HALEY ALDRICH

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REPORT ON

SUPPLEMENTAL REMEDIAL INVESTIGATION WORK PLAN – 1,4-DIOXANE AND PFAS SAMPLING PHILIPS LIGHTING COMPANY BATH FACILITY BATH, NEW YORK

by Haley & Aldrich of New York
Rochester, New York

for New York State Department of Environmental Conservation
Avon, New York

File No. 127981-012
November 2018

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18 October 2018
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New York State Department of Environmental Conservation
Region 8 Division of Remediation
6274 East Avon-Lima Road
Avon, New York 14414

Attention: Mr. Timothy A. Schneider, P.E.

Subject: Emerging Contaminants Groundwater Sampling Work Plan
Philips Lighting Company Bath Facility
7265 State Route 54
Bath, New York
BCP Site # C851044

Dear Mr. Schneider:

Haley & Aldrich of New York (Haley & Aldrich) has prepared this letter Work Plan on behalf of the current owner of the subject site, Yort, Inc. and the former site owner (Philips North America LLC, formerly Philips Electronics North America Corporation; collectively "Philips"). In a letter dated July 31, 2018 (attached), the New York State Department of Environmental Conservation (NYSDEC) requested that Philips prepare and submit a letter Work Plan for the collection and analysis of groundwater samples for compounds that the NYSDEC has identified as "emerging contaminants", including 1,4-dioxane and per- and polyfluoroalkyl substances (PFAS). This work plan includes the rational for selection of a subset of existing monitor wells at the Philips Lighting Company Facility in Bath, New York (BCP Site # C81044) as well as describes activities and noted modifications to the existing NYSDEC-approved groundwater sampling plan for the collection and analysis of 1,4-dioxane and PFAS.

Background

Groundwater at the site is currently being monitored from an existing well network for volatile organic compounds (VOCs). The current groundwater sampling program is described in the NYSDEC-approved Supplemental Remedial Investigation Work Plan (SRIWP) dated April 2016, and the supporting plans in the NYSDEC-approved RIWP dated 2014, including the Quality Assurance Project Plan (QAPP), Health Safety Plan (HASP), and Field Sampling Plan (FSP). Recent groundwater sampling completed at the Site included collection of groundwater samples from the monitoring well network for VOCs in January 2018 and June 2018; a focused supplemental sampling event was also completed in August 2018 to confirm the June 2018 water quality results in six (6) of the monitor wells. Current NYSDEC-approved sampling procedures include the collection of VOC samples using passive diffusion bags (PDBs), and low flow sampling equipment for TAL metals at MW-9C. The next round of groundwater sampling is tentatively

scheduled to be completed in November 2018 pending NYSDEC-approval of this letter Work Plan. Once this letter Work Plan is approved, select monitoring wells will also be sampled for 1,4-Dioxane and PFAS as detailed below during the next scheduled groundwater sampling event.

PROPOSED GROUNDWATER SAMPLING LOCATIONS

As requested, the existing monitoring well network was evaluated to determine appropriate sampling locations for the expanded "emerging contaminants" and six (6) wells are proposed to be sampled for 1,4-dioxane and PFAS in groundwater. The selection criteria were based on the NYSDEC's recommendations to include upgradient wells to determine water quality conditions that may be migrating onto the site, and representative wells which are near or downgradient of suspected sources or release areas. Based on the criteria recommended by the NYSDEC, Philips proposes to collect samples for 1,4-dioxane and PFAS from wells as described in the table below. Locations of proposed wells to be sampled for the NYSDEC-requested emerging compounds are shown in Figure 1.

Monitoring Well	Location	Rationale
MW-19B	Offsite and anticipated to be upgradient of former manufacturing operations; VOCs have not been detected in samples from this well.	Detection of emerging compounds at this location could indicate that the source of the emerging compounds originated from an offsite upgradient source(s).
MW-3B	North of facility and within AOC-8; groundwater samples collected from this location (and nearby wells MW-4B and MP-11B) have similar water quality signatures, containing elevated levels of TCE.	Detection of an emerging compound(s) at this location may indicate historical activities conducted within AOC-8 as a potential source.
MW-2A	South of the facility within a perched groundwater zone containing TCE.	Detection of an emerging compound(s) at this location may indicate historical activities conducted in the southern portion of the developed portion of the facility as a potential source.
MW-1B	West of facility adjacent to IRM-5.	Detection of an emerging compound(s) at this location may indicate historical activities within the IRM as a potential source.
MW-6B	East of facility and suspected to be downgradient of AOCs 2, 3, 4, 5, and 8 and IRM-2.	Detection of an emerging compound(s) at this location may indicate historical activities within AOCs located north of the facility as a potential source.
MW-17B	West of facility and suspected to be downgradient of the facility.	Detection of an emerging compound(s) at this location may indicate historical activities west of the facility as a potential source.

ANALYTICAL METHODS

PFAS

Groundwater samples will be collected and analyzed for PFAS using modified (low level) EPA Method 537, which was indicated to be the NYSDEC preferred analytical method for analysis of groundwater samples for PFAS as stated in the April 2018 attachment entitled "Groundwater Sampling for Emerging Compounds" that was appended to the July 31, 2018 correspondence from NYSDEC. According to the NYSDEC guidance, modified EPA Method 537 can achieve the required detection limits for PFAS target analytes of 2 parts per trillion (ng/L). PFAS constituents that will be analyzed and reported are based on the NYSDEC target analyte list which is summarized in Table 1.

1,4-dioxane

Groundwater analysis has primarily been completed for VOCs using EPA Method 8260B, which includes the analysis and reporting of 1,4-dioxane; however, the method detection limit (MDL) for 1,4-dioxane using this method is higher than the current NYSDEC requirement of a detection limit of 0.28 micrograms per liter (ug/L). NYSDEC has recommended that samples be analyzed for low-level detection of 1,4-dioxane using either Method 8260B or 8270C with the gas chromatograph/mass spectrometer's (GC/MS) detector set in the selective ion monitoring (SIM) mode. While NYSDEC permits analysis of 1,4-dioxane by either EPA Method 8260 or 8270; the Department prefers that samples be analyzed using EPA Method 8270C, due a larger sample volume, less vulnerable interference with chlorinated compounds, and a more robust extraction procedure. Based on this, groundwater samples collected from proposed monitoring wells will be analyzed for 1,4-dioxane using EPA Method 8270C in SIM mode.

SAMPLING EQUIPMENT

Samples collected from the proposed wells for analysis of 1,4-dioxane and PFAS will be collected in accordance with the NYSDEC's guidance "Collection of Groundwater Samples for Perfluorooctanoic Acid (PFOA) and Per fluorinated Compounds from Monitor Wells Sampling Protocol, Revision 1.2, dated June 29, 2016" that was included as an attachment to the July 31, 2018 NYSDEC correspondence. Currently, PDBs are used to collect groundwater samples for VOCs analysis. However, PDBs only provide a limited volume of water for sample collection. PDBs also require that the compounds be able to diffuse through the sampling material. As a result, PDBs are not considered acceptable methods for the collection of either 1,4-dioxane or PFAS.

Since PDBs are not acceptable for the proposed expanded sampling, the existing NYSDEC-approved groundwater sampling method will be modified for the collection of samples for analysis of 1,4-dioxane and PFAS. Philips proposes to use HydraSleeve samplers to obtain sufficient volumes of groundwater from the selected wells for analysis of the expanded emerging contaminant list. HydraSleeve samplers are constructed of high-density polyethylene (HDPE), are flat when empty, displace a minimal volume of groundwater when installed, and fill slowly over several days, resulting in minimal disturbance during

sampling. The manufacturer's (GeoInsight) standard operating procedure for sampling using Hydrasleeve samples is included as an attachment to this letter Work Plan. Emerging contaminant samples collected using HydraSleeves will be completed prior to placement of PDBs, which will be used for VOC analysis.

PFAS AND 1,4-DIOXANE SAMPLING CONSIDERATIONS

Due to the prevalence of PFAS in many low-density polyethylene (LDPE) and Teflon products that are commonly used in groundwater sampling, special precautions need to be taken during sampling to reduce the potential for cross contamination of the samples.

Groundwater samples collected for the analysis of emerging contaminants will be collected prior to recording groundwater elevation data or before samples are collected for VOCs analysis using PDBs. Nitrile gloves will be changed prior to and after collecting each sample to mitigate potential cross contamination between wells. Nitrile gloves will also need to be worn when labelling bottles and preparing coolers for shipment to avoid contact with adhesives that are generally found on sampling labels or tapes used to seal coolers, since some of the adhesives may contain PFAS.

The following represents the proposed sampling procedures for the collection of samples for 1,4-dioxane and PFAS:

1. Field staff performing the sampling will be required to wash their hands with demonstrated PFAS-free water and Granulated Alconox® prior to handling the sampling equipment or bottles, touching the sampling ports, or putting on nitrile gloves.
2. Samples for PFAS analysis will be collected in two (2) laboratory supplied 250 mL, unpreserved polypropylene or HDPE with non-Teflon polypropylene or HDPE screw cap.
3. Samples for 1,4-dioxane will be collected in two (2) laboratory supplied 500 mL unpreserved glass amber jars with Teflon-line screw cap.
4. During sampling, new disposable nitrile gloves will be donned prior to sampling at each location and following contact with a potential contaminant source, the sample container and cap will always be held by the sampler (i.e., not placed on the ground or in clothing pockets), and the inside of the sampling container and cap will not be touched.
5. PFAS field blanks will be collected by opening the bottle of demonstrated PFAS-free water (provided by the laboratory) and leaving it exposed to air near the sampling port.
6. After filling and securely capping, the bottles will be inverted at least 5 times to distribute the preservative and then transferred into coolers and placed on ice to maintain sample temperatures at 4 +/-2 °C).
7. Following the collection of the 1,4-dioxane and PFAS samples, the laboratory provided demonstrated PFAS-free water will be poured from the container into the preserved bottles from the lab.

8. The now empty field blank water bottle used will be returned to the lab with the filled sample containers.

Many materials used during common environmental investigations can potentially contain PFAS. Due to the limited available published literature and/or guidance on which materials affect sampling results, a conservative approach will be used to exclude materials known or suspected to contain PFAS to limit the potential for cross contamination of the samples. Materials that will be avoided during sampling include:

- Teflon, polytetrafluoroethylene (PTFE)
- Waterproof coatings containing PFAS
- Fluorinated ethylene propylene (FEP)
- Ethylene tetrafluoroethylene (ETFE)
- Low density polyethylene (LDPE)
- Polyvinylidene fluoride (PVDF)

QUALITY ASSURANCE / QUALITY CONTROL PROCEDURES

Due to the low-level detection limit for PFAS compounds (2 ng/L) and MDL for 1,4-dioxane (0.28 ug/L), and the potential for false positive detections, the following QA/QC samples will be collected:

- 1 field/sampler blank (PFAS sampling only);
- 1 field duplicate sample; and
- 1 matrix spike/ 1 matrix spike duplicate (MS/MSD)

Six (6) groundwater samples plus four (4) QA/QC) samples (10 total samples) will be submitted for analysis of PFAS compounds via modified EPA Method 537 (PFAS), and six (6) groundwater samples and three (3) QA/QC) samples (9 total samples) will be submitted for the analysis of low-level 1,4-dioxane by EPA Method 8270-SIM. See Table 1 for the list of the target compounds and their reporting limits.

Field and QA/QC samples will be submitted to Alpha Analytical for the analysis of 1,4-dioxane and PFAS compounds. The analytical laboratory data report will be reviewed and validated.

REPORTING

The results of the groundwater sampling described above will be combined with remedial investigation (RI) data in the existing database for the site. Progress on the field work will be provided to the NYSDEC in the Monthly Progress Reports. Submission of validated sampling results will be provided to the NYSDEC in a data summary report, which will include an electronic data deliverable in EQuIS format and include an evaluation of results. Recommendations for further sampling for 1,4-dioxane and PFAS at currently approved or expanded locations will be evaluated, if warranted. The work plan report will be prepared and submitted to the NYSDEC for review and approval as described in the attached schedule.

Schedule

Currently, sitewide groundwater sampling for VOCs (and TAL metals at MW-9C, only) is being scheduled to be completed in November 2018. This routine sampling event would be completed in accordance with the procedures and methods presented in the NYSDEC-approved Supplemental Remedial Investigation Work Plan (SRIWP) dated April 2016 and the NYSDEC-approved RIWP dated 2014, including the Quality Assurance Project Plan (QAPP), Health and Safety Plan (HASP), and Field Sampling Plan (FSP). Additional sampling of selected wells for 1,4-dioxane and PFAS is proposed to be completed in accordance with this letter Work Plan immediately prior to the November 2018 sampling event as described in the schedule (Figure 2).

Closing

Should you have any questions with this supplemental work plan or wish to discuss the project further, please do not hesitate to contact either Mr. Dean Weeks of Philips or Haley & Aldrich.

Sincerely yours,
HALEY & ALDRICH OF NEW YORK

Keith M. Aragona
Senior Project Manager

W. Thomas West
Sr. Project Manager/VP

Enclosures:

- Table 1 – Sampling and Analysis Plan – Supplemental Groundwater Sampling – Target Compounds and Reporting Limits
- Table 2 – Sampling and Analysis Plan – Supplemental Groundwater Sampling – Sample Containers, Preservation, and Holding Times
- Table 3 - Sampling and Analysis Plan – Supplemental Groundwater Sampling – Data Quality Indicators/Corrective Actions
- Figure 1 – Site Plan
- Figure 2 – Emerging Compound Sampling Schedule
- July 31, 2018 NYSDEC correspondence to Philips
- HydraSleeve Standard Operating Procedure
- EPA Method 537
- EPA Method 8270C

c: Philips; Attn: D. Weeks, R. Farley
NYSDEC; Attn: D. Harkawik, B. Schilling
NYSDOH; Attn: J. Deming, C. Vooris, P.E.

TABLES

TABLE 1
SAMPLING AND ANALYSIS PLAN - SUPPLEMENTAL GROUNDWATER SAMPLING - TARGET COMPOUNDS AND REPORTING LIMITS
PHILIPS LIGHTING COMPANY – BATH FACILITY
BATH, NY
BCP SITE #C851044

PARAMETER	ACRONYM	CASRN	FORMULA	RL
FLUORINATED TELOMER SULFONATES				**ng/L (ppt)**
1H,1H,2H,2H-perfluorooctanesulfonic acid	6:2 FTS	27619-97-2	C8H5F13O3S	2.0
1H,1H,2H,2H-perfluorodecanesulfonic acid	8:2 FTS	39108-34-4	C10H5F17O3S	2.0
PERFLUOROALKANE SULFONAMIDES (FPASAs)				
Perfluorooctane sulfonamide	FOSA	754-91-6	C8H2F17NO2S	2.0
PERFLUOROOCTANE SULFONAMIDOACETIC ACIDS (FPOSAAs)				
N-methyl-perfluorooctanesulfonamidoacetic a	N-MeFOSAA	2355-31-9	C11H6F17NO4S	2.0
N-ethyl-perfluorooctanesulfonamidoacetic aci	N-EtFOSAA	2991-50-6	C12H8F17NO4S	2.0
PERFLUOROALKYL CARBOXYLATES (PFCAs)				
Perfluorobutanoic acid	PFBA	375-22-4	C4HF7O2	2.0
Perfluoropentanoic acid	PFPeA	2706-90-3	C5HF9O2	2.0
Perfluorohexanoic acid	PFHxA	307-24-4	C6HF11O2	2.0
Perfluoroheptanoic acid	PFHpA	375-85-9	C7HF13O2	2.0
Perfluorooctanoic acid	PFOA	335-67-1	C8HF15O2	2.0
Perfluorononanoic acid	PFNA	375-95-1	C9HF17O2	2.0
Perfluorodecanoic acid	PFDA	335-76-2	C10HF19O2	2.0
Perfluoroundecanoic acid	PFUnDA	2058-94-8	C11HF21O2	2.0
Perfluorododecanoic acid (Tricosafluorododec	PFDoDA	307-55-1	C12HF23O2	2.0
Perfluorotridecanoic acid	PFTrDA	72629-94-8	C13HF25O2	2.0
Perfluortetradecanoic acid	PFTeDA	376-06-7	C14HF27O2	2.0
PERFLUOROALKYL SULFONATES (PFSAs)				
Perfluorobutane Sulfonic Acid	PFBS	375-73-5	C4F9O3S	2.0
Perfluorohexane Sulfonic Acid	PFHxS	355-46-4	C6F13O3S	2.0
Perfluoroheptane Sulfonic Acid	PFHpS	375-92-8	C7F15O3S	2.0
Perfluorooctane Sulfonic Acid	PFOS	1763-23-1	C8F17O3S	2.0
Perfluorodecane Sulfonic Acid	PFDS	335-77-3	C10F21O3S	2.0
SEMI-VOLATILE ORGANIC COMPOUNDS (SVOC)				**ug/L (ppb)**
1,4-Dioxane	1,4-D	123-91-1	C4H8O2	0.15

Notes:
ng/L = nanograms per liter; ug/L = micrograms per liter
PPT = parts per trillion
ppb = parts per billion
RL = Reporting Limit

TABLE 2
SAMPLING AND ANALYSIS PLAN - SUPPLEMENTAL GROUNDWATER SAMPLING -SAMPLE CONTAINERS, PRESERVATION, AND HOLDING TIMES
PHILIPS LIGHTING COMPANY – BATH FACILITY
BATH, NY
BCP SITE #C851044

Analytes	Matrix	Collection Method	Locations	No. of Locations	Analytical Method	Sample Containers	Preservation and Holding Time	Project-Specific Qualty Control Samples
1,4-dioxane (1,4 D)	Groundwater	HydraSleeve	MW-19B MW-3B MW-2A MW-1B MW-6B MW-17B	6	EPA Method 8270C SIM	2-500 mL amber glass, unpreserved	4 +/-2 °C 7 Days Extraction 40 Days Analysis	1 Field Duplicate 1 Matrix Spike 1 Matrix Spike Duplicate 1 Field Blank
PerFluoro Akyl Substances (PFAS)	Groundwater	HydraSleeve	MW-19B MW-3B MW-2A MW-1B MW-6B MW-17B	6	EPA Method 537 Modified	1-250 mL polypropylene or HDPE	4 +/-2 °C 14 Days Extraction 28 Days Analysis	

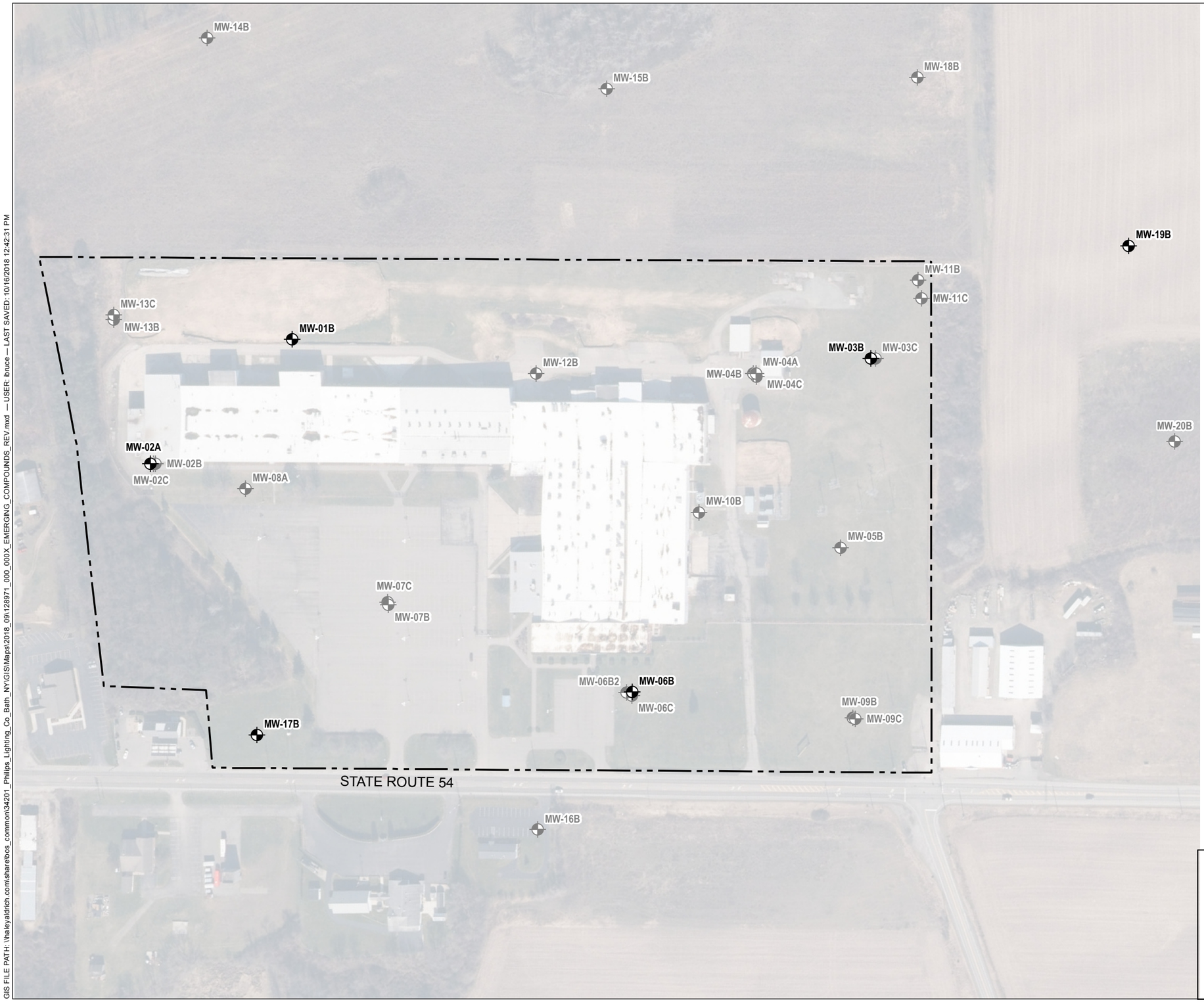
1. SIM - Selective Ion Mode

TABLE 3
SAMPLING AND ANALYSIS PLAN - SUPPLEMENTAL GROUNDWATER SAMPLING - DATA QUALITY INDICATORS/CORRECTIVE ACTIONS
PHILIPS LIGHTING COMPANY – BATH FACILITY
BATH, NY
BCP SITE #C851044

FIELD QA/QC SAMPLES	Data Quality Indicator	Frequency	Project Acceptance Criteria	Corrective Action
Field Duplicate	Precision	1 per sampling event	RPD <35% Water	Qualify Reported Results or Collect Additional Samples and Re-analyze
Equipment Rinse Blank	Accuracy	1 per method per event per sampler for non-dedicated sampling equipment	<RL	
Field Blank	Accuracy	1 per event per sampler	<RL	
LABORATORY QA/QC SAMPLES	**Data Quality Indicator**	**Frequency**	**Project Acceptance Criteria**	**Corrective Action**
Method Blank	Accuracy	1 per batch of 20 samples	[analyte] < 1/2 RL or sample [analyte] 10 times [Blank]	Re-prep and re-analyze blank and associated samples, or qualify reported results
Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)	Precision and accuracy	1 per batch of 20 samples	PFAS - %R = 50-150% True Value 1,4 D -%R = 40-140% True Value PFAS and 1,4 D - RPD <30%	Re-prep and re-analyze LCS and associated samples, or qualify reported results
Matrix Spike/Matrix Spike Duplicate Sample (MS/MSD)	Precision and accuracy	1 per 20 project samples	PFAS - %R = 50-150% True Value 1,4 D -%R = 40-140% True Value PFAS and 1,4 D - RPD <30%	Re-prep and re-analyze MS/MSD and associated samples, or qualify reported results
Surrogate Compound	Accuracy	Each Sample	1,4 D-D8 %R = 15 -110% True Value PFAS -C13 Standards %R = 50-150 % True Value	Re-Analyze Sample or qualify the reported results

NOTES:
1. RL = Reporting limit.
2. DQI = Data quality indicator.
3. NA = Not applicable.
4. QA/QC = Quality assurance/quality control
5. RDP = Relative percent difference.
6. [ ] = Concentration
7. %R = Percent recovery.

FIGURES



LEGEND

- EMERGING COMPOUND SAMPLING LOCATION
- NETWORK MONITORING WELL
- SITE BOUNDARY

NOTES

1. ALL LOCATIONS AND DIMENSIONS ARE APPROXIMATE.
2. AERIAL IMAGERY SOURCE: ESRI
3. TAX PARCEL BOUNDARY SOURCE: STEUBEN COUNTY PLANNING DEPARTMENT 2005

0 200 400
SCALE IN FEET

HALEY ALDRICH

PHILIPS LIGHTING COMPANY
BATH FACILITY
7265 STATE ROUTE 54
BATH, NEW YORK

PROPOSED EMERGING COMPOUND SAMPLING LOCATIONS

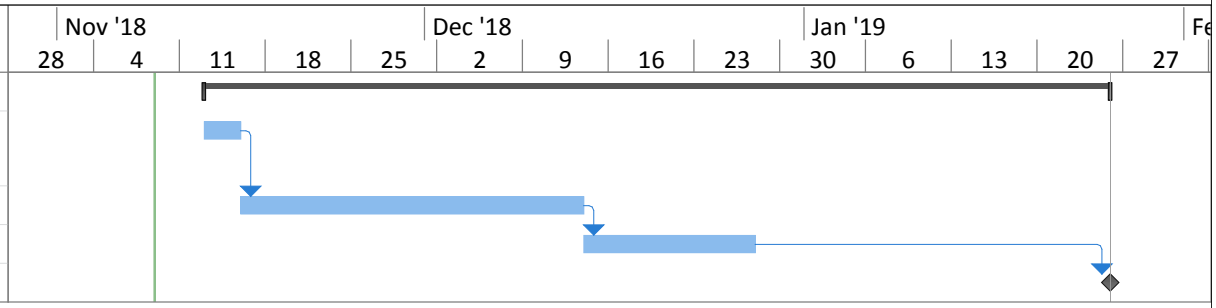
OCTOBER 2018

FIGURE 1

GIS FILE PATH: \\haleyaldrich.com\share\bos_common\34201_Philips_Lighting_Co_Bath_NY\GIS\Maps\2018_09\128971_000_000X_EMERGING_COMPOUNDS_REV.mxd — USER: bruce — LAST SAVED: 10/16/2018 12:42:31 PM

FIGURE 2
EMERGING COMPOUND SAMPLING SCHEDULE

ID	Task Mode	Task Name
1		**Emerging Compound Sampling**
2		Collect groundwater samples for emerging compounds
3		Laboratory analysis
4		Evaluate data
5		Reporting



Project: msproj11
Date: Fri 11/9/18

Task		Inactive Task		Start-only	
Split		Inactive Milestone		Finish-only	
Milestone		Inactive Summary		Deadline	
Summary		Manual Task		Progress	
Project Summary		Duration-only		Manual Progress	
External Tasks		Manual Summary Rollup			
External Milestone		Manual Summary			

July 31, 2018 NYSDEC Correspondence

HALEY ALDRICH

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

Division of Environmental Remediation, Region 8
6274 East Avon-Lima Road, Avon, NY 14414-9516
P: (585) 226-5353 I F: (585) 226-8139
www.dec.ny.gov

Via E-mail

Mr. Dean Weeks
Philips Lighting North America
200 Franklin Square Drive
Somerset, NJ 08873

July 31, 2018

RE: Request for sampling of Emerging Contaminants
Philips Lighting Site #c851044

Dear Mr. Weeks:

The New York State Department of Environmental Conservation (DEC) is undertaking a Statewide evaluation of remediation sites to better understand the risk posed to New Yorkers by 1,4-dioxane and per- and polyfluoroalkyl substances (PFAS). PFAS have historically not been evaluated at remediation sites, and 1,4-dioxane has not been evaluated at the levels that are now thought to represent a health concern. This initiative is being undertaken as a result of these "emerging contaminants" having been found in a number of drinking water supplies in New York. Accordingly, the DEC is requiring that you test site groundwater for these chemicals. To accommodate this requirement, a select number of existing monitoring wells, representative of the potential of the above-referenced site to be a source of these emerging contaminants, must be sampled. DEC recommends that at least one of these wells should be upgradient of the site.

The attached guidance provides information on the analytical methods and reporting requirements. A second guidance document describes special precautions that need to be considered when sampling for PFAS.

Please prepare a draft letter work plan that identifies the wells proposed for sampling, brief description of the sampling methods, and anticipated sampling date within the next 60 days. If you wish to discuss the scope of the requested water testing, please contact me at 585-226-5480 or timothy.schneider@dec.ny.gov.

Sincerely,

Timothy Schneider, P.E.
Professional Engineer 1

B. Schilling

M. Cruden
D. Harkawik
D. Hettrick
T. West
K. Aragona

HydraSleeve Standard Operating Procedure

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Groundwater Sampling for Emerging Contaminants

April 2018

Issue: NYSDEC has committed to analyzing representative groundwater samples at remediation sites for emerging contaminants (1,4-dioxane and PFAS) as described in the below guidance.

Implementation

NYSDEC project managers will be contacting site owners to schedule sampling for these chemicals. Only groundwater sampling is required. The number of samples required will be similar to the number of samples where "full TAL/TCL sampling" would typically be required in a remedial investigation. If sampling is not feasible (e.g., the site no longer has any monitoring wells in place), sampling may be waived on a site-specific basis after first considering potential sources of these chemicals and whether there are water supplies nearby.

Upon a new site being brought into any program (i.e., SSF, BCP), PFAS and 1,4-dioxane will be incorporated into the investigation of groundwater as part of the standard "full TAL/TCL" sampling. Until an SCO is established for PFAS, soil samples do not need to be analyzed for PFAS unless groundwater contamination is detected. Separate guidance will be developed to address sites where emerging contaminants are found in the groundwater. The analysis currently performed for SVOCs in soil is adequate for evaluation of 1,4-dioxane, which already has an established SCO.

Analysis and Reporting

Labs should provide a full category B deliverable, and a DUSR should be prepared by a data validator, and the electronic data submission should meet the requirements provided at: https://www.dec.ny.gov/chemical/62440.html ,

The work plan should explicitly describe analysis and reporting requirements.

PFAS sample analysis: Currently, ELAP does not offer certification for PFAS compounds in matrices other than finished drinking water. However, laboratories analyzing environmental samples (ex. soil, sediments, and groundwater) are required, by DER, to hold ELAP certification for PFOA and PFOS in drinking water by EPA Method 537 or ISO 25101.

Modified EPA Method 537 is the preferred method to use for groundwater samples due to the ability to achieve 2 ng/L (ppt) detection limits. If contract labs or work plans submitted by responsible parties indicate that they are not able to achieve similar reporting limits, the project manager should discuss this with a DER chemist. Note: Reporting limits for PFOA and PFOS should not exceed 2 ng/L.

