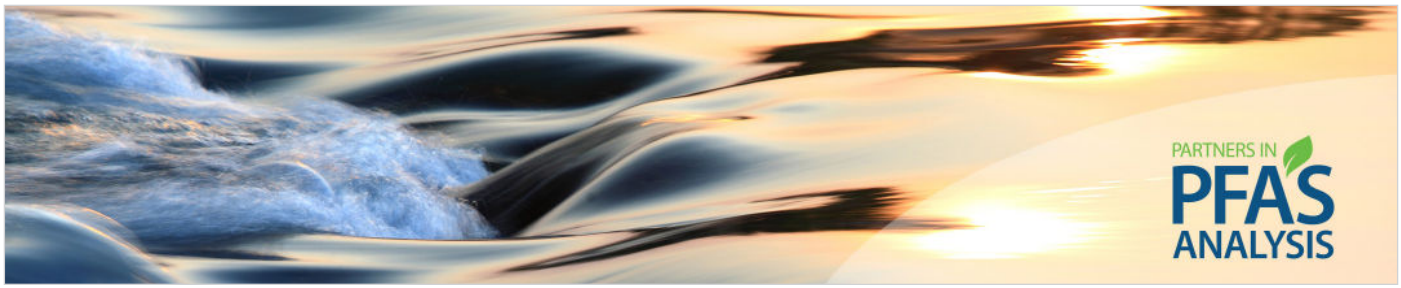

Incorporating Ultrashort-Chain Compounds into Comprehensive PFAS Analysis in Waters

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Abstract

A simple and reliable workflow was established here for analyzing 45 PFAS compounds in both potable and non-potable waters. The target analytes included C2 to C14 perfluoroalkyl carboxylic acids (PFCA); C1 to C13 perfluoroalkyl sulfonic acids (PFSA); fluorotelomer carboxylic acids and sulfonic acids; perfluorooctane sulfonamides and sulfonamidoacetic acids; and per- and polyfluoroether carboxylic acids and sulfonic acids. Method suitability was evaluated in terms of linearity, accuracy, precision, and suitability for a range of water types. The method produced exceptional chromatographic performance, providing a tool for comprehensive PFAS analysis that overcomes the challenges associated with conventional reversed-phase liquid chromatography (RPLC).

Related Products

- *Ultra Inert IBD 3 µm, 100 mm x 2.1 mm (cat.# 9175312-T)*
- *PFAS delay column (cat.# 27854)*
- *PFAS 28 calibration standard (cat.# 30734)*
- *Norm-Ject syringe (cat.# 22775)*
- *Polypropylene syringe filter (cat.# 28936)*
- *Polypropylene centrifuge tubes (cat.# 25846)*

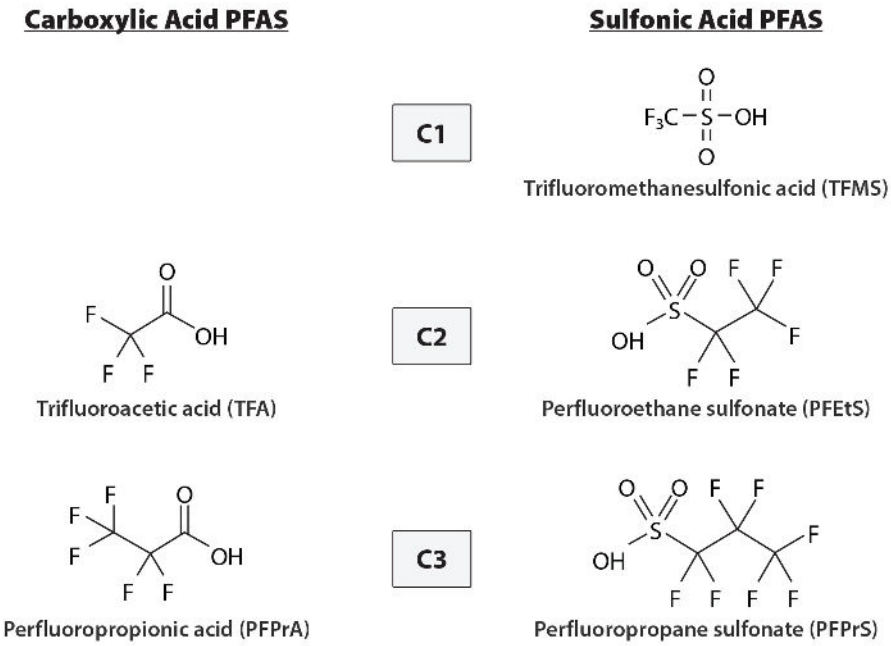
Introduction

Ultrashort-chain per- and polyfluoroalkyl substances (PFAS) are small, very polar compounds with carbon chain lengths shorter than C4 (Figure 1). Their ubiquitous presence and high levels in environmental aquatic systems are emerging as a significant concern, rivaling the well-established issues associated with long-chain PFAS contamination. Therefore, it is important to analyze both ultrashort-chain and longer chain PFAS together in water samples to comprehensively assess the full spectrum of PFAS contamination. Methods allowing concurrent analysis of C1-C14 PFAS will be important tools in PFAS testing because they will allow a better understanding of environmental fate and potential human exposure, which is critical to developing effective regulations and remediation strategies.

The development of comprehensive PFAS methods that include ultrashort-chain compounds is challenging because the high polarity of ultrashort-chain PFAS makes it difficult to obtain adequate retention with an RPLC method and C18 column, which is the typical approach for analyzing C4 and longer PFAS in water. Obtaining adequate retention and separation from matrix interferences is particularly problematic for early eluting compounds, such as TFA. GC-MS has been used for analyzing TFA and C4-C6 PFCA in water samples, but it requires an extra step for PFCA derivatization and does not allow simultaneous analysis of PFSA [1]. Ultrashort-chain PFAS have also been analyzed using anion-exchange LC, but method run times exceed 20 minutes and broad peaks were observed [2]. We have previously developed a rapid method for the analysis of ultrashort- and short-chain PFAS in water samples using a hybrid HILIC and ion-exchange LC column [3], but it did not incorporate long-chain PFAS. More recently, we developed a method to quantify C1 to C10 PFAS in human plasma and serum utilizing a polar-embedded alkyl phase LC column [4]. Based on the effectiveness of that method, we used it as a starting point for the current study, which aims to develop a new method for testing a broader range of PFAS in water matrices.

The method developed here uses an LC column with a polar-embedded alkyl stationary phase to ensure adequate retention of early eluting polar compounds. In addition, the column is made with hardware treated with an inert coating, which improves sensitivity by preventing any unwanted analyte interactions with the stainless-steel column. Using this Ultra Inert IBD column, a simple and reliable workflow was developed for the simultaneous analysis of C1 to C14 perfluoroalkyl carboxylic and sulfonic acids along with other groups of PFAS. Method performance was assessed for linearity, accuracy, precision, and suitability across a wide range of potable and non-potable water matrices.

Figure 1: Structures of C1 to C3 PFAS



Experimental

Water Samples

Wastewater samples were gifts from General Dynamics Information Technology (Falls Church, VA). These included effluents from a publicly owned treatment works (POTW); a hospital; a metal finisher; and a chemical manufacturer. Bottled waters were obtained from local grocery stores. Tap waters were collected from Restek Corporation (Bellefonte, PA) and local households served by different borough water authorities. In addition, a natural spring water, two well waters, and three creek waters were collected from regions in central Pennsylvania.

