane	0.300
1,2-Dichlorobenzene	0.010	bis(2-Chloroethyl)ether	0.700
1,3-Dichlorobenzene	0.010	Bis(2-chloroisopropyl)ether	0.010
1,4-Dichlorobenzene	0.010	bis(2-Ethylhexyl)phthalate	0.010
2,4,5-Trichlorophenol	0.200	Butylbenzylphthalate	0.010
2,4,6-Trichlorophenol	0.200	Chrysene	0.700
2,4-Dichlorophenol	0.200	Dibenzo(a,h)anthracene	0.400
2,4-Dimethylphenol	0.200	Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200	Diethyl phthalate	0.010
2,6-Dinitrotoluene	0.200	Dimethyl phthalate	0.010
2-Chloronaphthalene	0.800	Di-n-butyl phthalate	0.010
2-Chlorophenol	0.800	Di-n-octyl phthalate	0.010

2-Methylnaphthalene	0.400	Fluoranthene	0.600
2-Methylphenol	0.700	Fluorene	0.900
2-Nitrophenol	0.100	Hexachlorobenzene	0.100
4-Bromophenyl-phenylether	0.100	Hexachlorobutadiene	0.010
4-Chloro-3-methylphenol	0.200	Hexachlorocyclopentadiene	0.050
4-Chloroaniline	0.010	Hexachloroethane	0.300
4-Chlorophenyl-phenylether	0.400	Indeno(1,2,3-cd)pyrene	0.500
4-Methylphenol	0.600	Isophorone	0.400
Acenaphthene	0.900	Naphthalene	0.700
Acenaphthylene	0.900	Nitrobenzene	0.200
Anthracene	0.700	N-Nitroso-di-n-propylamine	0.500
Benzo(a)anthracene	0.800	N-Nitrosodiphenylamine	0.010
Benzo(a)pyrene	0.700	Pentachlorophenol	0.050
Benzo(b)fluoranthene	0.700	Phenanthrene	0.700
Benzo(g,h,i)perylene	0.500	Phenol	0.800
Benzo(k)fluoranthene	0.700	Pyrene	0.600
Benzyl Alcohol	0.010		

18.8 TABLE 8
Surrogate Recovery Limits[1]

Surrogate	% Recovery Limit (1L, LVI)	% Recovery Limit (3350C/3546)	% Recovery Limit (LL)	% Recovery Limit (LL_PAH)	% Recovery Limit (SIM)
2,4,6-Tribromophenol	41-120	54-120	24-146	---	---
2-Fluorobiphenyl	48-120	60-120	37-120	37-120	---
2-Fluorophenol	35-120	52-120	10-120	---	---
Nitrobenzene-d5	46-120	53-120	26-120	34-132	---
Phenol-d5	22-120	54-120	11-120	---	---
p-Terphenyl-d14	59-136	65-121	64-127	58-147	---
1,4-Dioxane-d8 (analog)	---	---	---	---	15-110

[1] Limits are updated and entered annually into LIMS

18.9 TABLE 9
Allowable CCV Failures

Total CCVs Analyzed in a Batch	Total # of Analytes	# Allowed out between CCVs (20%)
List 1	94	18
List 1, List 2	148	29
List 1, List 3	109	21
List 1, List 2, List 3	163	32

Note: this is based on the laboratory's main list of calibrated analytes.
Additional analytes/CCVs may be analyzed and the total number may be adjusted accordingly.

18.10 TABLE 10
Sample Dilutions

Dilution Factor	uL of Sample Extract	uL of $MeCl_2$	Total Volume (uL)	uL of IS
2	500	500	1000	20
4	250	750	1000	20
5	200	800	1000	20
10	100	900	1000	20
20	50	950	1000	20
25	40	960	1000	20
40	25	975	1000	20
50	20	980	1000	20
100	10	990	1000	20

Dilutions greater than 100X must be performed by serial dilution.