PFAS sample reporting: DER has developed a PFAS target analyte list (below) with the intent of achieving reporting consistency between labs for commonly reportable analytes. It is expected that reported results for PFAS will include, at a minimum, all the compounds listed. This list may be updated in the future as new information is learned and as labs develop new capabilities. If lab and/or matrix specific issues are encountered for any particular compounds, the NYSDEC project manager will make case-by-case decisions as to whether particular analytes may be temporarily or permanently discontinued from analysis for each site. Any technical lab issues should be brought to the attention of a NYSDEC chemist.

Some sampling using this full PFAS target analyte list is needed to understand the nature of contamination. It may also be critical to differentiate PFAS compounds associated with a site from other

sources of these chemicals. Like routine refinements to parameter lists based on investigative findings, the full PFAS target analyte list may not be needed for all sampling intended to define the extent of contamination. Project managers may approve a shorter analyte list (e.g., just the UCMR3 list) for some reporting on a case by case basis.

1,4-Dioxane Analysis and Reporting: The method detection limit (MDL) for 1,4-dioxane should be no higher than 0.28 µg/l (ppb). ELAP offers certification for both EPA Methods 8260 and 8270. In order to get the appropriate detection limits, the lab would need to run either of these methods in "selective ion monitoring" (SIM) mode. DER is advising the use of method 8270, since this method provides a more robust extraction procedure, uses a larger sample volume, and is less vulnerable to interference from chlorinated solvents (we acknowledge that 8260 has been shown to have a higher recovery in some studies).

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
	Perfluorooctanessulfonic 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 6 original UCMR3 chemicals

Collection of Groundwater Samples for Perfluorooctanoic Acid (PFOA) and Perfluorinated Compounds (PFCs) from Monitoring Wells Sample Protocol

Samples collected using this protocol are intended to be analyzed for perfluorooctanoic acid (PFOA) and other perfluorinated compounds by Modified (Low Level) Test Method 537.

The procedure used must be consistent with the NYSDEC March 1991 Sampling Guidelines and Protocols http://www.dec.ny.gov/docs/remediation_hudson_pdf/sgpsect5.pdf with the following materials limitations.

At this time acceptable materials for sampling include: stainless steel, high density polyethylene (HDPE), PVC, silicone, acetate and polypropylene. Equipment blanks should be generated at least daily. Additional materials may be acceptable if pre-approved by NYSDEC. Requests to use alternate equipment should include clean equipment blanks. **NOTE: Grunfos pumps and bladder pumps are known to contain PFC materials (e.g. Teflon™ washers for Grunfos pumps and LDPE bladders for bladder pumps).** All sampling equipment components and sample containers should not come in contact with aluminum foil, low density polyethylene (LDPE), glass or polytetrafluoroethylene (PTFE, Teflon™) materials including sample bottle cap liners with a PTFE layer. Standard two step decontamination using detergent and clean water rinse will be performed for equipment that does come in contact with PFC materials. Clothing that contains PTFE material (including GORE-TEX®) or that have been waterproofed with PFC materials must be avoided. Many food and drink packaging materials and “plumbers thread seal tape” contain PFCs.

All clothing worn by sampling personnel must have been laundered multiple times. The sampler must wear nitrile gloves while filling and sealing the sample bottles.

Pre-cleaned sample bottles with closures, coolers, ice, sample labels and a chain of custody form will be provided by the laboratory.

1. Fill two pre-cleaned 500 mL HDPE or polypropylene bottle with the sample.
2. Cap the bottles with an acceptable cap and liner closure system.
3. Label the sample bottles.
4. Fill out the chain of custody.
5. Place in a cooler maintained at 4 ± 2º Celsius.

Collect one equipment blank for every sample batch, not to exceed 20 samples.

Collect one field duplicate for every sample batch, not to exceed 20 samples.

Collect one matrix spike / matrix spike duplicate (MS/MSD) for every sample batch, not to exceed 20 samples.

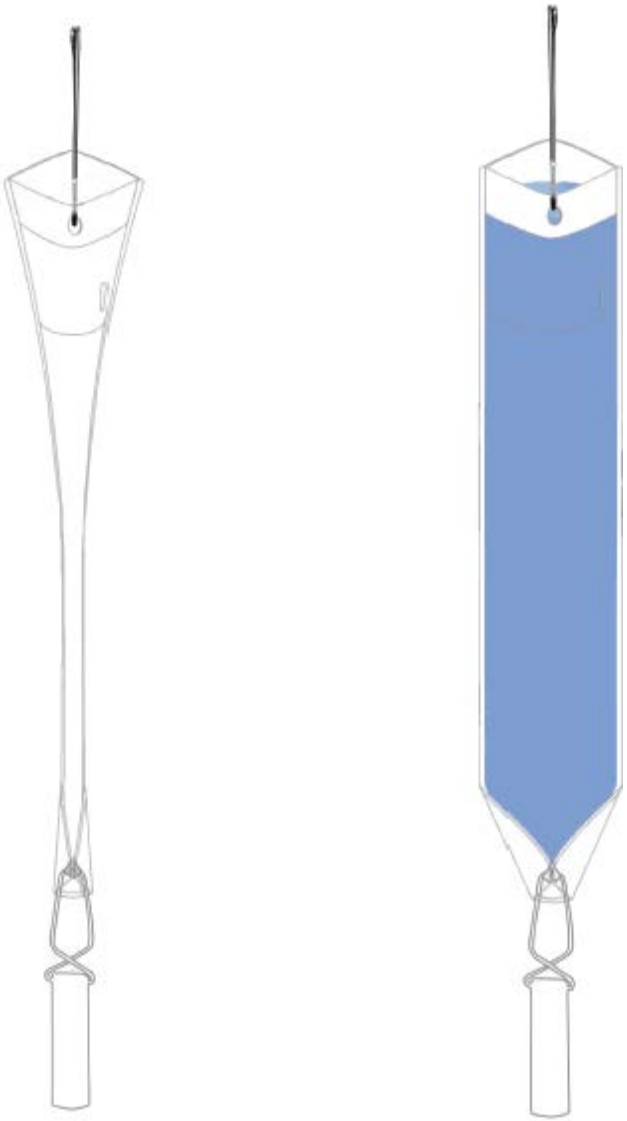
Request appropriate data deliverable (Category A or B) and an electronic data deliverable.

HYDRASleeve™

Simple by Design

US Patent No. 6,481,300; No. 6,837,120 others pending

Standard Operating Procedure: Sampling Groundwater with a HydraSleeve



This guide should be used in addition to field manuals and instructions appropriate to the chosen sampling device (i.e., HydraSleeve, SpeedBag or Super/Skinny Sleeve and W3 HybridSleeve).

Find the appropriate field manual and instructions on the HydraSleeve website at http://www.hydrasleeve.com.

For more information about the HydraSleeve, or if you have questions, contact:
GeoInsight, P.O. Box 1266, Mesilla Park, NM 88047
800-996-2225, info@hydrasleeve.com.

Table of Contents

Introduction

The HydraSleeve is classified as a no-purge (passive) grab sampling device, meaning that it is used to collect groundwater samples directly from the screened interval of a well without having to purge the well prior to sample collection. When it is used as described in this Standard Operating Procedure (SOP), the HydraSleeve causes no drawdown in the well (until the sample is withdrawn from the water column) and only minimal disturbance of the water column, because it has a very thin cross section and it displaces very little water (<100 ml) during deployment in the well. The HydraSleeve collects a sample from within the screen only. It excludes water from any other part of the water column in the well through the use of a self-sealing check valve at the top of the sampler. It is a single-use (disposable) sampler that is not intended for reuse, so there are no decontamination requirements for the sampler itself.

The use of no-purge sampling as a means of collecting representative groundwater samples depends on the natural movement of groundwater (under ambient hydraulic head) from the formation adjacent to the well screen through the screen. Robin and Gillham (1987) demonstrated the existence of a dynamic equilibrium between the water in a formation and the water in a well screen installed in that formation, which results in formation-quality water being available in the well screen for sampling at all times. No-purge sampling devices like the HydraSleeve collect this formation-quality water as the sample, under undisturbed (non-pumping) natural flow conditions. Samples collected in this manner generally provide more conservative (i.e., higher concentration) values than samples collected using well-volume purging, and values equivalent to samples collected using low-flow purging and sampling (Parsons, 2005).

Applications of the HydraSleeve

The HydraSleeve can be used to collect representative samples of groundwater for all analytes (volatile organic compounds [VOCs], semi-volatile organic compounds [SVOCs], common metals, trace metals, major cations and anions, dissolved gases, total dissolved solids, radionuclides, pesticides, PCBs, explosive compounds, and all other analytical parameters). Designs are available to collect samples from wells from 1” inside diameter and larger. The HydraSleeve can collect samples from wells of any yield, but it is especially well-suited to collecting samples from low-yield wells, where other sampling methods can’t be used reliably because their use results in dewatering of the well screen and alteration of sample chemistry (McAlary and Barker, 1987).

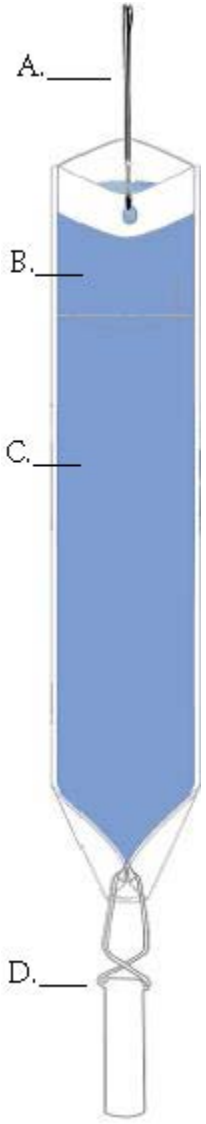
The HydraSleeve can collect samples from wells of any depth, and it can be used for single-event sampling or long-term groundwater monitoring programs. Because of its thin cross section and flexible construction, it can be used in narrow, constricted or damaged wells where rigid sampling devices may not fit. Using multiple HydraSleeves deployed in series along a single suspension line or tether, it is also possible to conduct in-well vertical profiling in wells in which contaminant concentrations are thought to be stratified.

As with all groundwater sampling devices, HydraSleeves should not be used to collect groundwater samples from wells in which separate (non-aqueous) phase hydrocarbons (i.e., gasoline, diesel fuel or jet fuel) are present because of the possibility of incorporating some of the separate-phase hydrocarbon into the sample.

Description of the HydraSleeve

The basic HydraSleeve (Figure 1) consists of the following components*:

- A suspension line or tether (A.), attached to the spring clip or directly to the top of the sleeve to deploy the device into and recover the device from the well. Tethers with depth indicators marked in 1-foot intervals are available from the manufacturer.
- A long, flexible, 4-mil thick lay-flat polyethylene sample sleeve (C.) sealed at the bottom (this is the sample chamber), which comes in different sizes, as discussed below with a self-sealing reed-type flexible polyethylene check valve built into the top of the sleeve (B.) to prevent water from entering or exiting the sampler except during sample acquisition.
- A reusable stainless-steel weight with clip (D.), which is attached to the bottom of the sleeve to carry it down the well to its intended depth in the water column. Bottom weights available from the manufacturer are 0.75" OD and are available in a variety of sizes. An optional top weight may be attached to the top of the HydraSleeve to carry it to depth and to compress it at the bottom of the well (not shown in Figure 1);
- A discharge tube that is used to puncture the HydraSleeve after it is recovered from the well so the sample can be decanted into sample bottles (not shown).
- Just above the self-sealing check valve at the top of the sleeve are two holes which provide attachment points for the spring clip and/or suspension line or tether. At the bottom of the sample sleeve are two holes which provide attachment points for the weight clip and weight.



*Other configurations such as top weighted assemblies, Super/SkinnySleeves, Speedbags, and W3 Hybrids are available.

Note: The sample sleeve and the discharge tube are designed for one-time use and are disposable. The spring clip, weight and weight clip may be reused after thorough cleaning. Suspension cord is generally disposed after one use although, if it is dedicated to the well, it may be reused at the discretion of the sampling personnel.

Selecting the HydraSleeve Size to Meet Site-Specific Sampling Objectives

It is important to understand that each HydraSleeve is able to collect a finite volume of sample because, after the HydraSleeve is deployed, you only get one chance to collect an undisturbed sample. Thus, the volume of sample required to meet your site-specific sampling and analytical requirements will dictate the size of HydraSleeve you need to meet these requirements.

Table 1. Dimensions and Volumes of HydraSleeve Models.

Diameter	Volume	Length	Lay-Flat Width	Filled Dia.
2-Inch HydraSleeves				
Standard 600 mls HydraSleeve	~600mls	30”	2.5”	1.4”
Standard 1-liter HydraSleeve	~1 Liter	38”	3”	1.9”
Super/SkinnySleeve 1-liter	~1 Liter	38”	2.5"	1.5”*
Super/SkinnySleeve 1.5-liter	~1.5 Liters	52”	2.5”	1.5”*
Super/SkinnySleeve 2-liter	*~2 Liters*	*66"*	*2.5"*	*1.5"**
4-Inch HydraSleeves				
Standard 2.5 liter	~2 Liters	38”	4”	2.7”

* outside diameter on the Heavy Duty Universal Super/SkinnySleeves is 1.5" however when using with schedule 40 hardware the O.D. of the assembly will be 1.9"

It's also recommended that you size the diameter of the HydraSleeve according to the diameter of the well (i.e. use 2-inch HydraSleeves in 2-inch wells). Using smaller sleeves in larger diameter wells (i.e. 2-inch HydraSleeves in 4-inch wells) will result in a longer fill rate and will require special retrieval instructions (explained later).

The volume of sample collected by the HydraSleeve varies with the diameter and length of the HydraSleeve. Dimensions and volumes of available HydraSleeve models are detailed in Table 1.

HydraSleeves can be custom-fabricated by GeoInsight in varying diameters and lengths to meet specific volume requirements. HydraSleeves can also be deployed in series (i.e., multiple HydraSleeves attached to one tether) to collect additional sample to meet specific volume requirements, as described below.

If you have questions regarding the availability of sufficient volume of sample to satisfy laboratory requirements for analysis, it is recommended that you contact the laboratory to discuss the minimum volumes needed for each suite of analytes. Laboratories often require only 10% to 25% of the volume they specify to complete analysis for specific suites of analytes, so they can often work with much smaller sample volumes that can easily be supplied using a HydraSleeve.

HydraSleeve Deployment

Information Required Before Deploying a HydraSleeve

Before installing a HydraSleeve in any well, you will need to know the following:

- The inside diameter of the well
- The length of the well screen
- The water level in the well
- The position of the well screen in the well
- The total depth of the well

The inside diameter of the well is used to determine the appropriate HydraSleeve diameter for use in the well. The other information is used to determine the proper placement of the HydraSleeve in the well to collect a representative sample from the screen (see HydraSleeve Placement, below), and to determine the appropriate length of tether to attach to the HydraSleeve to deploy it at the appropriate position in the well.

Most of this information (with the exception of the water level) should be available from the well log; if not, it will have to be collected by some other means. The inside diameter of the well can be measured at the top of the well casing, and the total depth of the well can be measured by sounding the bottom of the well with a weighted tape. The position and length of the well screen may have to be determined using a down-hole camera if a well log is not available. The water level in the well can be measured using any commonly available water-level gauge.

HydraSleeve Placement

The HydraSleeve is designed to collect a sample directly from the well screen. It fills by pulling it up through the screen a distance equivalent to the length of the sampler when correctly sized to the well diameter. This upward motion causes the top check valve to open, which allows the device to fill. To optimize sample recovery, it is recommended that the HydraSleeve be placed in the well so that the bottom weight rests on the bottom of the well and the top of the HydraSleeve is as close to the bottom of the well screen as possible. This should allow the sampler to fill before the top of the device reaches the top of the screen as it is pulled up through the water column, and ensure that only water from the screen is collected as the sample. In short-screen wells, or wells with a short water column, it may be necessary to use a top-weight on the HydraSleeve to compress it in the bottom of the well so that, when it is recovered, it has room to fill before it reaches the top of the screen.

Example

2" ID PVC well, 50' total depth, 10' screen at the bottom of the well, with water level above the screen (the entire screen contains water).

Correct Placement (figure 2): Using a standard HydraSleeve for a 2" well (2.5" flat width/1.5" filled OD x 30" long, 600 ml volume), deploy the sampler so the weight (a 5 oz., 2.5" long weight with a 2" long clip) rests at the bottom of the well. The top of the sleeve is thus set at ~34" above the bottom of the well. When the sampler is recovered, it will be pulled upward approximately 30" before it is filled; therefore, it is full (and the top check valve closes) at approximately 64" (5.3 feet) above the bottom of the well, which is well before the sampler reaches the top of the screen. In this example, only water from the screen is collected as a sample.

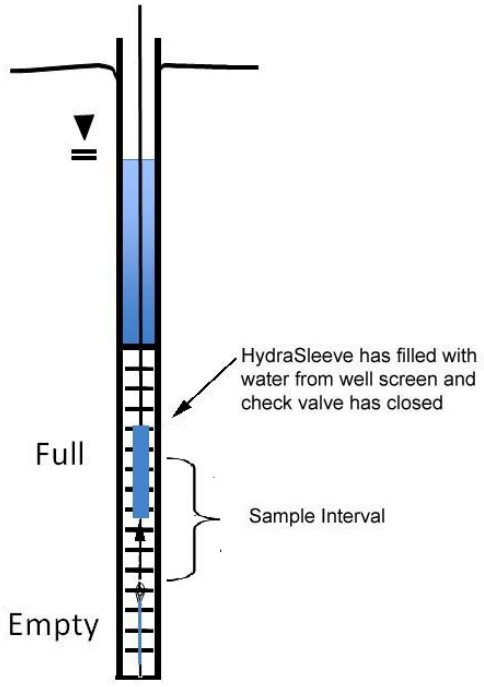


Figure 2. Correct Placement of HydraSleeve.

Incorrect Placement (figure 3): If the well screen in this example was only 5' long, and the HydraSleeve was placed as above, it would not fill before the top of the device reached the top of the well screen, so the sample would include water from above the screen, which may not have the same chemistry.

The solution? Deploy the HydraSleeve with a top weight, so that it is collapsed to within 6" of the bottom of the well. When the HydraSleeve is recovered, it will fill within 36" (3 feet) from the bottom of the well, or 2-feet before the sampler reaches the top of the screen, so it collects only water from the screen as the sample.

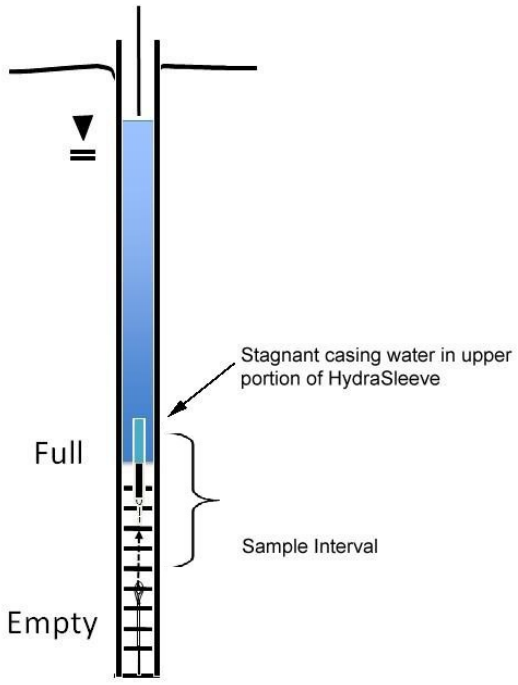


Figure 3. Incorrect placement of HydraSleeve.

This example illustrates one of many types of HydraSleeve placements. More complex placements are discussed in a later section.

NOTE: Using smaller diameter HydraSleeves (2-inch) in larger diameter wells (4-inch) causes a slower fill rate. Special retrieval methods are necessary if this is your set up (shown later in this document).

Procedures for Sampling with the HydraSleeve

Collecting a groundwater sample with a HydraSleeve is usually a simple one-person operation.

Note: Before deploying the HydraSleeve in the well, collect the depth-to-water measurement that you will use to determine the preferred position of the HydraSleeve in the well. This measurement may also be used with measurements from other wells to create a groundwater contour map. If necessary, also measure the depth to the bottom of the well to verify actual well depth to confirm your decision on placement of the HydraSleeve in the water column.

Measure the correct amount of tether needed to suspend the HydraSleeve in the well so that the weight will rest on the bottom of the well (or at your preferred position in the well). Make sure to account for the need to leave a few feet of tether at the top of the well to allow recovery of the sleeve.

Note: Always wear sterile gloves when handling and discharging the HydraSleeve.

I. Assembling the Basic HydraSleeve*

1. Remove the HydraSleeve from its packaging, unfold it, and hold it by its top.
2. Crimp the top of the HydraSleeve by folding the hard polyethylene reinforcing strips at the holes.
3. Attach the spring clip to the holes to ensure that the top will remain open until the sampler is retrieved.
4. Attach the tether to the spring clip by tying a knot in the tether.

Note: Alternatively, if spring clips are not being utilized, attach the tether to one (NOT both) of the holes at the top of the Hydrasleeve by tying a knot in the tether.

5. Fold the flaps with the two holes at the bottom of the HydraSleeve together to align the holes and slide the weight clip through the holes.
6. Attach a weight to the bottom of the weight clip to ensure that the HydraSleeve will descend to the bottom of the well.

*See Super/SkinnySleeve assembly manual and HydraSleeve Field Manual for other assembly instructions.

II. Deploying the HydraSleeve

1. Using the tether, carefully lower the HydraSleeve to the bottom of the well, or to your preferred depth in the water column

   During installation, hydrostatic pressure in the water column will keep the self-sealing check valve at the top of the HydraSleeve closed, and ensure that it retains its flat, empty profile for an indefinite period prior to recovery.

Note: Make sure that it is not pulled upward at any time during its descent. If the HydraSleeve is pulled upward at a rate greater than 0.5'/second at any time prior to recovery, the top check valve will open and water will enter the HydraSleeve prematurely.

2. Secure the tether at the top of the well by placing the well cap on the top of the well casing and over the tether.

Note: Alternatively, you can tie the tether to a hook on the bottom of the well cap (you will need to leave a few inches of slack in the line to avoid pulling the sampler up as the cap is removed at the next sampling event).

III. Equilibrating the Well

The equilibration time is the time it takes for conditions in the water column (primarily flow dynamics and contaminant distribution) to restabilize after vertical mixing occurs (caused by installation of a sampling device in the well).

- Situation: The HydraSleeve is deployed for the first time or for only one time in a well

  The basic HydraSleeve is very thin in cross section and displaces very little water (<100 ml) during deployment so, unlike most other sampling devices, it does not disturb the water column to the point at which long equilibration times are necessary to ensure recovery of a representative sample.

  In some cases, like when useing the SpeedBags, the HydraSleeve can be recovered immediately (with no equilibration time) or within a few hours. In regulatory jurisdictions that impose specific requirements for equilibration times prior to recovery of no-purge sampling devices, these requirements should be followed.

  NOTE: If using top weights additional equilibration time is needed to allow the top weight time to compress the HydraSleeve into the bottom of the well.

- Situation: The HydraSleeve is being deployed for recovery during a future sampling event.

  In periodic (i.e., quarterly, semi-annual, or annual) sampling programs, the sampler for the current sampling event can be recovered and a new sampler (for the next sampling event) deployed immediately thereafter, so the new sampler remains in the well until the next sampling event.

Thus, a long equilibration time is ensured and, at the next sampling event, the sampler can be recovered immediately. This means that separate mobilizations, to deploy and then to recover the sampler, are not required. HydraSleeves can be left in a well for an indefinite period of time without concern.

IV. HydraSleeve Recovery and Sample Collection

1. Hold on to the tether while removing the well cap.
2. Secure the tether at the top of the well while maintaining tension on the tether (but without pulling the tether upwards)
3. Measure the water level in the well.
4. Use one of the following 3 retrieval methods. In all 3 scenarios, when the HydraSleeve is full, the top check valve will close. You should begin to feel the weight of the HydraSleeve on the tether and it will begin to displace water. The closed check valve prevents loss of sample and entry of water from zones above the well screen as the HydraSleeve is recovered.

   a. In one smooth motion, pull the tether up 30"-60" (the length of the sampler) at a rate of about 1 foot per second (or faster). The motion will open the top check valve and allow the HydraSleeve to fill (it should fill in about 1:1 ratio or the length of the HydraSleeve if the sleeve is sized to fit the well). This is analogous to coring the water column in the well from the bottom up.

   b. There are times it is recommended that the HydraSleeve be oscillated in the screen zone to ensure it is full before leaving the screen area. Pull up 1-3 feet, let the sleeve assembly drop back down and repeat 3-5 times before pulling the sleeve to the surface. The collection zone will be the oscillation zone. ***When in doubt use this retrieval method.***

   c. SpeedBags require check valve activation and oscillation during recovery: When retrieving the SpeedBag, pull up hard 1-2 feet to open the check valve; let the assembly drop back down to the starting point; REPEAT THIS PROCESS 4 TIMES; and then quickly recover the SpeedBag through the well sceen to the surface.

5. Continue pulling the tether upward until the HydraSleeve is at the top of the well.
6. Discard the small volume of water trapped in the Hydrasleeve above the check valve by pinching it off at the top under the stiffeners (above the check valve).

v. Sample Discharge

NOTE: Sample collection should be done immediately after the HydraSleeve has been brought to the surface to preserve sample integrity.

Be sure you have discarded the water sitting above the check valve – see step #6 above.

1. Remove the discharge tube from its sleeve.
2. Hold the HydraSleeve at the check valve
3. Puncture the HydraSleeve at least 3-4 inches below the reinforcement strips with the pointed end of the discharge tube. NOTE: For some contaminants (VOC's/sinkers) the best location for discharge is the middle to bottom of the sampler. This would be representative of the deeper portion of the well screen.
4. Discharge water from the HydraSleeve into your sample containers. Control the discharge from the HydraSleeve by either raising the bottom of the sleeve, by squeezing it like a tube of toothpaste, or both.
5. Continue filling sample containers until all are full.

Measurement of Field Indicator Parameters

Field indicator parameter measurement is generally done during well purging and sampling to confirm when parameters are stable and sampling can begin. Because no-purge sampling does not require purging, field indicator parameter measurement is not necessary for the purpose of confirming when purging is complete.

If field indicator parameter measurement is required to meet a specific non-purging regulatory requirement, it can be done by taking measurements from water within a HydraSleeve that is not used for collecting a sample to submit for laboratory analysis (i.e., a second HydraSleeve installed in conjunction with the primary sample collection HydraSleeve [see Multiple Sampler Deployment below]).

Alternate Deployment Strategies

Deployment in Wells with Limited Water Columns

For wells in which only a limited water column needs to be sampled, the HydraSleeve can be deployed with an optional top weight in addition to a bottom weight. The top weight will collapse the HydraSleeve to a very short (approximately 6" to 24") length, depending on the length and volume of the sampler. This allows the HydraSleeve to fill in a water column only 3' to 10' in height (again) depending on the sampler size. Note the SuperSleeves accomplish the same thing but provide greater sample volume at a lower per sample cost.

Multiple Sampler Deployment

Multiple sampler deployment in a single well screen can accomplish two purposes:

1. It can collect additional sample volume to satisfy site or laboratory-specific sample volume requirements.
2. It can be used to collect samples from multiple intervals in the screen to allow identification of possible contaminant stratification.

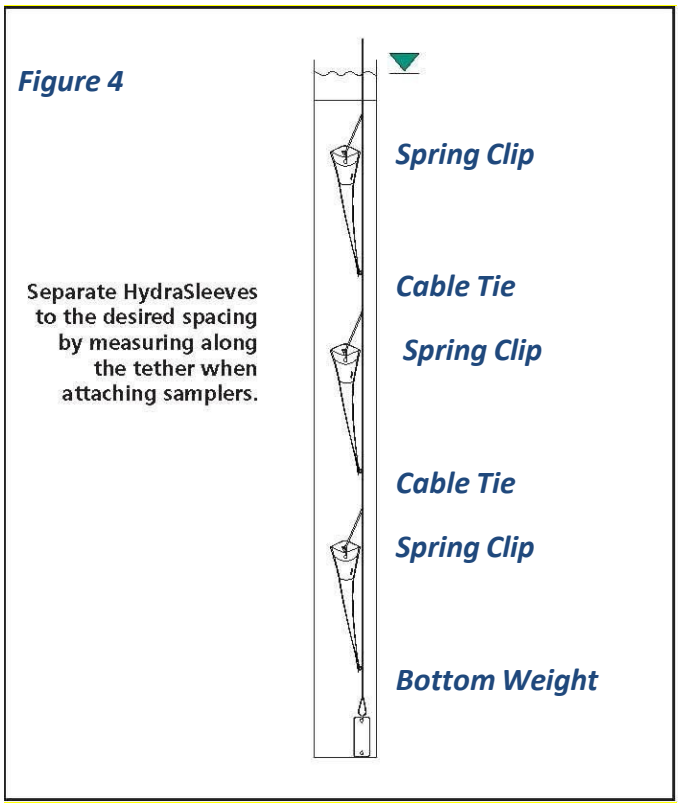


Figure 5. Multiple HydraSleeve deployment

If there is a need for only 2 samplers, they can be installed as follows. The first sampler can be attached to the tether as described above, a second attached to the bottom of the first using your desired length of tether between the two and the weight attached to the bottom of the second sampler (figure 6). This method can only be used with 2 samplers; 3 or more HydraSleeves in tandem need to be attached as described above.

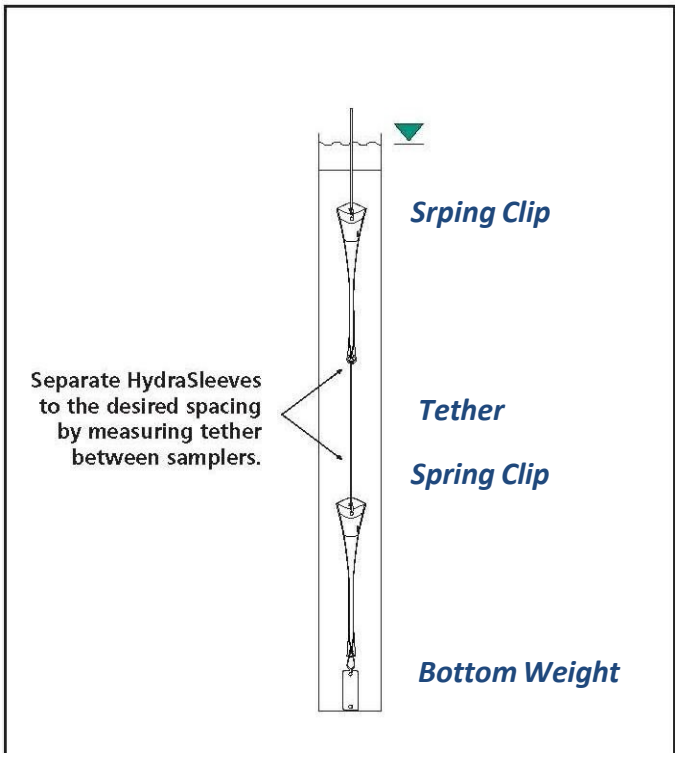


Figure 5. Alternative method for deploying multiple HydraSleeves.