Standard and Sample Preparation

The working calibration standard solutions (250 µL each) were prepared in reverse osmosis water across a range of 1 to 1000 ng/L in polypropylene HPLC vials. Five mass-labeled PFAS were used as quantitative internal standards (QIS) (Table I). A 2 µL aliquot of QIS working solution containing 40 ng/mL of $^{13}C_3$-PFBA; 20 ng/mL of $^{13}C_2$-PFHxA and $^{13}C_4$-PFOA; and 10 ng/mL of $^{13}C_5$-PFNA and $^{13}C_2$-PFDA was added to each standard solution, followed by mixing with 250 µL of methanol containing 1% acetic acid.

Tap water, bottled spring water, and treated sewage wastewater effluent from a POTW facility were used for the assessment of method accuracy and precision. Tap water and bottled water were used directly without filtration. The POTW water (~10 mL) was filtered with polypropylene syringe filters (cat.# 28936) and collected in 50-mL polypropylene tubes (cat.# 25846). These water samples (250 µL) were fortified at concentrations of 2, 4, 10, 50, and 250 ppt with native analytes and isotopically labeled ^{13}C-TFA, which served as a surrogate for the determination of TFA recovery. Each fortified sample was mixed with 2 µL of QIS working solution and 2.5 µL of extracted internal standards (EIS) working solution containing 10 ng/mL of mass-labeled PFAS as detailed in Table I. A 250 µL aliquot of methanol containing 1% acetic acid was then added and mixed with the fortified samples for LC-MS/MS analysis.

Analytical System

Analysis of C1-C14 PFAS in the water samples was performed by LC-MS/MS under the conditions shown below. A PFAS delay column was installed between the mixer and injector to prevent any potential PFAS contamination upstream of the injector from coeluting with PFAS in the samples. The MS/MS transition parameters for each analyte are provided in Table I.

System: Waters ACQUITY UPLC and Xevo TQ-S triple quadrupole mass spectrometer
Columns:

- Analytical column: Ultra Inert IBD, 100 mm x 2.1 mm, 3 µm (cat.# 9175312-T)
- PFAS delay column (cat.# 27854)

Injection volume: 45 µL
Mobile phase A: 5 mM ammonium formate, 0.1% formic acid in water
Mobile phase B: Acetonitrile
Flow rate: 0.4 mL/min
Temperature: 40 °C

Gradient:	Time (min)	%B
	0.00	50
	7.00	95
	10.00	95
	10.01	50
	12.00	50

Ion mode: Negative ESI
Mode: Scheduled MRM

Table I: MS Transitions and Analyte Retention Times

Compounds	Time (min)	Precursor Ion	Product Ions*	Cone (V)	Collision (V)	Internal Standard
Target Analytes						
Perfluoroalkyl carboxylic acids						
Trifluoroacetic acid (TFA)	2.12	113.03 [M-H]-	69.01	10	10	$^{13}C_3$-PFBA
Perfluoropropanoic acid (PFPrA)	2.69	162.97 [M-H]-	119.02	10	8	$^{13}C_3$-PFBA
Perfluorobutanoic acid (PFBA)	3.27	213.03 [M-H]-	168.98	14	8	$^{13}C_3$-PFBA
Perfluoropentanoic acid (PFPeA)	3.94	262.97 [M-H]-	218.97	2	6	$^{13}C_2$-PFHxA
Perfluorohexanoic acid (PFHxA)	4.59	313.10 [M-H]-	268.97/118.99	2	8/20	$^{13}C_2$-PFHxA
Perfluoroheptanoic acid (PFHpA)	5.24	363.16 [M-H]-	319.09/169.06	8	10/18	$^{13}C_4$-PFOA
Perfluorooctanoic acid (PFOA)	5.86	413.10 [M-H]-	368.96/168.90	2	10/16	$^{13}C_4$-PFOA
Perfluorononanoic acid (PFNA)	6.45	463.10 [M-H]-	419.01/219.02	4	10/16	$^{13}C_5$-PFNA
Perfluorodecanoic acid (PFDA)	7.03	513.17 [M-H]-	469.16/219.06	4	12/16	$^{13}C_2$-PFDA
Perfluoroundecanoic acid (PFUnA)	7.60	563.23 [M-H]-	519.24/269.07	6	12/18	$^{13}C_2$-PFDA
Perfluorododecanoic acid (PFDoA)	8.23	613.23 [M-H]-	569.19/169.06	8	12/26	$^{13}C_2$-PFDA
Perfluorotridecanoic acid (PFTrDA)	8.99	663.23 [M-H]-	619.21/169.06	8	14/28	$^{13}C_2$-PFDA
Perfluorotetradecanoic acid (PFTeDA)	9.83	712.67 [M-H]-	668.69/168.94	10	12/26	$^{13}C_2$-PFDA
Perfluoroalkyl sulfonic acids						
Trifluoromethanesulfonic acid (TFMS)	2.36	148.97 [M-H]-	79.93/98.92	62	18/18	$^{13}C_3$-PFBA
Perfluoroethanesulfonic acid (PFEtS)	2.89	198.90 [M-H]-	79.92/98.91	38	22/22	$^{13}C_3$-PFBA
Perfluoropropanesulfonic acid (PFPrS)	3.44	248.97 [M-H]-	79.92/98.91	2	24/24	$^{13}C_3$-PFBA
Perfluorobutanesulfonic acid (PFBS)	3.97	298.97 [M-H]-	79.97/98.89	2	26/26	$^{13}C_2$-PFHxA
Perfluoropentanesulfonic acid (PFPeS)	4.50	349.10 [M-H]-	79.98/98.98	6	32/30	$^{13}C_2$-PFHxA
Perfluorohexanesulfonic acid (PFHxS)	5.01	398.90 [M-H]-	79.97/98.89	56	32/34	$^{13}C_2$-PFHxA
Perfluoroheptanesulfonic acid (PFHpS)	5.50	449.17 [M-H]-	79.98/98.97	4	42/38	$^{13}C_4$-PFOA
Perfluorooctanesulfonic acid (PFOS)	5.96	499.03 [M-H]-	79.92/98.90	8	40/40	$^{13}C_4$-PFOA
Perfluorononanesulfonic acid (PFNS)	6.38	549.10 [M-H]-	79.92/98.83	12	42/40	$^{13}C_5$-PFNA
Perfluorodecanesulfonic acid (PFDS)	6.77	599.17 [M-H]-	79.98/98.83	8	44/46	$^{13}C_2$-PFDA
Perfluoroundecanesulfonic acid (PFUdS)	7.12	648.73 [M-H]-	79.94/98.94	38	50/44	$^{13}C_2$-PFDA
Perfluorododecanesulfonic acid (PFDoS)	7.44	698.77 [M-H]-	79.95/98.94	10	60/44	$^{13}C_2$-PFDA
Perfluorotridecanesulfonic acid (PFTrDS)	7.73	748.73 [M-H]-	79.94/98.94	8	76/52	$^{13}C_2$-PFDA

Table I: MS Transitions and Analyte Retention Times (cont.)

