Designation: D7968 – 17

Standard Test Method for Determination of Polyfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)[1]

This standard is issued under the fixed designation D7968; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This procedure covers the determination of selected polyfluorinated compounds (PFCs) in a soil matrix using solvent extraction, filtration, followed by liquid chromatography (LC) and detection with tandem mass spectrometry (MS/MS). These analytes are qualitatively and quantitatively determined by this method. This method adheres to multiple reaction monitoring (MRM) mass spectrometry. This procedure utilizes a quick extraction and is not intended to generate an exhaustive accounting of the content of PFCs in difficult soil matrices. An exhaustive extraction procedure for polyfluoralkyl substances, such as published by Washington et al.,[2] for difficult matrices should be considered when analyzing PFCs.

1.2 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 The Method of Detection Limit[3] and Reporting Range[4] for the target analytes are listed in Table 1.

1.3.1 The reporting limit in this test method is the minimum value below which data are documented as non-detects. Analyte detections between the method detection limit and the reporting limit are estimated concentrations and are not reported following this test method. In most cases, the reporting limit is calculated from the concentration of the Level 1 calibration standard as shown in Table 2 for the polyfluorinated compounds after taking into account a 2-g sample weight and a final extract volume of 10 mL, 50 % water/50 % MeOH with 0.1 % acetic acid. The final extract volume is assumed to be 10 mL because 10 mL of 50 % water/50 % MeOH with 0.1 % acetic acid was added to each soil sample and only the liquid layer after extraction is filtered, leaving the solid and any residual solvent behind. It is raised above the Level 1 calibration concentration for PFOS, PFHxA, FHEA, and FOEA; these compounds can be identified at the Level 1 concentration but the standard deviation among replicates at this lower spike level resulted in a higher reporting limit.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[5]

D653 Terminology Relating to Soil, Rock, and Contained Fluids

D1193 Specification for Reagent Water

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents

D3740 Practice for Minimum Requirements for Agencies Engaged in Testing and/or Inspection of Soil and Rock as Used in Engineering Design and Construction

[1] This test method is under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.01.06 on Analytical Methods.

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[2] Washington, J. W., Naile, J. E., Jenkins, T. M., and Lynch, D. G., "Characterizing Fluorotelomer and Polyfluoroalkyl Substances in New and Aged Fluorotelomer-Based Polymers for Degradation Studies with GC/MS and LC/MS/MS," *Environmental Science and Technology*, Vol 48, 2014, pp. 5762–5769.

[3] The MDL is determined following the Code of Federal Regulations, 40 CFR Part 136, Appendix B utilizing solvent extraction of soil. Two-gram sample of Ottawa sand was utilized. A detailed process determining the MDL is explained in the reference and is beyond the scope of this standard to be explained here.

[4] Reporting range concentration is calculated from Table 2 concentrations assuming a 30-µL injection of the Level 1 calibration standard for the PFCs, and the highest level calibration standard with a 10-mL final extract volume of a 2-g soil sample. Volume variations will change the reporting limit and ranges.

[5] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

TABLE 1 Method Detection Limit and Reporting Range[A]

Analyte	MDL (ng/kg)	Reporting Limit (ng/kg)
PFTreA	6.76	25–1000
PFTriA	5.26	25–1000
PFDoA	3.56	25–1000
PFUnA	2.45	25–1000
PFDA	5.54	25–1000
PFOS	18.83	50–1000
PFNA	2.82	25–1000
PFecHS	2.41	25–1000
PFOA	6.24	25–1000
PFHxS	7.75	25–1000
PFHpA	5.80	25–1000
PFHxA	15.44	50–1000
PFBS	6.49	25–1000
PFPeA	20.93	125–5000
PFBA	22.01	125–5000
FHEA	199.04	600–20 000
FOEA	258.37	750–20 000
FDEA	137.46	500–20 000
FOUEA	4.85	25–1000
FhpPa	5.09	25–1000
FHUEA	3.50	25–1000

[A]Abbreviations are defined in 3.2.

D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water

D5681 Terminology for Waste and Waste Management

D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

E2554 Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques

2.2 *Other Documents:*[6]

EPA SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods

40 CFR Part 136 Appendix B Definition and Procedure for the Determination of the Method Detection Limit

3. Terminology

3.1 *Definitions:*

3.1.1 *reporting limit, RL, n*—the minimum concentration below which data are documented as non-detects.

3.1.2 *polyfluorinated compounds, PFCs, n*—in this test method, eleven perfluoroalkyl carboxylic acids, three perfluoroalkylsulfonates, Decafluoro-4-(pentafluoroethyl)cyclohexanesulfonate, and six fluorotelomer acids listed in Table 1 collectively (not including mass labeled surrogates).

3.2 *Abbreviations:*

3.2.1 *CCC*—Continuing Calibration Check

3.2.2 *IC*—Initial Calibration

3.2.3 *ppt*—parts per trillion, ng/kg or ng/L

3.2.4 *LC*—Liquid Chromatography

3.2.5 *LCS/LCSD*—Laboratory Control Sample/Laboratory Control Sample Duplicate

3.2.6 *MDL*—Method Detection Limit

3.2.7 *MeOH*—Methanol

3.2.8 *mM*—millimolar, 1×10^{-3} moles/L

3.2.9 *MRM*—Multiple Reaction Monitoring

3.2.10 *MS/MSD*—Matrix Spike/Matrix Spike Duplicate

3.2.11 *NA*—Not available

3.2.12 *ND*—non-detect

3.2.13 *P&A*—Precision and Accuracy

3.2.14 *PFAS*—Perfluoroalkylsulfonate

3.2.15 *PFBS*—perfluorobutylsulfonate

3.2.16 *PFHxS*—perfluorohexylsulfonate

3.2.17 *PFOS*—Perfluorooctylsulfonate

3.2.18 *PFecHS*—Decaluoro-4-(pentafluoroethyl)cyclohexanesulfonate

3.2.19 *PFAC*—Perfluoroalkyl Carboxylic Acid

3.2.20 *PFBA*—Perfluorobutanoate

3.2.21 *PFPeA*—Perfluoropentanoate

3.2.22 *PFHxA*—Perfluorohexanoate

3.2.23 *PFHpA*—Perfluoroheptanoate

3.2.24 *PFOA*—Perfluorooctanoate

3.2.25 *PFNA*—Perfluorononanoate

3.2.26 *PFDA*—Perfluorodecanoate

3.2.27 *PFUnA*—Perfluoroundecanoate

3.2.28 *PFTriA*—Perfluorotridecanoate

3.2.29 *PFTreA*—Perfluorotetradecanoate

3.2.30 *FTAs and FTUAs*—Fluorotelomer and Unsaturated Fluorotelomer Acids

3.2.31 *FHpPA—3*-perfluoropheptyl propanoic acid

3.2.32 *FOUEA—2H*-perfluoro-2-decenoic acid

3.2.33 *FDEA—2*-perfluorodecyl ethanoic acid

3.2.34 *FOEA—2*-perfluorooctyl ethanoic acid

3.2.35 *FHUEA—2H*-perfluoro-2-octenoic acid

3.2.36 *FHEA—2*-perfluorohexyl ethanoic acid

3.2.37 *MPFAS*—Isotopically labeled Perfluoroalkylsulfonates

3.2.38 *MPFHxS*—$^{18}O_2$-Perfluorohexylsulfonate

3.2.39 *MPFOS*—$^{13}C_4$-Perfluorooctylsulfonate

3.2.40 *MPFCA*—Isotopically labeled Perfluoroalkylcarboxylates

3.2.41 *MPFBA*—$^{13}C_4$-Perfluorobutanoate

3.2.42 *MPFHxA*—$^{13}C_2$-Perfluorohexanoate

3.2.43 *MPFOA*—$^{13}C_4$-Perfluorooctanoate

3.2.44 *MPFNA*—$^{13}C_5$-Perfluorononanoate

3.2.45 *MPFDA*—$^{13}C_2$-Perfluorodecanoate

3.2.46 *MPFUnA*—$^{13}C_2$-Perfluoroundecanoate

3.2.47 *MPFDoA*—$^{13}C_2$-Perfluorodecanoate

3.2.48 *QA*—Quality Assurance

[6] Available from National Technical Information Service (NTIS), U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA, 22161, http://www.epa.gov/epawaste/hazard/testmethods/index.htm

TABLE 2 Concentrations of Calibration Standards (ng/L)

Analyte/Surrogate	LV1	LV2	LV3	LV4	LV5	LV6	LV7	LV8	LV9
PFPeA, PFBA	25	50	100	200	300	400	500	750	1000
PFTreA, PFTriA, PFDoA, PFUnA, PFDA, PFOS, PFNA, PFHxA, PFHpA, PFBS, PFechS, PFOA, PFHxS, FOUEA, FHUEA, FHpPA, MPFBS, MPFHxA, MPFUnA, MPFOA, MPFDA, MPFOS, MPFNA, MPFHxS, MPFBA	5	10	20	40	60	80	100	150	200
FHEA, FOEA, FDEA	100	200	400	800	1200	1600	2000	3000	4000

3.2.49 *QC*—Quality Control

3.2.50 *RL*—Reporting Limit

3.2.51 *RLCS*—Reporting Limit Check Sample

3.2.52 *RSD*—Relative Standard Deviation

3.2.53 *RT*—Retention Time

3.2.54 *SRM*—Single Reaction Monitoring

3.2.55 *SS*—Surrogate Standard

3.2.56 *TC*—Target Compound

4. Summary of Test Method

4.1 The operating conditions presented in this test method have been successfully used in the determination of polyfluorinated compounds in soil; however, this test method is intended to be performance based and alternative operating conditions can be used to perform this method provided data quality objectives are attained.

4.2 For PFC analysis, samples are shipped to the lab on ice and analyzed within 28 d of collection. A sample (2 g) is transferred to a polypropylene tube, spiked with surrogates (all samples) and target PFC compounds (laboratory control and matrix spike samples). The analytes are tumbled for an hour with 10 mL of methanol:water (50:50) under basic condition (pH ~ 9-10 adjusted with ~20 µL ammonium hydroxide). The samples are centrifuged and the extract, leaving the solid behind, is filtered through a polypropylene filter unit. Acetic acid (~50 µL) is added to all the filtered samples to adjust the pH ~3-4 and then analyzed by LC/MS/MS.

4.3 Most of the PFC target compounds are identified by comparing the single reaction monitoring (SRM) transition and its confirmatory SRM transition if correlated to the known standard SRM (Table 3) and quantitated utilizing an external calibration. The surrogates and some PFC target analytes (PFPeA, PFBA, FOUEA, and FHUEA) only utilize one SRM transition due to a less sensitive or non-existent secondary SRM transition. As an additional quality control measure, isotopically labeled PFC surrogates (listed in 12.4) recoveries are monitored. There is no correction to the data based upon surrogate recoveries. The final report issued for each sample lists the concentration of PFCs, if detected, or RL, if not detected, in ng/kg (dry weight basis) and the surrogate recoveries.

5. Significance and Use

5.1 This test method has been developed by the U.S. EPA Region 5 Chicago Regional Laboratory (CRL).

5.2 PFCs are widely used in various industrial and commercial products; they are persistent, bio-accumulative, and ubiquitous in the environment. PFCs have been reported to exhibit developmental toxicity, hepatotoxicity, immunotoxicity, and hormone disturbance. A draft Toxicological Profile for Perfluoroalkyls from the U.S. Department of Health and Human Services is available.[7] PFCs have been detected in soils, sludges, and surface and drinking waters. Hence, there is a need for a quick, easy, and robust method to determine these compounds at trace levels in various soil matrices for understanding of the sources and pathways of exposure.

5.3 This method has been used to determine selected polyfluorinated compounds in sand (Table 4) and four ASTM reference soils (Table 5).

6. Interferences

6.1 All glassware is washed in hot water with detergent and rinsed in hot water followed by distilled water. The glassware is then dried and heated in an oven at 250 °C for 15 to 30 min. All glassware is subsequently rinsed with methanol or acetonitrile.

6.2 All reagents and solvents should be pesticide residue purity or higher to minimize interference problems. The use of PFC-containing caps should be avoided.

6.3 Matrix interferences may be caused by contaminants in the sample. The extent of matrix interferences can vary considerably depending on variations in the sample matrices.

6.4 Contaminants have been found in reagents, glassware, tubing, glass disposable pipettes, filters, degassers, and other apparatus that release polyfluorinated compounds. All of these materials and supplies are routinely demonstrated to be free from interferences by analyzing laboratory reagent blanks under the same conditions as the samples. If found, measures should be taken to remove the contamination or data should be qualified; background subtraction of blank contamination is not allowed.

6.5 The liquid chromatography system used should consist, as much as practical, of sample solution or eluent contacting components free of PFC target analytes of interest.

6.6 Polyethylene LC vial caps or any other target analyte-free vial caps should be used.

6.7 Polyethylene disposable pipettes or target analyte-free pipettes should be used. All disposable pipettes should be checked for release of target analytes of interest.

6.8 Degassers are important to continuous LC operation and most commonly are made of fluorinated polymers. To enable use, an isolator column should be placed after the degasser and

[7] A draft Toxicological Profile for Perfluroalkyls can be found at http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=1117&tid=237 (2014).

TABLE 3 Retention Times, SRM Ions, and Analyte-Specific Mass Spectrometer Parameters

Chemical	Primary/ Confirmatory	Retention Times (min)	Cone (V)	Collision (eV)	MRM Transition	Primary/ Confirmatory SRM Area Ratio
PFTreA	Primary	10.63	20	13	712.9→668.9	7.4
	Confirmatory		20	30	712.9→169	
PFTriA	Primary	10.17	25	12	662.9→618.9	7.4
	Confirmatory		25	28	662.9→169	
PFDoA	Primary	9.61	10	12	612.9→568.9	8.2
	Confirmatory		10	25	612.9→169	
PFUnA	Primary	9.05	15	10	562.9→519	7.2
	Confirmatory		15	18	562.9→269	
PFDA	Primary	8.45	20	10	512.9→468.9	6.5
	Confirmatory		20	16	512.9→219	
PFOS	Primary	8.78	10	42	498.9→80.1	1.3
	Confirmatory		10	40	498.9→99.1	
PFNA	Primary	7.78	20	10	462.9→418.9	4.9
	Confirmatory		20	16	462.9→219	
PFecHS	Primary	8.1	10	25	460.9→381	2.2
	Confirmatory		10	25	460.9→99.1	
PFOA	Primary	7.11	20	10	412.9→369	3.6
	Confirmatory		20	16	412.9→169	
PFHxS	Primary	7.39	15	32	398.9→80.1	1
	Confirmatory		15	32	398.9→99.1	
PFHpA	Primary	6.35	15	10	362.9→319	4.1
	Confirmatory		15	15	362.9→169	
PFHxA	Primary	5.54	15	8	312.9→269	24.1
	Confirmatory		15	18	312.9→119.1	
PFBS	Primary	5.66	10	30	298.9→80.1	1.6
	Confirmatory		10	25	298.9→99.1	
PFPeA	Primary	4.68	10	8	263→219	NA
PFBA	Primary	3.67	10	8	212.9→169	NA
FHEA	Primary	6.14	15	20	376.9→293	3.6
	Confirmatory		15	6	376.9→313	
FOEA	Primary	7.54	15	18	476.9→393	4.3
	Confirmatory		15	12	476.9→413	
FDEA	Primary	8.83	15	8	576.8→493	3.2
	Confirmatory		15	15	576.8→513	
FOUEA	Primary	7.54	20	12	456.9→392.9	NA
FHpPA	Primary	7.54	15	12	440.9→337	1.1
	Confirmatory		15	20	440.9→317	
FHUEA	Primary	6.08	10	12	357→293	NA
MPFBA	Primary	3.67	10	7	217→172.1	NA
MPFHxA	Primary	5.54	15	8	315→270	NA
MPFHxS	Primary	7.39	15	34	402.9→84.1	NA
MPFOA	Primary	7.11	15	10	417→372	NA
MPFNA	Primary	7.81	15	9	467.9→423	NA
MPFOS	Primary	8.78	15	40	502.9→80.1	NA
MPFDA	Primary	8.45	15	10	514.9→470	NA
MPFUnA	Primary	9.05	15	10	564.9→519.9	NA
MPFDoA	Primary	9.61	15	12	614.9→569.9	NA

prior to the sample injection valve to separate the PFCs in the sample from the PFCs in the LC system.

