



Designation: D7968 – 17a

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 polyfluoroalkyl 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 Limit³ and Reporting Range⁴ 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, health and environmental 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
- [D1193 Specification for Reagent Water](#)
 - [D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)
 - [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- μ L 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

^AAbbreviations 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 *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*—Decafluoro-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*—¹⁸O₂-Perfluorohexylsulfonate
- 3.2.39 *MPFOS*—¹³C₄-Perfluorooctylsulfonate
- 3.2.40 *MPFCA*—Isotopically labeled Perfluoroalkylcarboxylates
- 3.2.41 *MPFBA*—¹³C₄-Perfluorobutanoate
- 3.2.42 *MPFHxA*—¹³C₂-Perfluorohexanoate
- 3.2.43 *MPFOA*—¹³C₄-Perfluorooctanoate
- 3.2.44 *MPFNA*—¹³C₅-Perfluorononanoate
- 3.2.45 *MPFDA*—¹³C₂-Perfluorodecanoate
- 3.2.46 *MPFUnA*—¹³C₂-Perfluoroundecanoate
- 3.2.47 *MPFDoA*—¹³C₂-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 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 quantifiable, 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 acetone-trile.

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

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