Compounds	Time (min)	Precursor Ion	Product Ions*	Cone (V)	Collision (V)	Internal Standard
Fluorotelomer sulfonic acids						
1H,1H,2H,2H-Perfluorohexane sulfonic acid (4:2 FTS)	4.22	327.10 [M-H]-	307.08/80.83	50	18/24	$^{13}C_2$-PFHxA
1H,1H,2H,2H-Perfluorooctane sulfonic acid (6:2 FTS)	5.75	427.17 [M-H]-	407.18/80.71	2	22/32	13C_4-PFOA
1H,1H,2H,2H-Perfluorodecane sulfonic acid (8:2 FTS)	7.22	527.17 [M-H]-	507.16/80.83	66	26/32	$^{13}C_2$-PFDA
Fluorotelomer carboxylic acids						
3-Perfluoropropyl propanoic acid (3:3 FTCA)	1.64	241.00 [M-H]-	177.00/117.00	2	6/6	$^{13}C_3$-PFBA
3-Perfluoropentyl propanoic acid (5:3 FTCA)	2.49	340.93 [M-H]-	216.96/236.93	2	24/14	$^{13}C_3$-PFBA
3-Perfluoroheptyl propanoic acid (7:3 FTCA)	3.61	440.90 [M-H]-	336.88/316.91	20	12/22	$^{13}C_3$-PFBA
Perfluorooctane sulfonamides						
Perfluorooctanesulfonamide (FOSA)	3.36	498.17 [M-H]-	77.97/477.76	8	28/26	$^{13}C_3$-PFBA
N-methyl perfluorooctanesulfonamide (NMeFOSA)	3.96	511.77 [M-H]-	168.95/218.91	2	26/24	$^{13}C_2$-PFHxA
N-ethyl perfluorooctanesulfonamide (NEtFOSA)	4.26	525.83 [M-H]-	168.96/218.92	10	26/24	$^{13}C_2$-PFHxA
Perfluorooctane sulfonamidoacetic acids						
N-methyl perfluorooctanesulfonamidoacetic acid (NMeFOSAA)	6.44	570.20 [M-H]-	419.17/483.16	46	20/14	$^{13}C_5$-PFNA
N-ethyl perfluorooctanesulfonamidoacetic acid (NEtFOSAA)	6.56	584.20 [M-H]-	419.18/483.11	6	20/16	$^{13}C_5$-PFNA
Per- and Polyfluoroether carboxylic acids						
Perfluoro-3-methoxypropanoic acid (PFMPA)	3.40	228.93 [M-H]-	84.97/198.94	10	10/14	$^{13}C_3$-PFBA
Perfluoro-4-methoxybutanoic acid (PFMBA)	4.00	278.87 [M-H]-	84.96/234.93	8	10/6	$^{13}C_2$-PFHxA
Nonafluoro-3,6-dioxaheptanoic acid (NFDHA)	4.06	294.93 [M-H]-	200.91/85.02	8	4/22	$^{13}C_2$-PFHxA
Hexafluoropropylene oxide dimer acid (HFPO-DA)	4.46	285.03 [M-COOH]-	169.02/185.02	2	6/16	$^{13}C_2$-PFHxA
4,8-Dioxa-3H-perfluorononanoic acid (ADONA)	4.63	376.90 [M-H]-	250.93/84.97	22	12/26	$^{13}C_2$-PFHxA
Ether sulfonic acids						
Perfluoro(2-ethoxyethane)sulfonic acid (PFEESA)	4.04	314.83 [M-H]-	134.94/83.01	4	22/16	$^{13}C_2$-PFHxA
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (9Cl-PF3ONS)	5.88	530.78 [M-H]-	350.85/82.96	12	26/24	$^{13}C_4$-PFOA
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS)	6.56	630.78 [M-H]-	450.80/82.95	8	26/32	$^{13}C_5$-PFNA
Extracted Internal Standards						
$^{13}C_3$-PFPrA	2.69	165.97 [M-H]-	120.96	10	11	$^{13}C_3$-PFBA
$^{13}C_4$-PFBA	3.27	217.03 [M-H]-	171.98	2	8	$^{13}C_3$-PFBA
$^{13}C_5$-PFPeA	3.94	267.97 [M-H]-	222.99	2	6	$^{13}C_2$-PFHxA
$^{13}C_5$-PFHxA	4.59	318.03 [M-H]-	272.93	2	7	$^{13}C_2$-PFHxA
$^{13}C_4$-PFHpA	5.24	366.90 [M-H]-	321.93	2	10	$^{13}C_4$-PFOA
$^{13}C_8$-PFOA	5.86	420.97 [M-H]-	375.94	2	10	$^{13}C_4$-PFOA
$^{13}C_6$-PFDA	7.03	518.90 [M-H]-	473.87	4	13	$^{13}C_2$-PFDA
$^{13}C_7$-PFUnA	7.60	569.90 [M-H]-	524.87	2	12	$^{13}C_2$-PFDA
$^{13}C_2$-PFDoA	8.23	614.84 [M-H]-	569.87	2	12	$^{13}C_2$-PFDA
$^{13}C_2$-PFTeDA	9.83	714.78 [M-H]-	669.80	8	14	$^{13}C_2$-PFDA
$^{13}C_3$-PFBS	3.97	301.97 [M-H]-	79.97	2	28	$^{13}C_2$-PFHxA

Table I: MS Transitions and Analyte Retention Times (cont.)

Compounds	Time (min)	Precursor Ion	Product Ions*	Cone (V)	Collision (V)	Internal Standard
$^{13}C_3$-PFHxS	5.01	401.90 [M-H]-	79.97	2	36	$^{13}C_2$-PFHxA
$^{13}C_8$-PFOS	5.96	506.84 [M-H]-	79.97	4	42	$^{13}C_4$-PFOA
$^{13}C_2$-4:2 FTS	4.22	328.97 [M-H]-	308.96	2	18	$^{13}C_2$-PFHxA
$^{13}C_2$-8:2 FTS	7.22	528.90 [M-H]-	508.90	2	24	$^{13}C_2$-PFDA
$^{13}C_8$-FOSA	3.36	505.91 [M-H]-	77.95	4	32	$^{13}C_3$-PFBA
d3-NMeFOSAA	6.44	572.90 [M-H]-	418.91	50	18	$^{13}C_5$-PFNA
d5-NEtFOSAA	6.56	588.97 [M-H]-	418.86	48	20	$^{13}C_5$-PFNA
Quantification Internal Standards						
$^{13}C_3$-PFBA	3.27	215.97 [M-H]-	171.97	10	8	
$^{13}C_2$-PFHxA	4.59	314.97 [M-H]-	269.93	8	8	
$^{13}C_4$-PFOA	5.86	416.87 [M-H]-	371.88	2	8	
$^{13}C_5$-PFNA	6.45	467.87 [M-H]-	422.89	16	10	
$^{13}C_2$-PFDA	7.03	514.87 [M-H]-	469.84	8	10	

*Quantifier ion/qualifier ion.

Results and Discussion

LC-MS/MS Method Development

An effective chromatographic method was established for the comprehensive analysis of 45 PFAS, including ultrashort-chain compounds, in potable and non-potable water samples (Figure 2). The Ultra Inert IBD column exhibited excellent chromatographic performance under reversed-phased conditions, with the embedded polar group providing good retention of TFA and other early eluting PFAS. In addition, as shown in Figure 3, the inert hardware resulted in a notable enhancement in detection sensitivity for most of the analytes (3-70% increase in peak area and 5-75% increase in peak height) compared to columns with uncoated hardware.

