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Designation: ~~D7979 – 15~~ D7979 – 15ε1

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.

ε[1] NOTE—Editorial corrections were made throughout in November 2015.

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~~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

iTeh Standards (https://standards.iteh.ai) Document Preview ASTM D7979-15e1 https://standards.iteh.ai/catalog/standards/sist/3bf14f22-c8ed-44d9-b89e-c2a062741363/astm-d7979-15e1

[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

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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~~

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.

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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 *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

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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 ~~Table 3)~~ 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] A Draft Toxicological Profile for Perfluoroalkyls can be found at: http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=1117&tid=237 (2014).

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.

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7.2 *Tandem Mass Spectrometer System*[10]—A MS/MS system capable of multiple reaction monitoring (MRM) analysis or any system that is capable of performing at the requirements in this test method shall be used.

7.3 *Filtration Device:*

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

7.3.2 A 10 mL Lock Tip Glass Syringe size is recommended since a 10 mL sample size is used in this test method.

7.3.3 *Filter Unit*[11]—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.[12] 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.

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[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~~ 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~~ 2.1 × 50 mm and 1.7 µm particle size column, or equivalent, has been found suitable for use.

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

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

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

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 *Polypropylene Tubes*—15 and 50 mL.

8.8 *pH Paper* (pH range 1–14).

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 *PFC Standards:*[13]

8.18.1 *Perfluorobutylsulfonate* (PFBS, CAS# 29420-49-3).
8.18.2 *Perfluorohexylsulfonate* (PFHxS, CAS# 3871-99-6).
8.18.3 *Perfluorooctylsulfonate* (PFOS, CAS # 1763-23-1).
8.18.4 *Perfluorobutanoate* (PFBA, CAS # ~~375-73-5).~~375-22-4).
8.18.5 *Perfluoropentanoate* (PFPeA, CAS# 2706-90-3).
8.18.6 *Perfluorohexanoate* (PFHxA, CAS#307-24-4).
8.18.7 *Perfluoroheptanoate* (PFHpA, CAS# 375-85-9).
8.18.8 *Perfluorooctanoate* (PFOA, CAS # 335-67-1).
8.18.9 *Perfluorononanoate* (PFNA, CAS# 375-95-1).
8.18.10 *Perfluorodecanoate* (PFDA, CAS# 335-76-2).
8.18.11 *Perfluoroundecanoate* (PFUnA, CAS# 2058-94-8).
8.18.12 *Perfluorododecanoate* (PFDoA, CAS# 307-55-1).
8.18.13 *Perfluorotridecanoate* (PFTriA, CAS# 72629-94-8).
8.18.14 *Perfluorotetradecanoate* (PFTreA, CAS# 376-06-7).
8.18.15 *Decafluoro-4-(pentafluoroethyl)cyclohexanesulfonate* (PFecHS, CAS # 67584-42-3).
8.18.16 *3-perfluoropheptyl propanoic acid* (FHpPA, CAS # 812-70-4).
8.18.17 *2H-perfluoro-2-decenoic acid* (FOUEA, CAS # 70887-84-2).
8.18.18 *2-perfluorodecyl ethanoic acid* (FDEA, CAS# not available).
8.18.19 *2-perfluorooctyl ethanoic acid* (FOEA, CAS # 27854-31-5).
8.18.20 *2H-perfluoro-2-octenoic acid* (FHUEA, CAS# not available).
8.18.21 *2-perfluorohexyl ethanoic acid* (FHEA, CAS # 53826-12-3).

8.19 *PFC Surrogates*[14]

8.19.1 $^{18}O_2$-*Perfluorohexylsulfonate* (MPFHxS).
8.19.2 $^{13}C_4$-*Perfluorooctylsulfonate* (MPFOS).
8.19.3 $^{13}C_4$-*Perfluorobutanoate* (MPFBA).
8.19.4 $^{13}C_2$-*Perfluorohexanoate* (MPFHxA).
8.19.5 $^{13}C_4$-*Perfluorooctanoate* (MPFOA).
8.19.6 $^{13}C_5$-*Perfluorononanoate* (MPFNA).
8.19.7 $^{13}C_2$-*Perfluorodecanoate* (MPFDA).
8.19.8 $^{13}C_2$-*Perfluoroundecanoate* (MPFUnA).
8.19.9 $^{13}C_2$-*Perfluorododecanoate* (MPFDoA).

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[13] 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.

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

TABLE 2 Gradient Conditions for Liquid Chromatography

Time (min)	Flow (mL/min)	95 % Water: 5 % Acetonitrile %	Acetonitrile %	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

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 Safety Data Sheets (SDS) for all reagents used in this method.

10. Sampling

10.1 *Sampling and Preservation*—Grab samples are collected in 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. Surface binding may bias data. This test method is based on a 5 mL 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 Publication SW-846, Guide D3856, and Practices D3694 may be used as guides. 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°C and 6°C from the time of collection until analysis. Analyze the sample within 28 days of collection. No holding time study has been done on the different water 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.[15]

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 samples 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 carry-over between samples. The LC utilized to develop this test method has a flow through needle design. The gradient conditions for liquid chromatography are shown in Table 2.

