Nota de aplicación

Large Volume Direct Injection Method for the Analysis of Perfluorinated Alkyl Substances (PFAS) in Environmental Water Samples in Accordance with ASTM 7979-17

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Abstract

In this application note we describe the use of the recently developed ASTM 7979-17 method (EPA Region 5, Dr. Lawrence B. Zintek) to analyze PFASs of interest in environmental waters, not only as described by U.S. legislation, but also those of interest elsewhere, including newer compounds (ADONA, 9Cl-PF3ONS, and 11Cl-PF3OUdS).

Benefits

Performing the ASTM 7979-17 method on the Xevo TQ-XS allows:

- Limited sample preparation of small sample volumes to speed up analysis time and enhance sample throughput.
- Sensitive analysis of PFAS compounds in the low ng/L range to meet regulatory requirements.
- A robust and reliable solution for monitoring PFAS compounds in non-drinking water matrices.

Introduction

Perfluoroalkyl substances (PFASs) are a class of anthropogenic compounds that are found in a range of consumer goods and industrial processes due to their chemical properties. Common uses include firefighting foams, insecticide formulations, water-resistant coating, floor polishes, and oilresistant coatings for paper products approved for food contact. Due to their widespread use and subsequent leaching from materials, PFASs are so ubiquitous that they are frequently detected throughout the environment and in 2009, they were classified as persistent organic pollutants (POPs) within the Stockholm Convention.[1] Due to their persistent, ubiquitous nature, and possible toxicity, most regulatory agencies worldwide closely monitor the use, occurrence, and impact of both traditional/common and newer, replacement short-chain PFASs.

For monitoring and research purposes, ng/L, or part-per-trillion (ppt), detection of PFASs is often required. Within the U.S. drinking water is regulated under the Safe Drinking Water Act, while other environmental waters are regulated under the Clean Water Act. In the third Unregulated Contaminant Monitoring rule (UCMR3)[2] for drinking water, the U.S. EPA has required monitoring of six different PFAS compounds with a minimum reporting level in the range of 30 to 200 ng/L for each component. The U.S. EPA has also issued a health advisory[3] acute level at 70 ng/L based on the best available peer-reviewed studies of PFAS effects.

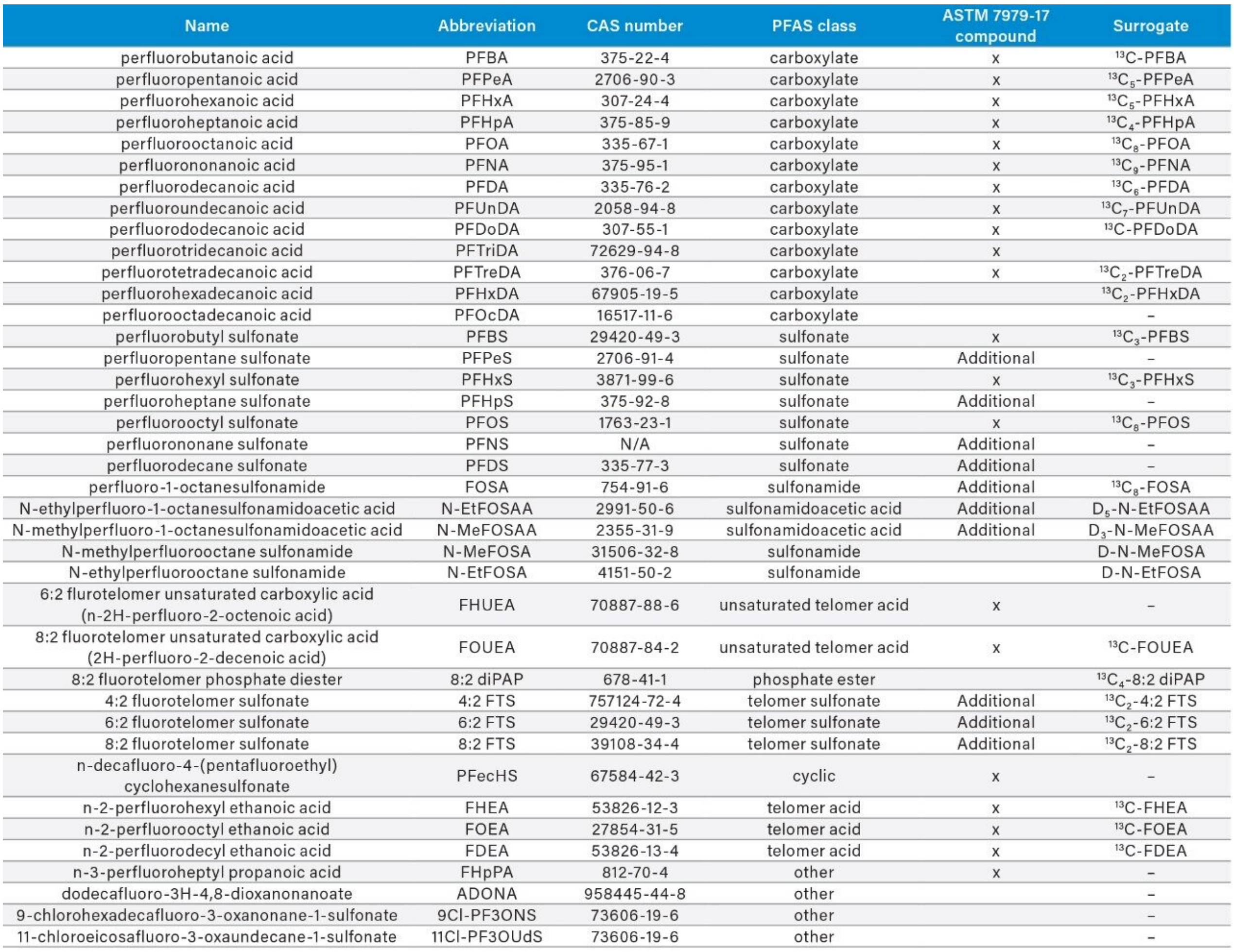
Within the EU, drinking water is regulated under the Drinking Water Directive, 98/83/EC, while other environmental waters are regulated under the EC Water Framework Directive (WFD), 2013/39/EU.[4] In the WFD, PFOS is specifically identified as a "priority hazardous substance."

In this application note we describe the use of the recently developed ASTM 7979-17 method (EPA Region 5, Dr. Lawrence B. Zintek)[5] to analyze PFASs of interest in environmental waters, not only as described by U.S. legislation, but also those of interest elsewhere, including newer compounds (ADONA, 9Cl-PF3ONS, and 11Cl-PF3OUdS). Since many countries look to the U.S. EPA and other agencies for guidance, it was decided to include as many compounds in a single analysis as was feasible at relevant detection levels.