Figure 2: Analysis of a 500 ppt PFAS Standard

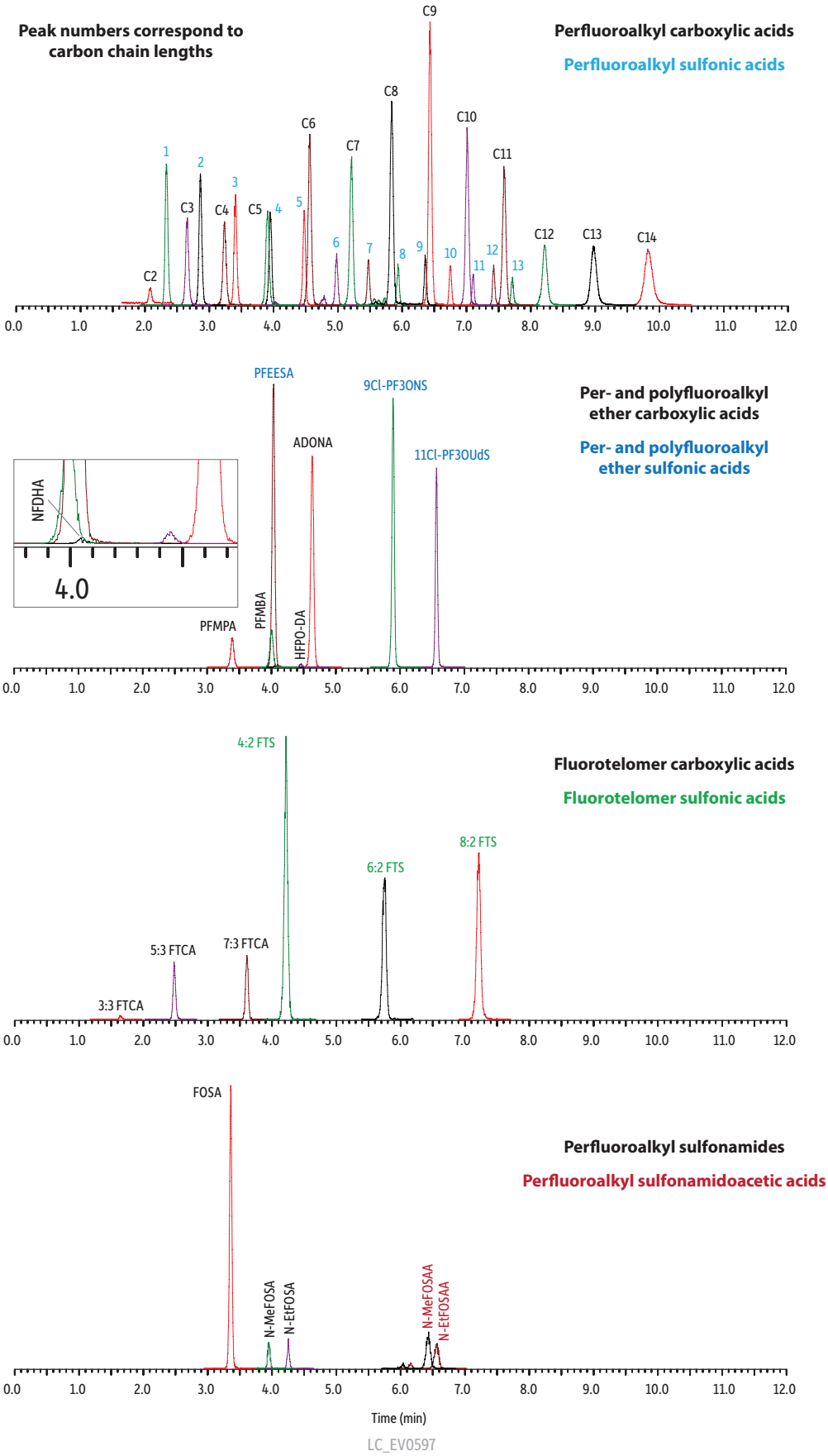
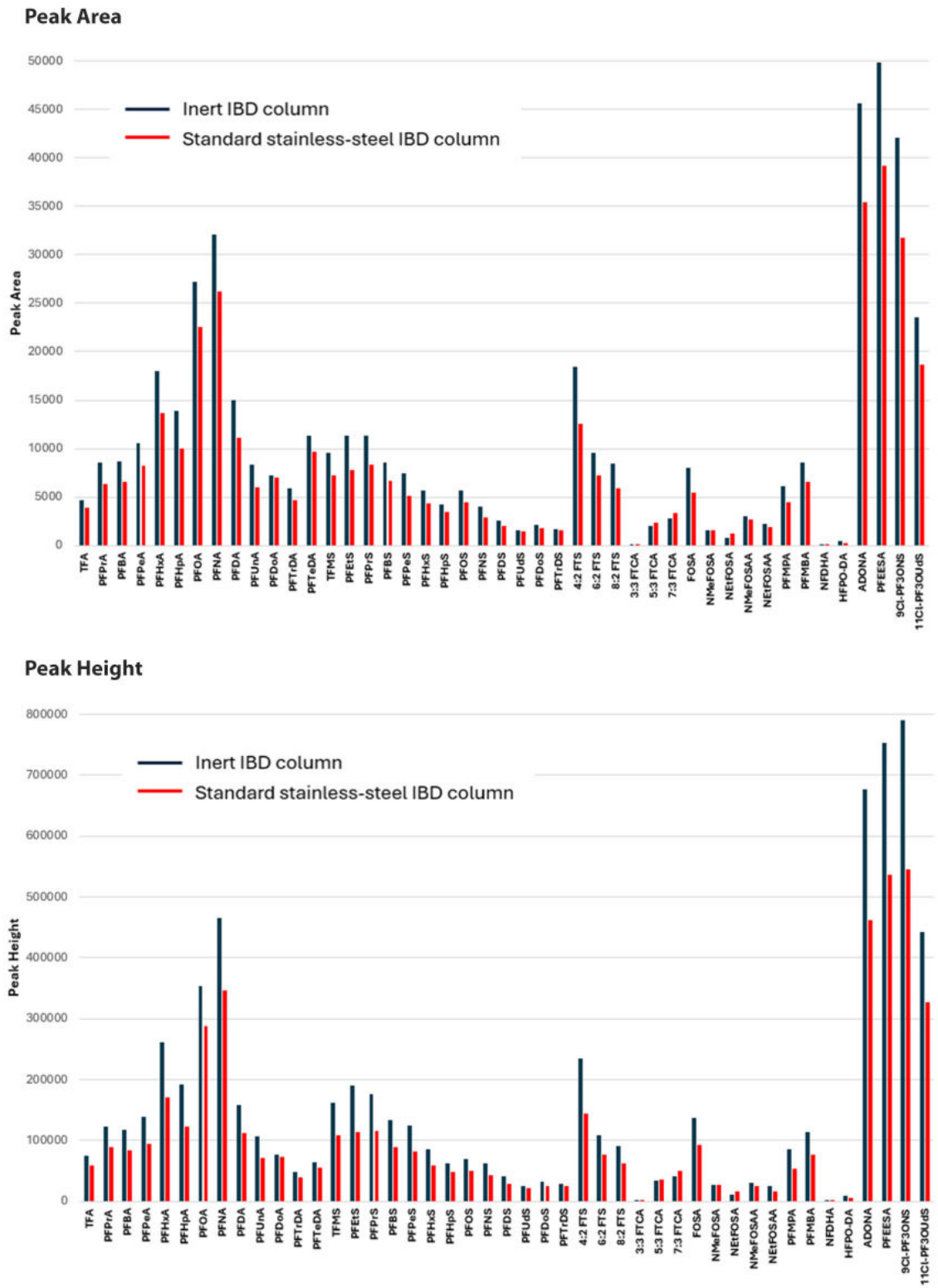


Figure 3: Inert LC column hardware increased peak area and height for most PFAS compared to columns made with traditional stainless-steel hardware.



