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Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Accordance With EPA 1633 Part 2: Analysis of Aqueous Matrices

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Abstract

US EPA Method 1633 has become the foundation method for analysis of PFAS in non-potable water matrices, soils, biosolids and tissues in the United States. The method consists of sample preparation using weak anion exchange (WAX) solid phase extraction (SPE) with graphitized carbon black (GCB) clean up. This application note is the second in a series demonstrating a comprehensive solution for performing the EPA 1633 methodology. The focus of this note is preparation and analysis of authentic water samples utilizing a prototype bilayer dual-phase SPE cartridge and LC-MS/MS method on an ACQUITY™ Premier BSM FTN LC System coupled to a Xevo™ TQ Absolute Tandem Quadrupole Mass Spectrometer.

Benefits

· An end-to-end workflow is presented for PFAS analysis in authentic water samples following the EPA 1633 procedure

· Performance criteria of EPA 1633 are met using only 250 mL water sample providing reduced requirements for sample collection, shipment, and storage as well as reduced sample preparation time

· A prototype bilayer dual-phase SPE cartridge containing WAX and GCB was utilized to reduce the debris and

hazards of working with dispersive GCB as well as further reducing sample preparation time

· Performance of the workflow is demonstrated by easily passing qualifications of a Waters™ ERA certified reference material

Introduction

US EPA Method 1633 was first introduced in August 2021 to become the foundational method for analysis of PFAS in non-potable water matrices, soils, biosolids, and tissues.[1] At the time of writing this document, Method 1633 is in the 4th Draft Phase with the final version expected to be released at the end of 2023.[2] By the final release of EPA 1633, it will have been multi-lab validated for each type of sample matrix included in the method. The method covers 40 PFAS and utilizes isotope dilution calibration and quantitation. Required sample preparation differs slightly depending on sample type, but all sample types utilize SPE on a WAX cartridge in combination with GCB clean up. EPA 1633 was created to support sample analysis for the Clean Water Act (CWA) and Department of Defense (DoD) monitoring and remediation, but it covers such a wide range of matrices and compounds that its applicability is expected to be widespread.

This is the second in a series of application notes addressing sample preparation, analysis and method performance of EPA 1633 using a comprehensive workflow of Waters technologies. This application note will focus on the preparation of authentic water samples with analysis utilizing the LC-MS/MS method established in Part 1 on an ACQUITY Premier BSM FTN UPLC System coupled to a Xevo TQ Absolute Mass Spectrometer.[3] The use of a combined WAX and GCB sample extraction and clean-up workflow is demonstrated on ground water, surface water, and wastewater (influent and effluent).

Experimental

Sample Preparation

Samples discussed in this application note include ground water and surface water that were collected locally, and influent and effluent wastewater that were kindly provided by a municipal wastewater treatment facility in the Midwest United States. All water samples were collected using grab sampling directly into 250 mL high

density polypropylene bottles. Samples were frozen until sample analysis according to EPA 1633 guidelines and holding times. Sample bottles were weighed prior to sample preparation (full) and after sample preparation (empty) to determine the exact volume collected in each bottle. In addition to authentic samples, the Waters ERA PFAS in Wastewater (Item No. 404 <https://www.eraqc.com/pfas-in-wastewater-wp-era001663?returnurl=%2fpfas-products%2f>) certified reference material (CRM) was processed with the samples.

A prototype bilayer dual-phase SPE cartridge containing both Weak Anion Exchange (WAX) and Graphitized Carbon Black (GCB) sorbents was used for sample preparation instead of adding dispersive GCB into the sample for cleanup.

Full sample preparation details are listed in Figure 1 and are adapted directly from the EPA 1633 method. Two changes to the method were made including a sample volume change and combining the dispersive GCB step into the SPE cartridge, as described previously. Sample volume was reduced to 250 mL from the suggested 500 mL sample in the method due to instrument sensitivity of the Xevo TQ Absolute Mass Spectrometer. Reducing sample volume reduces sample shipping and storage costs, as well as allowing for faster sample preparation when loading half the volume of sample onto an SPE cartridge. Combining the GCB and WAX into the same cartridge provides the convenience of minimizing complications from using loose material and reducing the number of steps during sample preparation without compromising the method.