11.2 *LC Sample Manager Conditions:*

11.2.1 *Needle Wash Solvent*—60 % acetonitrile/40 % 2-propanol. 8 second wash time before and after injection. Instrument manufacturer's specifications should be followed in order to eliminate sample carry-over.

11.2.2 *Temperatures*—Column, 35°C; Sample compartment, 15°C.

11.2.3 *Seal Wash*—Solvent: 60 % acetonitrile/40 % 2-propanol; Time: 5 minutes.

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 your instrument. Each peak requires at least 10 scans per peak for adequate quantitation. This test method contains nine surrogates, which are isotopically labeled PFCs, and 21 PFCs which were split up into eighteen 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:

The instrument is set in the Electrospray negative source setting.
Capillary Voltage: 0.75 kV
Cone: Variable depending on analyte
Extractor: 2 Volts

[15] Guides to help determine holding times can be found at: http://www.epa.gov/esd/cmb/research/bs_033cmb06.pdf (2014) and Practice D4841.

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

iTeh Standards (https://standards.iteh.ai) Document Preview
ASTM D7979-15e1
https://standards.iteh.ai/catalog/standards/sist/3bf14f2...c8ed-44d9-b8...e-c2a0627...astm-d7979-15e1

Source Temperature: 150°C
Desolvation Gas Temperature: 450°C
Desolvation Gas Flow: 800 L/hr
Cone Gas Flow: 200 L/hr
Collision Gas Flow: 0.15 mL/min
Low Mass Resolution 1: 2.6
High Mass Resolution 1: 14
Ion Energy 1: 1
Entrance Energy: 1
Collision Energy: Variable depending on analyte
Exit Energy: 1
Low Mass Resolution 2: 2.5
High Mass resolution 2: 14
Ion Energy 2: 3
Gain: 1.0
Multiplier: 511.1
Inter-Scan Delay: 0.004 seconds

12. Calibration and Standardization

12.1 The mass spectrometer shall be calibrated as in accordance with 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.

TABLE 4 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

12.2 *Calibration and Standardization*—To calibrate the instrument, analyze nine calibration standards containing the perfluorinated compounds prior to analysis as shown in Table 4. Calibration stock standard solution is prepared from the target and surrogate spike solutions directly to ensure consistency. Stock standard Solution A containing the perfluorinated 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 4. 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 calibration points if the individual laboratory's instrument can't achieve low 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 4) is prepared from the target and surrogate spike solutions directly to ensure consistency. 500 µL of the surrogate spike (20 µg/L), 500 µL of PFC Target Spike I and 500 µL of PFC Target Spike II (refer to ~~Table 6)~~ Table 6) is added to a 50 ml volumetric flask and diluted to 50 ml volume 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 in accordance with a particular laboratory's standard procedure. It is critical to ensure that the 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 hours 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 A second source verification may be incorporated into this test method at the discretion of the laboratory or project requirements. A second source standard should be analyzed near the midpoint of the calibration range to determine if the standards used are within ±30 % of the second source concentration. If they are not within ±30 %, the data shall be qualified stating in the narrative that the two different sources of standards did not match the acceptance criteria.

12.2.4 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~~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 and the confirmatory SRM transition for confirmation. This gives added confirmation by isolating the parent ion, forming two product ions by means of fragmentation, and relating it to the retention time in the calibration standard.

12.2.5 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 generated data. A new primary/confirmatory ion ratio will then be determined if switching the SRM transitions used to quantitate and confirm. The primary/confirmatory SRM transition area ratio shall be required to be within 35 % of the individual labs' new primary/confirmatory SRM transition area ratio.

12.2.6 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.

12.2.7 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 of 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.

12.2.8 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.

12.2.9 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.

12.2.10 A midpoint calibration check standard shall be analyzed at the end of each batch of 30 samples or within 24 hours after the initial calibration curve was generated, the criteria in the individual labs' quality system may be more restrictive pertaining to the number of samples. This end calibration check, in 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 re-occurrence 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 water sample containing the PFCs and surrogates at a prepared sample concentration in the calibration range of Levels 4–7. 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 pretreatment 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 5.

12.3.3 This study should be repeated until the single operator precision and mean recovery are within the limits in Table 5. 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 5 were generated from the single-laboratory data shown in the Precision and Bias Section 16. Data from reagent, surface, and wastewater matrices are shown in the Precision and Bias Section 16. It is recommended that the laboratory generate their own in-house QC acceptance criteria which meet or exceed the criteria in this test method. References on how to generate QC acceptance criteria are Practices D2777, D5847, and E2554, or Method 8000 in EPA Publication SW-846.

12.4 *Surrogate Spiking Solution:*

12.4.1 A surrogate spiking solution containing nine isotopically labeled PFCs – MPFBA, MPFHxA, MPFHxS, MPFDA, MPFOA, MPFOS, MPFNA, MPFUnA and MPFDoA are added to all samples; including 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 5 mL water sample results in a concentration of 160 ng/L of the surrogate in the sample. The results obtained for the surrogate recoveries shall fall within the limits of Table 5. 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[16] 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 water to investigate for contamination during sample preparation and extraction. The concentration of target analytes in either/both blank(s) shall be less than half the reporting limit

[16] Surrogate Mix from Wellington Laboratories Inc. has been found suitable for use.