Linearity

Employing quadratic regression (1/x weighted), all analytes exhibited acceptable linearities with r^2 >0.995 and deviations <30%. Table II shows the different linearity ranges for each target PFAS, which ranged from 1 ppt to 1000 ppt, with variation occurring at the lowest calibration concentration. LOQ and LOD values are also presented (LOQ values were defined as the concentration of the lowest calibration standard for each analyte).

Table II: LOQ* and LOD Values for PFAS in Tap, Bottled, and POTW Water

	Linearity Range	LOD (ng/L)		
Analytes	**(ng/L)**	**Tap Water**	**Bottled Water**	**POTW**
TFA	10–1000	1.7	1.4	2.1
PFPrA	1–1000	0.3	0.3	0.3
PFBA	2–1000	0.7	0.6	0.6
PFPeA	1–1000	0.5	0.4	0.3
PFHxA	1–1000	0.4	0.4	0.4
PFHpA	1–1000	0.4	0.4	0.5
PFOA	1–1000	0.4	0.4	0.4
PFNA	1–1000	0.3	0.3	0.3
PFDA	1–1000	0.4	0.3	0.5
PFUnA	1–1000	0.5	0.3	0.4
PFDoA	2–1000	0.7	0.4	0.5
PFTrDA	2–1000	0.8	0.6	0.6
PFTeDA	2–1000	0.8	0.7	0.6
TFMS	1–1000	0.2	0.2	0.2
PFEtS	1–1000	0.1	0.3	0.2
PFPrS	1–1000	0.2	0.2	0.4
PFBS	1–1000	0.2	0.2	0.5
PFPeS	1–1000	0.2	0.3	0.2
PFHxS	1–1000	0.3	0.6	0.5
PFHpS	2–1000	0.5	0.4	0.4
PFOS	2–1000	0.5	0.9	0.8
PFNS	2–1000	0.6	0.6	0.6
PFDS	2–1000	0.6	0.7	0.9
PFUdS	2–1000	0.5	0.7	0.9
PFDoS	2–1000	0.4	0.6	0.6
PFTrDS	2–1000	0.9	0.6	0.8
4:2 FTS	2–1000	0.4	0.6	0.5
6:2 FTS	2–1000	0.6	0.4	0.5
8:2 FTS	2–1000	0.4	0.4	0.5
3:3 FTCA	20–1000	8.3	7.4	-
5:3 FTCA	4–1000	1.2	1.1	1.5
7:3 FTCA	4–1000	1.6	1.3	1.2
FOSA	1–1000	0.2	0.2	0.2
NMeFOSA	10–1000	3.8	4.0	4.0
NEtFOSA	10–1000	4.6	4.0	4.0
NMeFOSAA	4–1000	1.2	1.2	1.9
NEtFOSAA	10–1000	4.3	2.5	3.3
PFMPA	1–1000	0.3	0.2	0.4
PFMBA	1–1000	0.4	0.3	0.4
NFDHA	20–1000	10.0	8.8	7.9

Table II: LOQ* and LOD Values for PFAS in Tap, Bottled, and POTW Water (cont.)

	Linearity Range	LOD (ng/L)		
Analytes	**(ng/L)**	**Tap Water**	**Bottled Water**	**POTW**
HFPO-DA	10–1000	3.8	3.3	5.2
ADONA	1–1000	0.1	0.1	0.2
PFEESA	1–1000	0.1	0.1	0.1
9Cl-PF3ONS	1–1000	0.2	0.2	0.2
11Cl-PF3OUdS	1–1000	0.2	0.1	0.3

*LOQ = concentration of the lowest calibration standard solution.

Accuracy and Precision

Three batches of samples were analyzed on different days, totaling nine replicates for each fortification level. The average recoveries and relative standard deviations (RSD) are presented in Tables III-V. All analytes exhibited good recovery values within the range of 70–130% across all fortification levels. Satisfactory method precision was demonstrated by %RSD values of <20%. Additionally, the results indicated that all extracted internal standards (EIS) had recovery values within 30% of the nominal concentration.

Table III: Accuracy and Precision Results for Tap Water Samples

Analytes	**Average Recovery (RSD, %), n=9**				
	Fortified Concentration (ng/L)				
	2	**4**	**10**	**50**	**250**
^{13}C-TFA	-	-	110 (9.61)	89.8 (5.10)	91.5 (2.04)
PFPrA	102 (6.88)	100 (3.72)	98.6 (6.71)	105 (8.98)	101 (6.85)
PFBA	108 (8.17)	107 (7.28)	104 (9.06)	104 (5.13)	103 (7.20)
PFPeA	109 (9.02)	115 (2.98)	105 (7.90)	111 (6.13)	107 (8.17)
PFHxA	88.2 (8.36)	99.8 (8.44)	92.0 (6.26)	105 (7.96)	103 (8.06)
PFHpA	88.7 (6.44)	101 (8.38)	86.2 (6.26)	95.1 (6.97)	91.2 (7.28)
PFOA	111 (6.58)	117 (4.67)	103 (9.51)	104 (8.34)	101 (8.98)
PFNA	108 (7.53)	110 (5.46)	97.8 (3.83)	104 (6.23)	99.5 (8.40)
PFDA	99.4 (6.34)	104 (5.56)	95.1 (5.35)	98.6 (9.37)	95.8 (8.66)
PFUnA	110 (14.0)	109 (11.4)	108 (14.6)	107 (8.05)	95.5 (7.14)
PFDoA	103 (14.2)	104 (9.98)	96.5 (14.1)	101 (5.81)	102 (3.95)
PFTrDA	101 (13.3)	91.1 (11.0)	87.5 (7.09)	82.3 (5.23)	86.5 (3.05)
PFTeDA	103 (6.04)	91.2 (10.6)	90.1 (8.18)	86.5 (10.9)	93.4 (4.21)
TFMS	112 (9.16)	108 (10.4)	97.3 (8.16)	105 (6.42)	104 (7.25)
PFEtS	103 (8.31)	115 (5.52)	103 (3.25)	106 (4.64)	107 (5.60)
PFPrS	109 (9.22)	114 (7.23)	99.3 (8.52)	106 (7.76)	107 (7.32)
PFBS	109 (6.89)	109 (10.7)	94.3 (8.59)	101 (5.45)	102 (6.53)
PFPeS	104 (5.33)	113 (3.79)	97.9 (4.84)	106 (7.29)	104 (9.30)
PFHxS	84.1 (16.7)	105 (7.50)	90.8 (12.8)	104 (4.37)	102 (3.77)
PFHpS	111 (7.72)	108 (6.82)	99.7 (7.04)	108 (5.65)	105 (6.59)
PFOS	112 (7.55)	106 (7.10)	95.5 (10.2)	107 (7.39)	107 (6.83)
PFNS	117 (13.8)	104 (10.7)	91.9 (10.2)	104 (4.92)	99.1 (6.15)
PFDS	107 (15.0)	106 (8.32)	94.4 (17.2)	97.9 (11.1)	94.4 (3.40)
PFUdS	108 (13.5)	92.4 (15.5)	88.1 (1.58)	85.7 (2.32)	93.4 (3.38)
PFDoS	114 (13.4)	96.5 (11.9)	85.9 (5.01)	83.5 (11.6)	93.9 (2.71)
PFTrDS	91.0 (17.8)	72.5 (18.2)	72.0 (13.8)	72.9 (14.4)	84.6 (3.55)

Table III: Accuracy and Precision Results for Tap Water Samples (cont.)