In either case, when attaching multiple HydraSleeves in series, more weight will be required to hold the samplers in place in the well than would be required with a single sampler. Recovery of multiple samplers and collection of samples is done in the same manner as for single sampler deployments.

Post-Sampling Activities

The recovered HydraSleeve and the sample discharge tubing should be disposed as per the solid waste management plan for the site. To prepare for the next sampling event, a new HydraSleeve can be deployed in the well (as described previously) and left in the well until the next sampling event, at which time it can be recovered.

The weight and weight clip can be reused on this sampler after they have been thoroughly cleaned as per the site equipment decontamination plan. The tether may be dedicated to the well and reused or discarded at the discretion of sampling personnel.

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EPA Method 537

HALEY ALDRICH

EPA Document #: EPA/600/R-08/092

METHOD 537. DETERMINATION OF SELECTED PERFLUORINATED ALKYL ACIDS IN DRINKING WATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (LC/MS/MS)

Version 1.1
September 2009

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METHOD 537

DETERMINATION OF SELECTED PERFLUORINATED ALKYL ACIDS IN DRINKING WATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (LC/MS/MS)

1. SCOPE AND APPLICATION

1.1 This is a liquid chromatography/tandem mass spectrometry (LC/MS/MS) method for the determination of selected perfluorinated alkyl acids (PFAAs) in drinking water. Accuracy and precision data have been generated in reagent water, and finished ground and surface waters for the compounds listed in the table below.

Analyte	Acronym	Chemical Abstract Services Registry Number (CASRN)
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	—
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	—
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluorononanoic acid	PFNA	375-95-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorotetradecanoic acid	PFTA	376-06-7
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluoroundecanoic acid	PFUnA	2058-94-8

1.2 The Minimum Reporting Level (MRL) is the lowest analyte concentration that meets Data Quality Objectives (DQOs) that are developed based on the intended use of this method. The single laboratory lowest concentration MRL (LCMRL) is the lowest true concentration for which the future recovery is predicted to fall, with high confidence (99%), between 50 and 150% recovery. Single laboratory LCMRLs for analytes in this method range from 2.9-14 ng/L, and are listed in Table 5. The procedure used to determine the LCMRL is described elsewhere.[1]

1.3 Laboratories using this method will not be required to determine the LCMRL for this method, but will need to demonstrate that their laboratory MRL for this method meets the requirements described in Section 9.2.5.

1.4 Determining the Detection Limit (DL) for analytes in this method is optional (Sect. 9.2.7). Detection limit is defined as the statistically calculated minimum concentration that can be measured with 99% confidence that the reported value is greater than zero.[2] The DL is compound dependent and is dependent on extraction efficiency, sample matrix, fortification concentration, and instrument performance.

1.5 This method is intended for use by analysts skilled in solid phase extractions, the operation of LC/MS/MS instruments, and the interpretation of the associated data.

1.6 METHOD FLEXIBILITY – In recognition of technological advances in analytical systems and techniques, the laboratory is permitted to modify the evaporation technique, separation technique, LC column, mobile phase composition, LC conditions and MS and MS/MS conditions (Sect. 6.12, 9.1.1, 10.2, and 12.1). Changes may not be made to sample collection and preservation (Sect. 8), the sample extraction steps (Sect. 11), or to the quality control requirements (Sect. 9). Method modifications should be considered only to improve method performance. Modifications that are introduced in the interest of reducing cost or sample processing time, but result in poorer method performance, should not be used. Analytes must be adequately resolved chromatographically in order to permit the mass spectrometer to dwell on a minimum number of compounds eluting within a retention time window. Instrumental sensitivity (or signal-to-noise) will decrease if too many compounds are permitted to elute within a retention time window. In all cases where method modifications are proposed, the analyst must perform the procedures outlined in the initial demonstration of capability (IDC, Sect. 9.2), verify that all Quality Control (QC) acceptance criteria in this method (Sect. 9) are met, and that acceptable method performance can be verified in a real sample matrix (Sect. 9.3.6).

NOTE: The above method flexibility section is intended as an abbreviated summation of method flexibility. Sections 4-12 provide detailed information of specific portions of the method that may be modified. If there is any perceived conflict between the general method flexibility statement in Section 1.6 and specific information in Sections 4-12, Sections 4-12 supersede Section 1.6.

2. SUMMARY OF METHOD

2.1 A 250-mL water sample is fortified with surrogates and passed through a solid phase extraction (SPE) cartridge containing polystyrenedivinylbenzene (SDVB) to extract the method analytes and surrogates. The compounds are eluted from the solid phase with a small amount of methanol. The extract is concentrated to dryness with nitrogen in a heated water bath, and then adjusted to a 1-mL volume with 96:4% (vol/vol) methanol:water after adding the IS(s). A 10-µL injection is made into an LC equipped with a C_{18} column that is interfaced to an MS/MS. The analytes are separated and

identified by comparing the acquired mass spectra and retention times to reference spectra and retention times for calibration standards acquired under identical LC/MS/MS conditions. The concentration of each analyte is determined by using the internal standard technique. Surrogate analytes are added to all Field and QC Samples to monitor the extraction efficiency of the method analytes.

3. DEFINITIONS

3.1 ANALYSIS BATCH – A set of samples that is analyzed on the same instrument during a 24-hour period, including no more than 20 Field Samples, that begins and ends with the analysis of the appropriate Continuing Calibration Check (CCC) standards. Additional CCCs may be required depending on the length of the analysis batch and/or the number of Field Samples.

3.2 CALIBRATION STANDARD (CAL) – A solution prepared from the primary dilution standard solution and/or stock standard solution, internal standard(s), and the surrogate(s). The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 COLLISIONALLY ACTIVATED DISSOCIATION (CAD) – The process of converting the precursor ion's translational energy into internal energy by collisions with neutral gas molecules to bring about dissociation into product ions.

3.4 CONTINUING CALIBRATION CHECK (CCC) – A calibration standard containing the method analytes, internal standard(s) and surrogate(s). The CCC is analyzed periodically to verify the accuracy of the existing calibration for those analytes.

3.5 DETECTION LIMIT (DL) – The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero. This is a statistical determination of precision (Sect. 9.2.7), and accurate quantitation is not expected at this level.[2]

3.6 EXTRACTION BATCH – A set of up to 20 Field Samples (not including QC samples) extracted together by the same person(s) during a work day using the same lot of SPE devices, solvents, surrogate, internal standard and fortifying solutions. Required QC samples include Laboratory Reagent Blank, Laboratory Fortified Blank, Laboratory Fortified Sample Matrix, and either a Field Duplicate or Laboratory Fortified Sample Matrix Duplicate.

3.7 FIELD DUPLICATES (FD1 and FD2) – Two separate samples collected at the same time and place under identical circumstances, and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

3.8 FIELD REAGENT BLANK (FRB) – An aliquot of reagent water that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.9 INTERNAL STANDARD (IS) – A pure chemical added to an extract or standard solution in a known amount(s) and used to measure the relative response of other method analytes and surrogates that are components of the same solution. The internal standard must be a chemical that is structurally similar to the method analytes, has no potential to be present in water samples, and is not a method analyte.

3.10 LABORATORY FORTIFIED BLANK (LFB) – A volume of reagent water or other blank matrix to which known quantities of the method analytes and all the preservation compounds are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.11 LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) – A preserved field sample to which known quantities of the method analytes are added in the laboratory. The LFSM is processed and analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate sample extraction and the measured values in the LFSM corrected for background concentrations.

3.12 LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LFSMD) – A duplicate of the Field Sample used to prepare the LFSM. The LFSMD is fortified, extracted, and analyzed identically to the LFSM. The LFSMD is used instead of the Field Duplicate to assess method precision when the occurrence of method analytes is low.

3.13 LABORATORY REAGENT BLANK (LRB) – An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents and reagents, sample preservatives, internal standard, and surrogates that are used in the analysis batch. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.14 LOWEST CONCENTRATION MINIMUM REPORTING LEVEL (LCMRL) – The single laboratory LCMRL is the lowest true concentration for which a future recovery is expected, with 99% confidence, to be between 50 and 150% recovery.[1]

3.15 MATERIAL SAFETY DATA SHEET (MSDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.16 MINIMUM REPORTING LEVEL (MRL) – The minimum concentration that can be reported as a quantitated value for a method analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard for that analyte and can only be used if acceptable QC criteria for this standard are met. A procedure for verifying a laboratory's MRL is provided in Section 9.2.5.

3.17 PRECURSOR ION – For the purpose of this method, the precursor ion is the deprotonated molecule ($[M-H]^-$) of the method analyte. In MS/MS, the precursor ion is mass selected and fragmented by collisionally activated dissociation to produce distinctive product ions of smaller *m/z*.

3.18 PRIMARY DILUTION STANDARD (PDS) SOLUTION – A solution containing the analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.19 PRODUCT ION – For the purpose of this method, a product ion is one of the fragment ions produced in MS/MS by collisionally activated dissociation of the precursor ion.

3.20 QUALITY CONTROL SAMPLE (QCS) – A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the source of calibration standards. The second source SSS is used to fortify the QCS at a known concentration. The QCS is used to check calibration standard integrity.

3.21 STOCK STANDARD SOLUTION (SSS) – A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.22 SURROGATE ANALYTE (SUR) – A pure chemical which chemically resembles method analytes and is extremely unlikely to be found in any sample. This chemical is added to a sample aliquot in known amount(s) before processing and is measured with the same procedures used to measure other method analytes. The purpose of the SUR is to monitor method performance with each sample.

4. INTERFERENCES

4.1 All glassware must be meticulously cleaned. Wash glassware with detergent and tap water, rinse with tap water, followed by a reagent water rinse. Non-volumetric glassware can be heated in a muffle furnace at 400 °C for 2 h or solvent rinsed. Volumetric glassware should be solvent rinsed and not be heated in an oven above 120 °C. Store clean glassware inverted or capped. Do not cover with aluminum foil because PFAAs can be potentially transferred from the aluminum foil to the glassware.

NOTE: PFAA standards, extracts and samples should not come in contact with any glass containers or pipettes as these analytes can potentially adsorb to glass surfaces. PFAA analyte, IS and SUR standards commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be prepared and stored in polypropylene containers.

4.2 Method interferences may be caused by contaminants in solvents, reagents (including reagent water), sample bottles and caps, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. The method analytes in this method can also be found in many common laboratory supplies and equipment, such as PTFE (polytetrafluoroethylene) products, LC solvent lines, methanol, aluminum foil, SPE sample transfer lines, etc.[3] All items such as these must be routinely demonstrated to be free from interferences (less than 1/3 the MRL for each method analyte) under the conditions of the analysis by analyzing laboratory reagent blanks as described in Section 9.3.1. **Subtracting blank values from sample results is not permitted.**

4.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the water. Humic and/or fulvic material can be co-extracted during SPE and high levels can cause enhancement and/or suppression in the electrospray ionization source or low recoveries on the SPE sorbent.[4-5] Total organic carbon (TOC) is a good indicator of humic content of the sample. Under the LC conditions used during method development, matrix effects due to total organic carbon (TOC) were not observed.

4.4 Relatively large quantities of the preservative (Sect. 8.1.2) are added to sample bottles. The potential exists for trace-level organic contaminants in these reagents. Interferences from these sources should be monitored by analysis of laboratory reagent blanks (Sect. 9.3.1), particularly when new lots of reagents are acquired.

4.5 SPE cartridges can be a source of interferences. The analysis of field and laboratory reagent blanks can provide important information regarding the presence or absence of such interferences. Brands and lots of SPE devices should be tested to ensure that contamination does not preclude analyte identification and quantitation.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining an awareness of OSHA regulations regarding safe handling of chemicals used in this method. A reference file of MSDSs should be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.[6-8]

5.2 PFOA has been described as "likely to be carcinogenic to humans."[9] Pure standard materials and stock standard solutions of these method analytes should be handled with suitable protection to skin and eyes, and care should be taken not to breathe the vapors or ingest the materials.

6. <u>EQUIPMENT AND SUPPLIES</u> (Brand names and/or catalog numbers are included for illustration only, and do not imply endorsement of the product.) Due to potential adsorption of analytes onto glass, polypropylene containers were used for all standard, sample and extraction preparations. Other plastic materials (e.g., polyethylene) which meet the QC requirements of Section 9 may be substituted.

6.1 SAMPLE CONTAINERS – 250-mL polypropylene bottles fitted with polypropylene screw caps. Sample bottles must be discarded after use.

6.2 POLYPROPYLENE BOTTLES – 4-mL narrow-mouth polypropylene bottles (VWR Cat. No.: 16066-960 or equivalent).

6.3 CENTRIFUGE TUBES – 15-mL conical polypropylene tubes with polypropylene screw caps for storing standard solutions and for collection of the extracts (Thomas Scientific Cat. No.: 2602A10 or equivalent).

6.4 AUTOSAMPLER VIALS – Polypropylene 0.3-mL autosampler vials (SUN SRi Cat. No.: 501-354) with polypropylene caps (SUN SRi Cat. No.: 501-357 or equivalent).

NOTE: Polypropylene vials and caps are necessary to prevent contamination of the sample from PTFE coated septa. However, polypropylene caps do not reseal, so evaporation occurs after injection. Thus, multiple injections from the same vial are not possible.

6.5 POLYPROPYLENE GRADUATED CYLINDERS – Suggested sizes include 25, 50, 100 and 1000-mL cylinders.

6.6 MICRO SYRINGES – Suggested sizes include 5, 10, 25, 50, 100, 250, 500 and 1000-µL syringes.

6.7 PLASTIC PIPETS – Polypropylene or polyethylene disposable pipets (Fisher Cat. No.: 13-711-7 or equivalent).

6.8 ANALYTICAL BALANCE – Capable of weighing to the nearest 0.0001 g.

6.9 SOLID PHASE EXTRACTION (SPE) APPARATUS FOR USING CARTRIDGES

6.9.1 SPE CARTRIDGES – 0.5 g, 6-mL SPE cartridges containing styrenedivinyl-benzene (SDVB) sorbent phase (Varian Cat. No.: 1225-5021 or equivalent).

6.9.2 VACUUM EXTRACTION MANIFOLD – A manual vacuum manifold with Visiprep™ large volume sampler (Supelco Cat. No. 57030 and 57275 or equivalent) for cartridge extractions, or an automatic/robotic sample preparation system designed for use with SPE cartridges, may be used if all QC requirements discussed in Section 9 are met. Extraction and/or elution steps may not be changed or omitted to accommodate the use of an automated system. Care must be taken with automated SPE systems to ensure the PTFE commonly used in these systems does not contribute to unacceptable analyte concentrations in the LRB (Sect. 9.3.1).

6.9.3 SAMPLE DELIVERY SYSTEM – Use of a polypropylene transfer tube system, which transfers the sample directly from the sample container to the SPE cartridge, is recommended, but not mandatory. Standard extraction manifolds come equipped with PTFE transfer tube systems. These can be replaced with 1/8" O.D. x 1/16" I.D. polypropylene or polyethylene tubing (Hudson Extrusions LLDPE or equivalent) cut to an appropriate length to ensure no sample contamination from the sample transfer lines. Other types of non-PTFE tubing may be used provided it meets the LRB (Sect. 9.3.1) and LFB (Sect. 9.3.3) QC requirements. The PTFE transfer tubes may be used, but an LRB must be run on each PFTE transfer tube and the QC requirements in Section 9.2.1 must be met. In the case of automated SPE, the removal of PTFE lines may not be feasible; therefore, LRBs will need to be rotated among the ports and must meet the QC requirements of Sections 9.2.1 and 9.3.1.

6.10 EXTRACT CONCENTRATION SYSTEM – Extracts are concentrated by evaporation with nitrogen using a water bath set no higher than 65 °C (Meyer N-Evap, Model 111, Organomation Associates, Inc. or equivalent).

6.11 LABORATORY OR ASPIRATOR VACUUM SYSTEM – Sufficient capacity to maintain a vacuum of approximately 10 to 15 inches of mercury for extraction cartridges.

6.12 LIQUID CHROMATOGRAPHY (LC)/TANDEM MASS SPECTROMETER (MS/MS) WITH DATA SYSTEM

6.12.1 LC SYSTEM – Instrument capable of reproducibly injecting up to 10-µL aliquots, and performing binary linear gradients at a constant flow rate near the flow rate used for development of this method (0.3 mL/min). The LC must be capable of pumping the water/methanol mobile phase without the use of a degasser which pulls vacuum on the mobile phase **bottle** (other types of degassers are acceptable). Degassers which pull vacuum on the mobile phase **bottle** will volatilize the ammonium acetate mobile phase causing the analyte peaks to shift to earlier retention times over the course of the analysis batch. The usage of a column heater is optional.

NOTE: During the course of method development, it was discovered that while idle for more than one day, PFAAs built up in the PTFE solvent transfer lines. To prevent long delays in purging high levels of PFAAs from the LC solvent lines, they were replaced with PEEK™ tubing and the PTFE solvent frits were replaced with stainless steel frits. It is not possible to remove all PFAA background contamination, but these measures help to minimize their background levels.

6.12.2 LC/TANDEM MASS SPECTROMETER – The LC/MS/MS must be capable of negative ion electrospray ionization (ESI) near the suggested LC flow rate of 0.3 mL/min. The system must be capable of performing MS/MS to produce unique product ions (Sect. 3.19) for the method analytes within specified retention time segments. A minimum of 10 scans across the chromatographic peak is required to ensure adequate precision. Data are demonstrated in Tables 5-9 using a triple quadrupole mass spectrometer (Waters Micromass Quattro Premier).

6.12.3 DATA SYSTEM – An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software should have the capability of processing stored LC/MS/MS data by recognizing an LC peak within any given retention time window. The software must allow integration of the ion abundance of any specific ion within specified time or scan number limits. The software must be able to calculate relative response factors, construct linear regressions or quadratic calibration curves, and calculate analyte concentrations.

6.12.4 ANALYTICAL COLUMN – An LC C_{18} column (2.1 x 150 mm) packed with 5 µm d_p C_{18} solid phase particles (Waters #: 186001301 or equivalent) was used. Any column that provides adequate resolution, peak shape, capacity, accuracy, and precision (Sect. 9) may be used.

7. REAGENTS AND STANDARDS

7.1 GASES, REAGENTS, AND SOLVENTS – Reagent grade or better chemicals should be used. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first determined that the reagent is of sufficiently high purity to permit its use without lessening the quality of the determination.

7.1.1 REAGENT WATER – Purified water which does not contain any measurable quantities of any method analytes or interfering compounds greater than 1/3 the MRL for each method analyte of interest. Prior to daily use, at least 3 L of reagent water should be flushed from the purification system to rinse out any build-up of analytes in the system's tubing.

7.1.2 METHANOL (CH_3OH, CAS#: 67-56-1) – High purity, demonstrated to be free of analytes and interferences (Tedia Absolv® grade or equivalent).

7.1.3 AMMONIUM ACETATE ($NH_4C_2H_3O_2$, CAS#: 631-61-8) – High purity, demonstrated to be free of analytes and interferences (Sigma-Aldrich ACS grade or equivalent).

7.1.4 20 mM AMMONIUM ACETATE/REAGENT WATER – To prepare 1 L, add 1.54 g ammonium acetate to 1 L of reagent water. This solution is prone to volatility losses and should be replaced at least every 48 hours.

7.1.5 TRIZMA® PRESET CRYSTALS, pH 7.0 (Sigma cat# T-7193 or equivalent) – Reagent grade. A premixed blend of Tris [Tris(hydroxymethyl)aminomethane] and Tris HCL [Tris(hydroxymethyl)aminomethane hydrochloride]. Alternatively, a mix of the two components with a weight ratio of 15.5/1 Tris HCL/Tris may be used. These blends are targeted to produce a pH near 7.0 at 25 °C in reagent water. Trizma® functions as a buffer, and removes free chlorine in chlorinated finished waters (Sect. 8.1.2).

7.1.6 NITROGEN – Used for the following purposes:

7.1.6.1 Nitrogen aids in aerosol generation of the ESI liquid spray and is used as collision gas in some MS/MS instruments. The nitrogen used should meet or exceed instrument manufacturer's specifications.

7.1.6.2 Nitrogen is used to concentrate sample extracts (Ultra High Purity or equivalent).

7.1.7 ARGON – Used as collision gas in MS/MS instruments. Argon should meet or exceed instrument manufacturer's specifications. Nitrogen gas may be used as the collision gas provided sufficient sensitivity (product ion formation) is achieved.

7.2 STANDARD SOLUTIONS – When a compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. PFAA analyte, IS and SUR standards commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be prepared and stored in polypropylene containers. Solution concentrations listed in this section were used to develop this method and are included as an example. Alternate concentrations may be used as necessary depending on instrument sensitivity and the calibration range used. Standards for sample fortification generally should be prepared in the smallest volume that can be accurately measured to minimize the addition of excess organic solvent to aqueous samples. **Even though stability times for standard solutions are suggested in the following sections, laboratories should use standard QC practices to determine when their standards need to be replaced.**

NOTE: Stock standards (Sect. 7.2.1.1, 7.2.2.1 and 7.2.3.1) were stored at ≤4 °C. Primary dilution standards (Sect. 7.2.1.2, 7.2.2.2 and 7.2.3.2) were stored at room temperature to prevent adsorption of the method analytes onto the container surfaces that may occur when refrigerated. Storing the standards at room temperature will also minimize daily imprecision due to the potential of inadequate room temperature stabilization.

7.2.1 INTERNAL (IS) STOCK STANDARD SOLUTIONS – This method uses three IS compounds listed in the table below. These isotopically labeled IS(s) were carefully chosen during method development because they encompass all the functional groups of the method analytes. Although alternate IS standards may be used provided they are isotopically labeled compounds with similar functional groups as the method analytes, the analyst must have documented reasons for using alternate IS(s). Alternate IS(s) must meet the QC requirements in Section 9.3.4. Note that different isotopic labels of the same IS(s) are acceptable (e.g., $^{13}C_2$-PFOA and $^{13}C_4$-PFOA) but will require modification of the MS/MS precursor and product ions.

Internal Standards	**Acronym**
Perfluoro-[1,2-$^{13}C_2$]octanoic acid	^{13}C-PFOA
Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate	^{13}C-PFOS
N-deuteriomethylperfluoro-1-octanesulfonamidoacetic acid	d_3-NMeFOSAA

7.2.1.1 IS STOCK STANDARD SOLUTIONS – These IS stocks can be obtained as individual certified stock standard solutions. During the development of this method, commercially obtained 50 µg/mL stock standard solutions in methanol were used (Wellington Labs, Perkin Elmer or equivalent). Analysis of the IS(s) is less complicated if the IS(s) purchased contains only the linear isomer. IS stock standard solutions were stable for at least 6 months when stored at 4 °C.

7.2.1.2 INTERNAL STANDARD PRIMARY DILUTION (IS PDS) STANDARD (1-4 ng/µL) – Prepare, or purchase commercially, the IS PDS at a suggested concentration of 1-4 ng/µL. If prepared from the individual stock standard solutions (Sect. 7.2.1.1), the table below can be used as a guideline for preparing the IS PDS. The IS PDS used in these studies was prepared in 96:4% (vol/vol) methanol:water. The IS PDS has been shown to be stable for at least two months when stored in polypropylene centrifuge tubes at room temperature. Use 10 µL of this 1-4 ng/µL solution to fortify the final 1-mL extracts (Sect. 11.5). This will yield a concentration of 10-40 pg/µL of each IS in the 1-mL extracts.

IS	Conc. of IS Stock (µg/mL)	Vol. Of IS Stock (µL)	Final Vol. of IS PDS (µL)	Final Conc. of IS PDS (ng/µL)
^{13}C-PFOA	1000	5.0	5000	1.0
^{13}C-PFOS	50	300.0	5000	3.0
d_3-NMeFOSAA	50	400.0	5000	4.0

7.2.2 SURROGATE (SUR) ANALYTE STANDARD SOLUTIONS – The three SUR(s) for this method are listed in the table below. These isotopically labeled SUR standards were carefully chosen during method development because they encompass most of the functional groups, as well as the water solubility range of the method analytes. Although alternate SUR standards may be used provided they are isotopically labeled compounds with similar functional groups as the method analytes, the analyst must have documented reasons for using alternate SUR standards. The alternate SUR standards chosen must still span the water solubility range of the method analytes. In addition, alternate SUR standards must meet the QC requirements in Section 9.3.5.

Surrogates	Acronym
Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid	^{13}C-PFHxA
Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	^{13}C-PFDA
N-deuterioethylperfluoro-1-octanesulfonamidoacetic acid	d_5-NEtFOSAA

7.2.2.1 SUR STOCK STANDARD SOLUTIONS – These SUR stocks can be obtained as individual certified stock standard solutions. During the development of this method, commercially obtained 50 µg/mL stock standard solutions in methanol containing 4% water (except for d_5-NEtFOSAA which was purchased in pure methanol) were used (Wellington Labs or equivalent). Analysis of the SUR(s) is less complicated if the SUR(s) purchased contains only the linear isomer. SUR stock standard solutions were stable for at least 6 months when stored at 4 °C.

7.2.2.2 SURROGATE PRIMARY DILUTION STANDARD (SUR PDS) (1-4 ng/µL) – Prepare, or purchase commercially, the SUR PDS at a suggested concentration of 1-4 ng/µL. If prepared from the individual stock standard solutions (Sect. 7.2.2.1), the table below can be used as a guideline for preparing the SUR PDS. The SUR PDS used in these studies was prepared in 96:4% (vol/vol) methanol:water. This solution is used to fortify all QC and Field Samples. The PDS has been shown to be stable for one year when stored in polypropylene centrifuge tubes at room temperature.

SUR	Conc. Of SUR Stock (µg/mL)	Vol. of SUR Stock (µL)	Final Vol. of SUR PDS (µL)	Final Conc. of SUR PDS (ng/µL)
^{13}C-PFHxA	50	100.0	5000	1.0
^{13}C-PFDA	50	100.0	5000	1.0
d_5-NEtFOSAA	50	400.0	5000	4.0

7.2.3 ANALYTE STANDARD SOLUTIONS – Analyte standards may be purchased commercially as ampoulized solutions or prepared from neat materials (see Table 3 for the analyte sources used during method development). If possible, purchase the method analytes as technical grade standards or neat materials. Standards or neat materials that contain only the linear isomer can be substituted only if technical grade (linear and branched isomers) standards or neat material cannot be purchased. PFHxS and PFOS must be purchased as technical grade (containing branched and linear isomers), as well as NEtFOSAA and NMeFOSAA (if commercially available). PFHxS and PFOS are not available as the acids listed in Section 1.1, but rather as their corresponding salts, such as Na^+ and K^+ (see Table 3). These salts are acceptable starting materials for the stock standards provided the measured mass is corrected for the salt content according to the equation below. Prepare the Analyte Stock and Primary Dilutions Standards as described below.

$$Mass_{acid} = Measured\ Mass_{salt} \times \frac{MW_{acid}}{MW_{salt}}$$

where:

MW_{acid} = the molecular weight of PFAA
MW_{salt} = the molecular weight of purchased salt

7.2.3.1 ANALYTE STOCK STANDARD SOLUTION – If preparing from neat material, accurately weigh approximately 5 mg of pure material to the nearest 0.1 mg into a 4-mL or larger polypropylene bottle (Sect. 6.2). Add 1 mL of the solvent indicated in the table below. Repeat for each method analyte. These stock standards were stable for at least 6 months when stored at -15 °C. When using these stock standards to prepare a PDS, care must be taken to ensure that these standards are at room temperature and adequately vortexed.

Analyte	Analyte Stock Solvent
PFHxA	96:4% (vol/vol) methanol:water
PFHpA	96:4% (vol/vol) methanol:water
PFOA	96:4% (vol/vol) methanol:water
PFNA	96:4% (vol/vol) methanol:water
PFDA	96:4% (vol/vol) methanol:water
PFUnA	96:4% (vol/vol) methanol:water
PFDoA	96:4% (vol/vol) methanol:water
PFTrDA	100% ethyl acetate
PFTA	100% ethyl acetate
PFBS	100% methanol
PFHxS	100% methanol
PFOS	100% methanol
NEtFOSAA	100% methanol
NMeFOSAA	100% methanol

7.2.3.2 ANALYTE PRIMARY DILUTION STANDARD (PDS) SOLUTION (0.5-2.5 ng/µL) – The analyte PDS contains all the method analytes of interest at various concentrations in methanol containing 4% water. The ESI and MS/MS response varies by compound; therefore, a mix of concentrations may be needed in the analyte PDS. See Tables 5-9 in Section 17 for suggested concentrations for each analyte. During method development, the analyte PDS was prepared such that approximately the same instrument response was obtained for all the analytes. The analyte PDS is prepared by dilution of the combined Analyte Stock Standard Solutions and is used to prepare the CAL standards, and fortify the LFBs, the LFSMs, the LFSMDs and FDs with the method analytes. The analyte PDS has been shown to be stable for 6 months when stored at room temperature.

7.2.4 CALIBRATION STANDARDS (CAL) – At least five calibration concentrations are required to prepare the initial calibration curve spanning a 20-fold concentration range (Sect. 10.2). Larger concentration ranges will require more calibration points. Prepare the CAL standards over the concentration range of interest from dilutions of the analyte PDS in methanol containing 4% reagent water. The suggested analyte concentrations found in Tables 5-9 can be used as a starting point for determining the calibration range. The IS and SUR are added to the CAL standards at a constant concentration. During method development, the concentrations of the SUR(s) were 10-40 pg/µL in the standard (40-160 ng/L in the sample) and the IS(s) were 10-40 pg/µL. The lowest concentration CAL standard must be at or below the MRL, which may depend on system sensitivity. The CAL standards may also be used as CCCs (Sect. 9.3.2). During method development, the CAL standards were shown to be stable for at least two weeks when stored at room temperature. Longer storage times are acceptable provided

appropriate QC measures are documented demonstrating the CAL standard stability.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE BOTTLE PREPARATION

8.1.1 Samples must be collected in a 250-mL polypropylene bottle fitted with a polypropylene screw-cap.

8.1.2 The preservation reagent, listed in the table below, is added to each sample bottle as a solid prior to shipment to the field (or prior to sample collection).

Compound	Amount	Purpose
Trizma®	5.0 g/L	buffering reagent and removes free chlorine

8.2 SAMPLE COLLECTION

8.2.1 The sample handler must wash their hands before sampling and wear nitrile gloves while filling and sealing the sample bottles. PFAA contamination during sampling can occur from a number of common sources, such as food packaging and certain foods and beverages. Proper hand washing and wearing nitrile gloves will aid in minimizing this type of accidental contamination of the samples.

8.2.2 Open the tap and allow the system to flush until the water temperature has stabilized (approximately 3 to 5 min). Collect samples from the flowing system.