Experimental

The ASTM 7979-17 currently covers the analysis of 21 PFAS compounds, with 10 additional compounds listed for consideration in the appendix of the method. For this analysis, eight additional compounds were added to the method to bring the total number of PFAS analytes to 39. Three of the compounds added to the method are emerging PFAS compounds of interest including ADONA, 9Cl-PF3ONS (the main component of F-53B), and 11Cl-PF3OUdS (minor component of F-53B). Table 1 contains the compound information for all of the PFAS compounds included in this method. All standards were obtained from Wellington Laboratories (Guelph, Ontario).

Table 1. PFAS compounds included in the analysis.



Name	Abbreviation	CAS number	PFAS class	ASTM 7979-17 compound	Surrogate
perfluorobutanoic acid	PFBA	375-22-4	carboxylate	x	^{13}C-PFBA
perfluoropentanoic acid	PFPeA	2706-90-3	carboxylate	x	$^{13}C_5$-PFPeA
perfluorohexanoic acid	PFHxA	307-24-4	carboxylate	x	$^{13}C_5$-PFHxA
perfluoroheptanoic acid	PFHpA	375-85-9	carboxylate	x	$^{13}C_4$-PFHpA
perfluorooctanoic acid	PFOA	335-67-1	carboxylate	x	$^{13}C_8$-PFOA
perfluorononanoic acid	PFNA	375-95-1	carboxylate	x	$^{13}C_9$-PFNA
perfluorodecanoic acid	PFDA	335-76-2	carboxylate	x	$^{13}C_6$-PFDA
perfluoroundecanoic acid	PFUnDA	2058-94-8	carboxylate	x	$^{13}C_7$-PFUnDA
perfluorododecanoic acid	PFDoDA	307-55-1	carboxylate	x	^{13}C-PFDoDA
perfluorotridecanoic acid	PFTriDA	72629-94-8	carboxylate	x	
perfluorotetradecanoic acid	PFTreDA	376-06-7	carboxylate	x	$^{13}C_2$-PFTreDA
perfluorohexadecanoic acid	PFHxDA	67905-19-5	carboxylate		$^{13}C_2$-PFHxDA
perfluorooctadecanoic acid	PFOcDA	16517-11-6	carboxylate		–
perfluorobutyl sulfonate	PFBS	29420-49-3	sulfonate	x	$^{13}C_3$-PFBS
perfluoropentane sulfonate	PFPeS	2706-91-4	sulfonate	Additional	–
perfluorohexyl sulfonate	PFHxS	3871-99-6	sulfonate	x	$^{13}C_3$-PFHxS
perfluoroheptane sulfonate	PFHpS	375-92-8	sulfonate	Additional	–
perfluorooctyl sulfonate	PFOS	1763-23-1	sulfonate	x	$^{13}C_8$-PFOS
perfluorononane sulfonate	PFNS	N/A	sulfonate	Additional	–
perfluorodecane sulfonate	PFDS	335-77-3	sulfonate	Additional	–
perfluoro-1-octanesulfonamide	FOSA	754-91-6	sulfonamide	Additional	$^{13}C_8$-FOSA
N-ethylperfluoro-1-octanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6	sulfonamidoacetic acid	Additional	D_5-N-EtFOSAA
N-methylperfluoro-1-octanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9	sulfonamidoacetic acid	Additional	D_3-N-MeFOSAA
N-methylperfluorooctane sulfonamide	N-MeFOSA	31506-32-8	sulfonamide		D-N-MeFOSA
N-ethylperfluorooctane sulfonamide	N-EtFOSA	4151-50-2	sulfonamide		D-N-EtFOSA
6:2 flurotelomer unsaturated carboxylic acid (n-2H-perfluoro-2-octenoic acid)	FHUEA	70887-88-6	unsaturated telomer acid	x	–
8:2 fluorotelomer unsaturated carboxylic acid (2H-perfluoro-2-decenoic acid)	FOUEA	70887-84-2	unsaturated telomer acid	x	^{13}C-FOUEA
8:2 fluorotelomer phosphate diester	8:2 diPAP	678-41-1	phosphate ester		$^{13}C_4$-8:2 diPAP
4:2 fluorotelomer sulfonate	4:2 FTS	757124-72-4	telomer sulfonate	Additional	$^{13}C_2$-4:2 FTS
6:2 fluorotelomer sulfonate	6:2 FTS	29420-49-3	telomer sulfonate	Additional	$^{13}C_2$-6:2 FTS
8:2 fluorotelomer sulfonate	8:2 FTS	39108-34-4	telomer sulfonate	Additional	$^{13}C_2$-8:2 FTS
n-decafluoro-4-(pentafluoroethyl) cyclohexanesulfonate	PFecHS	67584-42-3	cyclic	x	–
n-2-perfluorohexyl ethanoic acid	FHEA	53826-12-3	telomer acid	x	^{13}C-FHEA
n-2-perfluorooctyl ethanoic acid	FOEA	27854-31-5	telomer acid	x	^{13}C-FOEA
n-2-perfluorodecyl ethanoic acid	FDEA	53826-13-4	telomer acid	x	^{13}C-FDEA
n-3-perfluoroheptyl propanoic acid	FHpPA	812-70-4	other	x	–
dodecafluoro-3H-4,8-dioxanonanoate	ADONA	958445-44-8	other		–
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS	73606-19-6	other		–
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11Cl-PF3OUdS	73606-19-6	other		–

A Certified QC Standard (Cat #731) from ERA (Golden, CO), for use with ground and surface waters, was used as an instrumental QC check throughout the analysis. The standard contained a mix of 12 PFAS compounds. Certified values and QC Performance Acceptance Limits for each compound in the mix are provided with the standard, making instrumental QC evaluation fast and straightforward.

Since required detection limits are in the low ng/L range and as a result of the widespread use of PFASs, specific challenges must be addressed for sample collection, preparation, and analysis. There are many common sources of PFAS contamination in the field and laboratory. In the field, caution should be taken to avoid Teflon containing materials (such as waterproof clothing/jackets), plastic clipboards, waterproof notebooks, and chemical ice packs. In the lab, items to avoid include sticky notes, certain glass disposable pipettes, aluminum foil, vial caps with Teflon seals, and LDPE containers, to name a few. In fact, it is recommended that all laboratory supplies be checked for PFAS contamination before use, as is practical. Contamination is unavoidable from the chromatographic system. Therefore steps should be taken to minimize any system contribution, and as such, the Waters PFC Analysis Kit (p/n:176001744) for the UPLC system was utilized. The kit is comprised of PFAS-free components (such as PEEK tubing to replace the conventional Teflon coated solvent lines) and a PFC Isolator Column that helps to delay any residual background interferences from co-eluting with the analytical peak. Installation of the PFC Analysis Kit is straightforward and quick.[6]

Sample pretreatment

Samples were provided by the U.S. EPA Region 5 through a Cooperative Research and Development Agreement (EPA CRADA #884-16). Provided samples included reagent water, surface (river) water, ground water, influent waste water, and effluent waste water. Each water sample was spiked with a low and high level of a selection of PFAS compounds (three replicates of each concentration) prior to being received in the lab. Two blanks of each sample were also received.