7. Apparatus

7.1 *LC/MS/MS System:*

7.1.1 *Liquid Chromatography System*[8]—A complete LC system is required in order to analyze samples; this should include a sample injection system, a solvent pumping system capable of mixing solvents, a sample compartment capable of maintaining required temperature, and a temperature-controlled column compartment. An LC system that is capable of performing at the flows, pressures, controlled temperatures, sample volumes, and requirements of the standard shall be used.

7.1.2 *Analytical Column*[9]—A reverse phase Charged Surface Hybrid Phenyl-Hexyl particle column was used to develop this test method. Any column that achieves adequate resolution may be used. The retention times and order of elution may change depending on the column used and need to be monitored.

7.1.3 *Isolator Column*[10]—A reverse phase C18 column was used in this test method to separate the target analytes in the LC system and solvents from the target analytes in the analytical sample. This column was placed between the solvent mixing chamber and the injector sample loop.

[8] A Waters Acquity UPLC H-Class System, or equivalent, has been found suitable for use.

[9] A *Waters* Acquity UPLC CSH Phenyl-Hexyl, 2.1 × 100 mm and 1.7-µm particle size column, or equivalent, has been found suitable for use. It was used to develop this test method and generate the precision and bias data presented in Section 16.

[10] A *Waters* Acquity UPLC BEH C18, 2.1 × 50 mm and 1.7-µm particle size column, or equivalent, has been found suitable for use.

TABLE 4 Single-Laboratory Recovery Data in Ottawa Sand

Sample	Measured ng/kg from Ottawa Sand P&A Data (400 ng/kg spike for all PFCs except 2000 ng/kg for PFBA and PFPeA and 8000 ng/kg spike for FHEA, FDEA, and FOEA)										
	PFTreA	PFTriA	PFDoA	PFUnA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA
Unspiked 1	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Unspiked 2	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
P&A 1	389.6	394.3	384.7	376.7	362.1	347.6	345.8	232.9	222.2	1614.9	1344.5
P&A 2	462.1	424.6	397.2	379.1	378.4	376.9	365.9	247.9	229.8	1710.1	1388
P&A 3	402.7	387.7	383.1	365.9	374.7	363.3	347.1	242.4	222.9	1658.9	1376
P&A 4	403.9	397.1	395.4	381.5	379	359.4	342.7	246.8	225.8	1693.6	1401.9
P&A 5	467.2	445.8	412.6	388.5	376.8	370.3	369.7	249.3	231.4	1716.5	1433.4
P&A 6	392.1	385.3	374.2	370.9	353.2	351.7	340.3	236.7	220.5	1659	1366.4
Mean Recovery (ng/kg)	419.6	405.8	391.2	377.1	370.7	361.5	351.9	242.7	225.4	1675.5	1385
% Mean Recovery	104.9	101.4	97.8	94.3	92.7	90.4	88	60.7	56.4	83.8	69.3
Standard Deviation	35.4	24.1	13.5	8	10.6	11.1	12.6	6.6	4.4	38.5	30.7
RSD (%)	8.4	5.9	3.5	2.1	2.9	3.1	3.6	11	1.9	2.3	2.2

Sample	PFBS	PFHxS	PFOS	PFechS	FOUEA	FHpPA	FHUEA	FHEA	FOEA	FDEA
Unspiked 1	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Unspiked 2	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
P&A 1	337.4	349.1	340.3	342.8	389.5	371.3	372.5	7023.5	8202.6	8564.9
P&A 2	347.3	358.3	345.9	347.2	408.7	377.2	387.1	7346.1	8542.6	9308
P&A 3	366.3	330.1	331.7	345.4	401.5	361.4	379	6844.3	7402.4	8989.2
P&A 4	348.2	343.6	338.3	347.6	404.9	377.5	388.1	7258.2	7551.9	9173.4
P&A 5	351.8	361.7	365.6	362.6	417.5	395.1	391.8	7461.3	7821.2	9287.4
P&A 6	336.7	343.4	363.7	342.5	394.5	356.9	374.5	7559.3	8002.2	8367.1
Mean Recovery (ng/kg)	347.9	347.7	347.7	348	402.7	373.2	382.1	7248.8	7920.5	8948.3
% Mean Recovery	87	86.9	86.9	87	100.7	93.3	95.5	90.6	99	111.9
Standard Deviation	10.9	11.5	13.9	7.4	10	13.6	7.9	270.4	421.3	395.3
RSD (%)	3.1	3.3	4	2.1	2.5	3.6	2.1	3.7	5.3	4.4

TABLE 5 Single-Laboratory Surrogate Recovery Data in Ottawa Sand

Sample	Measured ng/kg from Ottawa Sand – 400 ng/kg spike								
	MPFBA	MPFHxA	MPFHxS	MPFOA	MPFNA	MPFOS	MPFDA	MPFUnA	MPFDoA
Unspiked 1	420.0	433.5	431.8	428.0	439.4	429.2	442.6	443.3	447.7
Unspiked 2	366.5	396.8	378.5	384.9	389.8	373.6	404.9	400.8	425.8
P&A 1	361.1	364.3	356.3	377.0	376.6	354.4	384.9	391.3	409.3
P&A 2	383.6	378.4	357.3	389.4	379.7	375.7	395.7	399.2	412.2
P&A 3	374.5	378.5	375.4	390.5	378.6	372.4	382.5	386.9	402.2
P&A 4	370.1	384.4	366.1	396.3	384.4	374.2	397.8	406.2	420.5
P&A 5	370.1	386.8	372.0	395.7	381.1	372.8	394.4	399.9	421.5
P&A 6	363.6	384.8	356.1	397.9	384.9	368.6	389.5	392.3	402.9
Mean Recovery (ng/kg dry weight)	376.2	388.4	374.2	394.9	389.3	377.6	399.0	402.5	417.7
% Mean Recovery	94.0	97.1	93.5	98.7	97.3	94.4	99.8	100.6	104.4
Standard Deviation	19.0	20.4	24.9	15.0	20.7	21.9	19.0	17.6	14.9
RSD (%)	5.1	5.3	6.7	3.8	5.3	5.8	4.8	4.4	3.6

7.2 *Tandem Mass Spectrometer System*[11]—A MS/MS system capable of multiple reaction monitoring (MRM) analysis or any system that is capable of meeting the requirements in this test method shall be used.

7.3 *Centrifuge*—A device to centrifuge the samples.

7.4 *Lab Rotator*[12]—A device to mix the samples by end-over-end rotation.

7.5 *Filtration Device:*

[11] A Waters Xevo TQ-S triple quadrupole mass spectrometer, or equivalent, has been found suitable for use.

[12] A Lab Rotator, or equivalent, has been found suitable to mix samples.

7.5.1 *Hypodermic Syringe*—A luer-lock tip glass syringe capable of holding a syringe driven filter unit.

7.5.2 A 10-mL lock tip glass syringe size is recommended since a 10-mL sample size is used in this test method.

7.5.3 *Filter Unit*[13]—Polypropylene filter units were used to filter the samples.

8. Reagents and Materials

8.1 *Purity of Reagents*—High performance liquid chromatography (HPLC) pesticide residue analysis and spectrophotometry grade chemicals shall be used in all tests. Unless indicated otherwise, it is intended that all reagents shall conform to the Committee on Analytical Reagents of the American Chemical Society.[14] Other reagent grades may be used provided they are first determined to be of sufficiently high purity to permit their use without affecting the accuracy of the measurements.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type 1 of Specification D1193. It shall be demonstrated that this water does not contain contaminants at concentrations sufficient to interfere with the analysis.

8.3 *Gases*—Ultrapure nitrogen and argon.

8.4 *Vials*—2-mL amber glass autosampler vials or equivalent.

8.5 Polyethylene autosampler vial caps or equivalent.

8.6 *Syringe*—10 or 25 mL filter-adaptable glass syringe with luer lock.

8.7 pH paper (pH range 1-14).

8.8 *Polypropylene Tubes*—15- and 50-mL.

8.9 Class A volumetric glassware.

8.10 *Pipette Tips*—Polypropylene pipette tips free of release agents or low retention coating of various sizes.

8.11 Polyethylene disposable pipettes.

8.12 Acetonitrile (CAS # 75-05-8).

8.13 Methanol (CAS # 67-56-1).

8.14 Ammonium acetate (CAS # 631-61-8).

8.15 Acetic acid (CAS # 64-19-7)

8.16 2-Propanol (isopropyl alcohol, CAS # 67-63-0).

8.17 Ammonium hydroxide (CAS # 1336-21-6).

8.18 Ottawa sand (CAS # 14808-60-7).

8.19 *PFC Standards*[15]:

8.19.1 Perfluorobutylsulfonate (PFBS, CAS # 29420-49-3).
8.19.2 Perfluorohexylsulfonate (PHFxS, CAS # 3871-99-6).
8.19.3 Perfluorooctylsulfonate (PFOS, CAS # 1763-23-1).
8.19.4 Perfluorobutanoate (PFBA, CAS # 375-22-4).
8.19.5 Perfluoropentanoate (PFPeA, CAS # 2706-90-3).
8.19.6 Perfluorohexanoate (PFHxA, CAS # 307-24-4).
8.19.7 Perfluoroheptanoate (PFHpA, CAS # 375-85-9).
8.19.8 Perfluorooctanoate (PFOA, CAS # 335-67-1).
8.19.9 Perfluorononanoate (PFNA, CAS # 375-95-1)
8.19.10 Perfluorodecanoate (PFDA, CAS # 335-76-2).
8.19.11 Perfluoroundecanoate (PFUnA, CAS # 2058-94-8).
8.19.12 Perfluorododecanoate (PFDoA, CAS # 307-55-1).
8.19.13 Perfluorotridecanoate (PFTriA, CAS # 72629-94-8).
8.19.14 Perfluorotetradecanoate (PFTreA, CAS # 376-06-7).
8.19.15 Decafluoro-4-(pentafluoroethyl)cyclohexanesulfonate (PFechS, CAS # 67584-42-3).
8.19.16 3-perfluoropheptyl propanoic acid (FHpPA, CAS # 812-70-4).
8.19.17 2H-perfluoro-2-decenoic acid (FOUEA, CAS # 70887-84-2).
8.19.18 2-perfluorodecyl ethanoic acid (FDEA, CAS # not available).
8.19.19 2-perfluorooctyl ethanoic acid (FOEA, CAS # 27854-31-5).
8.19.20 2H-perfluoro-2-octenoic acid (FHUEA, CAS # not available).
8.19.21 2-perfluorohexyl ethanoic acid (FHEA, CAS # 53826-12-3).

8.20 *PFC Surrogates:*[16]

8.20.1 $^{18}O_2$-Perfluorohexylsulfonate (MPFHxS).
8.20.2 $^{13}C_4$-Perfluorooctylsulfonate (MPFOS).
8.20.3 $^{13}C_4$-Perfluorobutanoate (MPFBA).
8.20.4 $^{13}C_2$-Perfluorohexanoate (MPFHxA).
8.20.5 $^{13}C_4$-Perfluorooctanoate (MPFOA).
8.20.6 $^{13}C_5$-Perfluorononanoate (MPFNA).
8.20.7 $^{13}C_2$-Perfluorodecanoate (MPFDA).
8.20.8 $^{13}C_2$-Perfluoroundecanoate (MPFUnA).
8.20.9 $^{13}C_2$-Perfluorododecanoate (MPFDoA).

9. Hazards

9.1 Normal laboratory safety applies to this method. Analysts should wear safety glasses, gloves, and lab coats when working in the lab. Analysts should review the material safety data sheets (MSDS) for all reagents used in this method.

10. Sampling

10.1 *Sampling and Preservation*—Grab samples are collected in glass or polypropylene containers. Sample containers and contact surfaces with PTFE shall be avoided. As part of the

[13] An Acrodisc GxF/0.2 µm GHP membrane syringe driven filter unit, or equivalent, has been found suitable for use.

[14] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, EDH Ltd., Poole, Dorset, U.K. and the *United States Pharmacopeia and National Formulary*, U. S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[15] PFC Standards may be difficult to find; some sources of PFC standards that have been found suitable for use were from Aldrich Chemical Company, Wellington Laboratories, Inc., and Wako Laboratory. Standards from other vendors may be used.

[16] PFC surrogates from Wellington Laboratories Inc., or equivalent, have been found suitable for use.

overall quality assurance program for this test method, field blanks exposed to the same field conditions as samples are collected and analyzed according to this test method to assess the potential for field contamination. This test method is based on a 2-g sample size per analysis. If different sample sizes are used, spiking solution amounts may need to be modified. Conventional sampling practices should be followed with the caution that PFC-containing products may be present in sampling equipment. All sampling equipment and supplies shall be PFC-free in order to prevent contamination of the samples. EPA publications SW-846 may be used as a sampling guide. Samples shall be shipped on ice with a trip blank. Once received, the sample temperature is taken and should be less than 6 °C. If the receiving temperature is greater than 6 °C, the sample temperature is noted in the case narrative accompanying the data. Samples should be stored refrigerated between 0 and 6 °C from the time of collection until analysis. The sample should be analyzed within 28 d of collection. No holding time study has been done on the various soil matrices tested in this test method. Holding time may vary depending on the matrix, and individual laboratories should determine the holding time in their matrix.[17]

11. Preparation of LC/MS/MS

11.1 *LC Chromatograph Operating Conditions:*

11.1.1 Injections of all standards and samples are made at a 30-µL volume. Other injection volumes may be used to optimize conditions. Standards and sample extracts shall be in a 50:50 methanol:water solution containing 0.1 % acetic acid. In the case of extreme concentration differences amongst samples, it is wise to analyze a blank after a concentrated sample and before a dilute sample to minimize carryover of analytes from injection to injection. However, there should not be carryover between samples. The LC utilized to develop this test method has a flow through LC needle design. The gradient conditions for liquid chromatography are shown in Table 6.

11.2 *LC Sample Manager Conditions:*

11.2.1 *Needle Wash Solvent*—60 % acetonitrile/40 % 2-propanol; Time: 5 min.