8.2.3 Fill sample bottles, taking care not to flush out the sample preservation reagent. Samples do not need to be collected headspace free.

8.2.4 After collecting the sample, cap the bottle and agitate by hand until preservative is dissolved. Keep the sample sealed from time of collection until extraction.

8.3 FIELD REAGENT BLANKS (FRB)

8.3.1 A FRB must be handled along with each sample set. The sample set is composed of samples collected from the same sample site and at the same time. At the laboratory, fill the field blank sample bottle with reagent water and preservatives, seal, and ship to the sampling site along with the sample bottles. For each FRB shipped, an empty sample bottle (no preservatives) must also be shipped. At the sampling site, the sampler must open the shipped FRB and pour the preserved reagent water into the empty shipped sample bottle, seal and label this bottle as the FRB. The FRB is shipped back to the laboratory along with the samples and analyzed to ensure that PFAAs were not introduced into the sample during sample collection/handling.

8.3.2 The same batch of preservative must be used for the FRBs as for the field samples.

8.3.3 The reagent water used for the FRBs must be initially analyzed for method analytes as a LRB and must meet the LRB criteria in Section 9.3.1 prior to use. This requirement will ensure samples are not being discarded due to contaminated reagent water rather than contamination during sampling.

8.4 SAMPLE SHIPMENT AND STORAGE – Samples must be chilled during shipment and must not exceed 10 °C during the first 48 hours after collection. Sample temperature must be confirmed to be at or below 10 °C when the samples are received at the laboratory. Samples stored in the lab must be held at or below 6 °C until extraction, but should not be frozen.

NOTE: Samples that are significantly above 10° C, at the time of collection, may need to be iced or refrigerated for a period of time, in order to chill them prior to shipping. This will allow them to be shipped with sufficient ice to meet the above requirements.

8.5 SAMPLE AND EXTRACT HOLDING TIMES – Results of the sample storage stability study (Table 10) indicated that all compounds listed in this method have adequate stability for 14 days when collected, preserved, shipped and stored as described in Sections 8.1, 8.2, and 8.4. Therefore, water samples should be extracted as soon as possible but must be extracted within 14 days. Extracts must be stored at room temperature and analyzed within 28 days after extraction. The extract storage stability study data are presented in Table 11.

9. QUALITY CONTROL

9.1 QC requirements include the Initial Demonstration of Capability (IDC) and ongoing QC requirements that must be met when preparing and analyzing Field Samples. This section describes the QC parameters, their required frequencies, and the performance criteria that must be met in order to meet EPA quality objectives. The QC criteria discussed in the following sections are summarized in Tables 12 and 13. These QC requirements are considered the minimum acceptable QC criteria. Laboratories are encouraged to institute additional QC practices to meet their specific needs.

9.1.1 METHOD MODIFICATIONS – The analyst is permitted to modify LC columns, LC conditions, evaporation techniques, internal standards or surrogate standards, and MS and MS/MS conditions. Each time such method modifications are made, the analyst must repeat the procedures of the IDC. **Modifications to LC conditions should still produce conditions such that co-elution of the method analytes is minimized to reduce the probability of suppression/enhancement effects.**

9.2 INITIAL DEMONSTRATION OF CAPABILITY – The IDC must be successfully performed prior to analyzing any Field Samples. Prior to conducting the IDC, the analyst must first generate an acceptable Initial Calibration following the procedure outlined in Section 10.2.

9.2.1 INITIAL DEMONSTRATION OF LOW SYSTEM BACKGROUND – Any time a new lot of SPE cartridges, solvents, centrifuge tubes, disposable pipets, and autosampler vials are used, it must be demonstrated that an LRB is reasonably free of contamination and that the criteria in Section 9.3.1 are met. If an automated extraction system is used, an LRB should be extracted on each port to ensure that all the valves and tubing are free from potential PFAA contamination.

9.2.2 INITIAL DEMONSTRATION OF PRECISION (IDP) – Prepare, extract, and analyze four to seven replicate LFBs fortified near the midrange of the initial calibration curve according to the procedure described in Section 11. Sample preservatives as described in Section 8.1.2 must be added to these samples. The relative standard deviation (RSD) of the results of the replicate analyses must be less than 20%.

9.2.3 INITIAL DEMONSTRATION OF ACCURACY (IDA) – Using the same set of replicate data generated for Section 9.2.2, calculate average recovery. The average recovery of the replicate values must be within ± 30% of the true value.

9.2.4 INITIAL DEMONSTRATION OF PEAK ASYMMETRY FACTOR – Peak asymmetry factors must be calculated using the equation in Section 9.3.9 for the first two eluting peaks (if only two analytes are being analyzed, both must be evaluated) in a mid-level CAL standard. The peak asymmetry factors must fall in the range of 0.8 to 1.5. See guidance in Section 10.2.4.1 if the calculated peak asymmetry factors do not meet the criteria.

9.2.5 MINIMUM REPORTING LEVEL (MRL) CONFIRMATION – Establish a target concentration for the MRL based on the intended use of the method. The MRL may be established by a laboratory for their specific purpose or may be set by a regulatory agency. Establish an Initial Calibration following the procedure outlined in Section 10.2. The lowest CAL standard used to establish the Initial Calibration (as well as the low-level CCC, Section 10.3) must be at or below the concentration of the MRL. Establishing the MRL concentration too low may cause repeated failure of ongoing QC requirements. Confirm the MRL following the procedure outlined below.

9.2.5.1 Fortify, extract, and analyze seven replicate LFBs at the proposed MRL concentration. These LFBs must contain all method preservatives described in Section 8.1.2. Calculate the mean measured concentration (*Mean*) and standard deviation for these replicates. Determine the Half Range for the prediction interval of results (HR_{PIR}) using the equation below

$$HR_{PIR} = 3.963s$$

where

s = the standard deviation

3.963 = a constant value for seven replicates.[1]

9.2.5.2 Confirm that the upper and lower limits for the Prediction Interval of Result ($PIR = Mean \pm HR_{PIR}$) meet the upper and lower recovery limits as shown below

The Upper PIR Limit must be ≤150% recovery.

$$\frac{Mean + HR_{PIR}}{FortifiedConcentration} \times 100\% \leq 150\%$$

The Lower PIR Limit must be ≥ 50% recovery.

$$\frac{Mean - HR_{PIR}}{FortifiedConcentration} \times 100\% \geq 50\%$$

9.2.5.3 The MRL is validated if both the Upper and Lower PIR Limits meet the criteria described above (Sect. 9.2.5.2). If these criteria are not met, the MRL has been set too low and must be determined again at a higher concentration.

9.2.6 CALIBRATION CONFIRMATION – Analyze a QCS as described in Section 9.3.10 to confirm the accuracy of the standards/calibration curve.

9.2.7 DETECTION LIMIT DETERMINATION *(optional) – While DL determination is not a specific requirement of this method, it may be required by various regulatory bodies associated with compliance monitoring. It is the responsibility of the laboratory to determine if DL determination is required based upon the intended use of the data.*

9.2.7.1 Replicate analyses for this procedure should be done over at least three days (i.e., both the sample extraction and the LC/MS/MS analyses should be done over at least three days). Prepare at least seven replicate LFBs at a concentration estimated to be near the DL. This concentration may be estimated by selecting a concentration at 2-5 times the noise level. The DLs in Table 5 were calculated from LFBs fortified at various concentrations as indicated in the table. The appropriate fortification concentrations will be dependent upon the sensitivity of the LC/MS/MS system used. All preservation reagents listed in Section 8.1.2 must also be added to these samples. Analyze the seven replicates through all steps of Section 11.

NOTE: If an MRL confirmation data set meets these requirements, a DL may be calculated from the MRL confirmation data, and no additional analyses are necessary.

Calculate the *DL* using the following equation

$$DL = s \times t_{(n-1,1-\alpha=0.99)}$$

where

s = standard deviation of replicate analyses
$t_{(n\text{-}1,\ 1\text{-}\alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = number of replicates.

NOTE: Do not subtract blank values when performing DL calculations. The DL is a statistical determination of precision only.[2] If the DL replicates are fortified at a low enough concentration, it is likely that they will not meet the precision and accuracy criteria for CCCs. Therefore, no precision and accuracy criteria are specified.

9.2.7.2 If a laboratory is establishing their own MRL, the calculated DLs should not be used as the MRL for analytes that commonly occur as background contaminants. Method analytes that are seen in the background should be reported as present in Field Samples, only after careful evaluation of the background levels. It is recommended that a MRL be established at the mean LRB concentrations + 3σ or 3 times the mean LRB concentration, whichever is greater. This value should be calculated over a period of time, to reflect variability in the blank measurements. It is recommended that this value be used as an MRL in order to avoid reporting false positive results.

9.3 ONGOING QC REQUIREMENTS – This section summarizes the ongoing QC criteria that must be followed when processing and analyzing Field Samples.

9.3.1 LABORATORY REAGENT BLANK (LRB) – An LRB is required with each extraction batch (Sect. 3.6) to confirm that potential background contaminants are not interfering with the identification or quantitation of method analytes. If more than 20 Field Samples are included in a batch, analyze an LRB for every 20 samples. If the LRB produces a peak within the retention time window of any analyte that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples. Background contamination must be reduced to an acceptable level before proceeding. Background from method analytes or other contaminants that interfere with the measurement of method analytes must be below 1/3 of the MRL. Blank contamination is estimated by extrapolation, if the concentration is below the lowest CAL standard. This extrapolation procedure is not allowed for sample results as it may not meet data quality objectives. If the method analytes are

detected in the LRB at concentrations equal to or greater than this level, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch. Because background contamination is a significant problem for several method analytes, it is highly recommended that the analyst maintain a historical record of LRB data.

9.3.2 CONTINUING CALIBRATION CHECK (CCC) – CCC Standards are analyzed at the beginning of each analysis batch, after every 10 Field Samples, and at the end of the analysis batch. See Section 10.3 for concentration requirements and acceptance criteria.

9.3.3 LABORATORY FORTIFIED BLANK (LFB) – An LFB is required with each extraction batch (Sect. 3.6). The fortified concentration of the LFB must be rotated between low, medium, and high concentrations from batch to batch. The low concentration LFB must be as near as practical to, but no more than two times, the MRL. Similarly, the high concentration LFB should be near the high end of the calibration range established during the initial calibration (Sect. 10.2). Results of the low-level LFB analyses must be 50-150% of the true value. Results of the medium and high-level LFB analyses must be 70-130% of the true value. If the LFB results do not meet these criteria for method analytes, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch.

9.3.4 INTERNAL STANDARDS (IS) – The analyst must monitor the peak areas of the IS(s) in all injections during each analysis day. The IS responses (peak areas) in any chromatographic run must be within 70-140% of the response in the most recent CCC and must not deviate by more than 50% from the average area measured during initial analyte calibration. If the IS areas in a chromatographic run do not meet these criteria, inject a second aliquot of that extract aliquotted into a new capped autosampler vial. Random evaporation losses have been observed with the polypropylene caps causing high IS(s) areas.

9.3.4.1 If the reinjected aliquot produces an acceptable IS response, report results for that aliquot.

9.3.4.2 If the reinjected extract fails again, the analyst should check the calibration by reanalyzing the most recently acceptable CAL standard. If the CAL standard fails the criteria of Section 10.3, recalibration is in order per Section 10.2. If the CAL standard is acceptable, extraction of the sample may need to be repeated provided the sample is still within the holding time. Otherwise, report results obtained from the reinjected extract, but annotate as suspect. Alternatively, collect a new sample and re-analyze.

9.3.5 SURROGATE RECOVERY – The SUR standard is fortified into all samples, CCCs, LRBs, LFBs, LFSMs, LFSMDs, FD, and FRB prior to extraction. It is also added to the CAL standards. The SUR is a means of assessing method

performance from extraction to final chromatographic measurement. Calculate the recovery (%R) for the SUR using the following equation

$$\%R = \left(\frac{A}{B}\right) \times 100$$

where

A = calculated SUR concentration for the QC or Field Sample
B = fortified concentration of the SUR.

9.3.5.1 SUR recovery must be in the range of 70-130%. When SUR recovery from a sample, blank, or CCC is less than 70% or greater than 130%, check 1) calculations to locate possible errors, 2) standard solutions for degradation, 3) contamination, and 4) instrument performance. Correct the problem and reanalyze the extract.

9.3.5.2 If the extract reanalysis meets the SUR recovery criterion, report only data for the reanalyzed extract.

9.3.5.3 If the extract reanalysis fails the 70-130% recovery criterion, the analyst should check the calibration by injecting the last CAL standard that passed. If the CAL standard fails the criteria of Section 10.3, recalibration is in order per Section 10.2. If the CAL standard is acceptable, extraction of the sample should be repeated provided the sample is still within the holding time. If the re-extracted sample also fails the recovery criterion, report all data for that sample as suspect/SUR recovery to inform the data user that the results are suspect due to SUR recovery. Alternatively, collect a new sample and re-analyze.

9.3.6 LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) – Analysis of an LFSM is required in each extraction batch and is used to determine that the sample matrix does not adversely affect method accuracy. Assessment of method precision is accomplished by analysis of a Field Duplicate (FD) (Sect. 9.3.7); however, infrequent occurrence of method analytes would hinder this assessment. If the occurrence of method analytes in the samples is infrequent, or if historical trends are unavailable, a second LFSM, or LFSMD, must be prepared, extracted, and analyzed from a duplicate of the Field Sample. Extraction batches that contain LFSMDs will not require the extraction of a FD. If a variety of different sample matrices are analyzed regularly, for example, drinking water from groundwater and surface water sources, method performance should be established for each. Over time, LFSM data should be documented by the laboratory for all routine sample sources.

9.3.6.1 Within each extraction batch (Sect. 3.6), a minimum of one Field Sample is fortified as an LFSM for every 20 Field Samples analyzed. The LFSM is prepared by spiking a sample with an appropriate amount of the Analyte

PDS (Sect. 7.2.3.2). Select a spiking concentration that is greater than or equal to the matrix background concentration, if known. Use historical data and rotate through the low, mid and high concentrations when selecting a fortifying concentration.

9.3.6.2 Calculate the percent recovery (%*R*) for each analyte using the equation

$$\%R = \frac{(A - B)}{C} \times 100$$

where

A = measured concentration in the fortified sample
B = measured concentration in the unfortified sample
C = fortification concentration.

9.3.6.3 Analyte recoveries may exhibit matrix bias. For samples fortified at or above their native concentration, recoveries should range between 70-130%, except for low-level fortification near or at the MRL (within a factor of 2-times the MRL concentration) where 50-150% recoveries are acceptable. If the accuracy of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCCs, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.3.7 FIELD DUPLICATE OR LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (FD or LFSMD) – Within each extraction batch (not to exceed 20 Field Samples, Sect. 3.6), a minimum of one FD or LFSMD must be analyzed. Duplicates check the precision associated with sample collection, preservation, storage, and laboratory procedures. If method analytes are not routinely observed in Field Samples, an LFSMD should be analyzed rather than an FD.

9.3.7.1 Calculate the relative percent difference (*RPD*) for duplicate measurements (*FD1* and *FD2*) using the equation

$$RPD = \frac{|FD1 - FD2|}{(FD1 + FD2)/2} \times 100$$

9.3.7.2 RPDs for FDs should be ≤30%. Greater variability may be observed when FDs have analyte concentrations that are within a factor of 2 of the MRL. At these concentrations, FDs should have RPDs that are ≤50%. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCC, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.3.7.3 If an LFSMD is analyzed instead of a FD, calculate the relative percent difference (RPD) for duplicate LFSMs (LFSM and LFSMD) using the equation

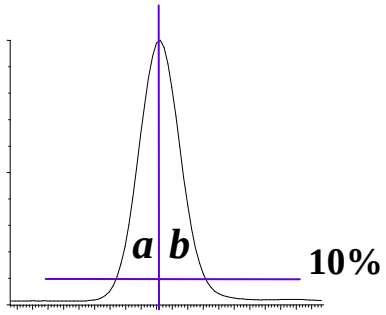
$$RPD = \frac{\left|LFSM - LFSMD\right|}{\left(LFSM + LFSMD\right)/2} \times 100$$

9.3.7.4 RPDs for duplicate LFSMs should be ≤30% for samples fortified at or above their native concentration. Greater variability may be observed when LFSMs are fortified at analyte concentrations that are within a factor of 2 of the MRL. LFSMs fortified at these concentrations should have RPDs that are ≤50% for samples fortified at or above their native concentration. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCC, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.3.8 FIELD REAGENT BLANK (FRB) – The purpose of the FRB is to ensure that PFAAs measured in the Field Samples were not inadvertently introduced into the sample during sample collection/handling. Analysis of the FRB is required only if a Field Sample contains a method analyte or analytes at or above the MRL. The FRB is processed, extracted and analyzed in exactly the same manner as a Field Sample. If the method analyte(s) found in the Field Sample is present in the FRB at a concentration greater than 1/3 the MRL, then all samples collected with that FRB are invalid and must be recollected and reanalyzed.

9.3.9 PEAK ASYMMETRY FACTOR – A peak asymmetry factor must be calculated using the equation below during the IDL and every time a calibration curve is generated. The peak asymmetry factor for the first two eluting peaks in a mid-level CAL standard (if only two analytes are being analyzed, both must be evaluated) must fall in the range of 0.8 to 1.5. Modifying the standard or extract composition to more aqueous content to prevent poor shape is not permitted. See guidance in Section 10.2.4.1 if the calculated peak asymmetry factors do not meet the criteria.

$$A_s = \frac{b}{a}$$



where:

A_s = peak asymmetry factor

B = width of the back half of the peak measured (at 10% peak height) from the trailing edge of the peak to a line dropped perpendicularly from the peak apex

a = the width of the front half of the peak measured (at 10% peak height) from the leading edge of the peak to a line dropped perpendicularly from the apex.

9.3.10 QUALITY CONTROL SAMPLES (QCS) – As part of the IDC (Sect. 9.2), each time a new Analyte PDS (Sect. 7.2.3.2) is prepared, and at least quarterly, analyze a QCS sample from a source different from the source of the CAL standards. If a second vendor is not available, then a different lot of the standard should be used. The QCS should be prepared and analyzed just like a CCC. Acceptance criteria for the QCS are identical to the CCCs; the calculated amount for each analyte must be ± 30% of the expected value. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem.

10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed. After the initial calibration is successful, a CCC is required at the beginning and end of each period in which analyses are performed, and after every tenth Field Sample.

10.2 INITIAL CALIBRATION

10.2.1 ESI-MS/MS TUNE

10.2.1.1 Calibrate the mass scale of the MS with the calibration compounds and procedures prescribed by the manufacturer.

10.2.1.2 Optimize the $[M-H]^-$ for each method analyte by infusing approximately 0.5-1.0 µg/mL of each analyte (prepared in the initial mobile phase conditions) directly into the MS at the chosen LC mobile phase flow rate (approximately 0.3 mL/min). This tune can be done on a mix of the method analytes. The MS parameters (voltages, temperatures, gas flows, etc.) are

varied until optimal analyte responses are determined. The method analytes may have different optima requiring some compromise between the optima. See Table 2 for ESI-MS conditions used in method development.

10.2.1.3 Optimize the product ion (Sect. 3.19) for each analyte by infusing approximately 0.5-1.0 µg/mL of each analyte (prepared in the initial mobile phase conditions) directly into the MS at the chosen LC mobile phase flow rate (approximately 0.3 mL/min). This tune can be done on a mix of the method analytes. The MS/MS parameters (collision gas pressure, collision energy, etc.) are varied until optimal analyte responses are determined. Typically, the carboxylic acids have very similar MS/MS conditions and the sulfonic acids have similar MS/MS conditions. See Table 4 for MS/MS conditions used in method development.

10.2.2 Establish LC operating parameters that optimize resolution and peak shape. Suggested LC suggested conditions can be found in Table 1. The LC conditions listed in Table 1 may not be optimum for all LC systems and may need to be optimized by the analyst (See Sect. 10.2.4.1). Modifying the standard or extract composition to more aqueous content to prevent poor shape is not permitted.

Cautions: LC system components, as well as the mobile phase constituents, contain many of the method analytes in this method. Thus, these PFAAs will build up on the head of the LC column during mobile phase equilibration. To minimize the background PFAA peaks and to keep background levels constant, the time the LC column sits at initial conditions must be kept constant and as short as possible (while ensuring reproducible retention times). In addition, prior to daily use, flush the column with 100% methanol for at least 20 min before initiating a sequence. It may be necessary on some systems to flush other LC components such as wash syringes, sample needles or any other system components before daily use.

Mobile phase modifiers other than 20 mM ammonium acetate may be used at the discretion of the analyst, provided that the retention time stability criteria in Sect. 11.7.2 can be met over a period of two weeks. During method development, retention times shifted to shorter and shorter times as days progressed when mobile phases with less then 20 mM ammonium acetate were used.

10.2.3 Inject a mid-level CAL standard under LC/MS conditions to obtain the retention times of each method analyte. If analyzing for PFTA, ensure that the LC conditions are adequate to prevent co-elution of PFTA and the mobile phase interferants shown in Figure 1. These interferants have the same precursor and products ions as PFTA, and under faster LC conditions may co-elute with PFTA. Divide the chromatogram into retention time windows each of which contains one

or more chromatographic peaks. During MS/MS analysis, fragment a small number of selected precursor ions ($[M-H]^-$; Sect. 3.17) for the analytes in each window and choose the most abundant product ion. The product ions (also the quantitation ions) chosen during method development are in Table 4, although these will be instrument dependent. For maximum sensitivity, small mass windows of ±0.5 daltons around the product ion mass were used for quantitation. If sufficient sensitivity exists to meet the MRL, wider mass ranges may be used to obtain more confirmation ions.

NOTE: As the NOTE in Section 10.2.4.1 indicates, PFOS has linear and branched isomers. There have been reports[10] that not all the products ions in the linear PFOS are produced in all the branched PFOS isomers. (This phenomenon probably exists for PFHxS and PFBS also, although it has not been studied to date.) Thus, in an attempt to reduce PFOS bias, it is required that the *m/z* 499 → *m/z* 80 transition be used as the quantitation transition. Some MS/MS instruments, such as conventional ion traps, may not be able to scan a product ion with such a wide mass difference from the precursor ion; therefore, they may not be used for this method if PFOS, PFBS, or PFHxS analysis is to be conducted. Literature reports[10] indicate for the most abundant PFOS isomer, which is the linear isomer, that all the products ions obtained on an ion trap have less than 10% relative abundance. In addition, there is not a single ion trap MS/MS transition that encompasses the linear isomer and the majority of the branch isomers; thus, the bias would be unacceptably high.

10.2.4 Inject a mid-level CAL standard under optimized LC/MS/MS conditions to ensure that each method analyte is observed in its MS/MS window and that there are at least 10 scans across the peak for optimum precision.

10.2.4.1 If broad, split or fronting peaks are observed for the first two eluting chromatographic peaks (if only two analytes are being analyzed, both must be evaluated), change the initial mobile phase conditions to higher aqueous content until the peak asymmetry ratio for each peak is 0.8 – 1.5. The peak asymmetry factor is calculated as described in Section 9.3.9 on a mid-level CAL standard. The peak asymmetry factor must meet the above criteria for the first two eluting peaks during the IDL and every time a new calibration curve is generated. Modifying the standard or extract composition to more aqueous content to prevent poor shape is not permitted.

NOTE: PFHxS, PFOS, NMeFOSAA, and NEtFOSAA have multiple chromatographic peaks using the LC conditions in Table 1 due to chromatographic resolution of the linear and branched isomers of these compounds. Most PFAAs are produced by two different processes. One process gives rise to linear

PFAAs only while the other process produces both linear and branched isomers. Thus, both branched and linear PFAAs can potentially be found in the environment. For the aforementioned compounds that give rise to more than one peak, all the chromatographic peaks observed in the standard must be integrated and the areas totaled. Chromatographic peaks in a sample must be integrated in the same way as the CAL standard.

10.2.5 Prepare a set of at least five CAL standards as described in Section 7.2.4. The lowest concentration CAL standard must be at or below the MRL, which may depend on system sensitivity. It is recommended that at least four of the CAL standards are at a concentration greater than or equal to the MRL.

10.2.6 The LC/MS/MS system is calibrated using the IS technique. Use the LC/MS/MS data system software to generate a linear regression or quadratic calibration curve for each of the analytes. This curve **must always** be forced through zero and may be concentration weighted, if necessary. Forcing zero allows for a better estimate of the background levels of method analytes.

10.2.6.1 The isotopically labeled IS(s) in this method may undergo suppression in the ESI source if the concentration of the co-eluting unlabeled method analyte(s) is too high. The analyte concentration at which suppression may occur can vary depending on the instrument, LC conditions, ESI conditions, IS concentration, etc. To evaluate whether suppression is occurring during calibration, calculate the relative percent difference (*RPD*) between the high (H) and low (L) areas for each IS using the equation

$$RPD = \frac{(H - L)}{(H + L)/2} \times 100$$

10.2.6.2 The RPD calculated above must be <20% for each IS during calibration. If the calculated RPD is >20% for any IS, the analyst must recalibrate at lower analyte concentrations until the IS RPDs are <20%.

10.2.7 CALIBRATION ACCEPTANCE CRITERIA – When quantitated using the initial calibration curve, each calibration point, except the lowest point, for each analyte should calculate to be within 70-130% of its true value. The lowest CAL point should calculate to be within 50-150% of its true value. If these criteria cannot be met, the analyst will have difficulty meeting ongoing QC criteria. It is recommended that corrective action is taken to reanalyze the CAL standards, restrict the range of calibration, or select an alternate method of calibration (forcing the curve through zero is still required).

CAUTION: When acquiring MS/MS data, LC operating conditions must be carefully reproduced for each analysis to provide reproducible

retention times. If this is not done, the correct ions will not be monitored at the appropriate times. As a precautionary measure, the chromatographic peaks in each window must not elute too close to the edge of the segment time window.

10.3 CONTINUING CALIBRATION CHECK (CCC) – Minimum daily calibration verification is as follows. Verify the initial calibration at the beginning and end of each group of analyses, and after every tenth sample during analyses. In this context, a "sample" is considered to be a Field Sample. LRBs, CCCs, LFBs, LFSMs, FDs FRBs and LFSMDs are not counted as samples. The beginning CCC of each analysis batch must be at or below the MRL in order to verify instrument sensitivity prior to any analyses. If standards have been prepared such that all low CAL points are not in the same CAL solution, it may be necessary to analyze two CAL standards to meet this requirement. Alternatively, the analyte concentrations in the analyte PDS may be customized to meet this criteria. Subsequent CCCs should alternate between a medium and high concentration CAL standard.

10.3.1 Inject an aliquot of the appropriate concentration CAL standard and analyze with the same conditions used during the initial calibration.

10.3.2 Determine that the absolute areas of the quantitation ions of the IS(s) are within 70-140% of the areas measured in the most recent continuing calibration check, and within 50-150% from the average areas measured during initial calibration. If any of the IS areas has changed by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may include cleaning of the MS ion source, or other maintenance as indicated in Section 10.3.4. Major instrument maintenance requires recalibration (Sect 10.2) and verification of sensitivity by analyzing a CCC at or below the MRL (Sect 10.3). Control charts are useful aids in documenting system sensitivity changes.

10.3.3 Calculate the concentration of each analyte and SUR in the CCC. The calculated amount for each analyte and SUR for medium and high level CCCs must be within ± 30% of the true value. The calculated amount for the lowest calibration point for each analyte must be within ± 50% and the SUR must be within ± 30% of the true value. If these conditions do not exist, then all data for the problem analyte must be considered invalid, and remedial action should be taken (Sect. 10.3.4) which may require recalibration. Any Field or QC Samples that have been analyzed since the last acceptable calibration verification should be reanalyzed after adequate calibration has been restored, with the following exception. **If the CCC fails because the calculated concentration is greater than 130% (150% for the low-level CCC) for a particular method analyte, and Field Sample extracts show no detection for that method analyte, non-detects may be reported without re-analysis.**

10.3.4 REMEDIAL ACTION – Failure to meet CCC QC performance criteria may require remedial action. Major maintenance, such as cleaning the electrospray

probe, atmospheric pressure ionization source, cleaning the mass analyzer, replacing the LC column, etc., requires recalibration (Sect 10.2) and verification of sensitivity by analyzing a CCC at or below the MRL (Sect 10.3).

11. PROCEDURE

11.1 This procedure may be performed manually or in an automated mode using a robotic or automatic sample preparation device. The data presented in Tables 5-11 demonstrate data collected by manual extraction. If an automated system is used to prepare samples, follow the manufacturer's operating instructions, but all extraction and elution steps must be the same as in the manual procedure. Extraction and/or elution steps may not be changed or omitted to accommodate the use of an automated system. If an automated system is used, the LRBs should be rotated among the ports to ensure that all the valves and tubing meet the LRB requirements (Sect. 9.3.1).

11.2 Some of the PFAAs adsorb to surfaces, including polypropylene. Therefore, the aqueous sample bottles must be rinsed with the elution solvent (Sect 11.4.4) whether extractions are performed manually or by automation. The bottle rinse is passed through the cartridge to elute the method analytes and is then collected (Sect. 11.4.4).

NOTE: The SPE cartridges and sample bottles described in this section are designed as single use items and should be discarded after use. They may not be refurbished for reuse in subsequent analyses.

11.3 SAMPLE PREPARATION

11.3.1 Samples are preserved, collected and stored as presented in Section 8. All Field and QC Samples, including the LRB, LFB and FRB, must contain the dechlorinating agent listed in Section 8.1.2. Determine sample volume. An indirect measurement may be done in one of two ways: by marking the level of the sample on the bottle or by weighing the sample and bottle to the nearest 10 g. After extraction, proceed to Section 11.6 for final volume determination. Some of the PFAAs adsorb to surfaces, thus the sample volume may **NOT** be transferred to a graduated cylinder for volume measurement. The LRB, LFB and FRB may be prepared by measuring 250 mL of reagent water with a polypropylene graduated cylinder or filling a 250-mL sample bottle to near the top.

11.3.2 Add an aliquot of the SUR PDS (Sect. 7.2.2.2) to each sample, cap and invert to mix. During method development, a 10-µL aliquot of the 1-4 ng/µL SUR PDS (Sect. 7.2.2.2) was added to 250 mL of sample for a final concentration of 40 ng/L for ^{13}C-PFHxA and ^{13}C-PFDA and 160 ng/L for d_5-NEtFOSAA.

11.3.3 In addition to the SUR(s) and dechlorination agent, if the sample is an LFB, FD, LFSM, or LFSMD, add the necessary amount of analyte PDS (Sect. 7.2.3.2). Cap and invert each sample to mix.

11.4 CARTRIDGE SPE PROCEDURE

11.4.1 CARTRIDGE CLEAN-UP AND CONDITIONING – DO NOT allow cartridge packing material to go dry during any of the conditioning steps. Rinse each cartridge with 15 mL of methanol. Next, rinse each cartridge with 18 mL of reagent water, without allowing the water to drop below the top edge of the packing. If the cartridge goes dry during the conditioning phase, the conditioning must be started over. Add 4-5 mL of reagent water to each cartridge, attach the sample transfer tubes (Sect. 6.9.3), turn on the vacuum, and begin adding sample to the cartridge.