The entirety of each 5-mL water sample was used to avoid any compound loss. Each sample was spiked with 160 ng/L of isotopically labeled surrogates (see Table 1). The surrogates are added to the sample prior to any preparation in order to determine method recoveries. 5 mL of methanol was then added to each water sample and vortexed for 2 min. The entire 10 mL sample was filtered using a disposable polypropylene syringe with a glass filter (25 mm diameter, 1.0 µm pore size) stacked on top of a polypropylene GHP filter (25 mm diameter, 0.2 µm pore size). Following filtration, 10 µL of acetic acid was added to each sample. An aliquot of each sample was transferred to a polypropylene autosampler vial and sealed with a Polyethylene Cap (p/n: 186005230).

LC conditions

LC system:	ACQUITY UPLC I-Class fitted with PFC Kit
Column:	ACQUITY UPLC CSH Phenyl Hexyl 1.7 µm , 2.1 × 100 mm
Column temp.:	35 °C
Sample temp.:	10 °C
Injection volume:	30 µL

Mobile phase A:	95:5 Water:methanol + 2 mM ammonium acetate
Mobile phase B:	Methanol + 2 mM ammonium acetate

Gradient:

Time (min)	Flow rate (mL/min)	%A	%B
0	0.3	100	0
1	0.3	80	20
6	0.3	55	45
13	0.3	20	80
14	0.4	5	95
17	0.4	5	95
18	0.3	100	0
22	0.3	100	0

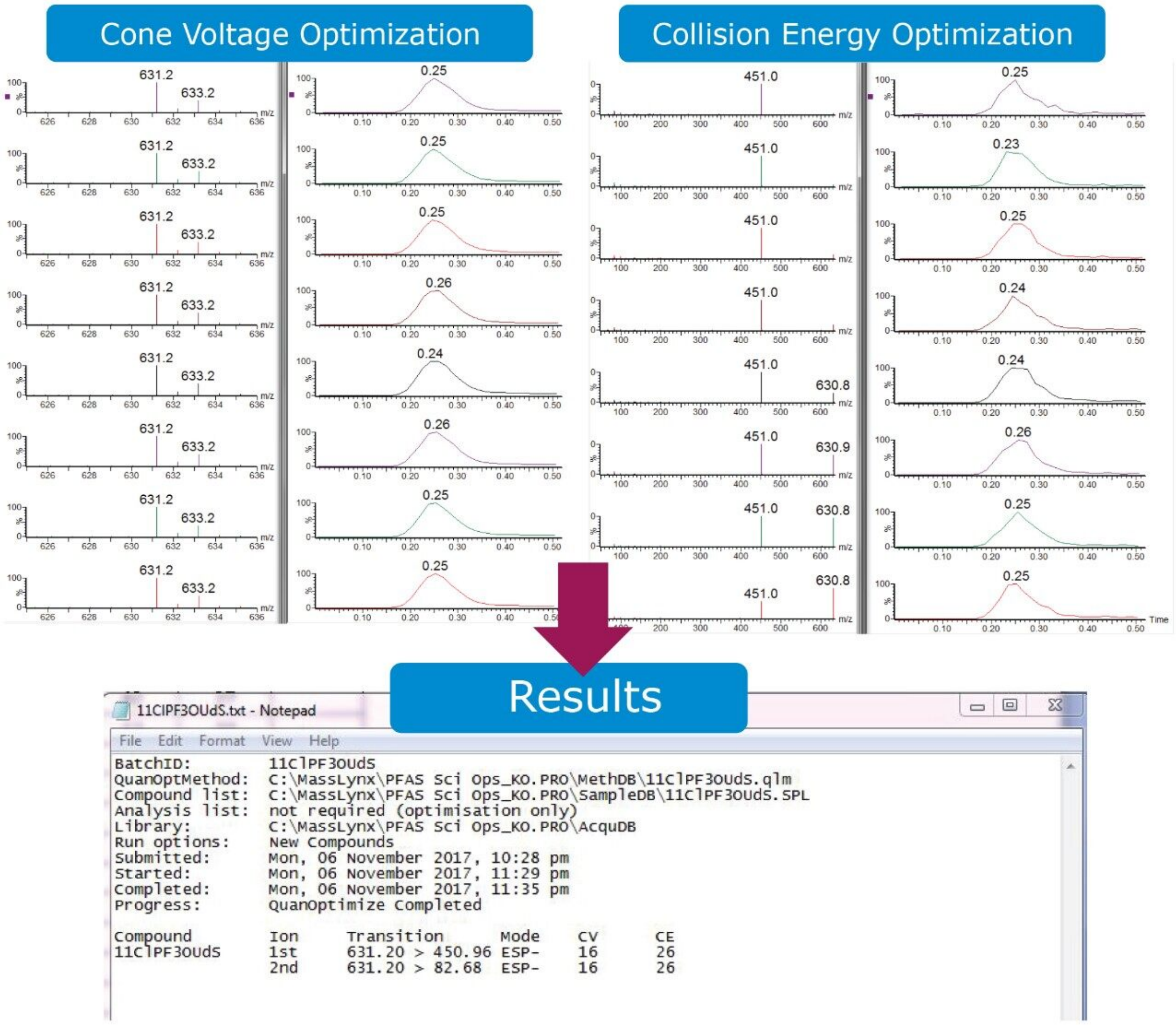
MS conditions

MS system:	Xevo TQ-XS
Ionization mode	ESI-
Capillary voltage:	1.0 kV

Desolvation temp.:	500 °C
Desolvation gas flow:	1100 L/hr
Cone gas flow:	150 L/hr
Source temp.:	120 °C
Method events:	Divert flow to waste from 15 to 21 min.

Method optimization using QuanOptimize

All MRM parameters for each compound were optimized using the QuanOptimize tool in MassLynx. QuanOptimize will automatically determine the parent ion, fragment ions, cone voltage, and collision energy required for each individual compound through injection. The MRMs generated from QuanOptimize for this method are detailed in Appendix Table A. By providing the mass or chemical formula in the MassLynx sample list, QuanOptimize will step through the cone voltages and collision energies designated in the QuanOptimize method. The software then automatically processes the results and generates a report with the MRM transition and corresponding cone voltage and collision energy (Figure 1). This tool also allows rapid and simple optimization of MRM method parameters for new compounds that may need to be added to the analysis method in the future.