1.
- Spike 250 mL water sample with Extracted Internal Standard Mix (MPFAC-HIF-ES from Wellington)
- Check pH and adjust to approximately 6 if necessary

2.
- Pack SPE cartridge with glass wool to half height of barrel
- Condition SPE cartridges
    - 15 mL 1% (v/v) ammonium hydroxide in methanol
    - 5 mL 0.3 M formic acid

3.
- Load sample at 5 mL/min
- Wash cartridge with 10 mL of reagent water, ensuring to rinse reservoir with this solution
- Wash with 5 mL of 1:1 0.1M formic acid:methanol, ensuring to rinse reservoir with this solution
- Dry cartridge for 15 seconds

4.
- Place collection tubes in manifold
- Rinse bottle with 5 mL 1% (v/v) ammonium hydroxide in methanol. Transfer to cartridge and elute
- Add 25 µL acetic acid to each sample
- Spike each sample with Non Extracted Internal Standard (MPFAC-HIF-IS from Wellington)

Figure 1. Full method details of the sample preparation process used for all water samples. Adapted from EPA Method 1633.

All samples were spiked with 5 ng/L (sample concentration equivalent) of the required extracted internal standard (EIS) prior to extraction and 5 ng/L (sample concentration equivalent) of the required non-extracted internal standard (NIS) after extraction. The calibration curve range for each analyte is listed in Appendix Table 2 and was determined from the data acquired and presented in Part 1 of this application note series.[3] All standards were obtained as mixes from Wellington Laboratories.

LC Conditions

LC system:	ACQUITY Premier BSM with FTN
Vials:	700 µL Polypropylene Screw Cap Vials (p/n: 186005219)
Analytical column:	ACQUITY Premier BEH™ C_{18} 2.1 x 50 mm, 1.7 µm

(p/n: 186009452)

Isolator column:	Atlantis™ Premier BEH C$_{18}$ AX 2.1 x 50 mm, 5.0 µm (p/n: 186009407)
Column temperature:	35 °C
Sample temperature:	10 °C
PFAS kit:	PFAS Install Kit with OASIS WAX 150 mg (p/n: 176004548)
Injection volume:	2 µL
Flow rate:	0.3 mL/min
Mobile phase A:	2 mM ammonium acetate in water
Mobile phase B:	2 mM ammonium acetate in acetonitrile

Gradient Table

Time (min)	%A	%B	Curve
0	95	5	initial
0.5	75	25	6
3	50	50	6
6.5	15	85	6
7	5	95	6
8.5	5	95	6
9	95	5	6
11	95	5	6

MS Conditions

MS system:	Xevo TQ Absolute
Ionization mode:	ESI-
Capillary voltage:	0.5 kV
Source temperature:	100 °C
Desolvation temperature:	350 °C
Desolvation flow:	900 L/hr
Cone flow:	150 L/hr
MRM method:	See Appendix for Full MRM Method details

Data Management

Software:	waters_connect™ for Quantitation

Results and Discussion

Recovery in Water Samples

EPA 1633 is a performance-based method that allows modifications as long as the performance criteria outlined in the method are all met. One major modification presented in this work is to use a bilayer dual-phase SPE cartridge that combines the otherwise dispersive GCB clean up step into the WAX SPE cartridge. GCB is difficult to work with and accurately measure, therefore utilizing a bilayer cartridge eliminates the untidy dispersive step. More importantly, combining the GCB cleanup step into the SPE extraction saves valuable time in the laboratory

during the sample preparation process. Additionally, less preparation steps allow for fewer opportunities for introduction of unintended PFAS sample contamination.