Analytes	Average Recovery (RSD, %), n=9				
	Fortified Concentration (ng/L)				
	2	4	10	50	250
4:2 FTS	106 (8.72)	109 (8.83)	90.2 (13.0)	103 (9.27)	101 (10.2)
6:2 FTS	108 (8.94)	112 (6.81)	96.4 (17.3)	102 (4.45)	99.4 (7.60)
8:2 FTS	111 (13.4)	107 (12.1)	92.6 (11.3)	101 (5.28)	94.6 (5.86)
3:3 FTCA	-	-	-	83.7 (8.92)	82.6 (5.64)
5:3 FTCA	-	120 (6.07)	106 (12.0)	103 (8.99)	103 (8.78)
7:3 FTCA	-	107 (8.36)	91.4 (16.2)	105 (7.98)	106 (7.36)
FOSA	107 (9.41)	107 (5.20)	95.4 (8.59)	95.7 (4.63)	95.5 (6.05)
NMeFOSA	-	-	106 (12.9)	105 (6.50)	104 (9.06)
NEtFOSA	-	-	105 (14.7)	112 (4.89)	105 (7.49)
NMeFOSAA	-	123 (7.06)	88.5 (14.6)	102 (8.37)	99.5 (7.89)
NEtFOSAA	-	-	106 (10.9)	96.1 (11.1)	92.6 (5.99)
PFMPA	99.0 (15.9)	103 (10.6)	90.2 (6.11)	103 (8.22)	103 (8.21)
PFMBA	105 (7.67)	107 (8.82)	95.8 (7.63)	107 (6.27)	103 (7.01)
NFDHA	-	-	-	115 (9.78)	115 (8.61)
HFPO-DA	-	-	115 (13.1)	108 (5.70)	106 (7.76)
ADONA	94.4 (11.5)	109 (5.71)	98.4 (7.58)	106 (7.56)	104 (8.94)
PFEESA	102 (8.88)	113 (4.75)	98.8 (7.11)	108 (6.06)	105 (8.76)
9Cl-PF3ONS	100 (8.99)	107 (4.54)	95.7 (2.88)	105 (6.31)	104 (9.09)
11Cl-PF3OUdS	88.2 (12.3)	96.8 (7.36)	87.8 (8.81)	96.7 (4.65)	95.1 (4.17)

Table IV: Accuracy and Precision Results for Bottled Water Samples

Analytes	Average Recovery (RSD, %), n=9				
	Fortified Concentration (ng/L)				
	2	4	10	50	250
^{13}C-TFA	-	-	104 (15.6)	99.4 (8.09)	103 (7.45)
PFPrA	96.7 (5.90)	101 (6.64)	97.9 (6.08)	107 (3.13)	114 (7.77)
PFBA	96.4 (5.81)	94.7 (8.49)	90.2 (6.21)	103 (6.58)	112 (6.78)
PFPeA	93.2 (8.17)	99.1 (13.9)	95.5 (10.2)	105 (5.95)	111 (8.53)
PFHxA	100 (13.1)	96.5 (9.30)	91.0 (8.66)	99.5 (4.92)	108 (8.20)
PFHpA	96.9 (8.26)	92.3 (3.67)	87.3 (4.82)	97.9 (6.15)	104 (5.56)
PFOA	94.4 (10.9)	100 (10.8)	101 (8.29)	105 (6.09)	112 (6.11)
PFNA	108 (9.34)	103 (8.32)	97.3 (3.99)	105 (5.46)	112 (7.09)
PFDA	101 (11.9)	96.9 (6.73)	92.2 (8.25)	100 (5.31)	109 (8.86)
PFUnA	109 (10.6)	104 (8.74)	90.6 (11.0)	97.7 (9.52)	105 (5.72)
PFDoA	97.5 (5.77)	95.2 (4.93)	78.5 (1.90)	85.1 (5.14)	103 (5.68)
PFTrDA	106 (9.03)	100 (8.97)	81.8 (13.1)	87.8 (18.6)	98.2 (9.05)
PFTeDA	116 (3.97)	109 (6.74)	90.5 (8.94)	93.5 (18.2)	114 (5.74)
TFMS	101 (9.04)	107 (6.85)	96.7 (4.30)	106 (2.88)	112 (7.17)
PFEtS	102 (7.45)	105 (4.66)	97.8 (3.00)	106 (2.01)	111 (7.50)
PFPrS	101 (10.4)	106 (7.28)	98.1 (6.13)	108 (1.98)	111 (6.44)
PFBS	103 (13.7)	101 (9.53)	85.8 (5.98)	101 (2.59)	108 (8.90)
PFPeS	95.6 (10.3)	102 (5.75)	92.3 (5.80)	102 (2.79)	109 (9.05)
PFHxS	110 (8.75)	99.4 (8.55)	90.9 (11.8)	96.5 (2.79)	103 (8.67)
PFHpS	99.8 (8.79)	94.2 (8.80)	90.9 (7.75)	105 (5.47)	110 (8.06)
PFOS	111 (12.9)	93.5 (8.65)	91.8 (9.70)	106 (6.02)	109 (6.08)
PFNS	102 (12.8)	90.8 (15.2)	86.8 (10.4)	101 (8.80)	112 (6.74)
PFDS	96.9 (19.1)	105 (12.1)	89.3 (11.4)	103 (10.2)	107 (5.82)
PFUdS	101 (18.5)	100 (16.3)	87.3 (10.5)	92.9 (14.5)	105 (5.71)
PFDoS	114 (7.52)	106 (10.7)	84.8 (14.6)	90.7 (14.5)	108 (7.49)
PFTrDS	126 (1.13)	109 (14.4)	86.2 (17.1)	88.4 (19.0)	112 (5.51)
4:2 FTS	103 (11.0)	98.1 (16.3)	88.6 (10.1)	94.3 (4.60)	108 (10.3)
6:2 FTS	108 (6.44)	95.2 (13.7)	88.0 (13.3)	97.7 (9.07)	106 (7.53)
8:2 FTS	112 (10.5)	109 (5.14)	95.0 (3.66)	103 (3.89)	109 (8.72)
3:3 FTCA	-	-	-	95.4 (10.4)	105 (6.94)
5:3 FTCA	-	103 (8.78)	94.3 (12.1)	105 (6.32)	109 (8.62)
7:3 FTCA	-	115 (5.16)	98.9 (9.92)	102 (8.75)	110 (7.09)
FOSA	111 (7.75)	103 (8.73)	91.6 (3.72)	104 (3.88)	112 (7.06)
NMeFOSA	-	-	105 (8.01)	101 (10.8)	115 (5.88)
NEtFOSA	-	-	121 (9.43)	100 (13.0)	110 (8.06)
NMeFOSAA	-	109 (12.1)	106 (10.1)	92.9 (13.8)	104 (9.53)
NEtFOSAA	-	-	101 (15.7)	100 (10.3)	105 (8.11)
PFMPA	99.5 (9.11)	99.6 (11.0)	92.2 (4.76)	103 (4.57)	112 (7.29)
PFMBA	92.3 (9.01)	102 (9.17)	90.1 (8.50)	100 (4.51)	109 (7.70)
NFDHA	-	-	-	111 (6.59)	111 (7.73)
HFPO-DA	-	-	106 (12.3)	101 (10.1)	112 (6.19)
ADONA	97.3 (11.4)	101 (6.41)	91.6 (3.35)	100 (4.26)	107 (10.3)
PFEESA	101 (8.99)	105 (8.33)	93.6 (5.67)	102 (3.03)	110 (9.16)
9Cl-PF3ONS	100 (8.53)	101 (7.16)	90.2 (4.28)	105 (4.22)	112 (8.47)
11Cl-PF3OUdS	91.0 (11.1)	96.8 (6.21)	85.0 (4.94)	100 (11.8)	108 (5.75)