11.4.2 SAMPLE EXTRACTON – Adjust the vacuum so that the approximate flow rate is 10-15 mL/min. Do not allow the cartridge to go dry before all the sample has passed through.

11.4.3 SAMPLE BOTTLE AND CARTRIDGE RINSE – After the entire sample has passed through the cartridge, rinse the sample bottles with two 7.5-mL aliquots of reagent water and draw each aliquot through the sample transfer tubes and the cartridges. Draw air or nitrogen through the cartridge for 5 min at high vacuum (10-15 in. Hg).

NOTE: If empty plastic reservoirs are used in place of the sample transfer tubes to pass the samples through the cartridges, these reservoirs must be treated like the transfer tubes. After the entire sample has passed through the cartridge, the reservoirs must be rinsed to waste with reagent water.

11.4.4 SAMPLE BOTTLE AND CARTRIDGE ELUTION – Turn off and release the vacuum. Lift the extraction manifold top and insert a rack with collection tubes into the extraction tank to collect the extracts as they are eluted from the cartridges. Rinse the sample bottles with 4 mL of methanol and elute the analytes from the cartridges by pulling the 4 mL of methanol through the sample transfer tubes and the cartridges. Use a low vacuum such that the solvent exits the cartridge in a dropwise fashion. Repeat sample bottle rinse and cartridge elution with a second 4-mL aliquot of methanol.

NOTE: If empty plastic reservoirs are used in place of the sample transfer tubes to pass the samples through the cartridges, these reservoirs must be treated like the transfer tubes. After the reservoirs have been rinsed in Section 11.4.3, the elution solvent used to rinse the sample bottles must be swirled down the sides of the reservoirs while eluting the cartridge to ensure that any method analytes on the surface of the reservoirs are transferred to the extract.

11.5 EXTRACT CONCENTRATION – Concentrate the extract to dryness under a gentle stream of nitrogen in a heated water bath (60-65 °C) to remove all the water/methanol

mix. Add the appropriate amount of 96:4% (vol/vol) methanol:water solution and the IS PDS (Sect. 7.2.1.2) to the collection vial to bring the volume to 1 mL and vortex. (10 µL of the 1-4 ng/µL IS PDS for extract concentrations of 10-40 pg/µL were used for method development). Transfer a small aliquot with a plastic pipet (Sect. 6.7) to a polypropylene autosampler vial.

NOTE: It is recommend that the entire 1-mL aliquot not be transferred to the autosampler vial because the polypropylene autosampler caps do not reseal after injection. Therefore, do not store the extracts in the autosampler vials as evaporation losses can occur occasionally in these autosampler vials. Extracts can be stored in 15-mL centrifuge tubes (Sect. 6.3).

11.6 SAMPLE VOLUME DETERMINATION – If the level of the sample was marked on the sample bottle, use a graduated cylinder to measure the volume of water required to fill the original sample bottle to the mark made prior to extraction. Determine to the nearest 10 mL. If using weight to determine volume, weigh the empty bottle to the nearest 10 g and determine the sample weight by subtraction of the empty bottle weight from the original sample weight (Sect. 11.3.1). Assume a sample density of 1.0 g/mL. In either case, the sample volume will be used in the final calculations of the analyte concentration (Sect. 12.2).

11.7 EXTRACT ANALYSIS

11.7.1 Establish operating conditions equivalent to those summarized in Tables 1-4 of Section 17. Instrument conditions and columns should be optimized prior to the initiation of the IDC.

11.7.2 Establish an appropriate retention time window for each analyte. This should be based on measurements of actual retention time variation for each method analyte in CAL standard solutions analyzed on the LC over the course of time. A value of plus or minus three times the standard deviation of the retention time obtained for each method analyte while establishing the initial calibration and completing the IDC can be used to calculate a suggested window size. However, the experience of the analyst should weigh heavily on the determination of the appropriate retention window size.

11.7.3 Calibrate the system by either the analysis of a calibration curve (Sect. 10.2) or by confirming the initial calibration is still valid by analyzing a CCC as described in Section 10.3. If establishing an initial calibration, complete the IDC as described in Section 9.2.

11.7.4 Begin analyzing Field Samples, including QC samples, at their appropriate frequency by injecting the same size aliquots (10 µL was used in method development), under the same conditions used to analyze the CAL standards.

11.7.5 At the conclusion of data acquisition, use the same software that was used in the calibration procedure to identify peaks of interest in predetermined retention time windows. Use the data system software to examine the ion abundances of the peaks in the chromatogram. Identify an analyte by comparison of its retention time with that of the corresponding method analyte peak in a reference standard. Comparison of the MS/MS mass spectra is not particularly useful given the limited ±0.5 dalton mass range around a single product ion for each method analyte.

11.7.6 The analyst must not extrapolate beyond the established calibration range. If an analyte peak area exceeds the range of the initial calibration curve, the extract may be diluted with 96%:4% (vol/vol) methanol:water solution and the appropriate amount of IS added to match the original concentration. Re-inject the diluted extract. Incorporate the dilution factor into the final concentration calculations. Acceptable SUR performance (Sect. 9.3.5.1) should be determined from the undiluted sample extract. The resulting data should be documented as a dilution, with an increased MRL.

12. DATA ANALYSIS AND CALCULATION

12.1. Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations using MS/MS. In validating this method, concentrations were calculated by measuring the product ions listed in Table 4. Other ions may be selected at the discretion of the analyst.

12.2. Calculate analyte and SUR concentrations using the multipoint calibration established in Section 10.2. Do not use daily calibration verification data to quantitate analytes in samples. Adjust final analyte concentrations to reflect the actual sample volume determined in Section 11.6.

12.3 Prior to reporting the data, the chromatogram should be reviewed for any incorrect peak identification or poor integration.

12.4 PFHxS, PFOS, NMeFOSAA, and NEtFOSAA have multiple chromatographic peaks using the LC conditions in Table 1 due to the linear and branch isomers of these compounds (Sect. 10.2.4.1). The areas of all the linear and branched isomer peaks observed in the CAL standards for each of these analytes must be summed and the concentrations reported as a total for each of these analytes.

12.5 Calculations must utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty), typically two, and not more than three significant figures.

NOTE: Some data in Section 17 of this method are reported with more than two significant figures. This is done to better illustrate the method performance.

13. METHOD PERFORMANCE

13.1 PRECISION, ACCURACY, AND MINIMUM REPORTING LEVELS – Tables for these data are presented in Section 17. LCMRLs and DLs for each method analyte are presented in Table 5. Precision and accuracy are presented for four water matrices: reagent water (Tables 6 and 7); chlorinated (finished) ground water (Table 8); high TOC chlorinated surface water (Table 9); and day zero of the aqueous holding time in chlorinated surface water (Table 10).

13.2 EVALUATION OF ADDITIONAL PERFLUORINATED ALKYL COMPOUNDS – Nine additional compounds were evaluated for inclusion in this method, but were not included for the following reasons. Due to volatility, low recoveries following evaporation were obtained for PFOSA (perfluorooctane sulfonylamide), NEtFOSE (2-N-ethylperfluorooctane sulfonamide ethanol), NMeFOSE (2-N-methylperfluorooctane sulfonamide ethanol), and NEtFOSA (N-ethylperfluorooctanesulfonamide). Poor chromatographic peak shape, which degraded with repeated injections, was obtained for PFOSAA (perfluorooctanesulfonamidoacetic acid). PFOSfn (perfluorosulfinate) degraded in aqueous samples in under 24 hours. PFOSF (perfluorooctane-1-sulfonylfluoride) had the same LC retention time as PFOS and appeared to undergo conversion in the ESI source to PFOS under method conditions. Finally, acceptable SPE recoveries were not obtained for PFBA (perfluorobutanoic acid) and PFPA (perfluoropentanoic acid).

13.3 SAMPLE STORAGE STABILITY STUDIES – An analyte storage stability study was conducted by fortifying the analytes into chlorinated surface water samples that were collected, preserved, and stored as described in Section 8. The precision and mean recovery (n=5) of analyses, conducted on Days 0, 7, and 14 are presented in Table 10.

13.4 EXTRACT STORAGE STABILITY STUDIES – Extract storage stability studies were conducted on extracts obtained from a chlorinated surface water fortified with the method analytes. The precision and mean recovery (n=5) of injections conducted on Days 0, 7, 14, 22, and 28 are reported in Table 11.

13.5 SECOND LABORATORY DEMONSTRATION – The performance of this method was demonstrated by multiple laboratories, with results similar to those reported in Section 17. The authors wish to acknowledge the work of the Suffolk County Water Authority Laboratory Hauppauge, NY and Lancaster Labs, a wholly owned subsidiary of Thermo Fisher Scientific, for their participation in the second laboratory demonstration.

14. POLLUTION PREVENTION

14.1 This method utilizes SPE to extract analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes, thereby minimizing the potential hazards to both the analyst and the environment as compared

to the use of large volumes of organic solvents in conventional liquid-liquid extractions.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C., 20036 or on-line at http://membership.acs.org/c/ccs/pub_9.htm (accessed August 2008).

15. WASTE MANAGEMENT

15.1 The analytical procedures described in this method generate relatively small amounts of waste since only small amounts of reagents and solvents are used. The matrices of concern are finished drinking water or source water. However, laboratory waste management practices must be conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions.

16. REFERENCES

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17. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1. LC METHOD CONDITIONS

Time (min)	% 20 mM ammonium acetate	% Methanol
Initial	60.0	40.0
1.0	60.0	40.0
25.0	10.0	90.0
32.0	10.0	90.0
32.1	60.0	40.0
37.0	60.0	40.0
Waters Atlantis® dC_{18} 2.1 x 150 mm packed with 5.0 µm C_{18} stationary phase Flow rate of 0.3 mL/min 10 µL injection		

TABLE 2. ESI-MS METHOD CONDITIONS

ESI Conditions	
Polarity	Negative ion
Capillary needle voltage	-3 kV
Cone gas flow	98 L/hr
Nitrogen desolvation gas	1100 L/hr
Desolvation gas temp.	350 °C

TABLE 3. METHOD ANALYTE SOURCE, RETENTION TIMES (RTs), AND SUGGESTED IS REFERENCES

Analyte	Method analyte Source[a]	Peak # (Fig. 1)	RT (min)	IS# Ref
PFBS	Aldrich	1	8.48	2
PFHxA	Fluka	2	11.38	1
PFHpA	Aldrich	4	14.33	1
PFHxS[b]	Fluka	5	14.48	2
PFOA	Aldrich	6	16.73	1
PFNA	Aldrich	8	18.76	1
PFOS[b]	Fluka	9	18.72	2
PFDA	Aldrich	11	20.47	1
NMeFOSAA	c	13	21.28	3
NEtFOSAA	c	15	22.01	3
PFUnA	Aldrich	17	21.95	1
PFDoA	Aldrich	18	23.20	1
PFTrDA	Exfluor	19	24.32	1
PFTA	Aldrich	20	25.27	1
^{13}C-PFHxA	Wellington Labs	3	11.38	1
^{13}C-PFDA	Wellington Labs	12	20.47	1
d_5-NEtFOSAA	Wellington Labs	16	21.99	3
^{13}C-PFOA– IS#1	PerkinElmer	7	16.73	-
^{13}C-PFOS– IS#2	Wellington Labs	10	18.71	-
d_3-NMeFOSAA–IS#3	Wellington Labs	14	21.24	-

[a] The data presented in this method were obtained using analytes purchased from these vendors. Other vendors' materials can be used provided the QC requirements in Section 9 can be met.

[b] PFHxS and PFOS neat materials were purchased as K^+ salts. The CASRN of the PFOS potassium salt is 2795-39-3 and the CASRN of the PFHxS potassium salt is 3871-99-6.

[c] These analytes were not commercially available at the time of method development as technical grade mixtures containing both linear and branched isomers.

TABLE 4. MS/MS METHOD CONDITIONS[a]

Segment[b]	Analyte	Precursor Ion[c] *(m/z)*	Product Ion[c,d] (*m/z*)	Cone Voltage (v)	Collision Energy[e] (v)
1	PFBS	299	80	40	25
2	PFHxA	313	269	15	10
3	PFHpA	363	319	12	10
3	PFHxS[f]	399	80	40	40
4	PFOA	413	369	15	10
4	PFNA	463	419	12	10
4	PFOS[f]	499	80	40	40
5	PFDA	513	469	15	10
5	NMeFOSAA[f]	570	419	25	20
5	NEtFOSAA[f]	584	419	25	20
5	PFUnA	563	519	15	10
5	PFDoA	613	569	15	10
6	PFTrDA	663	619	15	10
6	PFTA	713	669	15	10
2	^{13}C-PFHxA	315	270	15	10
5	^{13}C-PFDA	515	470	12	12
5	d_5-NEtFOSAA	589	419	25	20
4	^{13}C-PFOA	415	370	15	10
4	^{13}C-PFOS	503	80	40	40
5	d_3-NMeFOSAA	573	419	25	20

[a] An LC/MS/MS chromatogram of the analytes is shown in Figure 1.

[b] Segments are time durations in which single or multiple scan events occur.

[c] Precursor and product ions listed in this table are nominal masses. During MS and MS/MS optimization, the analyst should determine the precursor and product ion masses to one decimal place by locating the apex of the mass spectral peak place (e.g., *m/z* 498.9→79.9 for PFOS). These precursor and product ion masses (with one decimal place) should be used in the MS/MS method for all analyses.

[d] Ions used for quantitation purposes.

[e] Argon used as collision gas at a flow rate of 0.3 mL/min.

[f] Analyte has multiple resolved chromatographic peaks due to linear and branched isomers. All peaks summed for quantitation purposes.

TABLE 5. DLs AND LCMRLs IN REAGENT WATER

Analyte	Fortified Conc. (ng/L)[a]	DL[b] (ng/L)	LCMRL[c] (ng/L)
PFBS	9.1	3.1	3.7
PFHxA	5.0	1.6	2.9
PFHpA	4.1	0.5	3.8
PFHxS	11	2.0	8.0
PFOA	4.6	1.7	5.1
PFNA	4.8	0.7	5.5
PFOS	9.6	1.4	6.5
PFDA	3.7	0.7	3.8
NMeFOSAA	20	6.5	14
NEtFOSAA	21	4.2	14
PFUnA	5.4	2.8	6.9
PFDoA	3.7	1.1	3.5
PFTrDA	5.5	2.2	3.8
PFTA	4.4	1.7	4.7

[a] Spiking concentration used to determine DL.

[b] Detection limits were determined by analyzing seven replicates over three days according to Section 9.2.7.

[c] LCMRLs were calculated according to the procedure in reference 1.

TABLE 6. PRECISION AND ACCURACY OF LOW LEVEL FORTIFIED REAGENT WATER (n=7)

Analyte	Fortified Conc. (ng/L)	Mean % Recovery	% RSD
PFBS	9.1	93	12
PFHxA	5.0	108	9.3
PFHpA	8.3	111	6.2
PFHxS	11	116	4.9
PFOA	9.1	110	6.5
PFNA	9.6	121	7.5
PFOS	9.6	116	4.1
PFDA	7.3	114	4.1
NMeFOSAA	20	109	9.3
NEtFOSAA	21	113	5.5
PFUnA	11	120	5.4
PFDoA	7.3	116	4.6
PFTrDA	5.5	118	11
PFTA	8.7	117	2.4
^{13}C-PFHxA	40	89	6.1
^{13}C-PFDA	40	102	7.3
d_5-NEtFOSAA	160	100	4.9

TABLE 7. PRECISION AND ACCURACY OF HIGH LEVEL FORTIFIED REAGENT WATER (n=7)

Analyte	Fortified Conc. (ng/L)	Mean % Recovery	% RSD
PFBS	91	92	5.9
PFHxA	50	103	4.6
PFHpA	41	106	3.4
PFHxS	113	101	2.5
PFOA	46	104	3.6
PFNA	48	109	3.5
PFOS	96	101	3.8
PFDA	37	106	4.8
NMeFOSAA	202	100	3.7
NEtFOSAA	214	105	5.3
PFUnA	54	107	3.3
PFDoA	37	107	3.9
PFTrDA	55	107	1.9
PFTA	44	111	2.7
^{13}C-PFHxA	40	93	4.4
^{13}C-PFDA	40	99	3.5
d_5-NEtFOSAA	160	100	4.5

TABLE 8. PRECISION AND ACCURACY IN FORTIFIED CHLORINATED GROUND WATER[a] (n=7)

Analyte	Fortified Conc. (ng/L)	Mean % Recovery	% RSD
PFBS	91	101	3.9
PFHxA	50	112	0.9
PFHpA	41	105	1.8
PFHxS	113	103	2.2
PFOA	46	107	2.2
PFNA	48	103	2.4
PFOS	96	100[b]	2.2
PFDA	37	101	2.6
NMeFOSAA	202	96	2.6
NEtFOSAA	214	100	2.7
PFUnA	54	99	2.6
PFDoA	37	99	2.3
PFTrDA	55	96	3.4
PFTA	44	97	4.2
^{13}C-PFHxA	40	98	2.0
^{13}C-PFDA	40	98	2.1
d_5-NEtFOSAA	160	97	5.0

[a] TOC = 0.96 mg/L and hardness = 342 mg/L.

[b] Recovery is corrected for a matrix PFOS concentration of 40 ng/L.

TABLE 9. PRECISION AND ACCURACY IN FORTIFIED HIGH TOC CHLORINATED SURFACE WATER[a] (n=7)

Analyte	Fortified Conc. (ng/L)	Mean % Recovery	% RSD
PFBS	91	85	4.3
PFHxA	50	101	3.2
PFHpA	41	106	3.7
PFHxS	113	101	4.9
PFOA	46	110	3.1
PFNA	48	112	3.9
PFOS	96	104	4.0
PFDA	37	109	4.3
NMeFOSAA	202	95	4.0
NEtFOSAA	214	100	3.4
PFUnA	54	106	3.7
PFDoA	37	104	4.2
PFTrDA	55	102	4.7
PFTA	44	105	3.5
^{13}C-PFHxA	40	85	4.3
^{13}C-PFDA	40	101	3.2
d_5-NEtFOSAA	160	106	3.7

[a] TOC = 4.95 mg/L and hardness =137 mg/L.

TABLE 10. AQUEOUS SAMPLE HOLDING TIME DATA FOR SAMPLES FROM CHLORINATED SURFACE WATER[a], FORTIFIED WITH METHOD ANALYTES AND PRESERVED AND STORED ACCORDING TO SECTION 8 (n=5)

Analyte	Fortified Conc. (ng/L)	Day 0		Day 7		Day 14	
		Mean %Rec	% RSD	Mean %Rec	% RSD	Mean %Rec	% RSD
PFBS	91	83	8.5	87	3.3	90	12
PFHxA	50	99	4.3	98	3.4	104	10
PFHpA	41	105	1.1	97	4.2	102	7.0
PFHxS	113	98	2.8	98	3.8	92	9.0
PFOA[b]	46	98	2.5	94	3.2	96	7.6
PFNA	48	106	2.5	102	4.0	98	5.5
PFOS	96	103	4.9	100	3.1	104	6.7
PFDA	37	102	3.3	99	5.0	99	7.0
NMeFOSAA	202	97	3.6	95	4.0	97	5.1
NEtFOSAA	214	105	3.0	101	6.1	99	5.3
PFUnA	54	104	3.0	97	4.8	95	10
PFDoA	37	100	2.2	94	5.8	102	4.6
PFTrDA	55	102	2.8	93	3.8	104	5.3
PFTA	44	105	4.0	99	4.3	102	4.4

[a] TOC = 1.8 mg/L and hardness =205 mg/L.

[b] Recovery corrected for a native PFOA concentration of 14 ng/L in the tap water used for this study.

TABLE 11. EXTRACT HOLDING TIME DATA FOR SAMPLES FROM CHLORINATED SURFACE WATER, FORTIFIED WITH METHOD ANALYTES AND PRESERVED AND STORED ACCORDING TO SECTION 8 (n=5)

Analyte	Fortified Conc. (ng/L)	Day 0		Day 7		Day 14		Day 22		Day 28	
		Mean %Rec	RSD %	Mean %Rec	RSD %	Mean %Rec	RSD %	Mean %Rec	RSD %	Mean %Rec	RSD %
PFBS	91	83	8.5	89	10	91	8.3	92	11	90	7.5
PFHxA	50	99	4.3	101	4.7	103	5.7	105	5.2	102	4.1
PFHpA	41	105	1.1	101	3.4	109	3.5	110	2.9	108	1.7
PFHxS	113	98	2.8	101	2.1	107	3.5	106	3.1	104	2.5
PFOA[a]	46	98	2.5	100	1.4	102	2.7	101	3.4	101	2.8
PFNA	48	106	2.5	104	3.0	102	3.5	104	4.0	107	3.1
PFOS	96	103	4.9	100	1.6	109	1.4	103	3.6	105	1.9
PFDA	37	102	3.3	104	2.9	100	3.3	102	5.4	105	2.9
NMeFOSAA	202	97	3.6	96	1.8	96	2.8	102	3.4	99	3.9
NEtFOSAA	214	105	3.0	100	2.5	99	3.4	108	1.7	105	3.7
PFUnA	54	104	3.0	103	3.1	100	4.4	104	3.6	104	4.8
PFDoA	37	100	2.2	102	1.6	101	3.0	107	5.4	110	4.6
PFTrDA	55	102	2.8	95	3.8	97	2.5	104	4.1	104	2.3
PFTA	44	105	4.0	100	2.6	93	3.4	110	3.1	110	2.7

[a] Recovery corrected for a native PFOA concentration of 14 ng/L in the tap water used for this study.

TABLE 12. INITIAL DEMONSTRATION OF CAPABILITY QUALITY CONTROL REQUIREMENTS

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 9.2.1	Initial Demonstration of Low System Background	Analyze LRB prior to any other IDC steps.	Demonstrate that all method analytes are below 1/3 the MRL and that possible interferences from extraction media do not prevent the identification and quantification of method analytes.
Sect. 9.2.2	Initial Demonstration of Precision (IDP)	Analyze four to seven replicate LFBs fortified near the midrange calibration concentration.	%RSD must be <20%
Sect. 9.2.3	Initial Demonstration of Accuracy (IDA)	Calculate average recovery for replicates used in IDP.	Mean recovery ± 30% of true value
Sect. 9.2.4	Initial Demonstration of Peak Asymmetry Factor	Calculate the peak asymmetry factor using the equation in Section 9.3.9 for the first two eluting chromatographic peaks in a mid-level CAL standard.	Peak asymmetry factor of 0.8 - 1.5
Sect. 9.2.5	Minimum Reporting Limit (MRL) Confirmation	Fortify, extract and analyze seven replicate LFBs at the proposed MRL concentration. Calculate the Mean and the Half Range (HR). Confirm that the upper and lower limits for the Prediction Interval of Result (Upper PIR, and Lower PIR, Sect. 9.2.5.2) meet the recovery criteria.	Upper PIR ≤ 150% Lower PIR ≥ 50%
Sect. 9.2.6 and 9.3.10	Quality Control Sample (QCS)	Analyze a standard from a second source, as part of IDC.	Results must be within 70-130% of true value.
Sect. 9.2.7	Detection Limit (DL) Determination (optional)	Over a period of trhee days, prepare a minimum of seven replicate LFBs fortified at a concentration estimated to be near the DL. Analyze the replicates through all steps of the analysis. Calculate the DL using the equation in Sect. 9.2.7.1.	Data from DL replicates are not required to meet method precision and accuracy criteria. If the DL replicates are fortified at a low enough concentration, it is likely that they will not meet precision and accuracy criteria.

NOTE: Table 12 is intended as an abbreviated summary of QC requirements provided as a convenience to the method user. Because the information has been abbreviated to fit the table format, there may be issues that need additional clarification, or areas where important additional information from the method text is needed. In all cases, the full text of the QC in Section 9 supersedes any missing or conflicting information in this table.

TABLE 13. ONGOING QUALITY CONTROL REQUIREMENTS (SUMMARY)

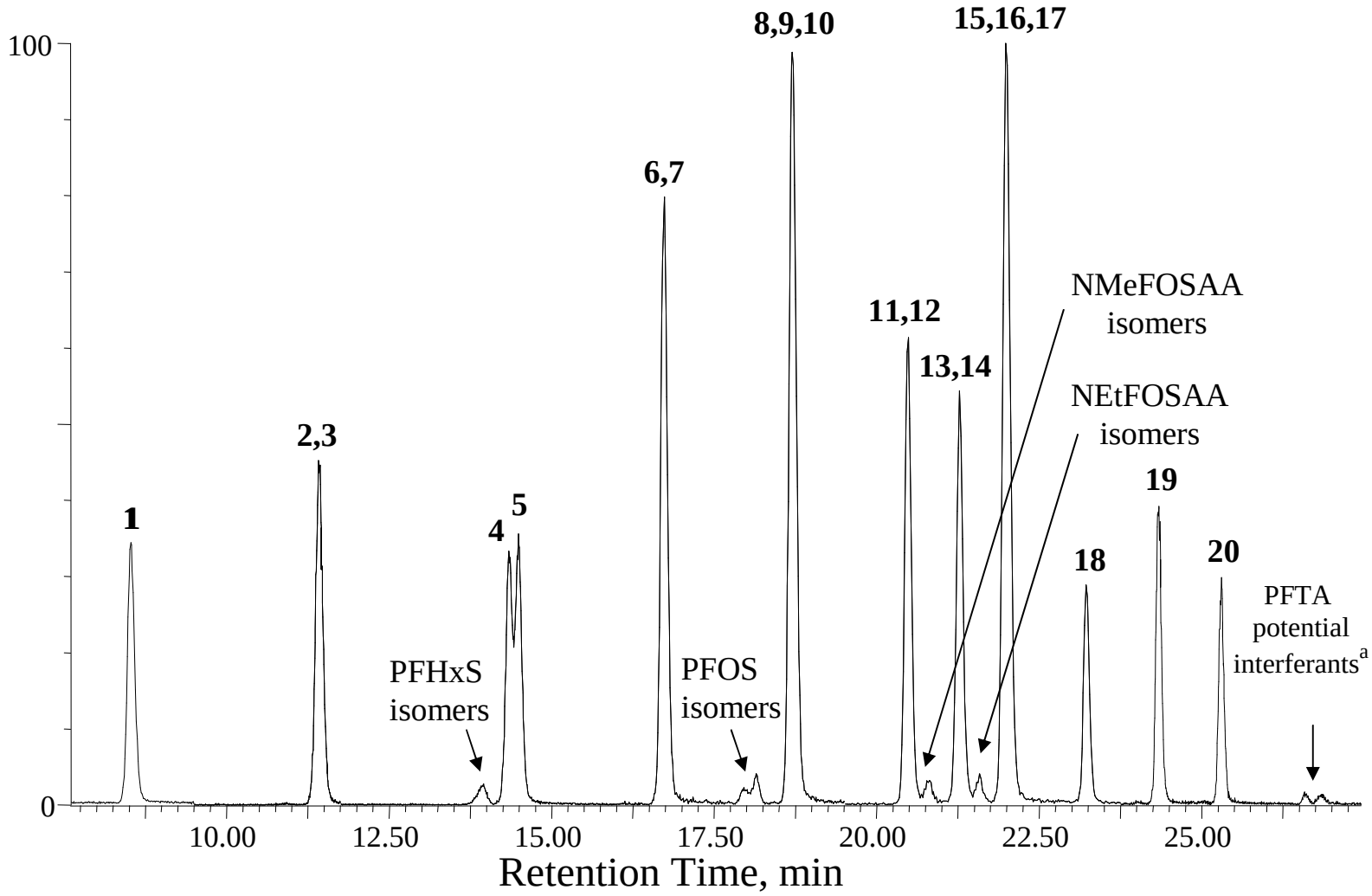
Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 8.1 - Sect. 8.5	Sample Holding Time	14 days with appropriate preservation and storage as described in Sections 8.1-8.5.	Sample results are valid only if samples are extracted within the sample holding time.
Sect. 8.5	Extract Holding Time	28 days when stored at room temperature in polypropylene centrifuge tubes.	Extract results are valid only if extracts are analyzed within the extract holding time.
Sect. 9.3.1	Laboratory Reagent Blank (LRB)	Daily, or with each extraction batch of up to 20 samples, whichever is more frequent.	Demonstrate that all method analytes are below 1/3 the MRL, and confirm that possible interferences do not prevent quantification of method analytes. If targets exceed 1/3 the MRL or if interferences are present, results for these subject analytes in the extraction batch are invalid.
Sect. 9.3.3	Laboratory Fortified Blank (LFB)	Analyze at least one LFB daily or one for each extraction batch of up to 20 Field Samples. Rotate the fortified concentrations between low, medium and high amounts.	Results of LFB analyses must be 70-130% of the true value for each method analyte for all fortified concentrations except the lowest CAL point. Results of the LFBs corresponding to the lowest CAL point for each method analyte must be 50-150% of the true value.
Sect. 9.3.4	Internal Standard (IS)	Internal standards, ^{13}C-PFOA (IS#1), ^{13}C-PFOS (IS#2), and d_3-NMeFOSAA (IS#3), are added to all standards and sample extracts, including QC samples. Compare IS areas to the average IS area in the initial calibration and to the most recent CCC.	Peak area counts for all ISs in all injections must be within ± 50% of the average peak area calculated during the initial calibration and 70-140% from the most recent CCC. If ISs do not meet this criterion, corresponding target results are invalid.
Sect. 9.3.5	Surrogate Standards (SUR)	Surrogate standards, ^{13}C-PFHxA, ^{13}C-PFDA, and d_5-NEtFOSAA, are added to all CAL standards and samples, including QC samples. Calculate SUR recoveries.	SUR recoveries must be 70-130% of the true value. If a SUR fails this criteria, report all results for sample as suspect/SUR recovery.