One of the important performance criteria that must be established in order to prove equivalence of this approach is the extracted internal standard (EIS) and non-extracted internal standard (NIS) recovery acceptance limits in the 4th Draft Method 1633 (See Table 6 within that document).[1] The individual recovery performance of the bilayer dual-phase SPE cartridge for ground water, surface water (with high organic matter content), influent wastewater (settled only), and effluent wastewater (fully treated discharge water) are listed for each EIS and NIS in Table 1. The data reported in Table 1 is the average recovery and %RSD for five replicate extractions of each matrix type. The mean recovery of all EIS among the 20 samples extracted was 91.2% with a mean RSD of 9.2%.

Compound	Ground water		Surface water		Influent water		Effluent water	
	Average recovery (%)	%RSD	Average recovery (%)	%RSD	Average recovery (%)	%RSD	Average recovery (%)	%RSD
$^{13}C_4$-PFBA	100.0	2.7	111.9	8.1	85.8	9.2	86.6	13.8
$^{13}C_5$-PFPeA	98.6	4.2	110.1	8.5	101.6	5.7	100.3	15.1
$^{13}C_5$-PFHxA	97.2	3.1	111.2	8.0	111.0	8.4	102.5	14.3
$^{13}C_4$-PFHpA	97.3	4.5	108.8	9.2	111.0	8.5	99.7	14.8
$^{13}C_8$-PFOA	98.8	2.5	110.6	9.0	113.0	13.3	100.7	16.5
$^{13}C_9$-PFNA	96.6	5.2	110.2	11.3	112.0	18.0	101.1	17.5
$^{13}C_6$-PFDA	92.1	2.9	108.1	9.5	103.8	18.1	97.0	17.5
$^{13}C_7$-PFUnDA	88.5	2.9	102.0	4.8	93.0	18.7	91.6	15.0
^{13}C-PFDoDA	83.1	2.8	89.8	8.5	63.8	18.2	82.5	14.0
$^{13}C_2$-PFTreDA	72.5	5.0	56.7	10.1	32.3	17.6	52.5	13.4
$^{13}C_3$-PFBS	97.8	2.3	110.9	6.5	116.8	12.3	102.6	13.5
$^{13}C_3$-PFHxS	97.0	5.0	113.1	6.9	112.5	8.3	104.8	14.5
$^{13}C_8$-PFOS	93.2	1.8	108.7	7.8	108.5	13.9	97.8	17.3
$^{13}C_2$-4:2 FTS	82.8	6.9	92.1	5.1	179.8	9.1	102.8	21.4
$^{13}C_2$-6:2 FTS	94.1	2.8	95.0	5.0	197.8	11.0	101.9	19.1
$^{13}C_2$-8:2 FTS	91.5	4.2	91.8	7.5	149.7	16.6	90.4	17.9
$^{13}C_8$-FOSA	92.3	3.6	99.4	5.8	101.3	19.8	96.7	18.7
$^{13}C_3$-GenX	98.0	3.5	105.9	6.6	85.2	7.5	98.6	14.8
D_5-N-EtFOSAA	91.3	3.4	91.9	6.0	127.0	15.4	93.3	18.3
D_3-N-MeFOSAA	89.0	4.8	90.3	5.5	137.4	16.2	91.6	20.3
d_3NMeFOSA	63.5	5.9	64.0	13.2	52.8	24.3	82.3	19.2
d_5NEtFOSA	61.1	7.0	61.9	13.5	38.9	23.8	78.5	19.6
d7-NMeFOSE	70.0	5.7	74.0	11.8	56.9	20.3	74.5	17.7
d9-NEtFOSE	67.2	5.9	71.1	12.3	52.9	20.2	71.1	18.3
$^{13}C_3$-PFBA	134.8	20.0	112.2	6.5	89.6	6.6	114.1	7.1
$^{13}C_2$-PFHxA	133.9	19.4	117.4	5.7	120.8	7.2	124.7	5.8
$^{13}C_4$-PFOA	127.9	22.7	116.3	7.8	132.2	8.1	123.5	8.0
$^{13}C_5$-PFNA	133.3	21.3	115.1	9.1	132.8	4.5	122.3	7.5
$^{13}C_2$-PFDA	136.8	20.3	115.8	6.3	155.9	4.0	124.4	7.7
$^{18}O_2$-PFHxS	133.6	21.4	115.7	7.4	112.2	7.0	119.8	6.6
$^{13}C_4$-PFOS	132.2	22.7	116.1	6.6	118.9	7.2	121.6	8.2