18.11 TABLE 11
8270D/MCP/RCP/SIM QC Requirements and Acceptance Criteria Summary

8270D			
QA Parameter	**Technical Acceptance**	**Allowable Failures**	**Narration Required**
DFTPP	1. Criteria listed in Table 3. 2. Tailing for Benzidine and PCP ≤2. 3. Breakdown of 4,4'-DDT ≤20 %	None	NA
ICAL	1. 20% RSD or r^2 ≥0.990 2. Minimum RF for all levels must meet criteria in Table 7. 3. ≤30% Readback on low point.	10% allowed out with passing RL check.	Detection only
ICV	1. 70-130%. 2. Meets min RF criteria in Table 7.	Recovery high - sample analysis ND.	Detection only
CCV	1. 20%D. 2. Meets min RF criteria in Table 7.	20% allowed out with passing RL check.	Yes
MB	Less than RL.	1. >RL with ND sample. 2. >RL with detection in sample >10X the MB.	Yes
LCS/LCSD	Historical limits for %R and %RPD.	1. Poor performers ≥10% recovery, ≥5% for benzidine. 2. High recovery, sample analysis ND.	Yes
MS/MSD	Historical limits for %R and %RPD.	Recoveries within limits in the LCS.	Recoveries ≤10% or ≥150% and/or RPD ≥50%.
Surrogates	Historical limits.	1. 1 acid and/or 1 B/N out, provided recovery is ≥10%. 2. Recovery high, samples ND. 3. Recovery low for 1 class, target analyte list requires compounds from other class only. 4. Obvious matrix interference. 5. Sample diluted 20X or greater.	Yes
Internal Standards	1. 50-200% of CCV to mid-level ICAL standard. 2. ≤30 sec shift of CCV to mid-level standard. 3. 50-200% recovery of samples to daily CCV. 4. ≤ 30 sec shift of samples to daily CCV.	None	NA

MCP

QA Parameter	Technical Acceptance	Allowable Failures	Narration Required
DFTPP	1. Criteria listed in Table 3. 2. Tailing for Benzidine and PCP ≤2. 3. Breakdown of 4,4'-DDT ≤20 %	None	NA
ICAL	1. 20% RSD or r^2 ≥0.990 2. Minimum RF must meet criteria in Table 7. 3. 0.05 min RF for other compounds on the low pt and average RF only. 4. ≤30% Readback on low point.	10% allowed out as long as %RSD is ≤40% or r^2 ≥0.980	Yes - RSD, r^2 and RF failures
ICV	1. 70-130% except "difficult" analytes**, which are 60-140%.	10% allowed out.	Yes
CCV	1. 20%D. 2. Meets min RF criteria in Table 7. 3. 0.05 min RF for remaining compounds.	20% allowed out, provided recovery is ≤40%.	Yes
MB	Less than RL.	1. >RL with ND sample. 2. >RL with detection in sample >10X the MB.	Yes
LCS/LCSD	1. 40-140% for base-neutral, 30-130% for acids, except "difficult" analytes**, which are 15-140%. 2. RPD ≤20% for waters, ≤30% for soils.	1. "Difficult" analytes 15-140%. 2. ≤10% allowed to fail provided recovery is ≥10%.	Yes
MS/MSD	1.40-140% for base-neutral, 30-130% for acids. 2. RPD ≤20% for waters, ≤30% for soils.	Recoveries within limits in the LCS.	Recoveries ≤10% or ≥150% and/or RPD ≥50%.
Surrogates	30-130% for soils, 30-130% for base-neutrals in water, 15-110% for acids in water.	1. 1 acid and/or 1 B/N out, provided recovery is ≥10%. 2. Recovery high, samples ND. 3. Recovery low for 1 class, target analyte list requires compounds from other class only. 4. Obvious matrix interference. 5. Sample diluted 20X or greater.	Yes
Internal Standards	1. 50-200% of CCV to mid-level ICAL standard. 2. ≤30 sec shift of CCV to mid-level standard. 3. 50-200% recovery of samples to daily CCV. 4. ≤ 30 sec shift of samples to daily CCV.	None	NA