11.3 *Mass Spectrometer Parameters:*

11.3.1 To acquire the maximum number of data points per SRM channel while maintaining adequate sensitivity, the tune parameters may be optimized according to the instrument used. Each peak requires at least ten scans per peak for adequate quantitation. This test method contains nine surrogates, which are isotopically labeled PFCs, and 21 PFCs which are split up into 18 MRM acquisition functions to optimize sensitivity. Variable parameters regarding retention times, SRM transitions, and cone and collision energies are shown in Table 3. Mass spectrometer parameters used in the development of this method are listed below:

11.3.1.1 The instrument is set in the Electrospray negative source setting.

11.3.1.2 Capillary Voltage: 0.75 kV.

11.3.1.3 Cone: Variable depending on analyte.

11.3.1.4 Extractor: 2 Volts.

11.3.1.5 Source Temperature: 150 °C.

11.3.1.6 Desolvation Gas Temperature: 450 °C.

11.3.1.7 Desolvation Gas Flow: 800 L/h.

11.3.1.8 Cone Gas Flow: 200 L/h.

11.3.1.9 Collision Gas Flow: 0.15 mL/min.

11.3.1.10 Low Mass Resolution 1: 2.6.

11.3.1.11 High Mass Resolution 1: 14.

11.3.1.12 Ion Energy 1: 1.

11.3.1.13 Entrance Energy: 1.

11.3.1.14 Collision Energy: Variable depending on analyte.

11.3.1.15 Exit Energy: 1.

11.3.1.16 Low Mass Resolution 2: 2.5.

11.3.1.17 High Mass Resolution 2: 14.

11.3.1.18 Ion Energy 2: 3.

11.3.1.19 Gain: 1.0.

11.3.1.20 Multiplier: 511.1.

11.3.1.21 Inter-Scan Delay: 0.004 s.

12. Calibration and Standardization

12.1 The mass spectrometer shall be calibrated as per manufacturer's specifications before analysis. Analytical values satisfying test method criteria have been achieved using the following procedures. Prepare all solutions in the lab using Class A volumetric glassware.

12.2 *Calibration and Standardization*—To calibrate the instrument, analyze nine calibration standards of the polyfluorinated compounds prior to sample analysis as shown in Table 2. Calibration stock standard solution is prepared from the target and surrogate spike solutions directly to ensure consistency. Stock standard Solution A containing the polyfluorinated compounds and surrogates is prepared at Level 9 concentration and aliquots of that solution are diluted to prepare Levels 1 through 8. The following steps will produce standards with the concentration values shown in Table 2. The analyst is responsible for recording initial component weights carefully when working with pure materials and correctly carrying the weights through the dilution calculations. At a minimum five calibration levels are required when using a linear calibration curve and six calibration levels are required when using a quadratic calibration curve. An initial nine-point curve may be used to allow for the dropping of the lower level calibration points if the individual laboratory's instrument cannot achieve low

[17] A guide to help and determine sample holding times can be found at http://www.epa.gov/esd/cmb/research/bs_033cmb06.pdf (2014).

TABLE 6 Gradient Conditions for Liquid Chromatography

Time (min)	Flow (mL/min)	Percent 95 % Water: 5 % Acetonitrile	Percent Acetonitrile	Percent 95 % Water: 5 % Acetonitrile, 400 mM Ammonium Acetate
0	0.3	95	0	5
1	0.3	75	20	5
6	0.3	50	45	5
13	0.3	15	80	5
14	0.4	0	95	5
17	0.4	0	95	5
18	0.4	95	0	5
21	0.4	95	0	5

detection limits on certain PFCs. This should allow for at least a five- or six-point calibration curve to be obtained. No problems were encountered while using the nine-point calibration curve in developing this test method.

12.2.1 Calibration stock standard Solution A (Level 9, Table 2) is prepared from the target and surrogate spike solutions directly to ensure consistency. 500 µL of surrogate spike (20 µg/L), 500 µL Target Spike I, and 500 µL of PFC Target Spike II (refer to Table 7) is added to a 50-mL volumetric flask and diluted to 50 mL with 50:50 methanol:water containing 0.1 % acetic acid. The preparation of the Level 9 standard can be accomplished using appropriate volumes and concentrations of stock solutions as per a particular laboratory's standard procedure. It is critical to ensure that analytes are solubilized in the Level 9 standard.

12.2.2 Aliquots of Solution A are then diluted with 50:50 methanol:water containing 0.1 % acetic acid to prepare the desired calibration levels in 2-mL amber glass LC vials. The calibration vials shall be used within 24 h to ensure optimum results. The end calibration check shall be prepared in a separate LC vial near the mid-level. All calibration standards should only be used once. The analyte concentration in the vial may change after the vial cap is pierced because the vial caps do not reseal after puncture. Changing the caps immediately after the injection should alleviate this problem. Calibration standards are not filtered.

12.2.3 Inject each standard and obtain its chromatogram. An external calibration technique is used to monitor the primary and confirmatory SRM transitions of each analyte. Calibration software is utilized to conduct the quantitation of the target analytes and surrogates using the primary SRM transition. The ratios of the primary/confirmatory SRM transition area counts are given in Table 3 and will vary depending on the individual tuning conditions. The primary/confirmatory SRM transition area ratio shall be within 35 % of the individual labs' accepted primary/confirmatory SRM transition area ratio. The primary SRM transition of each analyte is used for quantitation of and the confirmatory SRM transition for confirmation. This gives added confirmation by isolating the parent ion, forming two product ions via fragmentation, and relating it to the retention time in the calibration standard.

12.2.4 Depending on sensitivity and matrix interference issues dependent on sample type, the confirmatory SRM transition can be used as the primary SRM transition for quantitation during analysis. This shall be explained in a narrative accompanying the data. A new primary/confirmatory ion ratio will then be determined if switching the SRM transitions used to quantitate and confirm. The new primary/confirmatory SRM transition area ratio is required to be within 35 % of the individual labs' new primary/confirmatory SRM transition area ratio.

12.2.5 The calibration software manual should be consulted to use the software correctly. The quantitation method is set as an external calibration using the peak areas in ppt units. Concentrations may be calculated using the data system software to generate linear regression or quadratic calibration curves. Forcing the calibration curve through the origin (X = 0, Y = 0) is not recommended.

12.2.6 Linear calibration may be used if the coefficient of determination, r^2, is ≥0.98 for the analyte. The point of origin is excluded and a fit weighting 1/X is used in order to give more emphasis to the lower concentrations. If one of the calibration standards other than the high or low point causes the r^2 of the curve to be <0.98, this point shall be re-injected or a new calibration curve shall be regenerated. Each calibration point used to generate the curve shall have a calculated percent deviation less than 30 % from the generated curve. If the low or high point(s), or both, are excluded, minimally a five-point curve is acceptable but the reporting range shall be modified to reflect this change.

12.2.7 Quadratic calibration may be used if the coefficient of determination, r^2, is ≥0.99 for the analyte. The point of origin is excluded, and a fit weighting of 1/X is used in order to give more emphasis to the lower concentrations. If one of the calibration standards causes the curve to be <0.99, this point shall be re-injected or a new calibration curve shall be regenerated. If the low or high point(s), or both, are excluded, minimally a six-point curve is acceptable but the reporting range shall be modified to reflect this change. Each calibration point used to generate the curve shall have a calculated percent deviation less than 30 % from the generated curve.

12.2.8 The retention time window of the SRM transitions shall be within 5 % of the retention time of the analyte in a midpoint calibration standard. If this is not the case, re-analyze the calibration curve to determine if there was a shift in retention time during the analysis and the sample needs to be re-injected. If the retention time is still incorrect in the sample, refer to the analyte as an unknown.

12.2.9 A midpoint calibration check standard shall be analyzed at the end of each batch of 30 samples or within 24 h after the initial calibration curve was generated; the criteria in the individual labs' quality system may be more restrictive

TABLE 7 PFC Target Spike Solutions (PPB)

Analyte	Concentration of Analyte in PFC Target Spike Solutions		
	PFC High Target Spike Solutions		PFC Reporting Limit Spike Solution
	Target Spike I	Target Spike II	
PFTreA, PFTriA, PFDoA, PFUnA, PFDA, PFOS, PFNA, PFHxA, PFHpA, PFBS, PFechS, PFOA, PFHxS	20 µg/L	—	2 µg/L
PFBA, PFPeA	100 µg/L	—	10 µg/L
FOUEA, FHUEA, FHpPA	—	20 µg/L	2 µg/L
FHEA, FOEA, FDEA	—	400 µg/L	40 µg/L

pertaining to the number of samples. This end calibration check, a new not pierced sealed vial, should come from the same calibration standard solution that was used to generate the initial curve. The results from the end calibration check standard shall have a percent deviation less than 30 % from the calculated concentration for the target analytes and surrogates. If the results are not within these criteria, corrective action including reoccurrence minimization is performed and either all samples in the batch are re-analyzed against a new calibration curve or the affected results are qualified with an indication that they do not fall within the performance criteria of the test method. If the analyst inspects the vial containing the end calibration check standard and notices that the sample evaporated affecting the concentration or other anomaly, a new end calibration check standard may be made and analyzed. If this new end calibration check standard has a percent deviation less than 30 % from the calculated concentration for the target analytes and surrogates, the results may be reported unqualified.

12.3 If a laboratory has not performed the test before or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., an instrument qualification study including method detection limit (MDL), calibration range determination, and precision and bias determination shall be performed to demonstrate laboratory capability.

12.3.1 Analyze at least four replicates of a spiked sand sample containing the PFCs and surrogates at an extract concentration in the calibration range of Levels 4 through 7. The Level 6 concentration of the nine-point calibration curve was used to set the QC acceptance criteria in this method. The matrix and chemistry should be similar to the matrix used in this test method. Each replicate shall be taken through the complete analytical test method including any sample manipulation and extraction steps.

12.3.2 Calculate the mean (average) percent recovery and relative standard deviation (RSD) of the four values and compare to the acceptable ranges of the QC acceptance criteria for the Initial Demonstration of Performance in Table 8.

12.3.3 This study should be repeated until the single operator precision and mean recovery are within the limits in Table 8. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the *F* test and *t* test in evaluating the acceptability of the mean and standard deviation.

12.3.3.1 The QC acceptance criteria for the Initial Demonstration of Performance in Table 8 were generated from the single-laboratory data shown in Section 16. Data from Ottawa sand and four ASTM soil matrices are shown in Section 16. It is recommended that each laboratory determine in-house QC acceptance criteria which meet or exceed the criteria in this test method. References generating QC acceptance criteria are ASTM Practices D2777, D5847, E2554, or Method 8000 in EPA publications SW-846.

12.4 *Surrogate Spiking Solution:*

TABLE 8 QC Acceptance Criteria

NOTE 1—Table 8 data is preliminary until a multi-lab validation study is completed.

Analyte/Surrogate	Spike Conc. ng/kg	Initial Demonstration of Performance			Laboratory Control Sample	
		Recovery (%)		Precision	Recovery (%)	
		Lower Limit	Upper Limit	Maximum % RSD	Lower Control Limit (LCL) %	Upper Control Limit (UCL) %
PFTreA	400	70	130	30	70	130
PFTriA	400	70	130	30	70	130
PFDoA	400	70	130	30	70	130
PFUnA	400	70	130	30	70	130
PFDA	400	70	130	30	70	130
PFOS	400	70	130	30	70	130
PFNA	400	70	130	30	70	130
PFecHS	400	70	130	30	70	130
PFOA	400	70	130	30	70	130
PFHxS	400	70	130	30	70	130
PFHpA	400	50	130	30	50	130
PFHxA	400	50	130	30	50	130
PFBS	400	70	130	30	70	130
PFPeA	2000	70	130	30	70	130
PFBA	2000	50	130	30	50	130
FHEA	8000	70	130	30	70	130
FOEA	8000	70	130	30	70	130
FDEA	8000	70	130	30	70	130
FOUEA	400	70	130	30	70	130
FHpPA	400	70	130	30	70	130
FHUEA	400	70	130	30	70	130
MPFBA	400	70	130	30	70	130
MPFHxA	400	70	130	30	70	130
MPFHxS	400	70	130	30	70	130
MPFOA	400	70	130	30	70	130
MPFNA	400	70	130	30	70	130
MPFOS	400	70	130	30	70	130
MPFDA	400	70	130	30	70	130
MPFUnA	400	70	130	30	70	130
MPFDoA	400	70	130	30	70	130

12.4.1 A surrogate spiking solution containing nine isotopically labeled PFCs—MPFBA, MPFHxA, MPFHxS, MPFDA, MPFOA, MPFOS, MPFNA, MPFUnA, and MPFDoA—is added to all samples, method blanks, duplicates, laboratory control samples, matrix spikes, and reporting limit checks. A stock surrogate spiking solution is prepared at 20 µg/L in 95 % acetonitrile: 5 % water. Spiking 40 µL of this spiking solution into a 2-g soil sample results in a concentration of 400 ng/kg of the surrogate in the sample. The results obtained for the surrogate recoveries shall fall within the limits of Table 8. If the limits are not met, the affected results shall be qualified with an indication that they do not fall within the performance criteria of the test method.

12.4.1.1 The surrogate spiking solution was prepared by adding 250 µL of a 2-mg/L PFC surrogate mix[18] in a 50 mL volumetric and diluted to 50 mL with 95 % acetonitrile: 5 % water. Surrogate spiking solutions are routinely replaced every year if not previously discarded for quality control failure.

12.5 *Method Blank:*

12.5.1 At least two method blanks for every 30 samples are prepared in 2 g of Ottawa sand to investigate for contamination during sample preparation and extraction. The concentration of target analytes in either/both blank(s) shall be at less than half the reporting limit or the data shall be qualified as having a blank issue and the reporting limit shall be raised to at least three times above the blank contamination concentration. PFCs are common in the environment and laboratories requiring an additional method blank sample.

12.6 *Reporting Limit Check Sample (RLCS):*

12.6.1 Each batch or within the 24-h analysis window a reporting limit check sample shall be analyzed. The reporting limit check sample is processed like a laboratory control sample just spiked at or near (1 to 2 times) the reporting limit. The concentration of the RLCS may be reported below the reporting limit since the spike is at or near the reporting limit. This sample is to check if the analytes were present at the reporting limit, they would be identified. The recovery limits for the RLCS are 35 to 150 %, if any analytes are outside of these limits the QC failure is explained in a narrative accompanying the data.

12.6.2 Two grams of Ottawa sand is added to a 15-mL polypropylene centrifuge tube. The sample is spiked with 40 µL of PFC surrogate spiking solution and 25 µL of PFC reporting limit check solution (Table 7) and then taken through the sample preparation and analyzed.

