Designation: D7968 – 14

Standard Test Method for Determination of Perfluorinated 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 perfluorinated 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 perfluorinated 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.*

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

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

[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.

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 *perfluorinated 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

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

[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

3.2.56 *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 perfluorinated 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 days 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 US 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, surface and drinking waters. Hence, there is a need for 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 perfluorinated 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 minutes. 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 perfluorinated 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 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] 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

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. A 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.

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.

[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.

[11] A Waters Xevo TQ-S triple quadrupole mass spectrometer, 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

7.3 *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:*

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.

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

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 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

[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 Formulators, 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.