** "Difficult" analytes are 4-Chloroaniline, 4-Nitrophenol, Phenol and 2,4-Dinitrophenol.

RCP

QA Parameter	Technical Acceptance	Allowable Failures	Narration Required
DFTPP	1. Criteria listed in Table 3. 2. Tailing for Benzidine and PCP ≤2. 3. Breakdown of 4,4'-DDT ≤20 %	None	NA
ICAL	1. 20% RSD or r^2 ≥0.990 2. Minimum RF must meet 0.05 for all compounds.	20% allowed out.	Yes - RSD, r^2 and RF failures
ICV	80-120%.	20% allowed out as long as recovery within 65-135%.	Yes
CCV	20%D.	10% allowed out.	Yes
MB	Less than RL.	1. >RL with ND sample. 2. >RL with detection in sample >10X the MB.	Yes
LCS/LCSD	1. 40-140% for base-neutral, 30-130% for acids. 2. RPD ≤20% for waters, ≤30% for soils.	≤20% allowed to fail provided recovery is ≥10%.	Yes
MS/MSD	1. 40-140% for base-neutral, 30-130% for acids. 2. RPD ≤20% for waters, ≤30% for soils.	Recoveries within limits in the LCS.	Recoveries ≤10% or ≥150% and/or RPD ≥50%.
Surrogates	30-130% for soils, 30-130% for base-neutrals in water, 15-110% for acids in water.	1. 1 acid and/or 1 B/N out, provided recovery is ≥10%. 2. Recovery high, samples ND. 3. Recovery low for 1 class, target analyte list requires compounds from other class only. 4. Obvious matrix interference. 5. Sample diluted 20X or greater.	Yes
Internal Standards	1. 50-200% of CCV to mid-level ICAL standard. 2. ≤30 sec shift of CCV to mid-level standard. 3. 50-200% recovery of samples to daily CCV. 4. ≤ 30 sec shift of samples to daily CCV.	None	NA

SIM			
QA Parameter	**Technical Acceptance**	**Allowable Failures**	**Narration Required**
DFTPP	1. Criteria listed in Table 3.	None	NA
ICAL	1. 20% RSD or r^2 ≥0.990 2. ≤30% Readback on low point.	None	NA
ICV	80-120%.	Recovery high - sample analysis ND.	Detection only
CCV	20%D.	Recovery high - sample analysis ND.	Yes
MB	Less than RL.	1. >RL with ND sample. 2. >RL with detection in sample >10X the MB.	Yes
LCS/LCSD	1. 40-140%. 2. RPD ≤20%.	High recovery, sample analysis ND.	Yes
MS/MSD	1. 40-140%. 2. RPD ≤20%.	Recoveries within limits in the LCS.	Recoveries ≤10% or ≥150% and/or RPD ≥50%.
Analog	Historical limits.	1. Recovery high, samples ND. 2. Obvious matrix interference.	Yes
Internal Standards	1. 50-200% of CCV to mid-level ICAL standard. 2. ≤30 sec shift of CCV to mid-level standard. 3. 50-200% recovery of samples to daily CCV. 4. ≤ 30 sec shift of samples to daily CCV.	None	NA

Dieter, Gail A (DEC)

From: Dieter, Gail A (DEC)
Sent: Tuesday, August 28, 2018 11:59 AM
To: 'Eric D. Popken'
Subject: RE: For Review: Niagara Highway Garage #932163 - GWS Workplan

Eric,

I reviewed the Emerging Contaminants Sampling Workplan for the Niagara Highway Garage Site #932163. I have no questions or comments regarding the plan. You can assume with this email, that the NYSDEC accepts and approves the submitted sampling work plan.

If you could send me a tentative schedule for the sampling, I will need to get in contact with the Niagara County Supervisor to let him know that we will be taking samples at the site.

Thank you –

Gail

Gail A. Dieter
Environmental Chemist 2
NYS Dept. of Environmental Conservation
Division of Environmental Remediation
Bureau E, Section C
625 Broadway, 12th Floor
Albany, NY 12233-7017

Telephone: (518) 402-9645
Fax: (518) 402-9819
Email: gail.dieter@dec.ny.gov

From: Eric D. Popken [mailto:EPopken@gesonline.com]
Sent: Friday, August 24, 2018 4:46 PM
To: Dieter, Gail A (DEC) <gail.dieter@dec.ny.gov>
Subject: For Review: Niagara Highway Garage #932163 - GWS Workplan

Good afternoon Gail,

Attached for your review is the draft GWS workplan. Have a look over and let me know if you have any questions.

-Eric

Eric D. Popken, PG
Senior Project Manager

Office: 800.287.7857 ext. 4345
epopken@GESonline.com

Please note new address starting 5/18/18:
Groundwater & Environmental Services, Inc.
415 Lawrence Bell Drive, Suite 6
Williamsville, NY 14221

Follow Us: Website | LinkedIn | Twitter

Safety. From start to finish.

Licensed PG in New York