12.7 *Laboratory Control Sample (LCS):*

12.7.1 Analyze at least one LCS with the PFCs at a mid-level extract concentration. A concentration at the Level 6 concentration was used in this test method, any mid-level (Levels 4 through 7) concentration may be chosen using this test method. The LCS is prepared following the analytical method and analyzed with each batch of 30 samples or less. Prepare a stock matrix spiking solution—Target Spike I and II in 95 % acetonitrile: 5 % water containing the 21 PFCs at concentrations listed in Table 7. Spike 40 µL each of Target Spike I and Target Spike II into 2 g of Ottawa sand to yield a concentration of 2000 ng/kg (PFBA and PFPeA), 8000 ng/kg (FHEA, FDEA, and FOEA) and 400 ng/kg of remaining 16 PFCs (PFTreA, PFTriA, PFDoA, PFUnA, PFDA, PFOS, PFNA, PFHxA, PFHpA, PFBS, PFechS, PFOA, PFHxS, FOUEA, FHUEA, and FHpPA) in the sample. The result obtained for the LCS shall fall within the limits in Table 8. Spiking solutions are routinely replaced every year if not previously discarded for quality control failure.

12.7.2 If the result is not within these limits, sample analysis is halted until corrective action resolving the problem has been performed. Impacted samples in the batch are either re-analyzed or the results are flagged with a qualifier stating that they do not fall within the performance criteria of the test method.

12.8 *Matrix Spike (MS):*

12.8.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch of 30 or fewer samples by spiking the sample with a known concentration of PFCs and following the analytical method. Prepare a stock matrix spiking solution—Target Spike I and II in 95 % acetonitrile: 5 % water containing the 21 PFCs at concentrations listed in Table 7. Spike 40 µL of these stock solutions into 2 g of the site sample to yield a concentration of 2000 ng/kg (PFBA and PFPeA), 8000 ng/kg (FHEA, FDEA, and FOEA) and 400 ng/kg of remaining 16 PFCs (PFTreA, PFTriA, PFDoA, PFUnA, PFDA, PFOS, PFNA, PFHxA, PFHpA, PFBS, PFechS, PFOA, PFHxS, FOUEA, FHUEA, AND FHpPA) in the sample.

12.8.2 If the spiked concentration plus the background concentration exceeds that of the Level 9 calibration standard, the sample shall be diluted (using 50 % Methanol/50 % Water with 0.1 % acetic acid) to a level near the midpoint of the calibration curve.

12.8.3 Calculate the percent recovery of the spike (P) using Eq 1:

$$P = 100\frac{\left|A(V_s + V) - BV_s\right|}{CV} \quad (1)$$

where:

A = concentration found in spiked sample,
B = concentration found in unspiked sample,
C = concentration of analyte in spiking solution,
V_s = volume of sample used,
V = volume of spiking solution added, and
P = percent recovery.

12.8.4 The percent recovery of the spike shall fall within the limits in Table 9. If the percent recovery is not within these limits, a matrix interference may be present. Under these circumstances, either all samples in the batch may be analyzed by a test method not affected by the matrix interference, or the results shall be qualified indicating that they do not fall within the performance criteria of the test method. It has been found that in some cases the matrix spike concentration may be minimal compared to the concentration in the native sample. If this is the case, the sample may be spiked at a higher level or the generated data may be reported explaining in the narrative

[18] Surrogate mix from Wellington Laboratories, Inc. has been found suitable for use.

TABLE 9 MS/MSD QC Acceptance Criteria

NOTE 1—Table 9 data is preliminary until a multi-lab validation study is completed

Analyte	Spike Conc. ng/L	MS/MSD Recovery (%)		Precision RPD (%)
		Lower Limit	Upper Limit	
PFTreA	400	70	130	30
PFTriA	400	70	130	30
PFDoA	400	70	130	30
PFUnA	400	70	130	30
PFDA	400	70	130	30
PFOS	400	70	130	30
PFNA	400	70	130	30
PFecHS	400	70	130	30
PFOA	400	70	130	30
PFHxS	400	70	130	30
PFHpA	400	50	130	30
PFHxA	400	50	130	30
PFBS	400	70	130	30
PFPeA	2000	70	130	30
PFBA	2000	50	130	30
FHEA	8000	70	130	30
FOEA	8000	70	130	30
FDEA	8000	70	130	30
FOUEA	400	70	130	30
FHpPA	400	70	130	30
FHUEA	400	70	130	30
MPFBA	400	70	130	30
MPFHxA	400	70	130	30
MPFHxS	400	70	130	30
MPFOA	400	70	130	30
MPFNA	400	70	130	30
MPFOS	400	70	130	30
MPFDA	400	70	130	30
MPFUnA	400	70	130	30
MPFDoA	400	70	130	30

accompanying the data that the spike was negligible compared to the native concentration found in the sample.

12.8.5 The matrix spike/matrix spike duplicate (MS/MSD) limits in Table 9 were generated by a single-laboratory study using the data in Section 16. The limits in Table 9 are preliminary until a multi-lab validation study is completed. The matrix variation between different soils may have a tendency to generate significantly wider control limits than those generated for this test method. It is recommended that each laboratory determine in-house QC acceptance criteria meeting or exceeding the criteria stated in this test method.

12.8.5.1 Each laboratory should generate its own in-house QC acceptance criteria after the analysis of 15 to 20 matrix spike samples of a particular soil matrix. References on generating QC acceptance criteria are ASTM Practices D5847, D2777, E2554, or Method 8000 in EPA publication SW-846.

12.9 *Duplicate:*

12.9.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch of 30 or fewer samples. If the sample contains the analyte at a level greater than five times the detection limit of the method, the sample and duplicate may be analyzed unspiked; otherwise, a matrix spike/matrix spike duplicate should be used.

12.9.2 Calculate the relative percent difference (RPD) between the duplicate values (or MS/MSD values) as shown in Eq 2. Compare to the RPD limit in Table 9.

$$RPD = \frac{|MSR - MSDR|}{(MSR + MSDR)\div 2} \times 100 \quad (2)$$

where:

RPD = relative percent difference,
MSR = matrix spike recovery, and
MSDR = matrix spike duplicate recovery.

12.9.3 If the result exceeds the precision limit, the batch shall be re-analyzed or the results are flagged with a qualifier stating that they do not fall within the performance criteria of the test method.

13. Procedure

13.1 This test method is based upon a 2-g sample size per analysis. The samples shall be analyzed within 28 d of collection. If samples are received or stored above 6 °C, or are not analyzed within 28 d of collection, it is noted in the case narrative that accompanies the data.

13.2 Each batch of samples (30 or less) shall contain at least two method blanks, laboratory control sample, matrix spike, duplicate, and a reporting limit check sample at a minimum.

13.3 In the laboratory, 2 g of sample (measured to the hundredth of a gram) is placed in a 15-mL polypropylene centrifuge tube. Every sample is then spiked with the surrogates as described in Section 12. The laboratory control, reporting limit check, and matrix spike samples are then spiked with the target compounds as described in Section 12. The samples are then shaken as thoroughly as possible, depending on the soil, in order to mix the spike solutions throughout the sample.

13.4 To all samples, 10 mL of methanol:water (50:50) is added and hand shaken/vortexed for ~1 min. After vortexing, pH of the samples is adjusted pH ~9-10 with ammonium hydroxide (~20 µL) and hand shaken/vortexed again for ~1 min. The sample tubes are tumbled on a rotator for 1 h, then centrifuged at 1900 rpm for 10 min. The supernatant of the sample is filtered through an Acrodisc GxF/0.2 µm GHP membrane syringe driven filter unit (refer to 13.5 and 13.6 before use) to remove particulates in the samples, and leave solids behind. Acetic acid (~50 µL) is added to all samples to adjust the pH ~3-4 after filtration. An aliquot of the solution is transferred to a LC vial and a polyethylene cap is applied. The final volume of the solution is estimated to be 10 mL for quantitation purposes since 10 mL of MeOH/water was added.

13.5 The filters are washed with two volumes of 10 mL acetonitrile followed by two volumes of 10 mL methanol prior to use to ensure the removal of possible PFC contaminants.

13.6 The syringe shall be cleaned between each filtration. It is the analyst's responsibility to ensure that the syringe is clean. A suggested method for cleaning the syringe between filtrations is to first rinse with at least five syringe volumes of water, followed by at least three volumes of acetonitrile, then three volumes of methanol, and a final rinse with water.

13.7 Once a passing calibration curve is generated the analysis of samples may begin. An order of analysis may be method blank(s), reporting limit check, laboratory control sample(s), sample(s), duplicate(s), and matrix spike sample(s) followed by an end calibration check standard.

14. Calculation or Interpretation of Results

14.1 For quantitative analysis of the PFCs and surrogates, the SRM transitions are identified by comparison of retention times in the sample to those of the standards. The target compounds are identified by comparing the sample primary SRM transition and its confirmatory SRM transition if correlated to the known standard SRM transition. Confirmatory transitions are available for most of the target analytes (Table 3). The primary/confirmatory SRM ion ratio shall meet the criteria set in the quantitation method by ±35 %. The primary/confirmatory SRM ion ratio is the average of the individual levels primary/confirmatory SRM ion ratios in the calibration curve on the day of analysis. This ratio will vary depending on the instrument acquisition parameters and must be checked for every sample batch. External calibration curves are used to calculate the amounts of PFCs and surrogates. Calculate the concentration in ng/kg (dry weight basis, ppt) for each analyte. The individual PFCs may be reported if present at or above the reporting limit. If the concentration of the analyte is determined to be above the calibration range, the sample is diluted with a solution of 50 % Water/50 % MeOH containing 0.1 % acetic acid to obtain a concentration near the mid-point of the calibration range and re-analyzed. This method uses nine surrogates—MPFBA, MPFHxA, MPFHxS, MPFDA, MPFOA, MPFOS, MPFNA, MPFUnA, and MPFDoA—to monitor performance. The surrogate recoveries are provided with all data generated from this test method.

14.1.1 If there is no confirmatory transition for the analyte (refer to Table 3), and the presence of the analyte in the sample cannot be confirmed with the primary transition and retention time, the analyte is listed as a non-detect or as having a matrix interference present. This was the case for the PFPeA in the ASTM CL-1 soil and is listed as MI, that is, matrix interference (Table 10). The area where PFPeA eluted had multiple peaks present and without a confirmatory transition the correct peak could not be identified.

14.2 *Example Calculation of Sample Concentration Reported:*

14.2.1 The concentration of sample is calculated using the Eq 3.

$$C_s(\text{ng/kg}) = \frac{[C_i\ (\text{ng/L})] \times [V_s\ (\text{L})]}{[W_d\ (\text{kg})]} \quad (3)$$

where:

C_s = concentration of target analyte in sample,

TABLE 10 Single-Laboratory Target Compound Recovery Data in ASTM CL-1 Soil

NOTE 1—P&A concentration for each analyte are values after subtracting average unspiked concentration.

Sample	Measured ng/kg from ASTM CL-1 Soil (Lean Clay) P&A Data (400 ng/kg spike for all PFCs except 2000 ng/kg for PFBA and PFPeA and 8000 ng/kg spike for FHEA, FDEA, and FOEA)										
	PFTreA	PFTriA	PFDoA	PFUnA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA
Unspiked 1	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	MI	<RL
Unspiked 2	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	MI	<RL
P&A 1	175.8	237.1	248.9	269.3	274	272.1	276.2	288.5	281.2	MI	1023.8
P&A 2	229.6	286.2	304.5	320.7	320	328.4	325.3	312.6	296.1	MI	1592.4
P&A 3	184.6	262.6	298.1	318.8	318.1	307.1	316.2	306.1	286.5	MI	1673.7
P&A 4	220.9	282.2	290.7	318.3	296.9	305.7	311.8	306.2	317.9	MI	1780.7
P&A 5	227.8	284.8	306.1	319.3	328.9	323..7	331.4	308.7	316.1	MI	1803.3
P&A 6	204.9	263.5	280.7	296.9	294.6	292.2	317.4	277.8	294.6	MI	1502.5
Mean Recovery (ng/kg)	207.2	269.4	288.1	307.2	305.4	304.8	313	300	298.7	MI	1562.7
% Mean Recovery	51.8	67.3	72	76.8	76.3	76.2	78.3	75	74.7	MI	78.1
Standard Deviation	22.9	19	21.4	20.6	20.5	20.7	19.4	13.7	15.2	MI	287.3
RSD (%)	11	7.1	7.4	6.7	6.7	6.8	6.2	4.6	5.1	MI	18.4

Sample	PFBS	PFHxS	PFOS	PFechS	FOUEA	FHpPA	FHUEA	FHEA	FOEA	FDEA
Unspiked 1	<RL	<RL	37.5	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Unspiked 2	<RL	<RL	30.7	<RL	<RL	<RL	<RL	<RL	<RL	<RL
P&A 1	266.1	269.1	249.6	265	367.4	415.2	377.9	7463	8531.4	8466.7
P&A 2	306	303.5	289.9	313	371	395.9	362.1	7263.7	8324.9	8595.8
P&A 3	304.1	310.1	291.3	305.4	374.8	395.1	382.5	7227.6	8141.1	8656.5
P&A 4	319.2	318.2	280	303.7	373.1	388.3	387.6	7195.7	7304.5	7994.7
P&A 5	318.7	324.5	328.9	310.8	378.6	401.7	392.6	7034.7	8422.7	9070.4
P&A 6	284.2	288.1	275	298.9	370	385.1	373.1	6612.1	7980.6	8602.2
Mean Recovery (ng/kg)	299.7	302.2	285.8	299.4	372.5	396.9	379.3	7132.8	8117.5	8564.3
% Mean Recovery	74.9	75.6	71.4	74.9	93.1	99.2	94.8	89.2	101.5	107.1
Standard Deviation	20.8	20.5	25.9	17.6	3.9	10.7	10.9	289.8	444.5	346.7
RSD (%)	6.9	6.8	9.1	5.9	1.1	2.7	2.9	4.1	5.5	4

C_i = concentration of target analyte in sample from instrument,
V_s = volume of sample, and
W_d = dry weight of sample.

14.2.2 The analysis of PFCs may require dilution per sample. Example calculation is given in Eq 4.

$$\frac{V_f}{V_i}(C_u) = C_f \quad (4)$$

where:

V_f = final volume,
V_i = initial volume,
C_u = uncorrected concentration, and
C_f = final concentration (corrected for dilution).

14.3 There are nine labeled surrogates for this analysis. The labeled analyte represents the unlabeled native analytes. PFTreA and PFTriA are represented by MPFDoA. PFHpA is represented by MPFHxA, PFechS and PFBS are represented by MPFHxS, and PFPeA is represented by MPFBA. The six fluorotelomer acids do not have associated labeled surrogates. The recoveries of the nearest labeled surrogate should be monitored but do not represent the native compound. No qualifications based on surrogate recovery will be made for the six fluorotelomer acids. It is a user's judgement to qualify data based upon no-representative surrogates.

15. Report

15.1 Determine the results in units of ng/kg (ppt) in a soil sample on a dry weight basis. Calculate the concentration in the sample using the linear or quadratic calibration curve generated. All data that do not meet the specifications in the test method shall be appropriately qualified.

16. Precision and Bias

16.1 The determination of precision and bias was conducted by U.S. EPA Region 5 Chicago Regional Laboratory (CRL) and generated applicable to data to determine the precision and bias as described in Practice D2777 for a single laboratory validation study.