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BatchID:          11ClPF3OUdS
QuanOptMethod:    C:\MassLynx\PFAS Sci Ops_KO.PRO\MethDB\11ClPF3OUdS.qlm
Compound list:    C:\MassLynx\PFAS Sci Ops_KO.PRO\SampleDB\11ClPF3OUdS.SPL
Analysis list:    not required (optimisation only)
Library:          C:\MassLynx\PFAS Sci Ops_KO.PRO\AcquDB
Run options:      New Compounds
Submitted:        Mon, 06 November 2017, 10:28 pm
Started:          Mon, 06 November 2017, 11:29 pm
Completed:        Mon, 06 November 2017, 11:35 pm
Progress:         QuanOptimize Completed

Compound          Ion     Transition        Mode     CV      CE
11ClPF3OUdS       1st     631.20 > 450.96  ESP-     16      26
                  2nd     631.20 > 82.68   ESP-     16      26
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Figure 1. Example of the MassLynx QuanOptimize tool showing the process of cone voltage and collision energy optimization and the results from compound optimization.

Results and Discussion

Sample analysis was performed as described in ASTM 7979-17. One minor change was made to the mobile phase composition. For this work, methanol was used in place of acetonitrile. Also, the concentration of ammonium acetate added to both mobile phases was reduced to 2 mM from the suggested 20 mM in the official method. Both changes were made due to solubility concerns of ammonium acetate in acetonitrile.

These changes had no negative effects on method performance, such as peak resolution or response but made the LC method more robust. An overlaid chromatogram of all native compounds and isotope surrogates is demonstrated in Figure 2.

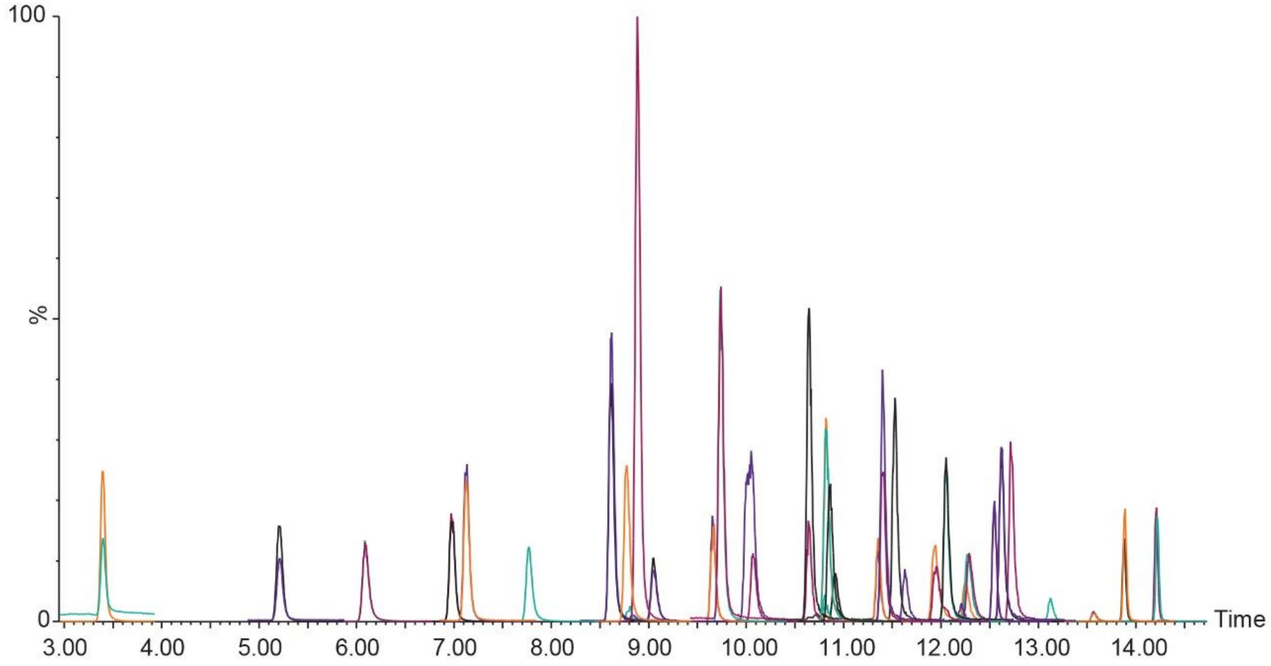

Figure 2. Overlay of all PFAS compounds analyzed in the method.

Method Detection Limits

A Method Detection Limit (MDL) study was performed to assess the sensitivity of the sample analysis method. Nine replicate samples were prepared by spiking reagent water with various concentrations of the PFAS analytes (Table 2) and 80 ng/L of the surrogate standard solution. All samples were taken through the sample pre-treatment procedure prior to analysis. MDL values were calculated using the equation:

MDL = SD x t_{n-1} , where SD = standard deviation of n replicates and t_{n-1} = 2.896 (student t value for n-1 samples)

The MDL values were all well below the required reporting limits stated in the ASTM 7979 method, indicating that this method is more than suitable for this analysis. An MDL value could not be calculated for telomer sulfonate isomer 6:2 FTS due to contamination of this compound in the solvents used for sample preparation. The remaining PFAS compounds experienced no background interference or contamination. Calibration curve requirements in ASTM 7979 require an R^2 value of 0.98 or greater for linear regression fit. All compounds were within this requirement, as highlighted in Table 2. Example calibration curves are also shown in Figure 3 for PFOA and PFOS. Figure 3 also shows chromatograms for PFOA and PFOS injected at 2.5 ng/L. This demonstrates the sensitivity at half the required reporting limit for these two compounds.

Table 2. Method Detection Limit (MDL) results for all compounds in method.

Compound	Sample spike (ng/L)	MDL (ng/L)	Reporting range (ng/L)*	R^2
PFBA	100	25.20	50–2000	0.993
PFPeA	10	1.04	50–2000	0.999
PFHxA	10	1.33	10–400	0.999
PFHpA	10	0.91	10–400	0.999
PFOA	10	1.42	10–400	0.999
PFNA	10	1.32	10–400	0.999
PFDA	10	0.84	10–400	0.998
PFUnDA	10	2.52	10–400	0.996
PFDoDA	10	1.76	10–400	0.993
PFTriDA	10	2.34	10–400	0.991
PFTreDA	10	1.99	10–400	0.993
PFHxDA	200	25.41	–	0.984
PFOcDA	400	41.99	–	0.983
PFBS	10	1.21	10–400	0.999
PFPeS	10	1.07	10–400	0.999
PFHxS	10	1.41	10–400	0.999
PFHpS	10	1.57	10–400	0.999
PFOS	10	1.61	10–400	0.999
PFNS	10	1.67	10–400	0.999
PFDS	10	1.44	10–400	0.997
FOSA	10	1.29	10–400	0.999
N-Et-FOSAA	10	1.90	10–400	0.997
N-Me-FOSAA	10	1.59	10–400	0.999
N-Et-FOSA	10	1.45	–	0.997
N-Me-FOSA	10	1.19	–	0.999
FHUEA	10	1.53	10–400	0.999
FOUEA	10	1.36	–	0.999
8:2 diPAP	300	50.16	–	0.988
4:2 FTS	10	1.50	10–400	0.999
6:2 FTS	10	N/A	10–400	0.999
8:2 FTS	10	2.62	10–400	0.997
PFecHS	10	1.17	10–400	0.998
FHEA	200	42.19	300–8000	0.994
FOEA	200	50.38	200–8000	0.997
FDEA	200	79.48	200–8000	0.993
FHpPA	10	1.47	10–400	0.999
ADONA	10	0.82	–	0.999
9Cl-PF3ONS	10	1.06	–	0.999
11Cl-PF3OUdS	10	1.45	–	0.998