Table V: Accuracy and Precision Results for POTW Water Samples

Analytes	Average Recovery (RSD, %), n=9				
	Fortified Concentration (ng/L)				
	2	4	10	50	250
^{13}C-TFA	-	-	-	104 (9.46)	108 (8.57)
PFPrA	99.7 (3.96)	101 (11.9)	99.7 (9.18)	109 (3.90)	113 (1.99)
PFBA	100 (8.79)	98.0 (6.35)	99.2 (7.44)	104 (8.77)	106 (4.82)
PFPeA	104 (9.17)	110 (6.19)	101 (5.66)	109 (2.80)	116 (2.05)
PFHxA	91.8 (12.1)	98.5 (10.0)	92.9 (9.53)	101(3.30)	103 (6.53)
PFHpA	115 (5.90)	111 (8.16)	97.6 (6.90)	97.1 (5.74)	99.5 (4.58)
PFOA	108 (8.67)	105 (8.15)	101 (4.86)	105 (4.68)	109 (5.20)
PFNA	113 (8.50)	117 (5.50)	95.1 (5.73)	103 (6.97)	107 (4.67)
PFDA	108 (10.6)	111 (8.44)	91.8 (5.90)	97.6 (4.10)	101 (3.49)
PFUnA	106 (12.6)	102 (9.97)	95.1 (8.99)	97.7 (3.90)	101 (6.28)
PFDoA	98.4 (16.6)	107 (9.05)	93.0 (3.83)	111 (11.9)	112 (12.2)
PFTrDA	94.1 (15.9)	94.4 (13.2)	79.7 (9.70)	90.3 (11.3)	96.7 (13.5)
PFTeDA	113 (12.7)	97.5 (18.9)	82.9 (12.4)	95.2 (13.3)	104 (18.0)
TFMS	104 (15.6)	108 (7.24)	94.9 (5.45)	94.9 (5.32)	96.0 (1.88)
PFEtS	93.1 (15.3)	108 (7.71)	87.9 (6.50)	95.7 (4.51)	97.9 (2.89)
PFPrS	105 (9.36)	114 (4.26)	91.5 (4.65)	99.5 (3.97)	102 (4.11)
PFBS	93.4 (12.3)	107 (6.18)	91.8 (7.88)	100 (5.38)	105 (6.90)
PFPeS	102 (13.3)	113 (8.62)	90.2 (4.13)	99.7 (2.68)	103 (4.89)
PFHxS	89.3 (17.7)	95.2 (8.96)	100 (12.7)	98.6 (6.64)	105 (6.83)
PFHpS	85.1 (16.1)	109 (9.59)	96.0 (7.89)	106 (3.56)	111 (2.42)
PFOS	79.0 (18.5)	107 (6.22)	86.1 (8.60)	101 (7.45)	110 (4.62)
PFNS	104 (9.28)	92.5 (14.2)	85.0 (9.21)	98.9 (4.69)	108 (3.95)
PFDS	109 (11.1)	106 (11.0)	92.6 (13.1)	101 (7.80)	101 (4.53)
PFUdS	95.6 (18.8)	102 (8.93)	77.9 (7.72)	90.2 (8.96)	96.4 (7.42)
PFDoS	111 (9.06)	95.0 (10.7)	80.0 (13.7)	83.1 (8.45)	99.5 (12.4)
PFTrDS	94.1 (14.9)	107 (15.1)	79.8 (12.5)	85.2 (12.4)	96.4 (15.1)
4:2 FTS	122 (5.65)	113 (4.55)	91.5 (7.23)	100 (3.92)	104 (5.01)
6:2 FTS	110 (10.3)	109 (12.0)	93.1 (10.0)	95.2 (7.65)	102 (5.42)
8:2 FTS	116 (10.0)	102 (16.1)	89.3 (12.6)	101 (5.81)	106 (3.58)
3:3 FTCA	-	-	-	-	-
5:3 FTCA	-	115 (7.21)	104 (8.42)	108 (7.38)	108 (5.05)
7:3 FTCA	-	122 (6.51)	92.6 (18.9)	99.7 (9.76)	105 (5.88)
FOSA	110 (8.60)	101 (10.9)	79.1 (4.69)	89.4 (5.01)	96.6 (6.21)
NMeFOSA	-	-	110 (18.8)	92.1 (10.3)	116 (3.63)
NEtFOSA	-	-	116 (9.55)	103 (11.9)	104 (11.6)
NMeFOSAA	-	118 (10.3)	98.2 (12.1)	98.8 (9.01)	100 (6.96)
NEtFOSAA	-	-	106 (10.9)	96.1 (11.1)	92.6 (5.99)
PFMPA	94.3 (11.0)	105 (7.54)	88.4 (7.38)	98.1 (3.33)	102 (4.66)
PFMBA	85.9 (7.17)	99.9 (10.5)	87.0 (8.69)	101 (4.18)	109 (5.75)
NFDHA	-	-	-	90.5 (13.9)	114 (3.75)
HFPO-DA	-	-	111 (6.49)	92.5 (16.2)	95.6 (12.4)
ADONA	90.8 (12.6)	116 (5.19)	90.9 (4.78)	103 (3.45)	106 (5.37)
PFEESA	89.4 (12.7)	113 (8.74)	92.8 (1.95)	102 (1.80)	108 (3.07)
9Cl-PF3ONS	95.4 (10.3)	102 (9.40)	85.4 (6.64)	101 (4.97)	106 (4.67)
11Cl-PF3OUdS	95.1 (8.68)	105 (3.84)	82.7 (4.07)	97.5 (7.82)	101 (6.36)

Measurement of 45 Targeted PFAS in Potable and Non-Potable Waters

Each sample was prepared in triplicate with the addition of EIS. Consistent with the accuracy and precision analysis, the recoveries of EIS were within 30% of the nominal concentration (100 ppt) across all source waters. This demonstrated that the established method was suitable for accurate measurement of targeted PFAS, including ultrashort-chain PFAS, in a wide range of water matrices (Table VI).