16.2 This test method was tested by CRL on Ottawa sand. The samples were spiked with the PFCs to obtain a 2000 ng/kg (PFBA and PFPeA), 8000 ng/kg (FHEA, FDEA, and FOEA), and 400 ng/kg of the remaining target analytes; PFTreA, PFTriA, PFDoA, PFUnA, PFDA, PFOS, PFNA, PFHxA, PFHpA, PFBS, PFechS, PFOA, PFHxS, FOUEA, FHUEA, FHpPA, and 400 ng/kg of each surrogate as described in Section 12. Table 4 contains the recoveries and standard deviations (SD) for the target compounds and Table 5 the surrogate recoveries.

16.3 This test method was tested by CRL on four ASTM reference soils (CH-1, ML-1, CL-1, and SP-1).[19] ASTM reference soil CH-1 is Fat Clay (CH)- Vicksburg Buckshot Clay, ASTM reference soil ML-1 is silt (ML)- Vicksburg silt, ASTM reference soil CL-1 is lean clay (CL)- Annapolis clay, and ASTM reference soil SP-1 is sand (SP)- Frederick sand. The samples were spiked with target compounds and surrogates as described in Section 12. Tables 10-17 contain the recoveries for the target compounds and surrogates in the ASTM soils.

17. Keywords

17.1 liquid chromatography; mass spectrometry; polyfluorinated compounds; soils

[19] Reference to the ASTM soils and soil reports can be found at http://www.durhamgeo.com/downloads/ASTM%20Soil%20Reports.html (2014).

TABLE 11 Single-Laboratory Target Compound Recovery Data in ASTM CH-1 Soil

NOTE 1—P&A concentration for each analyte are values after subtracting average unspiked concentration.

Sample	Measured ng/kg from ASTM CH-1 Soil (Fat Clay) P&A Data (400 ng/kg spike for all PFCs except 2000 ng/kg for PFBA and PFPeA and 8000 ng/kg spike for FHEA, FDEA, and FOEA)										
	PFTreA	PFTriA	PFDoA	PFUnA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA
Unspiked 1	<RL	<RL	<RL	<RL	<RL	<RL	88.4	<RL	71.3	118.3	<RL
Unspiked 2	<RL	<RL	<RL	<RL	<RL	<RL	86.4	<RL	65.4	<RL	<RL
P&A 1	304.2	348.4	352	384	370	376.1	366.2	353.3	354.2	1727.5	1824.1
P&A 2	309.1	353.9	363.2	380.8	366.8	369.1	373.1	368.5	361.6	1741.4	1791.8
P&A 3	303.9	356.5	365.4	379.1	370.4	387.3	369.5	376.2	374.2	1737.8	1854.7
P&A 4	313.9	352.8	354.2	381.5	367.5	368.4	369.9	359.6	347.1	1725.1	1794.8
P&A 5	314.9	355.1	359.5	382.3	377	371.5	359.2	364.3	357.8	1708.7	1587.3
P&A 6	302.8	359.5	363.3	372.8	366.6	387.2	377.4	366.1	355.3	1757.8	1805.9
Mean Recovery (ng/kg)	308.1	354.3	359.6	380.1	369.7	376.6	369.2	364.6	358.3	1733	1776.4
% Mean Recovery	77	88.6	89.9	95	92.4	94.1	92.3	91.2	89.6	86.7	88.8
Standard Deviation	5.3	3.8	5.4	3.9	3.9	8.7	6.2	7.8	9.1	16.7	95.5
RSD (%)	1.7	1.1	1.5	1	1.1	2.3	1.7	2.1	2.5	1	5.4

Sample	PFBS	PFHxS	PFOS	PFechS	FOUEA	FHpPA	FHUEA	FHEA	FOEA	FDEA
Unspiked 1	<RL	66	177.6	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Unspiked 2	<RL	58.8	172.8	<RL	<RL	<RL	<RL	<RL	<RL	<RL
P&A 1	266.1	354.1	354.4	359.1	428.3	399.6	377.9	7381.4	7037.1	7789.8
P&A 2	306	352.3	363.9	357	419.6	403.8	362.1	7408.4	7673.4	7286.4
P&A 3	304.1	345.5	342.7	379.7	432.9	396.7	382.5	8112.5	7451.6	7829.6
P&A 4	319.2	352.2	354.8	365.1	427.7	378.1	387.6	7660.8	7052.1	7470.3
P&A 5	318.7	343.1	333.6	352.5	408.1	342.6	392.6	6950.5	6572.5	7728.5
P&A 6	284.2	370.8	385.2	349.7	416.8	396.7	373.1	8018.1	7807.7	7431.3
Mean Recovery (ng/kg)	299.7	353	355.8	360.5	422.2	386.2	379.3	7588.6	7265.7	7589.3
% Mean Recovery	74.9	88.2	88.9	90.1	105.6	96.6	94.8	94.9	90.8	94.9
Standard Deviation	20.8	9.7	17.9	10.8	9.1	23.1	10.9	435.1	463.2	222.8
RSD (%)	6.9	2.8	5	3	2.2	6	2.9	5.7	6.4	2.9

TABLE 12 Single-Laboratory Surrogate Recovery Data in ASTM CH-1 Soil

Sample	Measured ng/kg from ASTM CH-1 Soil (Fat Clay, White Bucket) – 400 ng/kg spike								
	MPFBA	MPFHxA	MPFHxS	MPFOA	MPFNA	MPFOS	MPFDA	MPFUnA	MPFDoA
Unspiked 1	353.8	355.3	341.9	362.1	366.6	371.0	371.8	360.3	357.4
Unspiked 2	365.1	374.0	360.1	373.5	389.7	383.6	379.5	382.5	372.1
P&A 1	353.0	354.6	361.7	365.2	377.3	371.3	365.3	378.0	365.5
P&A 2	362.2	358.1	373.4	363.8	382.5	365.9	363.8	386.7	367.9
P&A 3	367.3	372.1	351.5	373.6	390.5	357.6	385.0	379.9	366.6
P&A 4	359.2	363.6	350.4	365.1	378.5	369.7	368.9	378.1	362.3
P&A 5	349.7	351.3	362.6	364.7	372.2	367.2	365.6	371.9	369.8
P&A 6	361.6	367.3	367.0	378.2	380.5	382.2	375.8	386.0	376.6
Mean Recovery (ng/kg dry weight)	359.0	362.0	358.5	368.3	379.7	371.0	371.9	377.9	367.2
% Mean Recovery	89.7	90.5	89.6	92.1	94.9	92.8	93.0	94.5	91.8
Standard Deviation	6.2	8.5	10.1	5.9	8.1	8.5	7.6	8.6	5.9
RSD (%)	1.7	2.3	2.8	1.6	2.1	2.3	2.0	2.3	1.6

TABLE 13 Single-Laboratory Target Compound Recovery Data in ASTM SP-1 Soil

NOTE 1—P&A concentration for each analyte are values after subtractive average unspiked concentration.

Sample	Measured ng/kg from ASTM SP-1 Soil (Frederick Sand) P&A Data (400 ng/kg spike for all PFCs except 2000 ng/kg for PFBA and PFPeA and 8000 ng/kg spike for FHEA, FDEA, and FOEA)										
	PFTreA	PFTriA	PFDoA	PFUnA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA
Unspiked 1	<RL	<RL	<RL	<RL	<RL	<RL	53.1	<RL	<RL	28.1	<RL
Unspiked 2	<RL	<RL	<RL	<RL	<RL	<RL	51.3	<RL	<RL	24.1	<RL
P&A 1	313	354.2	357.9	363.2	375.6	364.1	346.9	388.7	357.2	1748.6	1824.1
P&A 2	315.2	355.4	375.2	359.6	383.4	375	361	384.6	351.3	1789.8	1819.4
P&A 3	331.5	360.7	376.3	383.3	394.4	362.2	359.7	394.4	373.9	1784.7	1859.5
P&A 4	326.8	354.1	372.2	377.6	393	384.1	372	393.1	365.7	1775.9	1858.6
P&A 5	311.6	355.5	374.4	362.7	380.5	373.2	349.3	371.8	359.7	1763.7	1813.8
P&A 6	324.2	371.8	394.4	379.1	389.6	392.2	372.5	399.5	359.6	1774	1818.8
Mean Recovery (ng/kg)	320.3	358.6	375	370.9	386.1	375.1	360.2	388.7	361.2	1772.7	1832.3
% Mean Recovery	80.1	89.6	93.8	92.7	96.5	93.8	90.1	97.2	90.3	88.6	91.6
Standard Deviation	8.2	6.9	11.7	10.2	7.4	11.5	10.8	9.7	7.7	14.9	20.9
RSD (%)	2.6	1.9	3.1	2.7	1.9	3.1	3	2.5	2.1	0.8	1.1

Sample	PFBS	PFHxS	PFOS	PFechS	FOUEA	FHpPA	FHUEA	FHEA	FOEA	FDEA
Unspiked 1	<RL	24.4[A]	682.1	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Unspiked 2	<RL	25.3	606.3	<RL	<RL	<RL	<RL	<RL	<RL	<RL
P&A 1	357.2	349.9	171.3	351.6	459.5	376.5	429.1	8259.4	8160.3	8462.8
P&A 2	351.3	334.1	286.8	359.4	453.7	380	431.5	7702.5	8462.3	8302.9
P&A 3	373.9	373.9	268.9	368	454.1	387.6	436.3	8153.8	8600	8840.4
P&A 4	365.7	377.3	307.9	367.3	453.8	404.9	440.7	7945	7850.5	8532.8
P&A 5	359.7	366.1	372.4	352.4	436.5	415.2	418.9	7785.8	8119.7	8985.6
P&A 6	359.6	351	407.8	378.3	463.6	415.7	452.4	8677.1	9173.5	8837.9
Mean Recovery (ng/kg)	361.2	358.7	302.5	362.8	453.5	396.6	434.8	8087.3	8394.3	8660.4
% Mean Recovery	90.3	89.7	75.6	90.7	113.4	99.2	108.7	101.1	104.9	108.3
Standard Deviation	7.7	16.6	83.2	10.3	9.2	17.6	11.3	358.1	464.8	265.6
RSD (%)	2.1	4.6	27.5	2.8	2	4.4	2.6	4.4	5.5	3.1

[A] Slightly below Reporting Limit

TABLE 14 Single-Laboratory Surrogate Recovery Data in ASTM SP-1 Soil

Sample	Measured ng/kg from ASTM SP-1 Soil (Frederick Sand, Yellow Bucket) – 400 ng/kg spike								
	MPFBA	MPFHxA	MPFHxS	MPFOA	MPFNA	MPFOS	MPFDA	MPFUnA	MPFDoA
Unspiked 1	370.2	366.9	369.2	368.6	367.1	357.9	379.4	368.7	374.6
Unspiked 2	374.9	371.9	366.8	372.1	372.5	363.2	376.7	375.7	374.0
P&A 1	361.5	372.6	373.8	371.7	369.8	356.8	372.0	376.6	366.7
P&A 2	373.4	367.7	362.0	369.1	367.4	360.8	368.4	361.8	369.0
P&A 3	366.1	358.9	365.9	365.6	365.8	351.6	364.3	365.3	372.3
P&A 4	372.0	369.1	359.2	373.6	364.3	376.0	374.6	366.5	373.4
P&A 5	364.8	365.6	360.1	371.7	383.3	359.6	370.0	368.6	369.4
P&A 6	365.2	381.2	373.1	371.8	379.0	361.5	374.5	382.2	386.6
Mean Recovery (ng/kg dry weight)	368.5	369.2	366.2	370.5	371.1	360.9	372.5	370.6	373.2
% Mean Recovery	92.1	92.3	91.6	92.6	92.8	90.2	93.1	92.7	93.3
Standard Deviation	4.8	6.4	5.6	2.6	6.7	7.1	4.8	6.8	6.1
RSD (%)	1.3	1.7	1.5	0.7	1.8	2.0	1.3	1.8	1.6

TABLE 15 Single-Laboratory Surrogate Recovery Data in ASTM CL-1 Soil

Sample	Measured ng/kg from ASTM CL-1 Soil (Lean Clay, Red Bucket) – 400 ng/kg spike								
	MPFBA	MPFHxA	MPFHxS	MPFOA	MPFNA	MPFOS	MPFDA	MPFUnA	MPFDoA
Unspiked 1	347.9	337.6	350.5	348.5	360.6	367.7	350.7	354.6	345.8
Unspiked 2	335.1	325.9	319.4	319.2	321.7	329.5	323.1	305.8	296.4
P&A 1	259.3	263.3	281.3	275.1	278.0	270.9	273.5	276.9	259.0
P&A 2	318.4	309.5	300.7	308.2	325.2	312.8	321.8	312.2	299.5
P&A 3	321.5	302.4	316.8	313.8	324.1	320.9	317.6	311.0	308.0
P&A 4	323.9	308.0	304.2	316.6	325.4	328.1	314.8	321.8	310.7
P&A 5	299.9	297.9	289.0	298.6	305.0	306.5	298.8	396.5	282.8
P&A 6	292.3	286.7	294.5	295.1	301.8	308.4	296.3	299.5	285.8
Mean Recovery (ng/kg dry weight)	312.3	303.9	307.0	309.4	317.7	318.1	312.0	309.8	298.5
% Mean Recovery	78.1	76.0	76.8	77.3	79.4	79.5	78.0	77.4	74.6
Standard Deviation	27.8	22.8	21.8	21.4	23.9	27.2	22.9	22.5	25.2
RSD (%)	8.9	7.5	7.1	6.9	7.5	8.6	7.3	7.3	8.4

TABLE 16 Single-Laboratory Target Compound Recovery Data in ASTM ML-1 Soil

NOTE 1—P&A concentration for each analyte are values after subtracting average unspiked concentration.