TABLE 13. (Continued)

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 9.3.6	Laboratory Fortified Sample Matrix (LFSM)	Analyze one LFSM per extraction batch (20 samples or less) fortified with method analytes at a concentration close to but greater than the native concentration, if known. Calculate LFSM recoveries.	Recoveries at mid and high levels should be within 70-130% and within 50-150% at the low-level fortified amount (near the MRL). If these criteria are not met, results are labeled suspect due to matrix effects.
Sect. 9.3.7	Laboratory Fortified Sample Matrix Duplicate (LFSMD) or Field Duplicates (FD)	Extract and analyze at least one FD or LFSMD with each extraction batch (20 samples or less). A LFSMD may be substituted for a FD when the frequency of detects are low. Calculate RPDs.	Method analyte RPDs for the LFMD or FD should be ≤30% at mid and high levels of fortification and ≤50% near the MRL. If these criteria are not met, results are labeled suspect due to matrix effects.
Sect. 9.3.8	Field Reagent Blank (FRB)	Analysis of the FRB is required only if a Field Sample contains a method analyte or analytes at or above the MRL. The FRB is processed, extracted and analyzed in exactly the same manner as a Field Sample.	If the method analyte(s) found in the Field Sample is present in the FRB at a concentration greater than 1/3 the MRL, then all samples collected with that FRB are invalid and must be recollected and reanalyzed.
Sect. 9.3.9	Peak Asymmetry Factor	Calculate the peak asymmetry factor for the first two eluting chromatographic peaks in a mid-level CAL standard every time a calibration curve is generated.	Peak asymmetry factor of 0.8 - 1.5
Sect. 9.3.10	Quality Control Sample (QCS)	Analyze at least quarterly or when preparing new standards, as well as during the IDC.	Results must be within 70-130% of true value.
Sect. 10.2 and Sect. 9.3.2	Initial Calibration	Use IS calibration technique to generate a first or second order calibration curve forced through zero. Use at least five standard concentrations. Check the calibration curve as described in Sect. 10.2.7.	When each CAL standard is calculated as an unknown using the calibration curve, the analyte results should be 70-130% of the true value for all except the lowest standard, which should be 50-150% of the true value. Recalibration is recommended if these criteria are not met.
Sect. 9.3.2 and Sect. 10.3	Continuing Calibration Check (CCC)	Verify initial calibration by analyzing a low level (at the MRL or below) CCC prior to analyzing samples. CCCs are then injected after every 10 samples and after the last sample, rotating concentrations to cover the calibrated range of the instrument.	Recovery for each analyte and SUR must be within 70-130% of the true value for all but the lowest level of calibration. Recovery for each analyte in the lowest CAL level CCC must be within 50-150% of the true value and the SUR must be within 70-130% of the true value.

NOTE: Table 13 is intended as an abbreviated summary of QC requirements provided as a convenience to the method user. Because the information has been abbreviated to fit the table format, there may be issues that need additional clarification, or areas where important additional information from the method text is needed. In all cases, the full text of the QC in Section 8-10 supersedes any missing or conflicting information in this table.

FIGURE 1. EXAMPLE CHROMATOGRAM FOR REAGENT WATER FORTIFIED WITH METHOD 537 ANALYTES AT CONCENTRATION LEVELS INDICATED IN TABLE 6. NUMBERED PEAKS ARE IDENTIFIED IN TABLE 3.



[a] Abbreviated chromatographic conditions may lead to co-elution of PFTA and the potential interferants shown here. See Section 10.2.3 for more information.

EPA Method 8270C

HALEY ALDRICH

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. Direct injection of a sample may be used in limited applications. The following compounds can be determined by this method:

		Appropriate Preparation Techniques[b]				
Compounds	CAS No[a]	3510	3520	3540/ 3541	3550	3580
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthene-d_{10} (IS)		X	X	X	X	X
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	X
2-Acetylaminofluorene	53-96-3	X	ND	ND	ND	X
1-Acetyl-2-thiourea	591-08-2	LR	ND	ND	ND	LR
Aldrin	309-00-2	X	X	X	X	X
2-Aminoanthraquinone	117-79-3	X	ND	ND	ND	X
Aminoazobenzene	60-09-3	X	ND	ND	ND	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
3-Amino-9-ethylcarbazole	132-32-1	X	X	ND	ND	ND
Anilazine	101-05-3	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
o-Anisidine	90-04-0	X	ND	ND	ND	X
Anthracene	120-12-7	X	X	X	X	X
Aramite	140-57-8	HS(43)	ND	ND	ND	X
Aroclor 1016	12674-11-2	X	X	X	X	X
Aroclor 1221	11104-28-2	X	X	X	X	X
Aroclor 1232	11141-16-5	X	X	X	X	X
Aroclor 1242	53469-21-9	X	X	X	X	X
Aroclor 1248	12672-29-6	X	X	X	X	X
Aroclor 1254	11097-69-1	X	X	X	X	X
Aroclor 1260	11096-82-5	X	X	X	X	X
Azinphos-methyl	86-50-0	HS(62)	ND	ND	ND	X
Barban	101-27-9	LR	ND	ND	ND	LR
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	X
Benz(a)anthracene	56-55-3	X	X	X	X	X
Benzo(b)fluoranthene	205-99-2	X	X	X	X	X
Benzo(k)fluoranthene	207-08-9	X	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
p-Benzoquinone	106-51-4	OE	ND	ND	ND	X
Benzyl alcohol	100-51-6	X	X	ND	X	X
α-BHC	319-84-6	X	X	X	X	X
β-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
γ-BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X
Bis(2-chloroethyl) ether	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl) ether	108-60-1	X	X	X	X	X
Bis(2-ethylhexyl) phthalate	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
Bromoxynil	1689-84-5	X	ND	ND	ND	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X
Captafol	2425-06-1	HS(55)	ND	ND	ND	X
Captan	133-06-2	HS(40)	ND	ND	ND	X
Carbaryl	63-25-2	X	ND	ND	ND	X
Carbofuran	1563-66-2	X	ND	ND	ND	X
Carbophenothion	786-19-6	X	ND	ND	ND	X
Chlordane (NOS)	57-74-9	X	X	X	X	X
Chlorfenvinphos	470-90-6	X	ND	ND	ND	X
4-Chloroaniline	106-47-8	X	ND	ND	ND	X
Chlorobenzilate	510-15-6	X	ND	ND	ND	X
5-Chloro-2-methylaniline	95-79-4	X	ND	ND	ND	X
4-Chloro-3-methylphenol	59-50-7	X	X	X	X	X
3-(Chloromethyl)pyridine hydrochloride	6959-48-4	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	X	X	X	X
2-Chlorophenol	95-57-8	X	X	X	X	X
4-Chloro-1,2-phenylenediamine	95-83-0	X	X	ND	ND	ND
4-Chloro-1,3-phenylenediamine	5131-60-2	X	X	ND	ND	ND
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X
Chrysene	218-01-9	X	X	X	X	X
Chrysene-d_{12} (IS)		X	X	X	X	X
Coumaphos	56-72-4	X	ND	ND	ND	X
p-Cresidine	120-71-8	X	ND	ND	ND	X
Crotoxyphos	7700-17-6	X	ND	ND	ND	X
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5	X	ND	ND	ND	LR
4,4'-DDD	72-54-8	X	X	X	X	X
4,4'-DDE	72-55-9	X	X	X	X	X
4,4'-DDT	50-29-3	X	X	X	X	X
Demeton-O	298-03-3	HS(68)	ND	ND	ND	X
Demeton-S	126-75-0	X	ND	ND	ND	X
Diallate (cis or trans)	2303-16-4	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
2,4-Diaminotoluene	95-80-7	DC,0E(42)	ND	ND	ND	X
Dibenz(a,j)acridine	224-42-0	X	ND	ND	ND	X
Dibenz(a,h)anthracene	53-70-3	X	X	X	X	X
Dibenzofuran	132-64-9	X	X	ND	X	X
Dibenzo(a,e)pyrene	192-65-4	ND	ND	ND	ND	X
1,2-Dibromo-3-chloropropane	96-12-8	X	X	ND	ND	ND
Di-n-butyl phthalate	84-74-2	X	X	X	X	X
Dichlone	117-80-6	OE	ND	ND	ND	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
1,4-Dichlorobenzene-d_4 (IS)		X	X	X	X	X
3,3'-Dichlorobenzidine	91-94-1	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
Dichlorovos	62-73-7	X	ND	ND	ND	X
Dicrotophos	141-66-2	X	ND	ND	ND	X
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Diethylstilbestrol	56-53-1	AW,0S(67)	ND	ND	ND	X
Diethyl sulfate	64-67-5	LR	ND	ND	ND	LR
Dihydrosaffrole	56312-13-1	ND	ND	ND	ND	ND
Dimethoate	60-51-5	HE,HS(31)	ND	ND	ND	X
3,3'-Dimethoxybenzidine	119-90-4	X	ND	ND	ND	LR
Dimethylaminoazobenzene	60-11-7	X	ND	ND	ND	X
7,12-Dimethylbenz(a)-anthracene	57-97-6	CP(45)	ND	ND	ND	CP
3,3'-Dimethylbenzidine	119-93-7	X	ND	ND	ND	X
α,α-Dimethylphenethylamine	122-09-8	ND	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
Dimethyl phthalate	131-11-3	X	X	X	X	X
1,2-Dinitrobenzene	528-29-0	X	ND	ND	ND	X
1,3-Dinitrobenzene	99-65-0	X	ND	ND	ND	X
1,4-Dinitrobenzene	100-25-4	HE(14)	ND	ND	ND	X
4,6-Dinitro-2-methylphenol	534-52-1	X	X	X	X	X
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X	X	X	X	X
Dinocap	39300-45-3	CP,HS(28)	ND	ND	ND	CP
Dinoseb	88-85-7	X	ND	ND	ND	X
Dioxathion	78-34-2	ND	ND	ND	ND	ND
Diphenylamine	122-39-4	X	X	X	X	X
5,5-Diphenylhydantoin	57-41-0	X	ND	ND	ND	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Disulfoton	298-04-4	X	ND	ND	ND	X
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	ND	X	X
EPN	2104-64-5	X	ND	ND	ND	X
Ethion	563-12-2	X	ND	ND	ND	X
Ethyl carbamate	51-79-6	DC(28)	ND	ND	ND	X
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Famphur	52-85-7	X	ND	ND	ND	X
Fensulfothion	115-90-2	X	ND	ND	ND	X
Fenthion	55-38-9	X	ND	ND	ND	X
Fluchloralin	33245-39-5	X	ND	ND	ND	X
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X
2-Fluorobiphenyl (surr)	321-60-8	X	X	X	X	X
2-Fluorophenol (surr)	367-12-4	X	X	X	X	X
Heptachlor	76-44-8	X	X	X	X	X
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Hexachlorophene	70-30-4	AW,CP(62)	ND	ND	ND	CP
Hexachloropropene	1888-71-7	X	ND	ND	ND	X
Hexamethylphosphoramide	680-31-9	X	ND	ND	ND	X
Hydroquinone	123-31-9	ND	ND	ND	ND	X
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isodrin	465-73-6	X	ND	ND	ND	X
Isophorone	78-59-1	X	X	X	X	X
Isosafrole	120-58-1	DC(46)	ND	ND	ND	X
Kepone	143-50-0	X	ND	ND	ND	X
Leptophos	21609-90-5	X	ND	ND	ND	X
Malathion	121-75-5	HS(5)	ND	ND	ND	X
Maleic anhydride	108-31-6	HE	ND	ND	ND	X
Mestranol	72-33-3	X	ND	ND	ND	X
Methapyrilene	91-80-5	X	ND	ND	ND	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
4,4'-Methylenebis (2-chloroaniline)	101-14-4	OE,OS(0)	ND	ND	ND	LR

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
4,4'-Methylenebis (N,N-dimethylaniline)	101-61-1	X	X	ND	ND	ND
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
Methyl parathion	298-00-0	X	ND	ND	ND	X
2-Methylphenol	95-48-7	X	ND	ND	ND	X
3-Methylphenol	108-39-4	X	ND	ND	ND	X
4-Methylphenol	106-44-5	X	ND	ND	ND	X
Mevinphos	7786-34-7	X	ND	ND	ND	X
Mexacarbate	315-18-4	HE,HS(68)	ND	ND	ND	X
Mirex	2385-85-5	X	ND	ND	ND	X
Monocrotophos	6923-22-4	HE	ND	ND	ND	X
Naled	300-76-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
Naphthalene-d_8 (IS)		X	X	X	X	X
1,4-Naphthoquinone	130-15-4	X	ND	ND	ND	X
1-Naphthylamine	134-32-7	OS(44)	ND	ND	ND	X
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
Nicotine	54-11-5	DE(67)	ND	ND	ND	X
5-Nitroacenaphthene	602-87-9	X	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
3-Nitroaniline	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	X
5-Nitro-o-anisidine	99-59-2	X	ND	ND	ND	X
Nitrobenzene	98-95-3	X	X	X	X	X
Nitrobenzene-d_5 (surr)		X	X	X	X	X
4-Nitrobiphenyl	92-93-3	X	ND	ND	ND	X
Nitrofen	1836-75-5	X	ND	ND	ND	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
5-Nitro-o-toluidine	99-55-8	X	X	ND	ND	X
Nitroquinoline-1-oxide	56-57-5	X	ND	ND	ND	X
N-Nitrosodi-n-butylamine	924-16-3	X	ND	ND	ND	X
N-Nitrosodiethylamine	55-18-5	X	ND	ND	ND	X
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosomethylethylamine	10595-95-6	X	ND	ND	ND	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-n-propylamine	621-64-7	X	X	X	X	X
N-Nitrosomorpholine	59-89-2	ND	ND	ND	ND	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
N-Nitrosopyrrolidine	930-55-2	X	ND	ND	ND	X
Octamethyl pyrophosphoramide	152-16-9	LR	ND	ND	ND	LR
4,4'-Oxydianiline	101-80-4	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
Parathion	56-38-2	X	X	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X
Pentachloronitrobenzene	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Perylene-d_{12} (IS)		X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenanthrene-d_{10} (IS)		X	X	X	X	X
Phenobarbital	50-06-6	X	ND	ND	ND	X
Phenol	108-95-2	DC(28)	X	X	X	X
Phenol-d_6 (surr)		DC(28)	X	X	X	X
1,4-Phenylenediamine	106-50-3	X	ND	ND	ND	X
Phorate	298-02-2	X	ND	ND	ND	X
Phosalone	2310-17-0	HS(65)	ND	ND	ND	X
Phosmet	732-11-6	HS(15)	ND	ND	ND	X
Phosphamidon	13171-21-6	HE(63)	ND	ND	ND	X
Phthalic anhydride	85-44-9	CP,HE(1)	ND	ND	ND	CP
2-Picoline (2-Methylpyridine)	109-06-8	X	X	ND	ND	ND
Piperonyl sulfoxide	120-62-7	X	ND	ND	ND	X
Pronamide	23950-58-5	X	ND	ND	ND	X
Propylthiouracil	51-52-5	LR	ND	ND	ND	LR
Pyrene	129-00-0	X	X	X	X	X
Pyridine	110-86-1	ND	ND	ND	ND	ND
Resorcinol	108-46-3	DC,OE(10)	ND	ND	ND	X
Safrole	94-59-7	X	ND	ND	ND	X
Strychnine	57-24-9	AW,0S(55)	ND	ND	ND	X
Sulfallate	95-06-7	X	ND	ND	ND	X
Terbufos	13071-79-9	X	ND	ND	ND	X
Terphenyl-d_{14}(surr)	1718-51-0	X	X	ND	X	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X	ND	ND	ND	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X
Tetrachlorvinphos	961-11-5	X	ND	ND	ND	X
Tetraethyl dithiopyrophosphate	3689-24-5	X	X	ND	ND	ND
Tetraethyl pyrophosphate	107-49-3	X	ND	ND	ND	X
Thionazine	297-97-2	X	ND	ND	ND	X
Thiophenol (Benzenethiol)	108-98-5	X	ND	ND	ND	X
Toluene diisocyanate	584-84-9	HE(6)	ND	ND	ND	X
o-Toluidine	95-53-4	X	ND	ND	ND	X
Toxaphene	8001-35-2	X	X	X	X	X
2,4,6-Tribromophenol (surr)	118-79-6	X	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X
Trifluralin	1582-09-8	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
2,4,5-Trimethylaniline	137-17-7	X	ND	ND	ND	X
Trimethyl phosphate	512-56-1	HE(60)	ND	ND	ND	X
1,3,5-Trinitrobenzene	99-35-4	X	ND	ND	ND	X
Tris(2,3-dibromopropyl) phosphate	126-72-7	X	ND	ND	ND	LR
Tri-p-tolyl phosphate	78-32-0	X	ND	ND	ND	X
O,O,O-Triethyl phosphorothioate	126-68-1	X	ND	ND	ND	X

[a] Chemical Abstract Service Registry Number
[b] See Sec. 1.2 for other acceptable preparation methods.

KEY TO ANALYTE LIST

IS = This compound may be used as an internal standard.
surr = This compound may be used as a surrogate.
AW = Adsorption to walls of glassware during extraction and storage.
CP = Nonreproducible chromatographic performance.
DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).
HE = Hydrolysis during extraction accelerated by acidic or basic conditions (number in parenthesis is percent recovery).
HS = Hydrolysis during storage (number in parenthesis is percent stability).
LR = Low response.
ND = Not determined.
OE = Oxidation during extraction accelerated by basic conditions (number in parenthesis is percent recovery).
OS = Oxidation during storage (number in parenthesis is percent stability).
X = Greater than 70 percent recovery by this technique.

1.2 In addition to the sample preparation methods listed in the above analyte list, Method 3542 describes sample preparation for semivolatile organic compounds in air sampled by Method 0010 (Table 11 contains surrogate performance data), Method 3545 describes an automated solvent extraction device for semivolatiles in solids (Table 12 contains performance data), and Method 3561 describes a supercritical fluid extraction of solids for PAHs (see Tables 13, 14, and 15 for performance data).

1.3 Method 8270 can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated.

In most cases, Method 8270 is not appropriate for the quantitation of multicomponent analytes, e.g., Aroclors, Toxaphene, Chlordane, etc., because of limited sensitivity for those analytes. When these analytes have been identified by another technique, Method 8270 is appropriate for confirmation of the presence of these analytes when concentration in the extract permits. Refer to Sec. 7.0 of Methods 8081 and 8082 for guidance on calibration and quantitation of multicomponent analytes such as the Aroclors, Toxaphene, and Chlordane.

1.4 The following compounds may require special treatment when being determined by this method:

1.4.1 Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.

1.4.2 Under the alkaline conditions of the extraction step from aqueous matrices, α-BHC, γ-BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected.

1.4.3 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

1.4.4 N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.

1.4.5 N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.

1.4.6 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4.7 Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. The analyst needs to use caution if modifying the injection port temperature as the performance of other analytes may be adversely affected.

1.4.8 Toluene diisocyanate rapidly hydrolyses in water (half-life of less then 30 min.). Therefore, recoveries of this compound from aqueous matrices should not be expected. In addition, in solid matrices, toluene diisocyanate often reacts with alcohols and amines to produce urethane and ureas and consequently cannot usually coexist in a solution containing these materials.

1.4.9 In addition, analytes in the list provided above are flagged when there are limitations caused by sample preparation and/or chromatographic problems.

1.5 The estimated quantitation limit (EQL) of Method 8270 for determining an individual compound is approximately 660 µg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for ground water samples (see Table 2). EQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

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

2.0 SUMMARY OF METHOD

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to Method 3500) and, if necessary, sample cleanup procedures (refer to Method 3600).

2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.4 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

3.1 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.

3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system

4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2 Column - 30 m x 0.25 mm ID (or 0.32 mm ID) 1 µm film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.3 Mass spectrometer

4.1.3.1 Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria in Table 3 when 1 µL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.3.2 An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. The mass spectrometer must be capable of producing a mass spectrum for DFTPP which meets the criteria in Table 3 when 5 or 50 ng are introduced.

4.1.4 GC/MS interface - Any GC-to-MS interface may be used that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria. For a narrow-bore capillary column, the interface is usually capillary-direct into the mass spectrometer source.

4.1.5 Data system - A computer system should be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer should have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software should also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.1.6 Guard column (optional) - (J&W Deactivated Fused Silica, 0.25 mm ID x 6 m, or equivalent) between the injection port and the analytical column joined with column joiners (Hewlett-Packard Catalog No. 5062-3556, or equivalent).

4.2 Syringe - 10-µL.

4.3 Volumetric flasks, Class A - Appropriate sizes with ground-glass stoppers.

4.4 Balance - Analytical, capable of weighing 0.0001 g.

4.5 Bottles - glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

5.0 REAGENTS

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

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

5.3 Stock standard solutions (1000 mg/L) - Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 Transfer the stock standard solutions into bottles with PTFE-lined screw-caps. Store, protected from light, at -10°C or less or as recommended by the standard manufacturer. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

5.3.4 It is recommended that nitrosamine compounds be placed together in a separate calibration mix and not combined with other calibration mixes. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

5.3.5 Mixes with hydrochloride salts may contain hydrochloric acid, which can cause analytical difficulties. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

5.4 Internal standard solutions - The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} (see Table 5). Other compounds may be used as internal standards as long as the requirements given in Sec. 7.3.2 are met.

5.4.1 Dissolve 0.200 g of each compound with a small volume of carbon disulfide. Transfer to a 50 mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/µL. Each 1 mL sample extract undergoing analysis should be spiked with 10 µL of the internal standard solution, resulting in a concentration of 40 ng/µL of each internal standard. Store at -10°C or less when not in use. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.4.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute internal standard solution may be required. Area counts of the internal standard peaks should be between 50-200% of the area of the target analytes in the mid-point calibration analysis.

5.5 GC/MS tuning standard - A methylene chloride solution containing 50 ng/µL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/µL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at -10°C or less when not in use. If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute tuning solution may be necessary. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.6 Calibration standards - A minimum of five calibration standards should be prepared at five different concentrations. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in actual samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method.

5.6.1 It is the intent of EPA that all target analytes for a particular analysis be included in the calibration standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.6.2 Each 1-mL aliquot of calibration standard should be spiked with 10 µL of the internal standard solution prior to analysis. All standards should be stored at -10°C or less, and should be freshly prepared once a year, or sooner if check standards indicate a problem. The calibration verification standard should be prepared weekly and stored at 4°C. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.7 Surrogate standards - The recommended surrogates are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for instructions on preparing the surrogate solutions.

5.7.1 Surrogate Standard Check: Determine what the appropriate concentration should be for the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards. It is recommended that this check be done whenever a new surrogate spiking solution is prepared.

NOTE: Method 3561 (SFE Extraction of PAHs) recommends the use of bromobenzene and p-quaterphenyl to better cover the range of PAHs listed in the method.

5.7.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute surrogate solution may be necessary.

5.8 Matrix spike and laboratory control standards - See Method 3500 for instructions on preparing the matrix spike standard. The same standard may be used as the laboratory control standard (LCS).

5.8.1 Matrix Spike Check: Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery. It is recommended that this check be done whenever a new matrix spiking solution is prepared.

5.8.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute matrix and LCS spiking solution may be necessary.

5.8.3 Some projects may require the spiking of the specific compounds of interest, since the spiking compounds listed in Method 3500 would not be representative of the compounds of interest required for the project. When this occurs, the matrix and LCS spiking

standards should be prepared in methanol, with each compound present at a concentration appropriate for the project.

5.9 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents - All solvents should be pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Store the sample extracts at -10°C, protected from light, in sealed vials (e.g., screw-cap vials or crimp-capped vials) equipped with unpierced PTFE-lined septa.

7.0 PROCEDURE

7.1 Sample preparation

7.1.1 Samples are normally prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Air	3542
Water	3510, 3520, 3535
Soil/sediment	3540, 3541, 3545, 3550, 3560, 3561
Waste	3540, 3541, 3545, 3550, 3560, 3561, 3580

7.1.2 In very limited applications, direct injection of the sample into the GC/MS system with a 10-µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L). Therefore, it is only permitted where concentrations in excess of 10,000 µg/L are expected.

7.2 Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Analytes of interest	Methods
Aniline & aniline derivatives	3620
Phenols	3630, 3640, 8041[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3610, 3620, 3630, 3660, 3665
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620

Analytes of interest	Methods
Petroleum waste	3611, 3650
All base, neutral, and acid priority pollutants	3640

[a] Method 8041 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Initial calibration

Establish the GC/MS operating conditions, using the following recommendations as guidance.

Mass range:	35-500 amu
Scan time:	1 sec/scan
Initial temperature:	40°C, hold for 4 minutes
Temperature program:	40-270°C at 10°C/min
Final temperature:	270°C, hold until benzo[g,h,i]perylene elutes
Injector temperature:	250-300°C
Transfer line temperature:	250-300°C
Source temperature:	According to manufacturer's specifications
Injector:	Grob-type, splitless
Injection volume:	1-2 µL
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

Split injection is allowed if the sensitivity of the mass spectrometer is sufficient.

7.3.1 The GC/MS system must be hardware-tuned using a 50 ng injection of DFTPP. Analyses must not begin until the tuning criteria are met.

7.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of DFTPP from the instrument manufacturer, the following approach has been shown to be useful: Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.

7.3.1.2 Use the DFTPP mass intensity criteria in Table 3 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g. CLP, Method 525, or manufacturer's instructions), provided that method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

7.3.1.3 The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD

should not exceed 20%. (See Sec. 8.0 of Method 8081 for the percent breakdown calculation). Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible.

7.3.1.4 If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column. The use of a guard column (Sec. 4.1.6) between the injection port and the analytical column may help prolong analytical column performance.

7.3.2 The internal standards selected in Sec. 5.4 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for 1,4-dichlorobenzene-d_4, use 152 m/z for quantitation).

7.3.3 Analyze 1-2 µL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte (as indicated in Table 1). A set of at least five calibration standards is necessary (see Sec. 5.6 and Method 8000). The injection volume must be the same for all standards and sample extracts. Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes.

Calculate response factors (RFs) for each target analyte relative to one of the internal standards as follows:

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

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

7.3.4 System performance check compounds (SPCCs)

7.3.4.1 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol.

7.3.4.2 The minimum acceptable average RF for these compounds is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

7.3.4.3 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.3.5 Calibration check compounds (CCCs)

7.3.5.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Section 7.0 of Method 8000.

7.3.5.2 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte. The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual CCC (see Table 4) must be less than or equal to 30%.

$$\text{mean RF} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{RF}} \times 100$$

7.3.5.3 If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with Sec. 7.3.

7.3.5.4 If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, refer to Sec. 7.0 of Method 8000.

7.3.6 Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement.

7.3.7 Linearity of target analytes - If the RSD of any target analytes is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 7.6.2).

7.3.7.1 If the RSD of any target analyte is greater than 15%, refer to Sec. 7.0 in Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

NOTE: Method 8000 designates a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8270 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

7.3.7.2 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject 50 ng of the DFTPP standard into the GC/MS system. The resultant mass spectrum for DFTPP must meet the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

7.4.2 The initial calibration (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 7.4.4 through 7.4.7.

NOTE: The DFTPP and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

7.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Sec. 8.0 of Method 8000B for method blank performance criteria.

7.4.4 System performance check compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC in the calibration verification standard must meet a minimum response factor of 0.050. This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.4.5 Calibration check compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Table 4 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Sec. 7.0 of Method 8000 for guidance on calculating percent difference and drift.

7.4.5.2 If the percent difference for each CCC is less than or equal to 20%, then the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater than 20% difference or drift) for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCCs are not included in the list of analytes for a project,

and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.4.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.7 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 GC/MS analysis of samples

7.5.1 It is highly recommended that sample extracts be screened on a GC/FID or GC/PID using the same type of capillary column used in the GC/MS system. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Allow the sample extract to warm to room temperature. Just prior to analysis, add 10 µL of the internal standard solution to the 1-mL concentrated sample extract obtained from sample preparation.

7.5.3 Inject a 1-2 µL aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration (Sec. 7.3). The volume to be injected should contain 100 ng of base/neutral and 200 ng of acid surrogates (assuming 100% recovery), unless a more sensitive GC/MS system is being used and the surrogate solution is less concentrated then that listed in Sec. 5.7. The injection volume must be the same volume used for the calibration standards.

7.5.4 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed. Additional internal standard must be added to the diluted extract to maintain the same concentration as in the calibration standards (40 ng/µL, unless a more sensitive GC/MS system is being used).

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance.

7.5.5 The use of selected ion monitoring (SIM) is acceptable for applications requiring detection limits below the normal range of electron impact mass spectrometry. However, SIM

may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

7.6 Qualitative analysis

7.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. Compounds are identified when the following criteria are met.

7.6.1.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. Diastereomeric pairs (e.g., Aramite and Isosafrol) that may be separable by the GC should be identified, quantitated and reported as the sum of both compounds by the GC.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

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

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the

analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:

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

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

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

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

7.7.2 If the RSD of a compound's response factor is 15% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data (Sec. 7.3.5). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

7.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 7.6.2) should be estimated. The same formulae should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

7.7.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.7.5 Quantitation of multicomponent compounds (e.g., Toxaphene, Aroclors, etc.) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD, by Methods 8081 or 8082. However, Method 8270 may be used to confirm the identification of these compounds, when the concentrations are at least 10 ng/µL in the concentrated sample extract.

7.7.6 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are quantitated as isomeric pairs. Diastereomeric pairs (e.g., Aramite and Isosafrol) that may be separable by the GC should be summed and reported as the sum of both compounds.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Method 3500. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Sec. 7.0 of Method 8000 and include calibration verification and chromatographic analysis of samples. In addition, instrument QC requirements may be found in the following sections of Method 8270:

8.2.1 The GC/MS system must be tuned to meet the DFTPP criteria listed in Secs. 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as described in Sec. 7.3.

8.2.3 The GC/MS system must meet the calibration verification acceptance criteria in Sec. 7.4, each 12 hours.

8.2.4 The RRT of the sample component must fall within the RRT window of the standard component provided in Sec. 7.6.1.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed, a septum is changed), see the guidance in Sec 8.2 of Method 8000 regarding whether recalibration of the system must take place.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Method 8250 (the packed column version of Method 8270) was tested by 15 laboratories using organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations ranging from 5 to 1,300 µg/L. Single operator accuracy and precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7. These values are presented as guidance only and are not intended as absolute acceptance criteria. Laboratories should generate their own acceptance criteria for capillary column method performance. (See Method 8000.)

9.2 Chromatograms from calibration standards analyzed with Day 0 and Day 7 samples were compared to detect possible deterioration of GC performance. These recoveries (using Method 3510 extraction) are presented in Table 8.

9.3 Method performance data (using Method 3541 Automated Soxhlet extraction) are presented in Table 9. Single laboratory accuracy and precision data were obtained for semivolatile organics in a clay soil by spiking at a concentration of 6 mg/kg for each compound. The spiking solution was mixed into the soil during addition and then allowed to equilibrate for approximately 1 hour prior to extraction. The spiked samples were then extracted by Method 3541 (Automated Soxhlet). Three determinations were performed and each extract was analyzed by gas chromatography/ mass spectrometry following Method 8270. The low recovery of the more volatile compounds is probably due to volatilization losses during equilibration. These data are listed in Table 10 and were taken from Reference 7.

9.4 Surrogate precision and accuracy data are presented in Table 11 from a field dynamic spiking study based on air sampling by Method 0010. The trapping media were prepared for analysis by Method 3542 and subsequently analyzed by Method 8270.