**Reporting ranges listed are as set in the ASTM 7979-17 method.*[5]

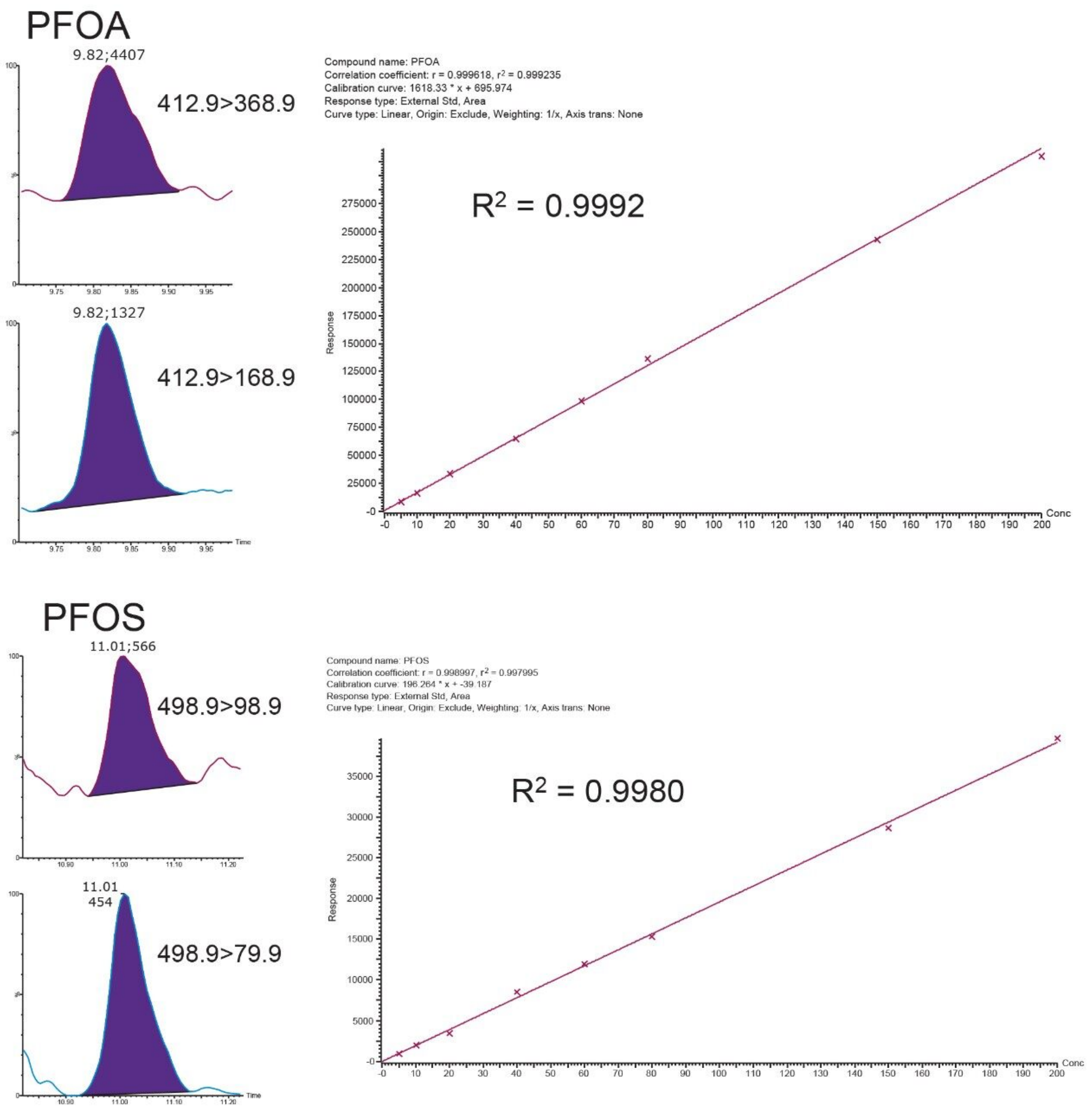

Figure 3. Example chromatograms and calibration curves for PFOA (top) and PFOS (bottom). Chromatograms are representative of an injection of 2.5 ng/L, which is half the required lower reporting limit.

Control Samples

The ASTM 7979-17 method requires control samples to be run with the criteria they must pass as outlined in Figure 4. All compounds passed the control criteria, with the exception of 6:2 FTS due to solvent contamination of that compound.

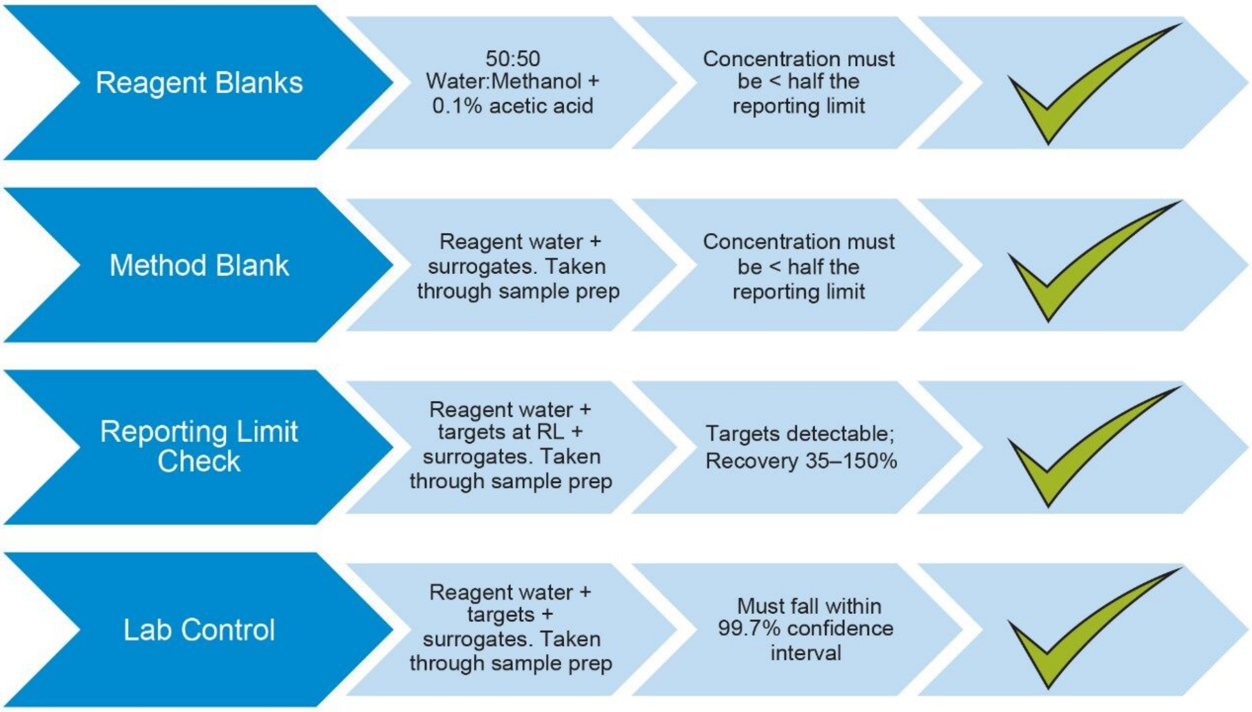

Figure 4. Criteria set by ASTM 7979-17 method for control samples.