Sample	Measured ng/kg from ASTM ML-1 Soil (Silt) P&A Data (400 ng/kg spike for all PFCs except 2000 ng/kg for PFBA and PFPeA and 8000 ng/kg spike for FHEA, FDEA, and FOEA)										
	PFTreA	PFTriA	PFDoA	PFUnA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA
Unspiked 1	<RL	<RL	<RL	<RL	<RL	<RL	108.2	24.3[A]	80	<RL	<RL
Unspiked 2	<RL	<RL	<RL	<RL	<RL	<RL	117.7	<RL	81.6	<RL	<RL
P&A 1	336.8	386	388.8	398.3	405.3	399.6	467.4	366.7	383.9	1841.3	1928.3
P&A 2	330	369.5	377.5	370.5	385.4	380.1	478.2	364.8	356.9	1806.7	1825.6
P&A 3	323.5	386.8	382.3	384.5	395.3	394.4	488.9	394.4	386	1856.4	1932.9
P&A 4	323.3	364.9	379.9	371.8	391.3	399.4	465.1	370	372	1794.6	1886.4
P&A 5	327	377.7	383.9	381.6	380.5	400	483.9	380.6	372	1842.6	1845
P&A 6	328.5	375.3	374.5	368.6	386.6	385	475.7	358.1	363.3	1789.8	1860.9
Mean Recovery (ng/kg)	328.2	376.7	381.1	379.2	390.7	393.1	476.5	372.4	372.4	1821.4	1879.8
% Mean Recovery	82	94.2	95.3	94.8	97.7	98.3	119.1	93.1	93.1	91.1	94
Standard Deviation	5	8.8	5	11.3	8.8	8.6	9.2	13	11.3	29	44.1
RSD (%)	1.5	2.3	1.3	3	2.2	2.2	1.9	3.5	3	1.6	2.3

Sample	PFBS	PFHxS	PFOS	PFechS	FOUEA	FHpPA	FHUEA	FHEA	FOEA	FDEA
Unspiked 1	23.8[A]	99.9	221.1	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Unspiked 2	<RL	127.5	490.3	<RL	<RL	<RL	<RL	<RL	<RL	<RL
P&A 1	363.7	365.2	214.8	376.4	487.6	410.3	455.2	7217	9101.6	8724.6
P&A 2	351.3	336.9	194.7	369.5	479.6	439.8	449.3	8160.6	8024	9020.2
P&A 3	408	359.7	398	381.5	486.9	409.4	440.3	8134.8	8114	8821.1
P&A 4	337.8	358.7	207.7	363.6	471.4	416.6	424.4	8936.9	7829.1	8852.5
P&A 5	369.2	350.5	229.8	366.3	463.5	402.5	462.5	8796.3	8045.3	8483.3
P&A 6	348.8	355.1	189.8	373.6	474	389.5	473	8295	8228.9	8780.7
Mean Recovery (ng/kg)	363.1	354.3	239.1	371.8	477.1	411.3	450.8	8256.8	8223.8	8780.4
% Mean Recovery	90.8	88.6	59.8	93	119.3	102.8	112.7	103.2	102.8	109.8
Standard Deviation	24.6	9.8	79.1	6.7	9.4	16.7	17.1	610	449.5	176.5
RSD (%)	6.8	2.8	33.1	1.8	2	4.1	3.8	7.4	5.5	2

[A]Slightly below Reporting Limit.

TABLE 17 Single-Laboratory Surrogate Recovery Data in ASTM ML-1 Soil

Sample	Measured ng/kg from ASTM ML-1 Soil (Silt, Green Bucket) – 400 ng/kg spike								
	MPFBA	MPFHxA	MPFHxS	MPFOA	MPFNA	MPFOS	MPFDA	MPFUnA	MPFDoA
Unspiked 1	375.8	363.7	367.3	374.7	383.1	372.2	376.2	379.1	381.3
Unspiked 2	369.7	371.4	361.2	364.7	375.2	361.2	372.6	377.9	377.3
P&A 1	375.8	387.2	380.4	375.3	385.8	374.3	396.3	387.2	397.2
P&A 2	369.7	358.3	375.0	372.5	377.3	355.4	376.2	380.1	379.6
P&A 3	383.9	374.9	369.0	377.4	384.8	362.4	380.0	371.8	374.7
P&A 4	361.3	375.0	352.4	363.4	377.1	378.0	372.0	371.4	372.6
P&A 5	368.1	378.1	378.5	371.2	385.7	361.5	376.6	388.7	394.1
P&A 6	353.9	362.2	365.5	370.7	374.4	360.5	373.6	372.5	377.3
Mean Recovery (ng/kg dry weight)	369.8	371.3	368.6	371.2	380.4	365.7	377.9	378.6	381.8
% Mean Recovery	92.4	92.8	92.2	92.8	95.1	91.4	94.5	94.6	95.4
Standard Deviation	9.3	9.5	9.3	5.0	4.9	8.0	7.9	6.7	9.0
RSD (%)	2.5	2.6	2.5	1.3	1.3	2.2	2.1	1.8	2.4

APPENDIX

(Nonmandatory Information)

X1. PRELIMINARY DATA SUGGESTS THAT OTHER PFC ANALYTES MAY BE DETERMINED BY THIS STANDARD AND THE APPENDIX INFORMATION MAY BE OF USEFUL INFORMATION TO THE USER

X1.1 Preliminary data for an additional ten PFC analytes and isotopically labelled surrogates show promise for their analysis in soil using this standard. These analytes are listed in Table X1.1 with their method detection limit (MDL) and reporting range. Table X1.2 lists their MRM transitions, cone and collision energies, retention times, and ion ratios. Table X1.3 lists their precision and accuracy in Ottawa sand. Tables X1.4-X1.15 list the precision and accuracy for the additional ten PFCs and 14 of the standard's analytes and surrogates in various ASTM soils referenced in the standard (unspiked sample concentration average subtracted from the spiked concentrations if detected).

X1.2 *Figures*:

X1.2.1 Some of the analytes are comprised of isomeric mixtures; this is the case for PFOS, PFecHS, and PFHxS in this test method. The entire isomeric group should be quantitated up to your data quality objectives for the project, and it should be clear in your data package how quantitation was done. This is one reason why a secondary transition is required and allows

TABLE X1.1 List of Additional Analytes, Surrogates, MDLs, and Reporting Ranges

NOTE 1—MDL determination followed Reference 3 in standard. Reporting range followed Reference 4 in standard.

Analyte	Abbreviation	Chemical Abstract Number	MDL (ng/Kg)	Reporting Range (ng/Kg)
Perfluoro-1-decanesulfonate	PFDS	2806-15-7	3.03	25-1000
Perfluoro-1-nonanesulfonate	PFNS	68259-12-1	2.89	25-1000
Perfluoro-1-heptanesulfonate	PFHpS	375-92-8	3.37	25-1000
Perfluoro-1-pentanesulfonate	PFPeS	2706-91-4	1.97	25-1000
1H, 1H, 2H, 2H-perfluorohexane sulfonate	4:2 FTS	757124-72-4	3.13	25-1000
1H, 1H, 2H, 2H-perfluorooctane sulfonate	6:2 FTS	27619-97-2	3.48	25-1000
1H, 1H, 2H, 2H-perfluordecane sulfonate	8:2 FTS	39108-34-4	7.42	25-1000
N-methylperfluoro-1-octanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9	4.22	25-1000
N-ethylperfluoro-1-octanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6	7.34	25-1000
Perfluoro-1-octanesulfonamide	FOSA	754-91-6	4.54	25-1000
Surrogates				
1H, 1H, 2H, 2H-perfluoro-(1,2-$^{13}C_2$)hexane sulfonate	M 4:2 FTS	NA	NA	NA
1H, 1H, 2H, 2H-perfluoro-1(1,2-$^{13}C_2$)octane sulfonate	M 6:2 FTS	NA	NA	NA
1H, 1H, 2H, 2H-perfluoro-1(1,2-$^{13}C_2$)decane sulfonate	M 8:2 FTS	NA	NA	NA
N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid	M N-MeFOSAA	NA	NA	NA
N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid	M N-EtFOSAA	NA	NA	NA

TABLE X1.2 Analyte MRM Transitions, Cone and Collision Energies, Retention Times, and Ion Ratios

Analyte	Primary/Confirmatory	MRM Transition	Cone (V)	Collision Energy (eV)	Retention Time (min)	Primary/Confirmatory SRM Area Ratio
PFDS	Primary	598.9→79.9	15	45	9.8	1.2
	Confirmatory	598.9→98.9	15	45		
PFNS	Primary	548.9→79.9	15	42	9.2	1.2
	Confirmatory	548.9→98.9	15	42		
PFHpS	Primary	448.9→79.9	15	38	7.9	1.3
	Confirmatory	448.9→98.9	15	36		
PFPeS	Primary	348.9→79.9	15	34	6.4	1.4
	Confirmatory	348.9→98.9	15	30		
4:2 FTS	Primary	327→307	10	20	5.2	3.5
	Confirmatory	327→80.9	10	24		
6:2 FTS	Primary	427→406.9	10	22	6.7	4.3
	Confirmatory	427→80.9	10	30		
8:2 FTS	Primary	526.9→506.9	10	26	8	4.5
	Confirmatory	526.9→80.9	10	34		
N-MeFOSAA	Primary	569.9→419	15	20	8.4	1.8
	Confirmatory	569.9→482.9	15	16		
N-EtFOSAA	Primary	583.9→419	15	20	8.7	1.7
	Confirmatory	583.9→482.9	15	16		
FOSA	Primary	497.9→77.9	15	28	9.8	NA
M 4:2 FTS	Primary	329→309	20	10	5.2	NA
M 6:2 FTS	Primary	429→408.9	10	22	6.7	NA
M 8:2 FTS	Primary	528.9→508.9	10	26	8	NA
M N-MeFOSAA	Primary	572.9→419	15	20	8.4	NA
M N-EtFOSAA	Primary	588.9→419	15	20	8.7	NA

TABLE X1.3 Precision and Accuracy Data in Ottawa Sand

Analyte	Spike Amount (ng/Kg)	Average Recovery (%)	Standard Deviation (%)	# of Replicates (n)
PFDS	400	94.2	3.3	6
PFNS	400	93.4	1.6	6
PFHpS	400	91.7	3.1	6
PFPeS	400	89.7	1.7	6
FOSA	400	99.4	2.1	6
4:2 FTS	400	91.9	1.8	6
6:2 FTS	400	92.9	2.8	6
8:2 FTS	400	99.6	4.1	6
N-EtFOSAA	400	96.3	5.3	6
N-MeFOSAA	400	90.7	3.1	6
M 4:2 FTS	400	91.8	4.8	8
M 6:2 FTS	400	95.1	5.8	8
M 8:2 FTS	400	97.9	7.2	8
M N-EtFOSAA	400	99.8	3.9	8
M N-MeFOSAA	400	91.7	4.6	8

easier determinations to be made by the analyst by comparing the two transitions. If there are parts of the isomeric mixture in the sample that do not match the retention times of the standard, they should not be included in the integration and this should be explained in the narrative accompanying the data.

X1.2.2 The confirmatory ion ratios in "weathered samples" may not match the ion ratios in the calibration standards for the target analytes that may contain isomeric mixtures. Figs. X1.1-X1.4 are examples of this for PFHxS and PFOS; these differences in isomer mixtures may be observed with analytes that have the possibility of containing isomeric mixtures. These differences for PFHxS and PFOS were found in actual samples and may either be the cause of different compositions used, weathering or degradation or the affinity of the branched isomers to certain matrices. If the ion ratios do not match the ion ratio criteria, document in the case narrative and the affected data should be qualified and explained in the narrative accompanying the data.

TABLE X1.4 Precision and Accuracy Study for PFCs in Frederick Sand, ASTM SP-1

Frederick Sand ASTM SP-1 Measured ng/Kg from 400 ng/Kg spike for all PFCAs except 2000 ng/Kg (PFBA and PFPeA)											
Sample	PFTreA	PFTriA	PFDoA	PFUnA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA
Unspiked 1	<RL	<RL	<RL	<RL	<RL	<RL	65.35	<RL	28.6	<RL	<RL
Unspiked 2	<RL	<RL	<RL	<RL	<RL	<RL	73.4	<RL	35.8	<RL	<RL
Spiked 1	383.25	376	358.3	348.25	366.45	361.85	329.9	357.25	342.35	1759.3	1558.45
Spiked 2	378.45	365.3	350.4	349.15	353.4	351.55	334.7	357.75	334.4	1740.5	1530.7
Spiked 3	365.4	359.15	342.65	347.9	350.3	351.55	337.35	348.65	322	1749.05	1507.55
Spiked 4	374.55	357.4	352.55	341.1	355.45	350	333.65	361.1	338.05	1735.25	1496.9
Spiked 5	354.05	352.3	336.15	339.2	345.7	344.85	326.3	354.15	330.9	1682.4	1469
Spiked 6	336.15	338.7	333.85	333.05	349.25	340.35	321.95	350.4	325.6	1655.2	1456.6
Average Recovery (ng/Kg)	365.31	358.14	345.65	343.11	353.43	350.03	330.64	354.88	332.22	1720.28	1503.20
% Average Recovery	91.33	89.54	86.41	85.78	88.36	87.51	82.66	88.72	83.05	86.01	75.16
Standard Deviation	17.65	12.52	9.68	6.42	7.22	7.28	5.75	4.73	7.63	41.60	37.97
RSD (%)	4.83	3.50	2.80	1.87	2.04	2.08	1.74	1.33	2.30	2.42	2.53

TABLE X1.5 Precision and Accuracy Study for PFCs in Frederick Sand, ASTM SP-1

Frederick Sand ASTM SP-1 Measured ng/Kg from 400 ng/Kg spike													
Sample	PFBS	PFHxS	PFOS	PFDS	PFNS	PFHpS	PFPeS	FOSA	4:2 FTS	6:2 FTS	8:2 FTS	N-EtFOSAA	N-MeFOSAA
Unspiked 1	29.55	26.6	624.9	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Unspiked 2	18.35	35.25	825.7	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Spiked 1	343.65	360.6	317.25	378.35	383.25	380.65	362.1	406.45	348.1	363.65	368.85	388.8	368.3
Spiked 2	332.35	342.8	214.75	352.9	362.6	361.55	345.3	391.95	351.8	356.25	363.6	370.25	361.55
Spiked 3	339.2	355.25	298.55	359.65	354.5	360.8	353.6	387.2	351.9	350.4	372.85	365.45	364.9
Spiked 4	345	347.15	270.35	375.25	359.95	363.2	363.55	398.75	355.25	360.7	395.75	353.05	368.7
Spiked 5	339.65	338.45	213.35	370	380.25	376.15	365.15	400.6	368.75	375.8	386.4	350.45	380.4
Spiked 6	330.35	349.95	299.25	359.85	349.7	359.2	361.9	378.25	343.65	351.15	380.6	347.85	355.25
Average Recovery (ng/Kg)	338.37	349.03	268.92	366.00	365.04	366.93	358.60	393.87	353.24	359.66	378.01	362.64	366.52
% Average Recovery	84.59	87.26	67.23	91.50	91.26	91.73	89.65	98.47	88.31	89.91	94.50	90.66	91.63
Standard Deviation	5.91	8.10	45.07	10.04	13.72	9.09	7.65	10.19	8.57	9.46	11.92	15.55	8.43
RSD (%)	1.75	2.32	16.76	2.74	3.76	2.48	2.13	2.59	2.42	2.63	3.15	4.29	2.30

TABLE X1.6 Precision and Accuracy Study for PFCs in Frederick Sand, ASTM SP-1

Surrogates – (Frederick Sand ASTM SP-1, 400 ng/Kg spike)														
Sample	MPFBA	MPFHxA	MPFHxS	MPFOA	MPFNA	MPFOS	MPFDA	MPFUnA	MPFDoA	M 4:2 FTS	M 6:2 FTS	M 8:2 FTS	M N-EtFOSAA	M N-MeFOSAA
Unspiked 1	315.5	360.85	372.4	349.3	351.2	358.7	347	348.9	358.9	354.55	368.5	353.15	384	357.55
Unspiked 2	322.35	352	364.95	355.2	349.95	367.9	338.85	340.95	346.6	350.75	353.15	368.95	375.8	359.3
Spiked 1	300.8	347	374.05	354.45	346.1	379.2	341.4	346.55	356.8	365.95	383.95	389.05	384.1	352.75
Spiked 2	298.6	349.05	365.55	346.5	336.3	353.25	342.1	339.2	344.35	357.15	362.45	385.65	383.3	354.9
Spiked 3	290.5	334.4	357.6	340.4	331.4	359.4	331.3	328.35	334.95	355.55	350.1	376.75	379.5	345.35
Spiked 4	292	336.85	357.65	342.35	336.95	359.85	338.35	335.3	335.3	365.1	369.45	388.2	373.6	363.5
Spiked 5	278.9	334.75	346.6	333.9	324.7	349.15	327.7	321.3	326.75	350.25	369.8	350.2	357.35	342.65
Spiked 6	280.1	317	325.2	327.35	315.95	355.5	317.65	312.6	318	345.2	353.6	364.3	353.2	339.35
Average Recovery (ng/Kg)	297.34	341.49	358.00	343.68	336.57	360.37	335.54	334.14	340.21	355.56	363.88	372.03	373.86	351.92
% Avg. Recovery	74.34	85.37	89.50	85.92	84.14	90.09	83.89	83.54	85.05	88.89	90.97	93.01	93.46	87.98
Standard Deviation	15.50	13.57	15.93	9.73	12.40	9.38	9.46	12.58	14.19	7.18	11.36	15.40	12.14	8.59
RSD (%)	5.21	3.97	4.45	2.83	3.69	2.60	2.82	3.76	4.17	2.02	3.12	4.14	3.25	2.44