Table VI: Measurement of 45 Targeted PFAS in Various Water Matrices (nd = non-detected)

Water Samples	Averaged Concentration (ng/L)												
	Ultrashort-Chain			Short-Chain						Long-Chain		Alternatives	
	TFA	PFPrA	TFMS	PFBA	PFBS	PFPeA	PFHxA	PFHxS	PFHpA	PFOA	PFOS	PFMPA	HFPO-DA
Potable Waters													
Tap Water #1	176	2.66	8.40	nd	nd	< 1.00	2.13	nd	nd	< 1.00	nd	nd	nd
Tap Water #2	317	1.54	7.14	nd	2.25	nd	nd	nd	nd	nd	< 2.00	nd	nd
Tap Water #3	166	3.15	10.9	nd	2.14	2.51	1.24	nd	nd	< 1.00	4.76	nd	nd
Tap Water #4	330	5.48	12.8	nd	1.68	1.97	nd	nd	nd	nd	nd	nd	nd
Tap Water #5	1186	29.0	25.4	13.2	8.58	13.7	17.7	nd	5.78	18.0	5.63	nd	nd
Bottled Water #1 (spring water)	107	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Bottled Water #2 (spring water)	257	1.66	< 1.00	< 2.00	1.21	nd	nd	nd	nd	nd	< 2.00	nd	nd
Bottled Water #3 (RO purified)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Natural Spring Water	486	2.91	4.81	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Well Water #1	557	1.82	1.74	nd	nd	nd	nd	nd	nd	< 1.00	nd	nd	nd
Well Water #2	171	1.16	< 1.00	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Non-Potable Waters													
Creek Water #1	605	4.88	6.75	5.82	19.5	3.50	1.52	nd	< 1.00	< 1.00	6.06	4.40	nd
Creek Water #2	626	3.07	2.26	nd	2.68	nd	nd	nd	nd	nd	< 2.00	nd	nd
Creek Water #3	627	10.9	8.28	< 2.00	2.19	4.94	2.35	nd	nd	3.08	5.97	nd	nd
POTW Water Effluent	1156	24.2	9.66	nd	2.84	6.50	24.0	2.28	< 1.00	12.9	3.88	nd	nd
Hospital Effluent	487	3.08	1.45	nd	nd	2.15	1.50	nd	nd	nd	nd	nd	nd
Metal Finisher Effluent	678	2.78	8.89	2.87	3.11	2.52	2.09	nd	nd	< 1.00	112	nd	nd
Chemical Manufacture Effluent	90,473	8540	13.3	62.8	1.13	100	7.22	nd	12.0	20.8	nd	14.0	5709

Conclusions

A simple and reliable dilute-and-shoot workflow was established in this study to provide a unique solution that incorporates ultrashort-chain PFAS into a comprehensive analysis of PFAS in various water matrices. Use of an Ultra Inert IBD column, which is a polar-embedded alkyl phase column with an inert coating on the hardware, ensured that the method was sensitive, accurate, and precise. Most important, this method can serve as a valuable tool for monitoring these emergent PFAS in environmental water systems and assist in generating guidelines for future regulatory actions. Visit www.restek.com/PFAS for additional products, methods, and technical resources supporting PFAS analysis.

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Ultra Inert IBD HPLC Column

Catalog No.	Product Name	Units
9175312-T	Ultra Inert IBD HPLC Column, 3 µm, 100 mm x 2.1 mm	ea.

PFAS Delay Column

- Traps system-related PFAS, preventing interference and ensuring accurate trace-level analysis of PFAS in samples.
- Universal compatibility: works with
  - any HPLC or UHPLC up to 15,000 psi (1034 bar);
  - both FPP and SPP analytical columns; and
  - all stationary phases.
- Highly retentive of system-related PFAS; no breakthrough even with extended equilibration times.
- Easy installation with standard fittings.

Catalog No.	Product Name	Units
27854	PFAS Delay Column, 5 µm, 50 x 2.1 mm HPLC Column	ea.

PFAS 28 Calibration Standard

Contains:
11-chloroeicosafluoro-3-oxaundecane-1sulfonic acid (11Cl-PF3OUdS) (763051-92-9)
1H,1H,2H,2H-Perfluorodecane sulfonic acid (8:2 FTS) (39108-34-4)
1H,1H,2H,2H-Perfluorohexane sulfonic acid (4:2 FTS) (757124-72-4)
1H,1H,2H,2H-Perfluorooctane sulfonic acid (6:2 FTS) (27619-97-2)
4,8-dioxa-3H-perfluorononanoic acid (ADONA) (919005-14-4)
9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (9Cl-PF3ONS) (756426-58-1)
2-(Heptafluoropropoxy)2,3,3,3tetrafluoropropionic acid (HFPO-DA) (13252-13-6)
N-ethylperfluoro-1-octanesulfonamidoacetic acid (NEtFOSAA)* (2991-50-6)
N-methylperfluoro-1-octanesulfonamidoacetic acid (NMeFOSAA)* (2355-31-9)
Perfluoro-1-decanesulfonic acid (PFDS) (335-77-3)
Perfluoro-1-nonanesulfonic acid (PFNS) (68259-12-1)
Perfluoro-1-octanesulfonamide (FOSA) (754-91-6)
Perfluoro-1-pentanesulfonic acid (PFPeS) (2706-91-4)
Perfluorobutanesulfonic acid (PFBS) (375-73-5)
Perfluorobutanoic acid (PFBA) (375-22-4)
Perfluorodecanoic acid (PFDA) (335-76-2)
Perfluorododecanoic acid (PFDOA) (307-55-1)
Perfluoroheptanesulfonic acid (PFHpS) (375-92-8)
Perfluoroheptanoic acid (PFHpA) (375-85-9)
Perfluorohexanesulfonic acid (PFHxS)* (355-46-4)
Perfluorohexanoic acid (PFHxA) (307-24-4)
Perfluorononanoic acid (PFNA) (375-95-1)
Heptadecafluorooctanesulfonic acid (PFOS)* (1763-23-1)
Perfluorooctanoic acid (PFOA)* (335-67-1)
Perfluoropentanoic acid (PFPeA) (2706-90-3)
Perfluorotetradecanoic acid (PFTeDA) (376-06-7)
Perfluorotridecanoic acid (PFTrDA) (72629-94-8)
Perfluoroundecanoic acid (PFUnA) (2058-94-8)

*Technical grade compound containing both branched and linear isomers; see certificate for details.

Catalog No.	Concentration	Solvent	Volume	Units
30734	1 µg/mL	Methanol (1 mM KOH)	1 mL/ampul	ea.

Norm-Ject Syringe

Catalog No.	Product Name	Units
22775	Norm-Ject Plastic Syringe, 10 mL Luer Lock Tip	100-pk.

Polypropylene Syringe Filter

Catalog No.	Product Name	Units
28936	25 mm Syringe Filter, 0.45 µm, Polypropylene, Black, Luer-Lock	100-pk.

Polypropylene Centrifuge Tubes

Catalog No.	Product Name	Units
25846	Empty Centrifuge Tubes, 50 mL, Polypropylene w/Cap	50-pk.

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