Sample Analysis

Triplicates of each spiked matrix at both concentrations were prepared and analyzed using the method according to ASTM 7979-17. Only the compounds currently written into the ASTM method were spiked into the water samples. All PFAS compounds that were spiked into the various water samples were detected at both the high and low concentration spike. PFBA and PFPeA were spiked at 300 ng/L and 1000 ng/L in the low and high spike samples, respectively. 4:2, 6:2, and 8:2 FTS were spiked at 1200 ng/L and 4000 ng/L in the low and high spike, respectively. All other PFAS compounds were spiked at 60 ng/L in the low spike samples and 200 ng/L in the high spike samples. Figure 5 shows an example of all the PFAS compounds spiked at the low concentration level in the surface (river) water sample.

Recovery of the PFAS compounds was determined using isotope labelled surrogate standards that were spiked into the samples prior to sample pre-treatment and analysis. For compounds that did not have a surrogate available, a compound close in retention time and chemical structure was used as the surrogate. Table 3 demonstrates the percent recovery of all PFAS compounds spiked into the five water samples. ASTM 7979 requires percent recoveries to be in the range of 70% to 130%. All compounds included in the method were within this range with the exception of PFTreDA, PFTriDA, and FDEA. These compounds exhibited an enhancement effect when analyzed from a prepared sample compared to the response exhibited in solvent standards. The enhancement could be associated with co-elution of these compounds with matrix components in the sample. Correction of sample concentration can be performed if necessary based on the percent recovery exhibited by the surrogate standard or by quantification using matrix matched calibration curves.

The method proved to be repeatable as well, demonstrated by the %RSD values highlighted in Appendix Table B. All matrix samples were processed in triplicate, which is demonstrated by the n=3 RSD values. These values represent the full method reproducibility. A single sample of reagent water and ground water were also injected 20 times to produce instrument repeatability data (%RSD values in Appendix Table B). Again, due to solvent contamination of 6:2 FTS, an accurate %RSD value for the method replicates could not be calculated. For the most part, the %RSD values fell below 10%, with a majority of compounds exhibiting RSDs below 5%.

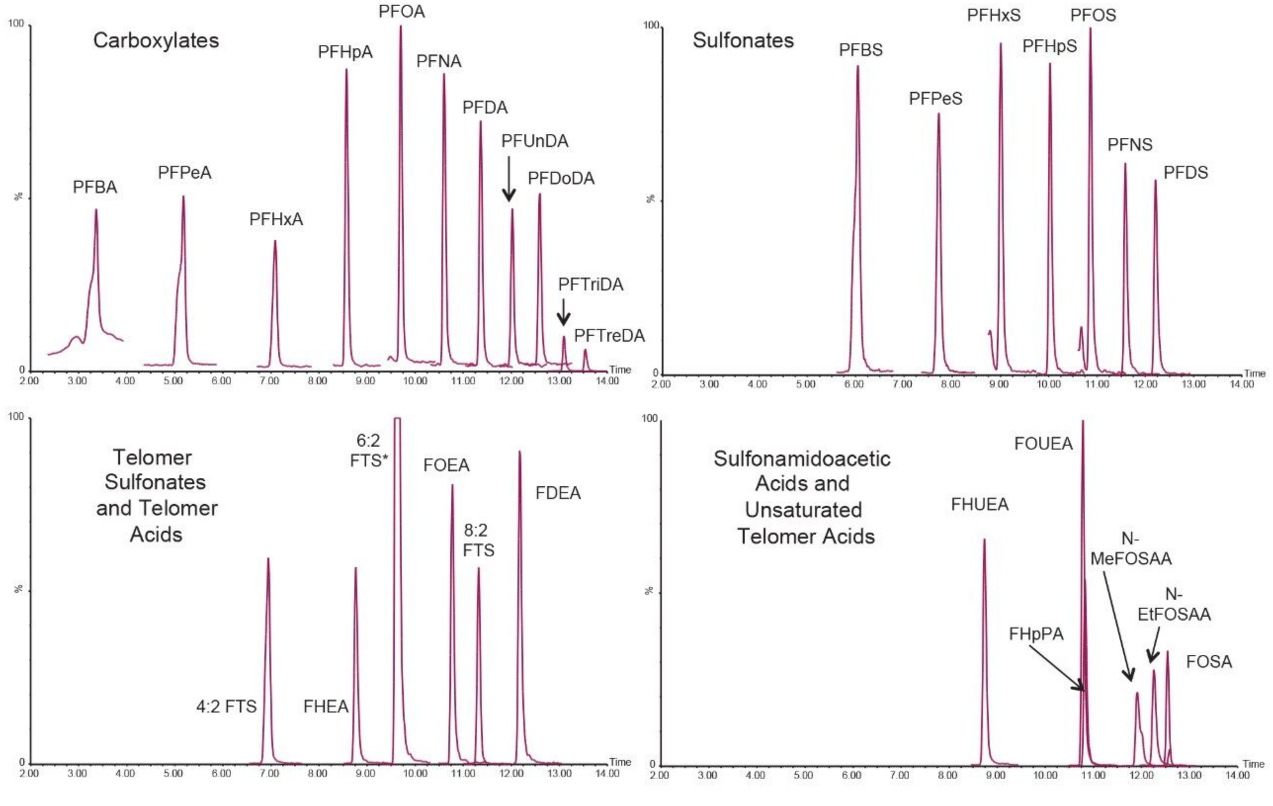

*Figure 5. All PFAS compounds detected in a low concentration spiked surface water sample. PFBA and PFPeA at 300 ng/L; 4:2, 6:2, and 8:2 FTS at 1200 ng/L; all other compounds at 60 ng/L. *Compound shown off scale.*

Table 3. Percent recoveries of all compounds spiked into water samples.

