



Designation: D7979 – 17

Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)¹

This standard is issued under the fixed designation D7979; 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 per- and polyfluoroalkyl substances (PFASs) in a water matrix using 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 a technique known as selected reaction monitoring (SRM) or sometimes referred to as multiple reaction monitoring (MRM). This is not a drinking water method, performance of this test method has not been evaluated on drinking water matrices.

1.2 The Method Detection Limit (MDL)² and Reporting Range³ for the target analytes are listed in [Table 1](#). The target concentration for the reporting limit for this test method was 10 ng/L for most of the target analytes at the time of development.

1.2.1 The reporting limit in this test method is the minimum value below which data are documented as non-detects. The reporting limit may be lowered providing your lab meets the minimum performance requirements of this test method at the lower concentrations, this method is performance based and modifications are allowed to improve performance. 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 the concentration of the Level 1 calibration standard as shown in [Table 4](#) for the PFASs after taking into account the 50 % dilution with methanol. It is above the Level 1 calibration concentration for 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.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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:*⁴

- [D1129 Terminology Relating to Water](#)
- [D1193 Specification for Reagent Water](#)
- [D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)
- [D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water](#)
- [D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents](#)
- [D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents](#)
- [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 D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

Current edition approved July 15, 2017. Published August 2017. Originally approved in 2015. Last previous edition approved in 2016 as D7979 – 16. DOI: 10.1520/D7979-17.

² The MDL is determined following the Code of Federal Regulations (CFR), 40 CFR Part 136, Appendix B utilizing dilution and filtration. 5 mL sample of water was utilized. A detailed process determining the MDL is explained in the reference and is beyond the scope of this test method to be explained here.

³ Reporting range concentration is calculated from [Table 4](#) concentrations assuming a 30 μ L injection of the Level 1 calibration standard for PFASs, and the highest level calibration standard with a 10 mL final extract volume of a 5 mL water sample. Volume variations will change the reporting limit and ranges.

⁴ 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

| Analyte ^A | MDL (ng/L) | Reporting Ranges (ng/L) |
|----------------------|------------|-------------------------|
| PFTreA ^B | 1.2 | 10 – 400 |
| PFTriA ^B | 0.7 | 10 – 400 |
| PFDoA ^B | 1.2 | 10 – 400 |
| PFUnA ^B | 1.2 | 10 – 400 |
| PFDA ^B | 1.4 | 10 – 400 |
| PFOS ^B | 2.2 | 10 – 400 |
| PFNA ^B | 1.1 | 10 – 400 |
| PFecHS ^B | 1.9 | 10 – 400 |
| PFOA ^B | 1.7 | 10 – 400 |
| PFHxS ^B | 1.2 | 10 – 400 |
| PFHpA ^B | 1.0 | 10 – 400 |
| PFHxA ^B | 2.0 | 10 – 400 |
| PFBS ^B | 0.8 | 10 – 400 |
| PFPeA ^B | 4.6 | 50 – 2000 |
| PFBA ^B | 4.6 | 50 – 2000 |
| FHEA | 92.9 | 300 – 8000 |
| FOEA | 106.8 | 300 – 8000 |
| FDEA | 47.2 | 200 – 8000 |
| FOUEA | 2.3 | 10 – 400 |
| FHpPA | 3.3 | 10 – 400 |
| FHUEA | 1.5 | 10 – 400 |

^A Acronyms are defined in 3.3.

^B New MDL study was reported in August 2016, which resulted in a reporting limit and range update.

2.2 Other Standards:⁵

EPA Publication SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods
Code of Federal Regulations 40 CFR Part 136, Appendix B

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *per- and polyfluoroalkyl substances*, *n*—in this test method, 11 perfluoroalkyl carboxylic acids, 3 perfluoroalkylsulfonates, Decafluoro-4-(pentafluoroethyl)cyclohexanesulfonate and 6 fluorotelomer acids listed in Table 1 collectively (not including any mass labeled surrogates).