9.5 Single laboratory precision and bias data (using Method 3545 Accelerated Solvent Extraction) for semivolatile organic compounds are presented in Table 12. The samples were conditioned spiked samples prepared and certified by a commercial supplier that contained 57 semivolatile organics at three concentrations (250, 2500, and 12,500 µg/kg) on three types of soil (clay, loam and sand). Spiked samples were extracted both by the Dionex Accelerated Solvent Extraction system and by Perstorp Environmental Soxtec™ (automated Soxhlet). The data presented in Table 12 represents seven replicate extractions and analyses for each individual sample and were taken from reference 9. The average recoveries from the three matrices for all analytes and all replicates relative to the automated Soxhlet data are as follows: clay 96.8%, loam 98.7% and sand 102.1%. The average recoveries from the three concentrations also relative to the automated Soxhlet data are as follows: low-101.2%, mid-97.2% and high-99.2%.

9.6 Single laboratory precision and bias data (using Method 3561 SFE Extraction of PAHs with a variable restrictor and solid trapping material) were obtained for the method analytes by the extraction of two certified reference materials (one, EC-1, a lake sediment from Environment Canada and the other, HS-3, a marine sediment from the National Science and Engineering Research Council of Canada, both naturally-contaminated with PAHs). The SFE instrument used for these extractions was a Hewlett-Packard Model 7680. Analysis was by GC/MS. Average recoveries from six replicate extractions range from 85 to 148% (overall average of 100%) based on the certified value (or a Soxhlet value if a certified value was unavailable for a specific analyte) for the lake sediment. Average recoveries from three replicate extractions range from 73 to 133% (overall average of 92%) based on the certified value for the marine sediment. The data are found in Tables 13 and 14 and were taken from Reference 10.

9.7 Single laboratory precision and accuracy data (using Method 3561 SFE Extraction of PAHs with a fixed restrictor and liquid trapping) were obtained for twelve of the method analytes by the extraction of a certified reference material (a soil naturally contaminated with PAHs). The SFE instrument used for these extractions was a Dionex Model 703-M. Analysis was by GC/MS. Average recoveries from four replicate extractions range from 60 to 122% (overall average of 89%) based on the certified value. Following are the instrument conditions that were utilized to extract a 3.4 g sample: Pressure - 300 atm; Time - 60 min.; Extraction fluid - CO_2; Modifier - 10% 1:1 (v/v) methanol/methylene chloride; Oven temperature - 80°C; Restrictor temperature - 120°C; and, Trapping fluid - chloroform (methylene chloride has also been used). The data are found in Table 15 and were taken from Reference 11.

10.0 REFERENCES

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TABLE 1

CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
2-Picoline	3.75[a]	93	66,92
Aniline	5.68	93	66,65
Phenol	5.77	94	65,66
Bis(2-chloroethyl) ether	5.82	93	63,95
2-Chlorophenol	5.97	128	64,130
1,3-Dichlorobenzene	6.27	146	148,111
1,4-Dichlorobenzene-d_4 (IS)	6.35	152	150,115
1,4-Dichlorobenzene	6.40	146	148,111
Benzyl alcohol	6.78	108	79,77
1,2-Dichlorobenzene	6.85	146	148,111
N-Nitrosomethylethylamine	6.97	88	42,43,56
Bis(2-chloroisopropyl) ether	7.22	45	77,121
Ethyl carbamate	7.27	62	44,45,74
Thiophenol (Benzenethiol)	7.42	110	66,109,84
Methyl methanesulfonate	7.48	80	79,65,95
N-Nitrosodi-n-propylamine	7.55	70	42,101,130
Hexachloroethane	7.65	117	201,199
Maleic anhydride	7.65	54	98,53,44
Nitrobenzene	7.87	77	123,65
Isophorone	8.53	82	95,138
N-Nitrosodiethylamine	8.70	102	42,57,44,56
2-Nitrophenol	8.75	139	109,65
2,4-Dimethylphenol	9.03	122	107,121
p-Benzoquinone	9.13	108	54,82,80
Bis(2-chloroethoxy)methane	9.23	93	95,123
Benzoic acid	9.38	122	105,77
2,4-Dichlorophenol	9.48	162	164,98
Trimethyl phosphate	9.53	110	79,95,109,140
Ethyl methanesulfonate	9.62	79	109,97,45,65
1,2,4-Trichlorobenzene	9.67	180	182,145
Naphthalene-d_8 (IS)	9.75	136	68
Naphthalene	9.82	128	129,127
Hexachlorobutadiene	10.43	225	223,227
Tetraethyl pyrophosphate	11.07	99	155,127,81,109
Diethyl sulfate	11.37	139	45,59,99,111,125
4-Chloro-3-methylphenol	11.68	107	144,142
2-Methylnaphthalene	11.87	142	141
2-Methylphenol	12.40	107	108,77,79,90
Hexachloropropene	12.45	213	211,215,117,106,141
Hexachlorocyclopentadiene	12.60	237	235,272

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
N-Nitrosopyrrolidine	12.65	100	41,42,68,69
Acetophenone	12.67	105	71,51,120
4-Methylphenol	12.82	107	108,77,79,90
2,4,6-Trichlorophenol	12.85	196	198,200
o-Toluidine	12.87	106	107,77,51,79
3-Methylphenol	12.93	107	108,77,79,90
2-Chloronaphthalene	13.30	162	127,164
N-Nitrosopiperidine	13.55	114	42,55,56,41
1,4-Phenylenediamine	13.62	108	80,53,54,52
1-Chloronaphthalene	13.65[a]	162	127,164
2-Nitroaniline	13.75	65	92,138
5-Chloro-2-methylaniline	14.28	106	141,140,77,89
Dimethyl phthalate	14.48	163	194,164
Acenaphthylene	14.57	152	151,153
2,6-Dinitrotoluene	14.62	165	63,89
Phthalic anhydride	14.62	104	76,50,148
o-Anisidine	15.00	108	80,123,52
3-Nitroaniline	15.02	138	108,92
Acenaphthene-d_{10} (IS)	15.05	164	162,160
Acenaphthene	15.13	154	153,152
2,4-Dinitrophenol	15.35	184	63,154
2,6-Dinitrophenol	15.47	162	164,126,98,63
4-Chloroaniline	15.50	127	129,65,92
Isosafrole	15.60	162	131,104,77,51
Dibenzofuran	15.63	168	139
2,4-Diaminotoluene	15.78	121	122,94,77,104
2,4-Dinitrotoluene	15.80	165	63,89
4-Nitrophenol	15.80	139	109,65
2-Naphthylamine	16.00[a]	143	115,116
1,4-Naphthoquinone	16.23	158	104,102,76,50,130
p-Cresidine	16.45	122	94,137,77,93
Dichlorovos	16.48	109	185,79,145
Diethyl phthalate	16.70	149	177,150
Fluorene	16.70	166	165,167
2,4,5-Trimethylaniline	16.70	120	135,134,91,77
N-Nitrosodi-n-butylamine	16.73	84	57,41,116,158
4-Chlorophenyl phenyl ether	16.78	204	206,141
Hydroquinone	16.93	110	81,53,55
4,6-Dinitro-2-methylphenol	17.05	198	51,105
Resorcinol	17.13	110	81,82,53,69
N-Nitrosodiphenylamine	17.17	169	168,167
Safrole	17.23	162	104,77,103,135

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Hexamethyl phosphoramide	17.33	135	44,179,92,42
3-(Chloromethyl)pyridine hydrochloride	17.50	92	127,129,65,39
Diphenylamine	17.54[a]	169	168,167
1,2,4,5-Tetrachlorobenzene	17.97	216	214,179,108,143,218
1-Naphthylamine	18.20	143	115,89,63
1-Acetyl-2-thiourea	18.22	118	43,42,76
4-Bromophenyl phenyl ether	18.27	248	250,141
Toluene diisocyanate	18.42	174	145,173,146,132,91
2,4,5-Trichlorophenol	18.47	196	198,97,132,99
Hexachlorobenzene	18.65	284	142,249
Nicotine	18.70	84	133,161,162
Pentachlorophenol	19.25	266	264,268
5-Nitro-o-toluidine	19.27	152	77,79,106,94
Thionazine	19.35	107	96,97,143,79,68
4-Nitroaniline	19.37	138	65,108,92,80,39
Phenanthrene-d_{10} (IS)	19.55	188	94,80
Phenanthrene	19.62	178	179,176
Anthracene	19.77	178	176,179
1,4-Dinitrobenzene	19.83	168	75,50,76,92,122
Mevinphos	19.90	127	192,109,67,164
Naled	20.03	109	145,147,301,79,189
1,3-Dinitrobenzene	20.18	168	76,50,75,92,122
Diallate (cis or trans)	20.57	86	234,43,70
1,2-Dinitrobenzene	20.58	168	50,63,74
Diallate (trans or cis)	20.78	86	234,43,70
Pentachlorobenzene	21.35	250	252,108,248,215,254
5-Nitro-o-anisidine	21.50	168	79,52,138,153,77
Pentachloronitrobenzene	21.72	237	142,214,249,295,265
4-Nitroquinoline-1-oxide	21.73	174	101,128,75,116
Di-n-butyl phthalate	21.78	149	150,104
2,3,4,6-Tetrachlorophenol	21.88	232	131,230,166,234,168
Dihydrosaffrole	22.42	135	64,77
Demeton-O	22.72	88	89,60,61,115,171
Fluoranthene	23.33	202	101,203
1,3,5-Trinitrobenzene	23.68	75	74,213,120,91,63
Dicrotophos	23.82	127	67,72,109,193,237
Benzidine	23.87	184	92,185
Trifluralin	23.88	306	43,264,41,290
Bromoxynil	23.90	277	279,88,275,168
Pyrene	24.02	202	200,203
Monocrotophos	24.08	127	192,67,97,109
Phorate	24.10	75	121,97,93,260

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Sulfallate	24.23	188	88,72,60,44
Demeton-S	24.30	88	60,81,89,114,115
Phenacetin	24.33	108	180,179,109,137,80
Dimethoate	24.70	87	93,125,143,229
Phenobarbital	24.70	204	117,232,146,161
Carbofuran	24.90	164	149,131,122
Octamethyl pyrophosphoramide	24.95	135	44,199,286,153,243
4-Aminobiphenyl	25.08	169	168,170,115
Dioxathion	25.25	97	125,270,153
Terbufos	25.35	231	57,97,153,103
α,α-Dimethylphenylamine	25.43	58	91,65,134,42
Pronamide	25.48	173	175,145,109,147
Aminoazobenzene	25.72	197	92,120,65,77
Dichlone	25.77	191	163,226,228,135,193
Dinoseb	25.83	211	163,147,117,240
Disulfoton	25.83	88	97,89,142,186
Fluchloralin	25.88	306	63,326,328,264,65
Mexacarbate	26.02	165	150,134,164,222
4,4'-Oxydianiline	26.08	200	108,171,80,65
Butyl benzyl phthalate	26.43	149	91,206
4-Nitrobiphenyl	26.55	199	152,141,169,151
Phosphamidon	26.85	127	264,72,109,138
2-Cyclohexyl-4,6-Dinitrophenol	26.87	231	185,41,193,266
Methyl parathion	27.03	109	125,263,79,93
Carbaryl	27.17	144	115,116,201
Dimethylaminoazobenzene	27.50	225	120,77,105,148,42
Propylthiouracil	27.68	170	142,114,83
Benz(a)anthracene	27.83	228	229,226
Chrysene-d_{12} (IS)	27.88	240	120,236
3,3'-Dichlorobenzidine	27.88	252	254,126
Chrysene	27.97	228	226,229
Malathion	28.08	173	125,127,93,158
Kepone	28.18	272	274,237,178,143,270
Fenthion	28.37	278	125,109,169,153
Parathion	28.40	109	97,291,139,155
Anilazine	28.47	239	241,143,178,89
Bis(2-ethylhexyl) phthalate	28.47	149	167,279
3,3'-Dimethylbenzidine	28.55	212	106,196,180
Carbophenothion	28.58	157	97,121,342,159,199
5-Nitroacenaphthene	28.73	199	152,169,141,115
Methapyrilene	28.77	97	50,191,71
Isodrin	28.95	193	66,195,263,265,147

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Captan	29.47	79	149,77,119,117
Chlorfenvinphos	29.53	267	269,323,325,295
Crotoxyphos	29.73	127	105,193,166
Phosmet	30.03	160	77,93,317,76
EPN	30.11	157	169,185,141,323
Tetrachlorvinphos	30.27	329	109,331,79,333
Di-n-octyl phthalate	30.48	149	167,43
2-Aminoanthraquinone	30.63	223	167,195
Barban	30.83	222	51,87,224,257,153
Aramite	30.92	185	191,319,334,197,321
Benzo(b)fluoranthene	31.45	252	253,125
Nitrofen	31.48	283	285,202,139,253
Benzo(k)fluoranthene	31.55	252	253,125
Chlorobenzilate	31.77	251	139,253,111,141
Fensulfothion	31.87	293	97,308,125,292
Ethion	32.08	231	97,153,125,121
Diethylstilbestrol	32.15	268	145,107,239,121,159
Famphur	32.67	218	125,93,109,217
Tri-p-tolyl phosphate[b]	32.75	368	367,107,165,198
Benzo(a)pyrene	32.80	252	253,125
Perylene-d_{12} (IS)	33.05	264	260,265
7,12-Dimethylbenz(a)anthracene	33.25	256	241,239,120
5,5-Diphenylhydantoin	33.40	180	104,252,223,209
Captafol	33.47	79	77,80,107
Dinocap	33.47	69	41,39
Methoxychlor	33.55	227	228,152,114,274,212
2-Acetylaminofluorene	33.58	181	180,223,152
4,4'-Methylenebis(2-chloroaniline)	34.38	231	266,268,140,195
3,3'-Dimethoxybenzidine	34.47	244	201,229
3-Methylcholanthrene	35.07	268	252,253,126,134,113
Phosalone	35.23	182	184,367,121,379
Azinphos-methyl	35.25	160	132,93,104,105
Leptophos	35.28	171	377,375,77,155,379
Mirex	35.43	272	237,274,270,239,235
Tris(2,3-dibromopropyl) phosphate	35.68	201	137,119,217,219,199
Dibenz(a,j)acridine	36.40	279	280,277,250
Mestranol	36.48	277	310,174,147,242
Coumaphos	37.08	362	226,210,364,97,109
Indeno(1,2,3-cd)pyrene	39.52	276	138,227
Dibenz(a,h)anthracene	39.82	278	139,279
Benzo(g,h,i)perylene	41.43	276	138,277
1,2:4,5-Dibenzopyrene	41.60	302	151,150,300

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Strychnine	45.15	334	334,335,333
Piperonyl sulfoxide	46.43	162	135,105,77
Hexachlorophene	47.98	196	198,209,211,406,408
Aldrin	--	66	263,220
Aroclor 1016	--	222	260,292
Aroclor 1221	--	190	224,260
Aroclor 1232	--	190	224,260
Aroclor 1242	--	222	256,292
Aroclor 1248	--	292	362,326
Aroclor 1254	--	292	362,326
Aroclor 1260	--	360	362,394
α-BHC	--	183	181,109
β-BHC	--	181	183,109
δ-BHC	--	183	181,109
γ-BHC (Lindane)	--	183	181,109
4,4'-DDD	--	235	237,165
4,4'-DDE	--	246	248,176
4,4'-DDT	--	235	237,165
Dieldrin	--	79	263,279
1,2-Diphenylhydrazine	--	77	105,182
Endosulfan I	--	195	339,341
Endosulfan II	--	337	339,341
Endosulfan sulfate	--	272	387,422
Endrin	--	263	82,81
Endrin aldehyde	--	67	345,250
Endrin ketone	--	317	67,319
2-Fluorobiphenyl (surr)	--	172	171
2-Fluorophenol (surr)	--	112	64
Heptachlor	--	100	272,274
Heptachlor epoxide	--	353	355,351
Nitrobenzene-d_5 (surr)	--	82	128,54
N-Nitrosodimethylamine	--	42	74,44
Phenol-d_6 (surr)	--	99	42,71
Terphenyl-d_{14} (surr)	--	244	122,212
2,4,6-Tribromophenol (surr)	--	330	332,141
Toxaphene	--	159	231,233

IS = internal standard
surr = surrogate
[a]Estimated retention times
[b]Substitute for the non-specific mixture, tricresyl phosphate

TABLE 2

ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Acenaphthene	10	660
Acenaphthylene	10	660
Acetophenone	10	ND
2-Acetylaminofluorene	20	ND
1-Acetyl-2-thiourea	1000	ND
2-Aminoanthraquinone	20	ND
Aminoazobenzene	10	ND
4-Aminobiphenyl	20	ND
Anilazine	100	ND
o-Anisidine	10	ND
Anthracene	10	660
Aramite	20	ND
Azinphos-methyl	100	ND
Barban	200	ND
Benz(a)anthracene	10	660
Benzo(b)fluoranthene	10	660
Benzo(k)fluoranthene	10	660
Benzoic acid	50	3300
Benzo(g,h,i)perylene	10	660
Benzo(a)pyrene	10	660
p-Benzoquinone	10	ND
Benzyl alcohol	20	1300
Bis(2-chloroethoxy)methane	10	660
Bis(2-chloroethyl) ether	10	660
Bis(2-chloroisopropyl) ether	10	660
4-Bromophenyl phenyl ether	10	660
Bromoxynil	10	ND
Butyl benzyl phthalate	10	660
Captafol	20	ND
Captan	50	ND
Carbaryl	10	ND
Carbofuran	10	ND
Carbophenothion	10	ND
Chlorfenvinphos	20	ND
4-Chloroaniline	20	1300
Chlorobenzilate	10	ND
5-Chloro-2-methylaniline	10	ND
4-Chloro-3-methylphenol	20	1300
3-(Chloromethyl)pyridine hydrochloride	100	ND
2-Chloronaphthalene	10	660

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
2-Chlorophenol	10	660
4-Chlorophenyl phenyl ether	10	660
Chrysene	10	660
Coumaphos	40	ND
p-Cresidine	10	ND
Crotoxyphos	20	ND
2-Cyclohexyl-4,6-dinitrophenol	100	ND
Demeton-O	10	ND
Demeton-S	10	ND
Diallate (cis or trans)	10	ND
Diallate (trans or cis)	10	ND
2,4-Diaminotoluene	20	ND
Dibenz(a,j)acridine	10	ND
Dibenz(a,h)anthracene	10	660
Dibenzofuran	10	660
Dibenzo(a,e)pyrene	10	ND
Di-n-butyl phthalate	10	ND
Dichlone	NA	ND
1,2-Dichlorobenzene	10	660
1,3-Dichlorobenzene	10	660
1,4-Dichlorobenzene	10	660
3,3'-Dichlorobenzidine	20	1300
2,4-Dichlorophenol	10	660
2,6-Dichlorophenol	10	ND
Dichlorovos	10	ND
Dicrotophos	10	ND
Diethyl phthalate	10	660
Diethylstilbestrol	20	ND
Diethyl sulfate	100	ND
Dimethoate	20	ND
3,3'-Dimethoxybenzidine	100	ND
Dimethylaminoazobenzene	10	ND
7,12-Dimethylbenz(a)anthracene	10	ND
3,3'-Dimethylbenzidine	10	ND
a,a-Dimethylphenethylamine	ND	ND
2,4-Dimethylphenol	10	660
Dimethyl phthalate	10	660
1,2-Dinitrobenzene	40	ND
1,3-Dinitrobenzene	20	ND
1,4-Dinitrobenzene	40	ND
4,6-Dinitro-2-methylphenol	50	3300
2,4-Dinitrophenol	50	3300

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
2,4-Dinitrotoluene	10	660
2,6-Dinitrotoluene	10	660
Dinocap	100	ND
Dinoseb	20	ND
5,5-Diphenylhydantoin	20	ND
Di-n-octyl phthalate	10	660
Disulfoton	10	ND
EPN	10	ND
Ethion	10	ND
Ethyl carbamate	50	ND
Bis(2-ethylhexyl) phthalate	10	660
Ethyl methanesulfonate	20	ND
Famphur	20	ND
Fensulfothion	40	ND
Fenthion	10	ND
Fluchloralin	20	ND
Fluoranthene	10	660
Fluorene	10	660
Hexachlorobenzene	10	660
Hexachlorobutadiene	10	660
Hexachlorocyclopentadiene	10	660
Hexachloroethane	10	660
Hexachlorophene	50	ND
Hexachloropropene	10	ND
Hexamethylphosphoramide	20	ND
Hydroquinone	ND	ND
Indeno(1,2,3-cd)pyrene	10	660
Isodrin	20	ND
Isophorone	10	660
Isosafrole	10	ND
Kepone	20	ND
Leptophos	10	ND
Malathion	50	ND
Maleic anhydride	NA	ND
Mestranol	20	ND
Methapyrilene	100	ND
Methoxychlor	10	ND
3-Methylcholanthrene	10	ND
4,4'-Methylenebis(2-chloroaniline)	NA	ND
Methyl methanesulfonate	10	ND
2-Methylnaphthalene	10	660
Methyl parathion	10	ND
2-Methylphenol	10	660
3-Methylphenol	10	ND

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
4-Methylphenol	10	660
Mevinphos	10	ND
Mexacarbate	20	ND
Mirex	10	ND
Monocrotophos	40	ND
Naled	20	ND
Naphthalene	10	660
1,4-Naphthoquinone	10	ND
1-Naphthylamine	10	ND
2-Naphthylamine	10	ND
Nicotine	20	ND
5-Nitroacenaphthene	10	ND
2-Nitroaniline	50	3300
3-Nitroaniline	50	3300
4-Nitroaniline	20	ND
5-Nitro-o-anisidine	10	ND
Nitrobenzene	10	660
4-Nitrobiphenyl	10	ND
Nitrofen	20	ND
2-Nitrophenol	10	660
4-Nitrophenol	50	3300
5-Nitro-o-toluidine	10	ND
4-Nitroquinoline-1-oxide	40	ND
N-Nitrosodi-n-butylamine	10	ND
N-Nitrosodiethylamine	20	ND
N-Nitrosodiphenylamine	10	660
N-Nitroso-di-n-propylamine	10	660
N-Nitrosopiperidine	20	ND
N-Nitrosopyrrolidine	40	ND
Octamethyl pyrophosphoramide	200	ND
4,4'-Oxydianiline	20	ND
Parathion	10	ND
Pentachlorobenzene	10	ND
Pentachloronitrobenzene	20	ND
Pentachlorophenol	50	3300
Phenacetin	20	ND
Phenanthrene	10	660
Phenobarbital	10	ND
Phenol	10	660
1,4-Phenylenediamine	10	ND
Phorate	10	ND
Phosalone	100	ND
Phosmet	40	ND
Phosphamidon	100	ND

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Phthalic anhydride	100	ND
2-Picoline	ND	ND
Piperonyl sulfoxide	100	ND
Pronamide	10	ND
Propylthiouracil	100	ND
Pyrene	10	660
Pyridine	ND	ND
Resorcinol	100	ND
Safrole	10	ND
Strychnine	40	ND
Sulfallate	10	ND
Terbufos	20	ND
1,2,4,5-Tetrachlorobenzene	10	ND
2,3,4,6-Tetrachlorophenol	10	ND
Tetrachlorvinphos	20	ND
Tetraethyl pyrophosphate	40	ND
Thionazine	20	ND
Thiophenol (Benzenethiol)	20	ND
o-Toluidine	10	ND
1,2,4-Trichlorobenzene	10	660
2,4,5-Trichlorophenol	10	660
2,4,6-Trichlorophenol	10	660
Trifluralin	10	ND
2,4,5-Trimethylaniline	10	ND
Trimethyl phosphate	10	ND
1,3,5-Trinitrobenzene	10	ND
Tris(2,3-dibromopropyl) phosphate	200	ND
Tri-p-tolyl phosphate(h)	10	ND
O,O,O-Triethyl phosphorothioate	NT	ND

[a] Sample EQLs are highly matrix-dependent. The EQLs listed here are provided for guidance and may not always be achievable.

[b] EQLs listed for soil/sediment are based on wet weight. Normally, data are reported on a dry weight basis, therefore, EQLs will be higher based on the % dry weight of each sample. These EQLs are based on a 30-g sample and gel permeation chromatography cleanup.

ND = Not Determined
NA = Not Applicable
NT = Not Tested

Other Matrices	Factor[c]
High-concentration soil and sludges by ultrasonic extractor	7.5
Non-water miscible waste	75

[c]EQL = (EQL for Low Soil/Sediment given above in Table 2) x (Factor)

TABLE 3

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a,b]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

[a] Data taken from Reference 3.

[b] Alternate tuning criteria may be used, (e.g., CLP, Method 525, or manufacturers' instructions), provided that method performance is not adversely affected.

TABLE 4

CALIBRATION CHECK COMPOUNDS (CCC)

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
Diphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

TABLE 5

SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr)
4-Methylphenol	Nitrobenzene	Hexachlorocyclo-pentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr)	1-Naphthylamine
N-Nitroso-di-n-propyl-amine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitrosodi-n-butylamine	2-Nitroaniline
Phenol-d_6 (surr)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetra-chlorobenzene
		2,3,4,6-Tetra-chlorophenol
		2,4,6-Tribromo-phenol (surr)
		2,4,6-Trichloro-phenol
		2,4,5-Trichloro-phenol

(surr) = surrogate

TABLE 5
(continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluor-anthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluor-anthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)-perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methyl-phenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)-anthracene
Fluoranthene	p-Dimethylaminoazobenzene	
Hexachlorobenzene	Pyrene	
N-Nitrosodiphenylamine	Terphenyl-d_{14} (surr)	
Pentachlorophenol	7,12-Dimethylbenz-(a)anthracene	
Pentachloronitrobenzene	Di-n-octyl phthalate	
Phenacetin	Indeno(1,2,3-cd) pyrene	
Phenanthrene	3-Methylchol-anthrene	
Pronamide		

(surr) = surrogate

TABLE 6

MULTILABORATORY PERFORMANCE DATA[a]

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range p, p_s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27-133
Benz(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(g,h,i)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl) ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl) ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl) phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octyl phthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192

TABLE 6
(continued)

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range p, p_s (%)
Heptachlor epoxide	100	54.7	70.9-109.4	26.155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9	D-230
Aroclor 1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in µg/L

$\bar{x}$ = Average recovery for four recovery measurements, in µg/L

p, p_s = Measured percent recovery

D = Detected; result must be greater than zero

[a] Criteria from 40 CFR Part 136 for Method 625, using a packed GC column. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7. These values are for guidance only. Appropriate derivation of acceptance criteria for capillary columns should result in much narrower ranges. See Method 8000 for information on developing and updating acceptance criteria for method performance.

TABLE 7

METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Compound	Accuracy, as recovery, x' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Acenaphthene	0.96C+0.19	0.15$\bar{x}$-0.12	0.21$\bar{x}$-0.67
Acenaphthylene	0.89C+0.74	0.24$\bar{x}$-1.06	0.26$\bar{x}$-0.54
Aldrin	0.78C+1.66	0.27$\bar{x}$-1.28	0.43$\bar{x}$+1.13
Anthracene	0.80C+0.68	0.21$\bar{x}$-0.32	0.27$\bar{x}$-0.64
Benz(a)anthracene	0.88C-0.60	0.15$\bar{x}$+0.93	0.26$\bar{x}$-0.21
Benzo(b)fluoranthene	0.93C-1.80	0.22$\bar{x}$+0.43	0.29$\bar{x}$+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19$\bar{x}$+1.03	0.35$\bar{x}$+0.40
Benzo(a)pyrene	0.90C-0.13	0.22$\bar{x}$+0.48	0.32$\bar{x}$+1.35
Benzo(g,h,i)perylene	0.98C-0.86	0.29$\bar{x}$+2.40	0.51$\bar{x}$-0.44
Benzyl butyl phthalate	0.66C-1.68	0.18$\bar{x}$+0.94	0.53$\bar{x}$+0.92
β-BHC	0.87C-0.94	0.20$\bar{x}$-0.58	0.30$\bar{x}$+1.94
δ-BHC	0.29C-1.09	0.34$\bar{x}$+0.86	0.93$\bar{x}$-0.17
Bis(2-chloroethyl) ether	0.86C-1.54	0.35$\bar{x}$-0.99	0.35$\bar{x}$+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16$\bar{x}$+1.34	0.26$\bar{x}$+2.01
Bis(2-chloroisopropyl) ether	1.03C-2.31	0.24$\bar{x}$+0.28	0.25$\bar{x}$+1.04
Bis(2-ethylhexyl) phthalate	0.84C-1.18	0.26$\bar{x}$+0.73	0.36$\bar{x}$+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13$\bar{x}$+0.66	0.16$\bar{x}$+0.66
2-Chloronaphthalene	0.89C+0.01	0.07$\bar{x}$+0.52	0.13$\bar{x}$+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20$\bar{x}$-0.94	0.30$\bar{x}$-0.46
Chrysene	0.93C-1.00	0.28$\bar{x}$+0.13	0.33$\bar{x}$-0.09
4,4'-DDD	0.56C-0.40	0.29$\bar{x}$-0.32	0.66$\bar{x}$-0.96
4,4'-DDE	0.70C-0.54	0.26$\bar{x}$-1.17	0.39$\bar{x}$-1.04
4,4'-DDT	0.79C-3.28	0.42$\bar{x}$+0.19	0.65$\bar{x}$-0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30$\bar{x}$+8.51	0.59$\bar{x}$+0.25
Di-n-butyl phthalate	0.59C+0.71	0.13$\bar{x}$+1.16	0.39$\bar{x}$+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20$\bar{x}$+0.47	0.24$\bar{x}$+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25$\bar{x}$+0.68	0.41$\bar{x}$+0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24$\bar{x}$+0.23	0.29$\bar{x}$+0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28$\bar{x}$+7.33	0.47$\bar{x}$+3.45
Dieldrin	0.82C-0.16	0.20$\bar{x}$-0.16	0.26$\bar{x}$-0.07
Diethyl phthalate	0.43C+1.00	0.28$\bar{x}$+1.44	0.52$\bar{x}$+0.22
Dimethyl phthalate	0.20C+1.03	0.54$\bar{x}$+0.19	1.05$\bar{x}$-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12$\bar{x}$+1.06	0.21$\bar{x}$+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14$\bar{x}$+1.26	0.19$\bar{x}$+0.35
Di-n-octyl phthalate	0.76C-0.79	0.21$\bar{x}$+1.19	0.37$\bar{x}$+1.19
Endosulfan sulfate	0.39C+0.41	0.12$\bar{x}$+2.47	0.63$\bar{x}$-1.03
Endrin aldehyde	0.76C-3.86	0.18$\bar{x}$+3.91	0.73$\bar{x}$-0.62
Fluoranthene	0.81C+1.10	0.22$\bar{x}$-0.73	0.28$\bar{x}$-0.60
Fluorene	0.90C-0.00	0.12$\bar{x}$+0.26	0.13$\bar{x}$+0.61
Heptachlor	0.87C-2.97	0.24$\bar{x}$-0.56	0.50$\bar{x}$-0.23
Heptachlor epoxide	0.92C-1.87	0.33$\bar{x}$-0.46	0.28$\bar{x}$+0.64

TABLE 7
(continued)

Compound	Accuracy, as recovery, x' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Hexachlorobenzene	0.74C+0.66	0.18$\bar{x}$-0.10	0.43$\bar{x}$-0.52
Hexachlorobutadiene	0.71C-1.01	0.19$\bar{x}$+0.92	0.26$\bar{x}$+0.49
Hexachloroethane	0.73C-0.83	0.17$\bar{x}$+0.67	0.17$\bar{x}$+0.80
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29$\bar{x}$+1.46	0.50$\bar{x}$-0.44
Isophorone	1.12C+1.41	0.27$\bar{x}$+0.77	0.33$\bar{x}$+0.26
Naphthalene	0.76C+1.58	0.21$\bar{x}$-0.41	0.30$\bar{x}$-0.68
Nitrobenzene	1.09C-3.05	0.19$\bar{x}$+0.92	0.27$\bar{x}$+0.21
N-Nitrosodi-n-propylamine	1.12C-6.22	0.27$\bar{x}$+0.68	0.44$\bar{x}$+0.47
Aroclor 1260	0.81C-10.86	0.35$\bar{x}$+3.61	0.43$\bar{x}$+1.82
Phenanthrene	0.87C+0.06	0.12$\bar{x}$+0.57	0.15$\bar{x}$+0.25
Pyrene	0.84C-0.16	0.16$\bar{x}$+0.06	0.15$\bar{x}$+0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15$\bar{x}$+0.85	0.21$\bar{x}$+0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23$\bar{x}$+0.75	0.29$\bar{x}$+1.31
2-Chlorophenol	0.78C+0.29	0.18$\bar{x}$+1.46	0.28$\bar{x}$+0.97
2,4-Dichlorophenol	0.87C-0.13	0.15$\bar{x}$+1.25	0.21$\bar{x}$+1.28
2,4-Dimethylphenol	0.71C+4.41	0.16$\bar{x}$+1.21	0.22$\bar{x}$+1.31
2,4-Dinitrophenol	0.81C-18.04	0.38$\bar{x}$+2.36	0.42$\bar{x}$+26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10$\bar{x}$+42.29	0.26$\bar{x}$+23.10
2-Nitrophenol	0.07C-1.15	0.16$\bar{x}$+1.94	0.27$\bar{x}$+2.60
4-Nitrophenol	0.61C-1.22	0.38$\bar{x}$+2.57	0.44$\bar{x}$+3.24
Pentachlorophenol	0.93C+1.99	0.24$\bar{x}$+3.03	0.30$\bar{x}$+4.33
Phenol	0.43C+1.26	0.26$\bar{x}$+0.73	0.35$\bar{x}$+0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16$\bar{x}$+2.22	0.22$\bar{x}$+1.81

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in µg/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in µg/L.