Average %recovery in matrix						
Compound	Reagent water	Ground water	Surface water	Influent water	Effluent water	Recovery compound
PFBA	82.7	82.1	80.9	80.8	85.5	^{13}C-PFBA
PFPeA	89.1	87.7	90.2	88.1	91.4	$^{13}C_5$-PFPeA
PFHxA	89.7	90.1	91.7	91.3	93.3	$^{13}C_5$-PFHxA
PFHpA	90.6	89.8	92.6	91.3	91.9	$^{13}C_4$-PFHpA
PFOA	92.5	92.0	94.2	94.7	94.3	$^{13}C_8$-PFOA
PFNA	93.0	92.2	94.3	94.8	95.2	$^{13}C_9$-PFNA
PFDA	97.0	97.1	100.2	100.7	99.2	$^{13}C_6$-PFDA
PFUnDA	106.4	102.9	107.1	106.2	108.0	$^{13}C_7$-PFUnDA
PFDoDA	116.3	113.3	119.0	118.5	120.0	^{13}C-PFDoDA
PFTriDA	198.3	183.7	205.5	228.0	197.1	$^{13}C_2$-PFTreDA
PFTreDA	198.3	183.7	205.5	228.0	197.1	$^{13}C_2$-PFTreDA
PFBS	94.6	92.1	96.8	93.8	96.1	$^{13}C_3$-PFBS
PFPeS	94.6	92.1	96.8	93.8	96.1	$^{13}C_3$-PFBS
PFHxS	89.8	88.1	91.3	91.9	93.5	$^{13}C_3$-PFHxS
PFHpS	92.8	90.6	94.6	94.1	93.5	$^{13}C_8$-PFOS
PFOS	92.8	90.6	94.6	94.1	93.5	$^{13}C_8$-PFOS
PFNS	92.8	90.6	94.6	94.1	93.5	$^{13}C_8$-PFOS
PFDS	92.8	90.6	94.6	94.1	93.5	$^{13}C_8$-PFOS
FOSA	92.9	92.8	95.1	94.3	95.9	$^{13}C_8$-FOSA
N-Et-FOSAA	127.4	120.6	127.7	129.4	130.0	D_5-N-EtFOSAA
N-Me-FOSAA	122.7	122.7	123.2	127.3	126.3	D_3-N-MeFOSAA
FHUEA	98.2	96.3	100.3	102.2	100.8	^{13}C-FOUEA
FOUEA	98.2	96.3	100.3	102.2	100.8	^{13}C-FOUEA
4:2 FTS	108.0	97.5	99.1	104.0	110.6	$^{13}C_2$-4:2 FTS
6:2 FTS	108.3	96.4	117.9	107.6	100.0	$^{13}C_2$-6:2 FTS
8:2 FTS	107.9	116.3	103.5	117.8	121.2	$^{13}C_2$-8:2 FTS
FHEA	100.2	98.4	104.3	105.3	110.4	^{13}C-FHEA
FOEA	100.5	94.9	99.1	101.1	102.6	^{13}C-FOEA
FDEA	155.0	140.8	164.1	162.3	159.1	^{13}C-FDEA
FHpPA	97.0	97.1	100.2	100.7	99.2	$^{13}C_6$-PFDA

Conclusion

- The ASTM 7979-17 method allows for quick sample turnaround time due to minimal sample preparation.
- The results described here meet and exceed the ASTM 7979-17 method.
- The results described here meet and exceed the EPA health advisory acute levels of 70 ng/L PFOS.
- The large volume direct injection method used on the Xevo TQ-XS was extremely sensitive with method detection limits in the low ng/L range for many compounds.
- All targeted PFAS compounds were detected in the water samples analyzed at both low and high concentrations with excellent recovery and reproducibility.

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Appendix Table A. MRM method details.

Compound	Parent	Fragment	CV	CE	RT
PFBA	213.0	169	8	5	3.01
PFPeA	262.9	218.9	5	5	4.78
PFHxA	312.9	268.9	16	6	6.68
		118.9	16	21	
PFHpA	362.9	318.9	14	8	8.18
		168.9	14	14	
PFOA	412.9	368.9	22	7	9.31
		168.9	22	15	
PFNA	462.9	418.9	18	9	10.23
		218.9	18	15	
PFDA	512.9	468.9	6	9	11.00
		218.9	6	15	
PFUnDA	562.9	518.9	8	8	11.66
		268.9	8	14	
PFDoDA	612.9	568.9	12	12	12.22
		168.9	12	21	
PFTriDA	662.9	168.9	14	22	12.73
		218.9	14	20	
PFTreDA	712.9	218.9	14	22	13.18
		168.9	14	20	
PFHxDA	812.9	168.9	22	28	13.86
		218.9	22	22	
PFODA	912.9	168.9	34	28	14.38
		218.9	34	28	
PFBS	289.9	80.1	7	27	5.62
		99.1	7	27	
PFPeS	348.9	79.9	32	31	7.31
		98.9	32	25	
PFHxS	398.9	80.1	38	35	8.59
		99.1	38	29	
PFHpS	448.9	79.9	16	34	9.62
		98.9	16	34	
PFOS	498.9	79.9	30	42	10.47
		98.9	30	40	
PFNS	548.9	80.1	24	40	11.20
		99.1	24	36	
PFDS	598.9	80.1	46	46	11.83
		99.1	46	46	
FOSA	498.0	77.9	40	29	12.25
N-EtFOSAA	584.0	418.9	34	15	11.89
		525.9	34	18	
N-MeFOSAA	569.9	418.9	36	15	11.55
		168.9	36	27	
N-EtFOSA	526.0	169	18	25	13.89
		219	18	21	
N-MeFOSA	511.9	168.9	16	25	13.56
		218.9	16	21	
FHUEA	356.9	292.9	20	12	8.34
		242.9	20	27	
FOUEA	456.9	392.9	20	11	10.41
		118.9	20	44	
8:2 diPAP	989.0	96.73	31	33	14.01
		542.9	31	25	
4:2 FTS	326.9	306.9	42	18	6.55
		80.9	42	27	
6:2 FTS	427.0	406.9	12	22	9.24
		80.1	12	32	
8:2 FTS	526.9	506.9	28	26	10.96
		80.9	28	37	
PFecHS	460.9	380.9	44	22	9.61
		99.1	44	22	
FHEA	376.9	292.9	13	11	8.37
		312.9	13	5	
FOEA	476.9	392.9	9	11	10.40
		242.9	9	22	
FDEA	576.9	492.9	5	24	11.83
		512.9	5	7	
FHpPA	440.9	336.9	26	10	10.48
		316.9	26	19	
ADONA	376.9	251	12	10	8.45
		84.9	12	22	
9Cl-PF3ONS	531.0	351	14	22	11.11
		82.9	14	20	
11Cl-PF3OUdS	631.0	450.9	16	26	12.31
		82.9	16	26	
^{13}C-PFBA	217	172	7	8	3.01
$^{13}C_5$-PFPeA	268	223	11	7	4.78
$^{13}C_5$-PFHxA	318	273	10	6	6.68
		120	10	18	
$^{13}C_4$-PFHpA	367	322	16	7	8.18
		172	16	15	
$^{13}C_8$-PFOA	421	376	6	8	9.31
		172	6	16	
$^{13}C_9$-PFNA	472	172	7	18	10.23
		223	7	18	
$^{13}C_6$-PFDA	519	473.9	25	7	11.00
		219	25	13	
$^{13}C_7$-PFUnDA	569.9	524.9	9	8	11.66
		273.9	9	14	
^{13}C-PFDoDA	615	569.9	23	10	12.22
		168.9	23	22	
$^{13}C_2$-PFTreDA	715	168.9	18	25	13.18
		219	18	25	
$^{13}C_2$-PFHxDA	815	169	14	31	13.86
		219	14	22	
$^{13}C_3$-PFBS	301.9	80.1	34	28	5.62
		99.1	34	24	
$^{13}C_3$-PFHxS	402	80.1	13	38	8.59
		99.1	13	30	
$^{13}C_8$-PFOS	507	80.1	36	34	10.47
		99.1	36	34	
$^{13}C_8$-FOSA	506	77.9	13	28	12.25
D_5-N-EtFOSAA	589	418.9	24	17	11.89
		482.9	24	13	
D_3-N-MeFOSAA	573	418.9	17	18	11.55
		515	17	18	
D-N-EtFOSA	531	168.9	15	25	13.89
		218.9	15	23	
D-N-MeFOSA	515	168.9	34	21	13.56
		218.9	34	21	
^{13}C-FOUEA	458.9	393.9	14	10	10.41
		395	14	18	
$^{13}C_4$-8:2 diPAP	993	97.1	38	33	14.01
$^{13}C_2$-4:2 FTS	329	309	14	18	6.55
		80.9	14	21	
$^{13}C_2$-6:2 FTS	429	409	48	21	9.24
		80.9	48	27	
$^{13}C_2$-8:2 FTS	529	509	20	27	10.96
		80.9	20	37	
^{13}C-FHEA	379	294	10	23	8.37
		63.9	10	5	
^{13}C-FOEA	478.9	393.9	14	14	10.40
		243.9	14	23	
^{13}C-FDEA	579	494	15	19	11.83
		244	15	40	