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

3.3 Acronyms:

3.3.1 *CCC*, *n*—Continuing Calibration Check

3.3.2 *FTAs and FTUAs*, *n*—Fluorotelomer and Unsaturated Fluorotelomer Acids

3.3.2.1 *FDEA*, *n*—2-perfluorodecyl ethanoic acid

3.3.2.2 *FHEA*, *n*—2-perfluorohexyl ethanoic acid

3.3.2.3 *FHpPA*, *n*—3-perfluoroheptyl propanoic acid

3.3.2.4 *FHUEA*, *n*—2H-perfluoro-2-octenoic acid

3.3.2.5 *FOEA*, *n*—2-perfluorooctyl ethanoic acid

3.3.2.6 *FOUEA*, *n*—2H-perfluoro-2-decenoic acid

3.3.3 *IC*, *n*—Initial Calibration

3.3.4 *LC*, *n*—Liquid Chromatography

3.3.5 *LCS/LCSD*, *n*—Laboratory Control Sample/Laboratory Control Sample Duplicate

3.3.6 *MDL*, *n*—Method Detection Limit

3.3.7 *MeOH*, *n*—Methanol

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

3.3.9 *MPFAC*, *n*—Isotopically labeled Perfluoroalkylcarboxylates

3.3.9.1 *MPFBA*, *n*—¹³C₄-Perfluorobutanoate

3.3.9.2 *MPFDA*, *n*—¹³C₂-Perfluorodecanoate

3.3.9.3 *MPFDoA*, *n*—¹³C₂-Perfluorododecanoate

3.3.9.4 *MPFHxA*, *n*—¹³C₂-Perfluorohexanoate

3.3.9.5 *MPFNA*, *n*—¹³C₅-Perfluorononanoate

3.3.9.6 *MPFOA*, *n*—¹³C₄-Perfluorooctanoate

3.3.9.7 *MPFUnA*, *n*—¹³C₂-Perfluoroundecanoate

3.3.10 *MPFAIS*, *n*—Isotopically labeled Perfluoroalkylsulfonates

3.3.10.1 *MPFHxS*, *n*—¹⁸O₂-Perfluorohexylsulfonate

3.3.10.2 *MPFOS*, *n*—¹³C₄-Perfluorooctylsulfonate

3.3.11 *MRM*, *n*—Multiple Reaction Monitoring

3.3.12 *MS/MSD*, *n*—Matrix Spike/Matrix Spike Duplicate

3.3.13 *NA*, *adj*—Not Available

3.3.14 *ND*, *n*—non-detect

3.3.15 *P&A*, *n*—Precision and Accuracy

3.3.16 *PFAC*, *n*—Perfluoroalkyl Carboxylic Acid

3.3.16.1 *PFBA*, *n*—Perfluorobutanoate

3.3.16.2 *PFDA*, *n*—Perfluorodecanoate

3.3.16.3 *PFDoA*, *n*—Perfluorododecanoate

3.3.16.4 *PFHpA*, *n*—Perfluoroheptanoate

3.3.16.5 *PFHxA*, *n*—Perfluorohexanoate

3.3.16.6 *PFNA*, *n*—Perfluorononanoate

3.3.16.7 *PFOA*, *n*—Perfluorooctanoate

3.3.16.8 *PFPeA*, *n*—Perfluoropentanoate

3.3.16.9 *PFTreA*, *n*—Perfluorotetradecanoate

3.3.16.10 *PFTriA*, *n*—Perfluorotridecanoate

3.3.16.11 *PFUnA*, *n*—Perfluoroundecanoate

3.3.17 *PFAIS*, *n*—Perfluoroalkylsulfonate

3.3.17.1 *PFBS*, *n*—Perfluorobutylsulfonate

3.3.17.2 *PFecHS*, *n*—Decafluoro-4-(pentafluoroethyl) cyclohexanesulfonate

3.3.17.3 *PFHxS*, *n*—Perfluorohexylsulfonate

3.3.17.4 *PFOS*, *n*—Perfluorooctylsulfonate

3.3.18 *PFASs*, *n*—Per- and Polyfluoroalkyl Substances

3.3.19 *ppt*, *n*—parts per trillion, ng/L

3.3.20 *QA*, *adj*—Quality-Assurance

3.3.21 *QC*, *adj*—Quality-Control

⁵ Available from National Technical Information Service (NTIS), U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA, 22161 or at <http://www.epa.gov/epawaste/hazard/testmethods/index.htm>