TABLE X1.7 Precision and Accuracy Study for PFCs in Silt, ASTM ML-1

Silt ASTM ML-1 Measured ng/Kg from 400 ng/Kg spike for all PFCAs except 2000 ng/Kg (PFBA and PFPeA)											
Sample	PFTreA	PFTriA	PFDoA	PFUnA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA
Unspiked 1	<RL	<RL	<RL	<RL	<RL	<RL	123.4	<RL	103.2	<RL	<RL
Unspiked 2	<RL	<RL	<RL	<RL	<RL	<RL	125.9	<RL	102.45	<RL	<RL
Spiked 1	406.35	397.4	384.4	353.95	381.6	376.7	388.25	388.55	383.35	1748.15	1667.4
Spiked 2	407.35	393.25	378	354.65	378.9	367.25	381.3	383.85	371.1	1756.1	1698.7
Spiked 3	406.65	397.95	381.85	356	373.25	369.45	363.4	380.1	358.25	1703.1	1657.95
Spiked 4	407.95	393.4	375.7	354.15	377.4	362.7	369.2	375.65	357.95	1656.55	1666.9
Spiked 5	398.15	390.85	371.55	348.55	369.15	358.65	377	375.3	374.7	1695.7	1587.45
Spiked 6	396.55	387.8	364.7	348.3	378.8	378.15	395.7	392.15	377.9	1742.15	1646.5
Average Recovery (ng/Kg)	403.83	393.44	376.03	352.60	376.52	368.82	379.14	382.60	370.54	1716.96	1654.15
% Average Recovery	100.96	98.36	94.01	88.15	94.13	92.20	94.79	95.65	92.64	85.85	82.71
Standard Deviation	5.08	3.86	7.16	3.31	4.53	7.65	11.94	6.87	10.44	38.56	37.00
RSD (%)	1.26	0.98	1.90	0.94	1.20	2.08	3.15	1.80	2.82	2.25	2.24

TABLE X1.8 Precision and Accuracy Study for PFCs in Silt, ASTM ML-1

Silt ASTM ML-1 Measured ng/Kg from 400 ng/Kg spike													
Sample	PFBS	PFHxS	PFOS	PFDS	PFNS	PFHpS	PFPeS	FOSA	4:2 FTS	6:2 FTS	8:2 FTS	N-EtFOSAA	N-MeFOSAA
Unspiked 1	27.75	96.2	201.35	<RL	<RL	<RL	<RL	125.15	<RL	<RL	<RL	101.25	<RL
Unspiked 2	24.55	98.05	202.2	<RL	<RL	<RL	<RL	123.5	<RL	<RL	<RL	99.6	<RL
Spiked 1	365.5	386.45	386.15	379.65	382.9	367.55	361.9	372.55	386.5	384.05	392.5	379.65	386.6
Spiked 2	369.2	381.8	381	373.4	378.4	382.4	366.95	379.7	377.7	379.15	380.35	383.75	379
Spiked 3	367.4	365.1	362.8	385.6	370.8	369.1	361.6	363.25	387	386.95	390.85	372.1	373.2
Spiked 4	369.15	360.95	404.4	391.9	379.9	389.25	369.35	368.2	386.1	384.85	400.95	385.65	390.3
Spiked 5	424.05	369.9	416.8	383.35	375.7	369.8	360.6	374.5	371.85	383.5	399.45	390.55	384.15
Spiked 6	407.55	389.25	402.25	376.3	358.75	367.15	378.25	340.8	385.9	382.55	387.25	350.8	377.35
Average Recovery (ng/Kg)	383.81	375.58	392.23	381.70	374.41	374.21	366.44	366.50	382.51	383.51	391.89	377.08	381.77
% Avg. Recovery	95.95	93.89	98.06	95.43	93.60	93.55	91.61	91.63	95.63	95.88	97.97	94.27	95.44
Standard Deviation	25.36	11.83	19.40	6.70	8.70	9.31	6.73	13.78	6.28	2.60	7.69	14.29	6.36
RSD (%)	6.61	3.15	4.95	1.75	2.32	2.49	1.84	3.76	1.64	0.68	1.96	3.79	1.67

TABLE X1.9 Precision and Accuracy Study for PFCs in Silt, ASTM ML-1

Surrogates – (Silt ASTM ML-1, 400 ng/Kg spike)														
Sample	MPFBA	MPFHxA	MPFHxS	MPFOA	MPFNA	MPFOS	MPFDA	MPFUnA	MPFDoA	M 4:2 FTS	M 6:2 FTS	M 8:2 FTS	M N-EtFOSAA	M N-MeFOSAA
Unspiked 1	346.85	382.45	375.25	368.25	372.8	394.05	383	353.85	384.7	370.05	371.7	389.15	399.9	390.7
Unspiked 2	335.8	384.15	356.55	370.45	362.35	383.1	372	354.05	369.85	379.6	361.5	379.6	388.9	375.5
Spiked 1	347.75	391.85	385.45	385.4	386.85	400.8	384.9	371.3	384.55	407	394.9	419.9	393.4	393.2
Spiked 2	349.7	383.45	382.3	370.5	368.95	396.9	372.7	354.7	374.45	394.7	397.35	416.85	388.2	398.5
Spiked 3	343.65	392.85	383.7	370.35	378.35	391.9	367.45	363.6	387.1	398.5	377.35	413.3	408	385.05
Spiked 4	324	377.6	376.45	373.75	367.9	367	383.35	361.4	379.85	386.05	386.75	429.85	399.05	375.85
Spiked 5	327.05	362.75	368.55	366.45	370.25	391	359.65	349.7	367	378.45	387.4	430.15	389.65	373.1
Spiked 6	344.8	373.4	371.5	365.5	360.6	385.65	367.7	342.4	361.05	392.15	379.65	392.45	375.15	380.1
Average Recovery (ng/Kg)	339.95	381.06	374.97	371.33	371.01	388.80	373.84	356.38	376.07	388.31	382.08	408.91	392.78	384.00
% Avg. Recovery	84.99	95.27	93.74	92.83	92.75	97.20	93.46	89.09	94.02	97.08	95.52	102.23	98.20	96.00
Standard Deviation	9.85	9.85	9.52	6.25	8.50	10.48	9.11	8.90	9.50	12.07	12.00	19.32	9.85	9.36
RSD (%)	2.90	2.58	2.54	1.68	2.29	2.70	2.44	2.50	2.53	3.11	3.14	4.73	2.51	2.44

TABLE X1.10 Precision and Accuracy Study for PFCs in Lean Clay, ASTM CL-1

Lean Clay ASTM CL-1 Measured ng/Kg from 400 ng/Kg spike for all PFCAs except 2000 ng/Kg (PFBA and PFPeA)											
Sample	PFTreA	PFTriA	PFDoA	PFUnA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA
Unspiked 1	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	M I	<RL
Unspiked 2	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	M I	<RL
Spiked 1	304.4	343.15	339	341.9	337.1	331.65	346.95	333.7	341.05	M I	1695.7
Spiked 2	290.95	328.35	336.65	343.5	350.9	340.1	361.1	334.3	345.6	M I	1677.35
Spiked 3	300.6	327.4	337.15	343.6	346.4	335.65	359.05	328.7	351.2	M I	1666.2
Spiked 4	289.45	319.9	333.4	333.9	326.85	323.8	337.1	327.8	349.1	M I	1655.9
Spiked 5	265.05	364.7	331.5	333	329	330.7	344.55	331.8	348.75	M I	1555.3
Spiked 6	310.55	384.3	347.6	346.4	341.35	334.3	358	333.9	352.9	M I	1645.85
Average Recovery (ng/Kg)	293.50	344.63	337.55	340.38	338.60	332.70	351.13	331.70	348.10		1649.38
% Average Recovery	73.38	86.16	84.39	85.10	84.65	83.18	87.78	82.93	87.03		82.47
Standard Deviation	16.08	25.11	5.62	5.57	9.51	5.48	9.66	2.82	4.24		49.23
RSD (%)	5.48	7.29	1.66	1.64	2.81	1.65	2.75	0.85	1.22		2.98

TABLE X1.11 Precision and Accuracy Study for PFCs in Lean Clay, ASTM CL-1

Lean Clay ASTM CL-1 Measured ng/Kg from 400 ng/Kg spike													
Sample	PFBS	PFHxS	PFOS	PFDS	PFNS	PFHpS	PFPeS	FOSA	4:2 FTS	6:2 FTS	8:2 FTS	N-EtFOSAA	N-MeFOSAA
Unspiked 1	<RL	<RL	29.1	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	36.55	<RL
Unspiked 2	<RL	<RL	24.1	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	24	<RL
Spiked 1	336.5	342.75	332.85	336.55	346.75	361.7	347.85	243.7	383.35	383.2	384.25	313.9	298.6
Spiked 2	357.5	360.85	358.7	319.45	342.4	357.7	347.5	224.45	391.7	374.15	398.35	334.6	311.45
Spiked 3	359.55	361.85	348.85	311.15	340.25	355.4	341.6	227.9	363.6	376.05	369.1	286.8	275.35
Spiked 4	358.25	350.15	357.25	330.95	335.95	334.2	335.8	231	382.4	365.55	378.1	283.75	277.45
Spiked 5	353.9	346.95	350.15	332.5	347.75	357.15	362.05	233.55	393.85	398.65	545.45	238.85	230.4
Spiked 6	355.1	350.95	349.05	335.6	350.7	345.8	337.6	228.05	378.65	373.65	511.7	303.85	285.2
Average Recovery (ng/Kg)	353.47	352.25	349.48	327.70	343.97	351.99	345.40	231.44	382.26	378.54	431.16	293.63	279.74
% Avg. Recovery	88.37	88.06	87.37	81.93	85.99	88.00	86.35	57.86	95.56	94.64	107.79	73.41	69.94
Standard Deviation	8.57	7.62	9.20	10.16	5.44	10.20	9.54	6.75	10.82	11.35	76.80	32.68	27.75
RSD (%)	2.42	2.16	2.63	3.10	1.58	2.90	2.76	2.92	2.83	3.00	17.81	11.13	9.92

TABLE X1.12 Precision and Accuracy Study for PFCs in Lean Clay, ASTM CL-1

Surrogates – (Lean Clay ASTM CL-1, 400 ng/Kg spike)													
Sample	MPFBA	MPFHxA	MPFHxS	MPFOA	MPFNA	MPFOS	MPFDA	MPFUnA	MPFDoA	M 4:2 FTS	M 6:2 FTS	M 8:2 FTS	M N-EtFOSAA	M N-MeFOSAA
Unspiked 1	309.05	353.15	370.7	359.15	350.2	391.65	358.65	362.3	351.4	389.6	382.4	374.95	333.95	328.95
Unspiked 2	310.5	351.05	364.4	344.2	335.2	368.55	356	353.8	344.3	386.1	385.15	378.95	363.1	345.55
Spiked 1	305	348.6	352.8	339	341.6	351.2	337.4	350.15	338.9	387.9	387.95	382.2	316.95	296.75
Spiked 2	307.6	342.2	365.8	350.15	328.05	367.9	337.7	344	339.55	391.4	403	396.95	333.15	320.05
Spiked 3	302.25	337.2	352.3	338.4	332.65	355.2	339.4	328.9	331.45	378.75	364.4	376.1	310.85	290.1
Spiked 4	303.8	343.1	358.85	331.6	340.65	361.3	343.3	333.65	333.7	375.4	374.25	387.5	297.45	283.8
Spiked 5	300.8	346.4	358.3	339.75	335.75	365.05	338.7	338.7	336.95	397.6	399.1	554.7	265.45	230.15
Spiked 6	296.9	336.6	350.7	338.65	335.75	357.45	354.7	344.95	350.1	395.6	404.55	497.4	299	281.85
Average Recovery (ng/Kg)	304.49	344.79	359.23	342.61	337.48	364.79	345.73	344.56	340.79	387.79	387.60	418.59	314.99	297.15
% Avg. Recovery	76.12	86.20	89.81	85.65	84.37	91.20	86.43	86.14	85.20	96.95	96.90	104.65	78.75	74.29
Standard Deviation	4.53	6.10	7.22	8.53	6.68	12.47	9.12	10.89	7.26	7.67	14.17	68.43	29.38	35.52
RSD (%)	1.49	1.77	2.01	2.49	1.98	3.42	2.64	3.16	2.13	1.98	3.66	16.35	9.33	11.95

TABLE X1.13 Precision and Accuracy Study for PFCs in Fat Clay, ASTM CH-1

	Fat Clay ASTM CH-1 Measured ng/Kg from 400 ng/Kg spike for all PFCAs except 2000 ng/Kg (PFBA and PFPeA)										
Sample	PFTreA	PFTriA	PFDoA	PFUnA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA
Unspiked 1	<RL	<RL	<RL	<RL	<RL	<RL	83.6	<RL	70.2	<RL	<RL
Unspiked 2	<RL	<RL	<RL	<RL	<RL	<RL	81	<RL	73.5	<RL	<RL
Spiked 1	361.85	350.45	339.45	345	344.45	338.5	338.65	348.7	340.4	1634.5	1579.8
Spiked 2	369.75	370	350.45	353.4	359.1	349.4	359.75	379.15	354	1805.5	1736.4
Spiked 3	372.35	369.9	358.8	356.5	342.05	348.2	350.65	358.8	346.25	1734.65	1560.15
Spiked 4	367	374.15	353.65	343.2	354.2	349.6	347.9	365.95	368.55	1684.35	1639.4
Spiked 5	379.95	384.4	364.25	367.2	364.15	361.5	362.65	356.85	362.55	1786.8	1613.05
Spiked 6	371.1	361.15	349.7	341.7	348.6	338.95	352.15	352.75	350.15	1757.75	1638.6
Average Recovery (ng/Kg)	370.33	368.34	352.72	351.17	352.09	347.69	351.96	360.37	353.65	1733.93	1627.90
% Average Recovery	92.58	92.09	88.18	87.79	88.02	86.92	87.99	90.09	88.41	86.70	81.40
Standard Deviation	6.01	11.56	8.50	9.81	8.61	8.47	8.61	10.89	10.43	64.54	61.88
RSD (%)	1.62	3.14	2.41	2.79	2.44	2.44	2.45	3.02	2.95	3.72	3.80