Appendix Table B. Reproducibility represented by %RSD of all compounds in each matrix. n=3 replicates represent the method reproducibility, n=20 replicates represent the instrument reproducibility.

	% RSD in matrix											
	Reagent water			Ground water			Surface water		Influent water		Effluent water	
	Low spike (n=3)	Low spike (n=20)	High spike (n=3)	Low spike (n=3)	Low spike (n=20)	High spike (n=3)	Low spike (n=3)	High spike (n=3)	Low spike (n=3)	High spike (n=3)	Low spike (n=3)	High spike (n=3)
PFBA	4.6	7.0	2.1	15.6	2.1	2.7	2.1	2.8	1.7	5.8	5.7	4.3
PFPeA	2.5	1.2	0.7	7.4	1.7	1.6	2.2	0.4	3.0	3.0	6.6	2.7
PFHxA	2.8	2.2	3.8	6.6	1.8	1.7	1.6	1.9	2.6	1.6	9.8	3.1
PFHpA	2.6	1.9	1.1	4.4	4.0	2.4	8.9	2.1	3.3	1.7	7.8	3.1
PFOA	8.8	5.6	1.0	5.9	5.1	1.5	9.5	2.5	4.5	1.5	5.1	2.3
PFNA	3.4	6.9	7.6	6.3	6.8	2.5	8.2	1.0	2.4	11.2	4.9	6.4
PFDA	1.4	4.2	2.7	8.7	5.1	1.3	5.2	1.9	2.2	4.3	8.8	5.1
PFUnDA	7.0	6.2	1.3	9.3	6.2	2.7	8.9	1.9	10.6	8.5	9.8	3.8
PFDoDA	1.0	5.8	2.4	2.0	6.5	11.5	8.1	0.5	4.8	8.2	7.0	4.2
PFTriDA	0.8	3.5	0.5	5.0	2.3	1.4	4.0	2.6	3.6	8.2	5.0	4.7
PFTreDA	4.0	5.5	3.1	8.4	6.0	2.2	2.3	1.5	1.5	14.4	8.2	2.5
PFBS	1.1	2.5	0.3	6.2	1.7	1.2	1.5	1.5	4.4	6.6	2.5	3.3
PFPeS	2.0	2.2	1.1	2.5	2.4	0.3	1.4	0.1	2.5	2.4	1.4	1.9
PFHxS	2.5	3.9	1.2	2.6	4.0	1.7	2.5	4.1	5.4	2.3	10.9	4.1
PFHpS	1.4	4.3	1.0	6.2	3.2	3.8	2.6	1.6	2.7	3.8	3.6	2.6
PFOS	9.0	4.4	1.8	7.9	5.7	3.1	7.2	1.5	4.9	1.5	9.5	3.0
PFNS	5.3	3.8	3.0	4.0	3.9	2.8	5.6	1.3	1.5	6.3	10.2	2.8
PFDS	5.7	6.6	1.6	3.0	5.5	3.7	3.0	1.8	3.8	4.0	0.3	3.3
FOSA	2.0	2.6	1.5	5.8	3.1	2.2	4.4	0.7	0.8	2.0	15.6	2.9
N-Et-FOSAA	4.4	5.0	3.5	2.8	4.9	3.0	2.3	4.1	6.9	7.5	1.0	4.2
N-Me-FOSAA	4.2	4.3	2.3	3.9	4.1	2.2	2.2	3.2	0.6	6.2	11.5	4.2
FHUEA	2.6	1.8	1.7	1.7	2.2	0.4	0.6	2.0	0.6	2.2	1.2	2.2
FOUEA	1.0	2.4	2.3	0.1	2.7	2.1	2.9	1.0	0.7	1.2	0.6	2.0
4:2 FTS	0.9	3.2	17.6	2.3	3.1	1.8	12.3	5.3	11.4	2.5	10.2	4.9
6:2 FTS	N/A	4.1	N/A	N/A	3.2	N/A	N/A	N/A	N/A	N/A	N/A	N/A
8:2 FTS	6.4	7.8	2.8	4.9	8.2	2.5	10.8	6.6	6.2	4.2	3.1	8.6
FHEA	4.8	5.3	6.3	3.2	7.6	1.5	8.2	0.6	3.6	4.5	9.1	3.5
FOEA	1.2	9.0	3.7	8.2	7.4	7.0	9.9	3.3	10.0	3.0	4.2	1.1
FDEA	6.2	6.8	4.4	3.6	7.4	4.6	7.8	5.1	8.6	11.2	9.5	7.8
FHpPA	2.1	2.9	0.9	1.5	3.2	2.6	2.1	1.8	0.9	1.3	0.3	2.4

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