Designation: D7979 – 16

Standard Test Method for Determination of Perfluorinated Compounds 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 perfluorinated compounds (PFCs) 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 multiple reaction monitoring (MRM) mass spectrometry.

1.2 The Method Detection Limit (MDL)[2] and Reporting Range[3] for the target analytes are listed in Table 1.

1.2.1 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 the concentration of the Level 1 calibration standard as shown in Table 4 for the perfluorinated compounds after taking into account the 50 % dilution with methanol. It is above the Level 1 calibration concentration for PFOS, PFBS, 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 *Units*—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 and health practices and determine the applicability of regulatory limitations prior to use.*

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

2.2 *Other Standards:*[5]

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

[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.

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[2] The MDL is determined following the Code of Federal Regulations, 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 µL injection of the Level 1 calibration standard for PFCs, 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.

[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

TABLE 1 Method Detection Limit and Reporting Range

Analyte[A]	MDL (ng/L)	Reporting Ranges (ng/L)
PFTreA	1.74	10 – 400
PFTriA	2.65	10 – 400
PFDoA	2.42	10 – 400
PFUnA	1.08	10 – 400
PFDA	3.03	10 – 400
PFOS	4.19	15 – 400
PFNA	1.76	10 – 400
PFecHS	1.93	10 – 400
PFOA	3.04	10 – 400
PFHxS	2.51	10 – 400
PFHpA	2.32	10 – 400
PFHxA	1.31	10 – 400
PFBS	7.60	30 – 400
PFPeA	11.59	50 – 2000
PFBA	13.85	50 – 2000
FHEA	92.93	300 – 8000
FOEA	106.75	300 – 8000
FDEA	47.17	200 – 8000
FOUEA	2.31	10 – 400
FHpPA	3.25	10 – 400
FHUEA	1.53	10 – 400

[A] Acronyms are defined in 3.3.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *perfluorinated compounds, 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 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 *MRM, n*—Multiple Reaction Monitoring

3.3.10 *MPFAS, n*—Isotopically labeled Perfluoroalkylsulfonates

3.3.10.1 *MPFHxS, n*—$^{18}O_2$-Perfluorohexylsulfonate

3.3.10.2 *MPFOS, n*—$^{13}C_4$-Perfluorooctylsulfonate

3.3.11 *MPFCA, n*—Isotopically labeled Perfluoroalkylcarboxylates

3.3.11.1 *MPFBA, n*—$^{13}C_4$-Perfluorobutanoate

3.3.11.2 *MPFDA, n*—$^{13}C_2$-Perfluorodecanoate

3.3.11.3 *MPFDoA, n*—$^{13}C_2$-Perfluorododecanoate

3.3.11.4 *MPFHxA, n*—$^{13}C_2$-Perfluorohexanoate

3.3.11.5 *MPFNA, n*—$^{13}C_5$-Perfluorononanoate

3.3.11.6 *MPFOA, n*—$^{13}C_4$-Perfluorooctanoate

3.3.11.7 *MPFUnA, n*—$^{13}C_2$-Perfluoroundecanoate

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 *PFAS, 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 *PFCs, n*—Perfluorinated Compounds

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

3.3.20 *QA, adj*—Quality-Assurance

3.3.21 *QC, adj*—Quality-Control

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*—Single 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 perfluorinated compounds 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 PFC 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 transferred to a polypropylene tube (or a 5 mL sample is collected in a polypropylene tube in the field to limit target analyte loss due to sample manipulation), spiked with surrogates (all samples) and target PFC compounds (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 approximately ≥0.2 % solids based upon a sample by weight.

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 transition (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/L 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.[6] 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 water matrices for understanding of the sources and pathways of exposure.

5.3 This method has been investigated for use with reagent, surface, sludge and wastewaters for selected perfluorinated compounds.

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 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 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:*

7.1.1 *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 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*[8]—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 needs to be monitored.

7.1.3 *Isolator Column*[9]—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.

[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.

[8] 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.

[9] 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.