TABLE X1.14 Surrogate Recoveries for Precision and Accuracy Study in Fat Clay, ASTM CH-1

	Fat Clay ASTM CH-1 Measured ng/Kg from 400 ng/Kg spike												
Sample	PFBS	PFHxS	PFOS	PFDS	PFNS	PFHpS	PFPeS	FOSA	4:2 FTS	6:2 FTS	8:2 FTS	N-EtFOSAA	N-MeFOSAA
Unspiked 1	<RL	54.25	146.05	<RL	<RL	<RL	<RL	68.6	<RL	<RL	<RL	<RL	<RL
Unspiked 2	<RL	56.75	141.6	<RL	<RL	<RL	<RL	64.55	<RL	<RL	<RL	<RL	<RL
Spiked 1	360.15	342.9	348.5	365.05	365.45	358.2	351.15	327.4	374.25	371	371.25	370	348
Spiked 2	373.65	366.9	369.95	368.7	361.15	361.35	358.35	339.85	393.2	376.6	381.65	374.55	352.5
Spiked 3	362.55	357.75	361.7	367.05	368.1	367.9	352.55	346.55	380.2	372.55	359.3	390.4	343.3
Spiked 4	367.25	365.5	380.7	370.1	366.45	357.7	349.95	346.35	390.05	377.9	383.65	382.05	344.85
Spiked 5	382.25	364.7	387.35	374.25	375.7	376	369.5	370.65	396.35	391.9	396.2	378.75	357.85
Spiked 6	369.35	361.85	367.55	365.35	361.7	364.85	344.6	342.85	377.9	382.65	363.5	387.55	341.7
Average Recovery (ng/Kg)	369.20	359.93	369.29	368.42	366.43	364.33	354.35	345.61	385.33	378.77	375.93	380.55	348.03
% Avg. Recovery	92.30	89.98	92.32	92.10	91.61	91.08	88.59	86.40	96.33	94.69	93.98	95.14	87.01
Standard Deviation	8.00	8.95	13.78	3.45	5.29	6.92	8.64	14.15	9.05	7.64	13.83	7.73	6.15
RSD (%)	2.17	2.49	3.73	0.94	1.44	1.90	2.44	4.09	2.35	2.02	3.68	2.03	1.77

TABLE X1.15 Surrogate Recoveries for Precision and Accuracy Study in Fat Clay, ASTM CH-1

	Surrogates – (Fat Clay ASTM CH -1, 400 ng/Kg spike)												
Sample	MPFBA	MPFHxA	MPFHxS	MPFOA	MPFNA	MPFOS	MPFDA	MPFUnA	MPFDoA	M 4:2 FTS	M 6:2 FTS	M 8:2 FTS	M N-EtFOSAA	M N-MeFOSAA
Unspiked 1	332.9	353.7	363.35	336.8	345.9	361.95	354.8	352.85	351.9	354.15	339.95	372.2	370.15	354.7
Unspiked 2	342.1	358.45	362.2	348	347.9	379.45	354.25	358.4	352.5	382.55	366.7	375.85	363.55	356.95
Spiked 1	323.35	344	352.8	345.25	329.4	370.6	347.2	344.55	344.8	380.95	361.1	375.15	351.7	343
Spiked 2	347.05	357.35	360.1	357.75	355.7	372.9	355.9	354	357.4	406.5	374.85	380	372.5	367.85
Spiked 3	322.9	355.8	364.95	347.45	356.6	371.4	355.1	359.25	354.25	386.45	380.85	401.5	370.5	357.3
Spiked 4	335.1	358.65	368.45	346.7	351.65	369.9	358.75	351.35	359	395.7	375.65	374.45	359.2	354.45
Spiked 5	343.75	359.35	371.5	364.55	350.95	379.65	364.6	364.3	359.25	398.95	397.75	402.7	377.75	365.1
Spiked 6	325.3	349.7	356.75	336.65	344.85	351.65	339.95	350.45	349.6	385.2	369.2	381.1	355.3	344.9
Average Recovery (ng/Kg)	334.06	354.63	362.51	347.89	347.87	369.69	353.82	354.39	353.59	386.31	370.76	382.87	365.08	355.53
% Avg. Recovery	83.51	88.66	90.63	86.97	86.97	92.42	88.45	88.60	88.40	96.58	92.69	95.72	91.27	88.88
Standard Deviation	9.60	5.34	6.05	9.51	8.58	9.21	7.40	6.12	4.98	15.74	16.61	12.22	9.12	8.62
RSD (%)	2.88	1.51	1.67	2.73	2.47	2.49	2.09	1.73	1.41	4.07	4.48	3.19	2.50	2.43

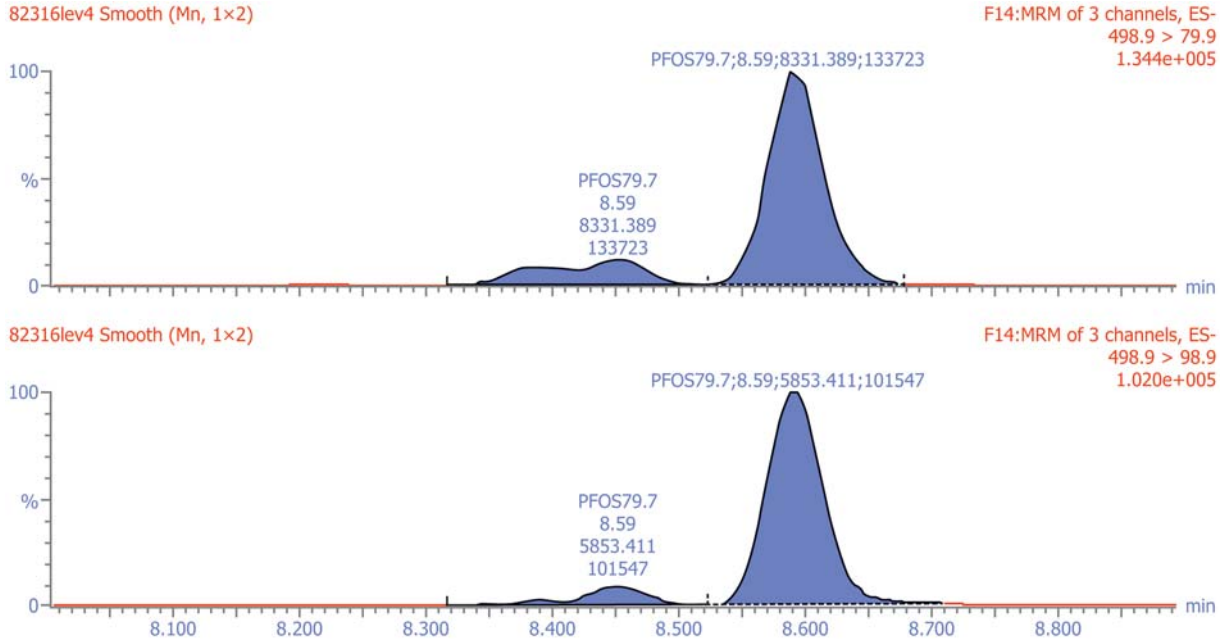
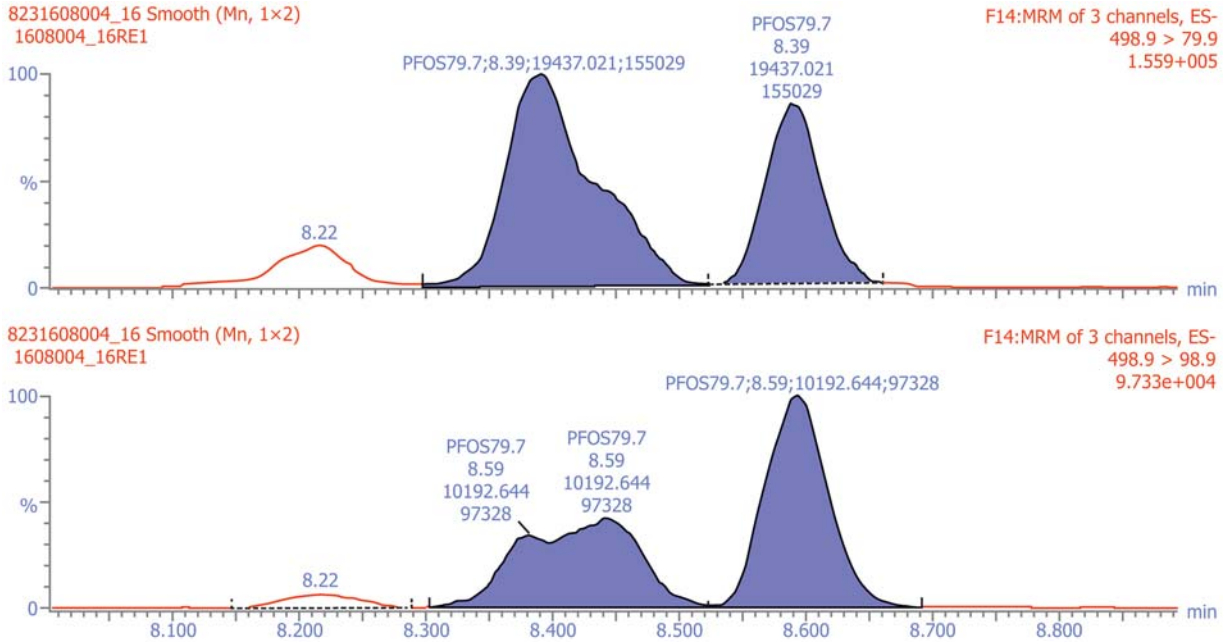


FIG. X1.1 PFOS in Calibration Standard



NOTE 1—The peak at 8.22 min is probably another isomer group of PFOS, but it is not included in the calibration standard so it can't be included here for quantitation.

FIG. X1.2 PFOS in Actual Sample

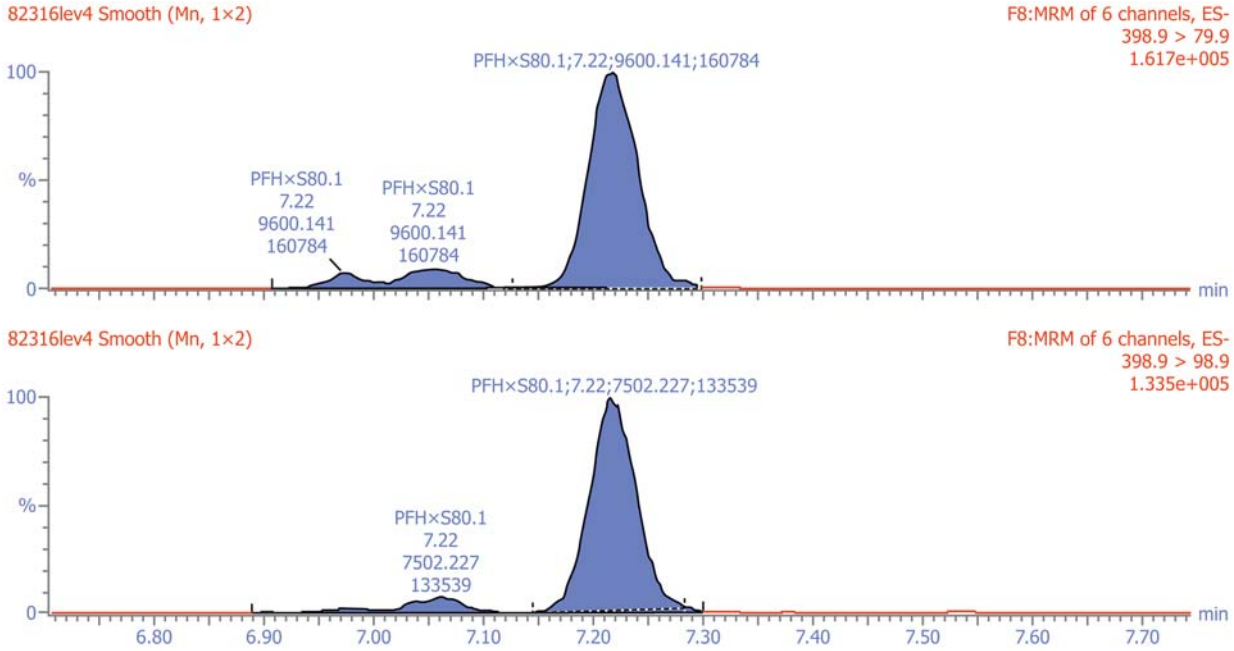


FIG. X1.3 PFHxS in Calibration Standard

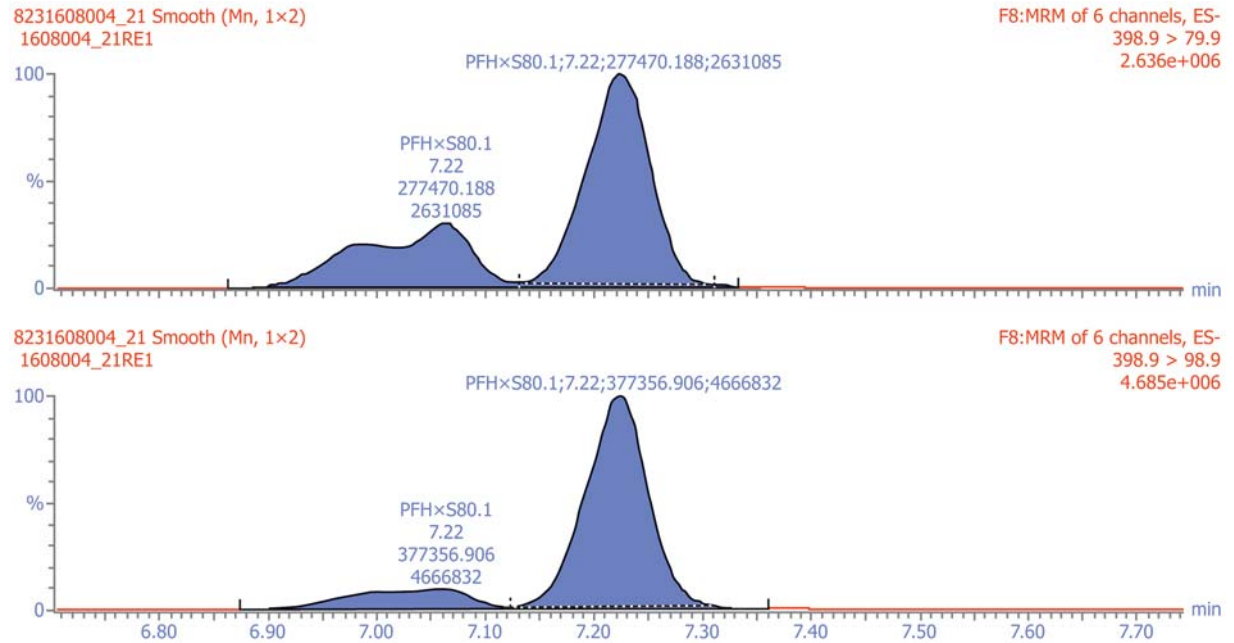


FIG. X1.4 PFHxS in Actual Sample