- 3.3.22 *RL, n*—Reporting Limit
- 3.3.23 *RLCS, n*—Reporting Limit Check Sample
- 3.3.24 *RSD, n*—Relative Standard Deviation
- 3.3.25 *RT, n*—Retention Time
- 3.3.26 *SRM, n*—Selected Reaction Monitoring
- 3.3.27 *SS, n*—Surrogate Standard
- 3.3.28 *TC, n*—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 PFASs in water; 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 PFASs analysis, samples are shipped to the lab at a temperature between 0°C and 6°C and analyzed within 28 days of collection. A sample (5 mL) is collected in a polypropylene tube in the field and that total sample is processed in order to limit target analyte loss due to sample manipulation and losses to surfaces, spiked with surrogates (all samples) and target PFASs (laboratory control and matrix spike samples) and hand shaken for 2 minutes after adding 5 mL of methanol. The samples are then filtered through a polypropylene filter unit. Acetic acid (~10 µL) is added to all the samples to adjust to pH ~3 and analyzed by LC/MS/MS. For 5 mL sludge samples; 5 mL methanol is added, adjusted to pH ~9 (adding ~20 µL of ammonium hydroxide), hand shaken, filtered, acidified to pH ~3 (~50 µL acetic acid) and then analyzed by LC/MS/MS.

NOTE 1—Sludge in this method is defined as sewage sample containing between 0.1 and 2% solids based upon a sample by weight.

NOTE 2—Since surface binding of target compounds may bias data, it is best to collect a 5.0 mL sample in a graduated 15 mL polypropylene BD Falcon tube in the field so that the whole sample is processed in the lab (NO ALIQUOTING). Once this 5.0 mL sample is spiked according to this Standard and methanol is added, it is then thoroughly shaken and transferred to a new 15 mL polypropylene tube during filtration. In order to have accurate volumes, the weight of the 15 mL polypropylene BD Falcon tube may be taken before and after sampling in order to obtain an exact volume. The density of water is assumed to be 1.0 g/mL unless the exact density of the water sample is known, then that conversion should be used.

4.3 Most of the PFASs are identified by comparing the SRM transition and its confirmatory SRM transition if correlated to the known standard SRM transition (Table 3) and quantitated utilizing an external calibration. The surrogates and some PFASs (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 PFASs 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 PFASs, if detected, or as a non-detect at the RL, if not detected, in ng/L and the surrogate recoveries.

5. Significance and Use

5.1 PFASs are widely used in various industrial and commercial products; they are persistent, bio-accumulative, and ubiquitous in the environment. PFASs 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.⁶ PFASs 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 water matrices for understanding of the sources and pathways of exposure.

5.2 This method has been investigated for use with reagent, surface, sludge and wastewaters for selected PFASs. This method has not been evaluated on drinking water matrices.

6. Interferences

6.1 All glassware is washed in hot water (typically > 45°C) with detergent and rinsed in hot water followed by distilled water. The glassware is then dried and heated in an oven (typically at 105°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 PFASs containing caps shall 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 of the sample matrices.

6.4 Contaminants have been found in reagents, glassware, tubing, glass disposable pipettes, filters, degassers and other apparatus that release PFASs. 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 PFASs 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 PFASs in the sample from the PFASs in the LC system.

7. Apparatus

7.1 *LC/MS/MS System:*

7.1.1 *Liquid Chromatography System*⁷—A complete LC system is required in order to analyze samples, this should include a sample injection system, a solvent pumping system

⁶ A Draft Toxicological Profile for Perfluoroalkyls can be found at: <http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=1117&tid=237> (2014).

⁷ A Waters Acquity UPLC H-Class System, or equivalent, has been found suitable for use.