C = True value for the concentration, in µg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

[a] Criteria from 40 CFR Part 136 for Method 625, using a packed GC column. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7. These values are for guidance only. Appropriate derivation of acceptance criteria for capillary columns should result in much narrower ranges. See Method 8000 for information on developing and updating acceptance criteria for method performance.

TABLE 8

EXTRACTION EFFICIENCY AND AQUEOUS STABILITY RESULTS

Compound	Percent Recovery on Day 0		Percent Recovery on Day 7	
	Mean	RSD	Mean	RSD
3-Amino-9-ethylcarbazole	80	8	73	3
4-Chloro-1,2-phenylenediamine	91	1	108	4
4-Chloro-1,3-phenylenediamine	84	3	70	3
1,2-Dibromo-3-chloropropane	97	2	98	5
Dinoseb	99	3	97	6
Parathion	100	2	103	4
4,4'-Methylenebis(N,N-dimethylaniline)	108	4	90	4
5-Nitro-o-toluidine	99	10	93	4
2-Picoline	80	4	83	4
Tetraethyl dithiopyrophosphate	92	7	70	1

Data taken from Reference 6.

TABLE 9

MEAN PERCENT RECOVERIES AND PERCENT RSD VALUES FOR SEMIVOLATILE ORGANICS FROM SPIKED CLAY SOIL AND TOPSOIL BY AUTOMATED SOXHLET EXTRACTION (METHOD 3541) WITH HEXANE-ACETONE (1:1)[a]

Compound	Clay Soil		Topsoil	
	Mean Recovery	RSD	Mean Recovery	RSD
1,3-Dichlorobenzene	0	--	0	--
1,2-Dichlorobenzene	0	--	0	--
Nitrobenzene	0	--	0	--
Benzal chloride	0	--	0	--
Benzotrichloride	0	--	0	--
4-Chloro-2-nitrotoluene	0	--	0	--
Hexachlorocyclopentadiene	4.1	15	7.8	23
2,4-Dichloronitrobenzene	35.2	7.6	21.2	15
3,4-Dichloronitrobenzene	34.9	15	20.4	11
Pentachlorobenzene	13.7	7.3	14.8	13
2,3,4,5-Tetrachloronitrobenzene	55.9	6.7	50.4	6.0
Benefin	62.6	4.8	62.7	2.9
alpha-BHC	58.2	7.3	54.8	4.8
Hexachlorobenzene	26.9	13	25.1	5.7
delta-BHC	95.8	4.6	99.2	1.3
Heptachlor	46.9	9.2	49.1	6.3
Aldrin	97.7	12	102	7.4
Isopropalin	102	4.3	105	2.3
Heptachlor epoxide	90.4	4.4	93.6	2.4
trans-Chlordane	90.1	4.5	95.0	2.3
Endosulfan I	96.3	4.4	101	2.2
Dieldrin	129	4.7	104	1.9
2,5-Dichlorophenyl-4-nitrophenyl ether	110	4.1	112	2.1
Endrin	102	4.5	106	3.7
Endosulfan II	104	4.1	105	0.4
p,p'-DDT	134	2.1	111	2.0
2,3,6-Trichlorophenyl-4'-nitrophenyl ether	110	4.8	110	2.8
2,3,4-Trichlorophenyl-4'-nitrophenyl ether	112	4.4	112	3.3
Mirex	104	5.3	108	2.2

[a] The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g; the spiking concentration was 500 ng/g, except for the surrogate compounds at 1000 ng/g, 2,5-Dichlorophenyl-4-nitrophenyl ether, 2,3,6-Trichlorophenyl-4-nitrophenyl ether, and 2,3,4-Trichlorophenyl-4-nitrophenyl ether at 1500 ng/g, Nitrobenzene at 2000 ng/g, and 1,3-Dichlorobenzene and 1,2-Dichlorobenzene at 5000 ng/g.

TABLE 10

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR THE EXTRACTION OF SEMIVOLATILE ORGANICS FROM SPIKED CLAY BY AUTOMATED SOXHLET (METHOD 3541)[a]

Compound	Mean Recovery	RSD
Phenol	47.8	5.6
Bis(2-chloroethyl)ether	25.4	13
2-Chlorophenol	42.7	4.3
Benzyl alcohol	55.9	7.2
2-Methylphenol	17.6	6.6
Bis(2-chloroisopropyl)ether	15.0	15
4-Methylphenol	23.4	6.7
N-Nitroso-di-n-propylamine	41.4	6.2
Nitrobenzene	28.2	7.7
Isophorone	56.1	4.2
2-Nitrophenol	36.0	6.5
2,4-Dimethylphenol	50.1	5.7
Benzoic acid	40.6	7.7
Bis(2-chloroethoxy)methane	44.1	3.0
2,4-Dichlorophenol	55.6	4.6
1,2,4-Trichlorobenzene	18.1	31
Naphthalene	26.2	15
4-Chloroaniline	55.7	12
4-Chloro-3-methylphenol	65.1	5.1
2-Methylnaphthalene	47.0	8.6
Hexachlorocyclopentadiene	19.3	19
2,4,6-Trichlorophenol	70.2	6.3
2,4,5-Trichlorophenol	26.8	2.9
2-Chloronaphthalene	61.2	6.0
2-Nitroaniline	73.8	6.0
Dimethyl phthalate	74.6	5.2
Acenaphthylene	71.6	5.7
3-Nitroaniline	77.6	5.3
Acenaphthene	79.2	4.0
2,4-Dinitrophenol	91.9	8.9
4-Nitrophenol	62.9	16
Dibenzofuran	82.1	5.9
2,4-Dinitrotoluene	84.2	5.4
2,6-Dinitrotoluene	68.3	5.8
Diethyl phthalate	74.9	5.4
4-Chlorophenyl-phenyl ether	67.2	3.2
Fluorene	82.1	3.4
4-Nitroaniline	79.0	7.9

TABLE 10
(continued)

Compound	Mean Recovery	RSD
4,6-Dinitro-2-methylphenol	63.4	6.8
N-Nitrosodiphenylamine	77.0	3.4
4-Bromophenyl-phenyl ether	62.4	3.0
Hexachlorobenzene	72.6	3.7
Pentachlorophenol	62.7	6.1
Phenanthrene	83.9	5.4
Anthracene	96.3	3.9
Di-n-butyl phthalate	78.3	40
Fluoranthene	87.7	6.9
Pyrene	102	0.8
Butyl benzyl phthalate	66.3	5.2
3,3'-Dichlorobenzidine	25.2	11
Benzo(a)anthracene	73.4	3.8
Bis(2-ethylhexyl) phthalate	77.2	4.8
Chrysene	76.2	4.4
Di-n-octyl phthalate	83.1	4.8
Benzo(b)fluoranthene	82.7	5.0
Benzo(k)fluoranthene	71.7	4.1
Benzo(a)pyrene	71.7	4.1
Indeno(1,2,3-cd)pyrene	72.2	4.3
Dibenzo(a,h)anthracene	66.7	6.3
Benzo(g,h,i)perylene	63.9	8.0
1,2-Dichlorobenzene	0	--
1,3-Dichlorobenzene	0	--
1,4-Dichlorobenzene	0	--
Hexachloroethane	0	--
Hexachlorobutadiene	0	--

[a] Number of determinations was three. The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil; the spike concentration was 6 mg/kg per compound. The sample was allowed to equilibrate 1 hour after spiking.

Data taken from Reference 7.

TABLE 11

PRECISION AND BIAS VALUES FOR METHOD 3542[1]

Compound	Mean Recovery	Standard Deviation	Relative Standard Deviation Percent
2-Fluorophenol	74.6	28.6	38.3
Phenol-d_5	77.8	27.7	35.6
Nitrobenzene-d_5	65.6	32.5	49.6
2-Fluorobiphenyl	75.9	30.3	39.9
2,4,6-Tribromophenol	67.0	34.0	50.7
Terphenyl-d_{14}	78.6	32.4	41.3

[1] The surrogate values shown in Table 11 represent mean recoveries for surrogates in all Method 0010 matrices in a field dynamic spiking study.

TABLE 12

ACCELERATED SOLVENT EXTRACTION (METHOD 3545) RECOVERY VALUES
AS PERCENT OF SOXTEC™

COMPOUND	CLAY			LOAM			SAND			AVE
	LOW	MID	HIGH	LOW	MID	HIGH	LOW	MID	HIGH	
Phenol	93.3	78.7	135.9	73.9	82.8	124.6	108.8	130.6	89.7	**102.0**
Bis(2-chloroethyl) ether	102.1	85.1	109.1	96.0	88.0	103.6	122.3	119.9	90.8	**101.9**
2-Chlorophenol	100.8	82.6	115.0	93.8	88.9	111.1	115.0	115.3	91.9	**101.6**
1,3-Dichlorobenzene	127.7	129.7	110.0	*364.2	129.9	119.0	*241.3	*163.7	107.1	**120.6**
1,4-Dichlorobenzene	127.9	127.0	110.5	*365.9	127.8	116.4	*309.6	*164.1	105.8	**119.2**
1,2-Dichlorobenzene	116.8	115.8	101.3	*159.2	113.4	105.5	*189.3	134.0	100.4	**112.5**
2-Methylphenol	98.9	82.1	119.7	87.6	89.4	111.0	133.2	128.0	92.1	**104.7**
Bis(2-chloroisopropyl)ether	109.4	71.5	108.0	81.8	81.0	88.6	118.1	148.3	94.8	**100.2**
o-Toluidine	100.0	89.7	117.2	100.0	*152.5	120.3	100.0	*199.5	102.7	**110.3**
N-Nitroso-di-n-propylamine	103.0	79.1	107.7	83.9	88.1	96.2	109.9	123.3	91.4	**98.1**
Hexachloroethane	97.1	125.1	111.0	*245.4	117.1	128.1	*566.7	147.9	103.7	**118.6**
Nitrobenzene	104.8	82.4	106.6	86.8	84.6	101.7	119.7	122.1	93.3	**100.2**
Isophorone	100.0	86.4	98.2	87.1	87.5	109.7	135.5	118.4	92.7	**101.7**
2,4-Dimethylphenol	100.0	104.5	140.0	100.0	114.4	123.1	100.0	*180.6	96.3	**109.8**
2-Nitrophenol	80.7	80.5	107.9	91.4	86.7	103.2	122.1	107.1	87.0	**96.3**
Bis(chloroethoxy)methane	94.4	80.6	94.7	86.5	84.4	99.6	130.6	110.7	93.2	**97.2**
2,4-Dichlorophenol	88.9	87.8	111.4	85.9	87.6	103.5	123.3	107.0	92.1	**98.6**
1,2,4-Trichlorobenzene	98.0	97.8	98.8	123.0	93.7	94.5	137.0	99.4	95.3	**104.2**
Naphthalene	101.7	97.2	123.6	113.2	102.9	129.5	*174.5	114.0	89.8	**106.1**
4-Chloroaniline	100.0	*150.2	*162.4	100.0	125.5	*263.6	100.0	*250.8	114.9	**108.1**
Hexachlorobutadiene	101.1	98.7	102.2	124.1	90.3	98.0	134.9	96.1	96.8	**104.7**
4-Chloro-3-methylphenol	90.4	80.2	114.7	79.0	85.2	109.8	131.6	116.2	90.1	**99.7**
2-Methylnaphthalene	93.2	89.9	94.6	104.1	92.2	105.9	146.2	99.1	93.3	**102.1**
Hexachlorocyclopentadiene	100.0	100.0	0.0	100.0	100.0	6.8	100.0	100.0	*238.3	**75.8**
2,4,6-Trichlorophenol	94.6	90.0	112.0	84.2	91.2	103.6	101.6	95.9	89.8	**95.9**
2,4,5-Trichlorophenol	84.4	91.9	109.6	96.1	80.7	103.6	108.9	83.9	87.9	**94.1**
2-Chloronaphthalene	100.0	91.3	93.6	97.6	93.4	98.3	106.8	93.0	92.0	**96.2**
2-Nitroaniline	90.0	83.4	97.4	71.3	88.4	89.9	112.1	113.3	87.7	**92.6**
2,6-Dinitrotoluene	83.1	90.6	91.6	86.4	90.6	90.3	104.3	84.7	90.9	**90.3**
Acenaphthylene	104.9	95.9	100.5	99.0	97.9	108.8	118.5	97.8	92.0	**101.7**
3-Nitroaniline	*224.0	115.6	97.6	100.0	111.8	107.8	0.0	111.7	99.0	**92.9**
Acenaphthene	102.1	92.6	97.6	97.2	96.9	104.4	114.2	92.0	89.0	**98.4**
4-Nitrophenol	0.0	93.2	121.5	18.1	87.1	116.6	69.1	90.5	84.5	**75.6**
2,4-Dinitrotoluene	73.9	91.9	100.2	84.7	93.8	98.9	100.9	84.3	87.3	**90.7**

TABLE 12 (cont.)

ACCELERATED SOLVENT EXTRACTION (METHOD 3545) RECOVERY VALUES
AS PERCENT OF SOXTEC™

COMPOUND	CLAY			LOAM			SAND			AVE
	LOW	MID	HIGH	LOW	MID	HIGH	LOW	MID	HIGH	
Dibenzofuran	89.5	91.7	109.3	98.5	92.2	111.4	113.8	92.7	90.4	**98.8**
4-Chlorophenyl phenyl ether	83.0	94.5	98.7	95.7	94.3	94.2	111.4	87.7	90.3	**94.4**
Fluorene	85.2	94.9	89.2	102.0	95.5	93.8	121.3	85.7	90.9	**95.4**
4-Nitroaniline	77.8	114.8	94.5	129.6	103.6	95.4	*154.1	89.3	87.5	**99.1**
N-Nitrosodiphenylamine	82.6	96.7	93.8	92.9	93.4	116.4	97.5	110.9	86.7	**96.8**
4-Bromophenyl phenyl ether	85.6	92.9	92.8	91.1	107.6	89.4	118.0	97.5	87.1	**95.8**
Hexachlorobenzene	95.4	91.7	92.3	95.4	93.6	83.7	106.8	94.3	90.0	**93.7**
Pentachlorophenol	68.2	85.9	107.7	53.2	89.8	88.1	96.6	59.8	81.3	**81.2**
Phenanthrene	92.1	93.7	93.3	100.0	97.8	113.3	124.4	101.0	89.9	**100.6**
Anthracene	101.6	95.0	93.5	92.5	101.8	118.4	123.0	94.5	90.6	**101.2**
Carbazole	94.4	99.3	96.6	105.5	96.7	111.4	115.7	83.2	88.9	**99.1**
Fluoranthene	109.9	101.4	94.3	111.6	96.6	109.6	123.2	85.4	92.7	**102.7**
Pyrene	106.5	105.8	107.6	116.7	90.7	127.5	103.4	95.5	93.2	**105.2**
3,3'-Dichlorobenzidine	100.0	*492.3	131.4	100.0	*217.6	*167.6	100.0	*748.8	100.0	**116.5**
Benzo(a)anthracene	98.1	107.0	98.4	119.3	98.6	104.0	105.0	93.4	89.3	**101.5**
Chrysene	100.0	108.5	100.2	116.8	93.0	117.0	106.7	93.6	90.2	**102.9**
Benzo(b)fluoranthene	106.6	109.9	75.6	121.7	100.7	93.9	106.9	81.9	93.6	**99.0**
Benzo(k)fluoranthene	102.4	105.2	88.4	125.5	99.4	95.1	144.7	89.2	78.1	**103.1**
Benzo(a)pyrene	107.9	105.5	80.8	122.3	97.7	104.6	101.7	86.2	92.0	**99.9**
Indeno(1,2,3-cd)pyrene	95.1	105.7	93.8	126.0	105.2	90.4	133.6	82.6	91.9	**102.7**
Dibenz(a,h)anthracene	85.0	102.6	82.0	118.8	100.7	91.9	142.3	71.0	93.1	**98.6**
Benzo(g,h,i)perylene	98.0	0.0	81.2	0.0	33.6	78.6	128.7	83.0	94.2	**66.4**
Average	**95.1**	**94.3**	**101.0**	**95.5**	**96.5**	**104.1**	**113.0**	**100.9**	**92.5**	

* Values greater than 150% were not used to determine the averages, but the 0% values were used.

TABLE 13

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT EC-1, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	(27.9)[b]	41.3 ± 3.6	(148)	8.7
Acenaphthylene	(0.8)	0.9 ± 0.1	(112)	11.1
Acenaphthene	(0.2)	0.2 ± 0.01	(100)	0.05
Fluorene	(15.3)	15.6 ± 1.8	(102)	11.5
Phenanthrene	15.8 ± 1.2	16.1 ± 1.8	102	11.2
Anthracene	(1.3)	1.1 ± 0.2	(88)	18.2
Fluoranthene	23.2 ± 2.0	24.1 ± 2.1	104	8.7
Pyrene	16.7 ± 2.0	17.2 ± 1.9	103	11.0
Benz(a)anthracene	8.7 ± 0.8	8.8 ± 1.0	101	11.4
Chrysene	(9.2)	7.9 ± 0.9	(86)	11.4
Benzo(b)fluoranthene	7.9 ± 0.9	8.5 ± 1.1	108	12.9
Benzo(k)fluoranthene	4.4 ± 0.5	4.1 ± 0.5	91	12.2
Benzo(a)pyrene	5.3 ± 0.7	5.1 ± 0.6	96	11.8
Indeno(1,2,3-cd)pyrene	5.7 ± 0.6	5.2 ± 0.6	91	11.5
Benzo(g,h,i)perylene	4.9 ± 0.7	4.3 ± 0.5	88	11.6
Dibenz(a,h)anthracene	(1.3)	1.1 ± 0.2	(85)	18.2

[a] Relative standard deviations for the SFE values are based on six replicate extractions.

[b] Values in parentheses were obtained from, or compared to, Soxhlet extraction results which were not certified.

Data are taken from Reference 10.

TABLE 14

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT HS-3, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	9.0 ± 0.7	7.4 ± 0.6	82	8.1
Acenaphthylene	0.3 ± 0.1	0.4 ± 0.1	133	25.0
Acenaphthene	4.5 ± 1.5	3.3 ± 0.3	73	9.0
Fluorene	13.6 ± 3.1	10.4 ± 1.3	77	12.5
Phenanthrene	85.0 ± 20.0	86.2 ± 9.5	101	11.0
Anthracene	13.4 ± 0.5	12.1 ± 1.5	90	12.4
Fluoranthene	60.0 ± 9.0	54.0 ± 6.1	90	11.3
Pyrene	39.0 ± 9.0	32.7 ± 3.7	84	11.3
Benz(a)anthracene	14.6 ± 2.0	12.1 ± 1.3	83	10.7
Chrysene	14.1 ± 2.0	12.0 ± 1.3	85	10.8
Benzo(b)fluoranthene	7.7 ± 1.2	8.4 ± 0.9	109	10.7
Benzo(k)fluoranthene	2.8 ± 2.0	3.2 ± 0.5	114	15.6
Benzo(a)pyrene	7.4 ± 3.6	6.6 ± 0.8	89	12.1
Indeno(1,2,3-cd)pyrene	5.0 ± 2.0	4.5 ± 0.6	90	13.3
Benzo(g,h,i)perylene	5.4 ± 1.3	4.4 ± 0.6	82	13.6
Dibenz(a,h)anthracene	1.3 ± 0.5	1.1 ± 0.3	85	27.3

[a] Relative standard deviations for the SFE values are based on three replicate extractions.

Data are taken from Reference 10.

TABLE 15

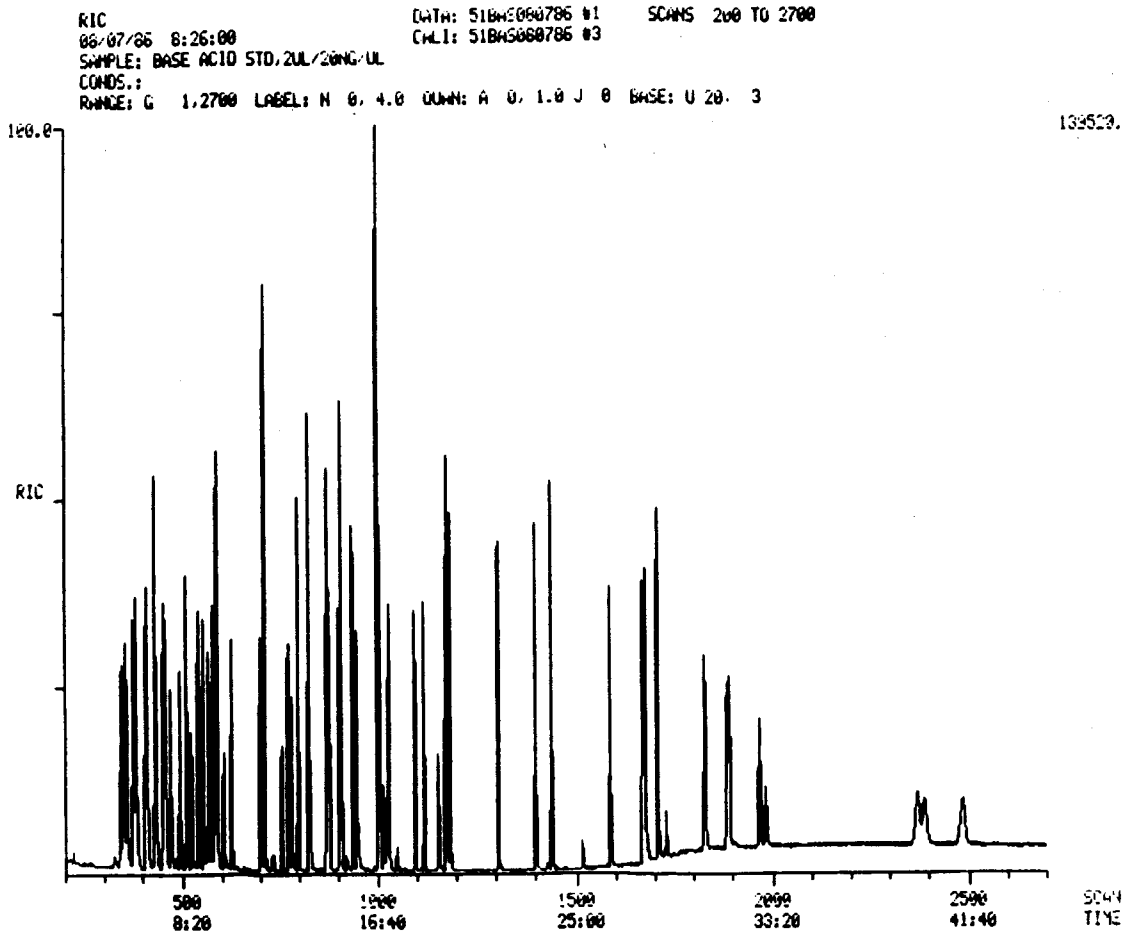
SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SOIL SRS103-100, USING METHOD 3561 (SFE - LIQUID TRAP)

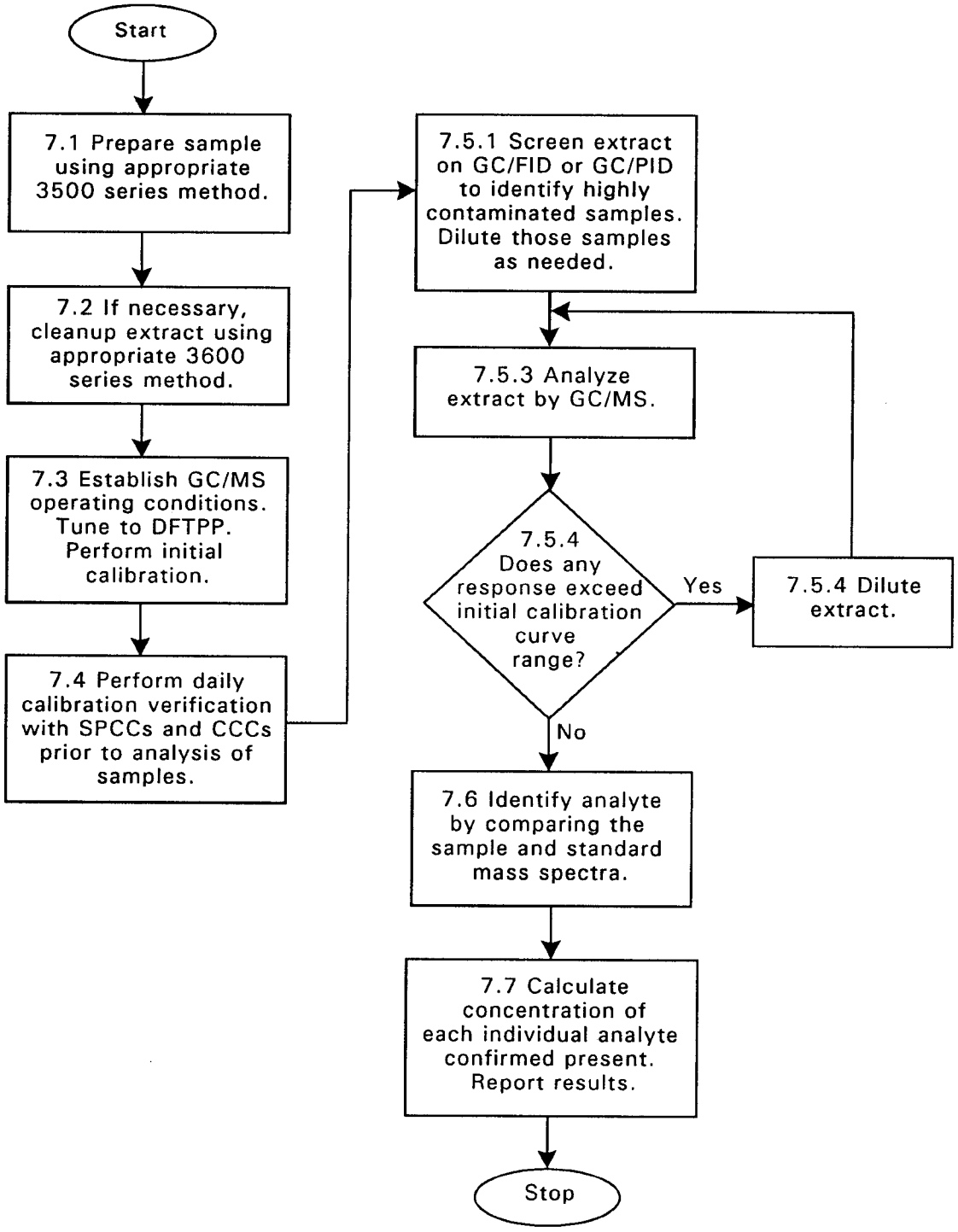
Compound	Certified Value (mg/kg)			SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	32.4	±	8.2	29.55	91	10.5
2-Methylnaphthalene	62.1	±	11.5	76.13	122	2.0
Acenaphthene	632	±	105	577.28	91	2.9
Dibenzofuran	307	±	49	302.25	98	4.1
Fluorene	492	±	78	427.15	87	3.0
Phenanthrene	1618	±	340	1278.03	79	3.4
Anthracene	422	±	49	400.80	95	2.6
Fluoranthene	1280	±	220	1019.13	80	4.5
Pyrene	1033	±	285	911.82	88	3.1
Benz(a)anthracene	252	±	38	225.50	89	4.8
Chrysene	297	±	26	283.00	95	3.8
Benzo(b)fluoranthene + Benzo(k)fluoranthene	153	±	22	130.88	86	10.7
Benzo(a)pyrene	97.2	±	17.1	58.28	60	6.5

[a] Relative standard deviations for the SFE values are based on four replicate extractions.

Data are taken from Reference 11.

FIGURE 1
GAS CHROMATOGRAM OF BASE/NEUTRAL AND ACID CALIBRATION STANDARD




Start
7.1 Prepare sample using appropriate 3500 series method.
7.2 If necessary, cleanup extract using appropriate 3600 series method.
7.3 Establish GC/MS operating conditions. Tune to DFTPP. Perform initial calibration.
7.4 Perform daily calibration verification with SPCCs and CCCs prior to analysis of samples.
7.5.1 Screen extract on GC/FID or GC/PID to identify highly contaminated samples. Dilute those samples as needed.
7.5.3 Analyze extract by GC/MS.
7.5.4 Does any response exceed initial calibration curve range?
Yes
7.5.4 Dilute extract.
No
7.6 Identify analyte by comparing the sample and standard mass spectra.
7.7 Calculate concentration of each individual analyte confirmed present. Report results.
Stop