Table 1. Average recovery of the extracted internal standards (EIS) and non-extracted internal standards (NIS) using the bilayer dual-phase SPE cartridge for each water sample type evaluated (n=5).

Figure 2 directly compares the average recovery across all water sample types with the allowable recoveries in EPA 1633 Table 6 (Draft 4). The recoveries in water samples were easily within the recovery acceptance limits for each compound, and in all cases were significantly above the minimum recovery level. This demonstrates that even in the more complex water matrices, the cartridge has equivalent performance as using dispersive GCB and is fit-for-purpose.
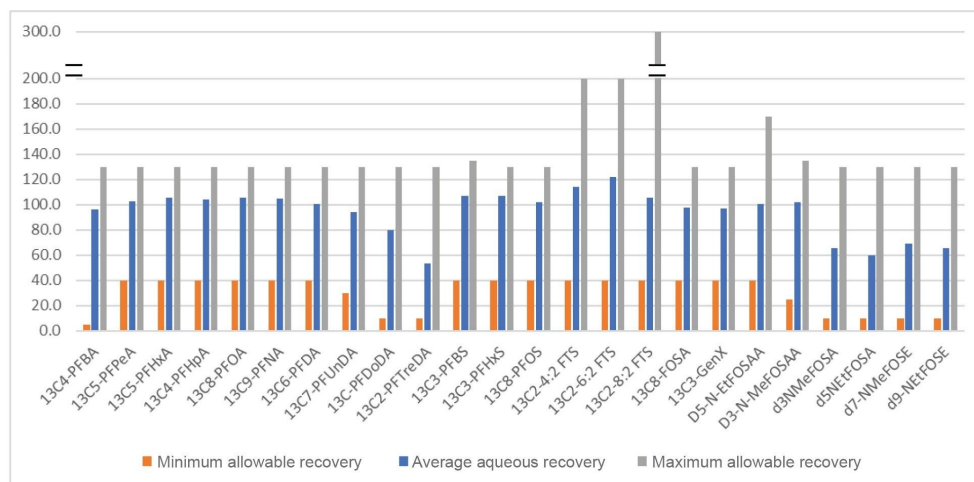
Figure 2. Average recovery of the extracted internal standards (EIS) in all four aqueous sample types (blue) compared to the minimum (orange) and maximum (gray) percent recoveries allowed in the EPA 1633 method (n=20). Note the split axis to accommodate the maximum recovery value for $^{13}C_2$-8:2 FTS.

Analysis of a Certified Reference Material

Accuracy of analysis is important for quantitating PFAS in customer samples. A certified reference material (CRM) from Waters ERA was processed with the authentic samples as a benchmark for workflow accuracy. The PFAS in Wastewater CRM is certified for all EPA 1633 analytes, giving a representative reference material for method performance without having to spike unknown matrix samples which can become complicated without a sample free from PFAS. Figure 3 shows the average quantitative results for three replicate extraction and analyses of the Wastewater CRM. The dotted and dashed red lines indicate the minimum and maximum certified value range of the CRM. The solid blue line represents the certified value. The solid gray line represents the average experimental quantitated value determined during sample analysis. All 40 target PFAS in EPA 1633 were quantified within the allowable minimum and maximum concentration range with a mean trueness of 92% and trueness range of 73–112%. This demonstrates confidence in accuracy of the sample preparation, analysis and data processing workflow using Waters solutions.
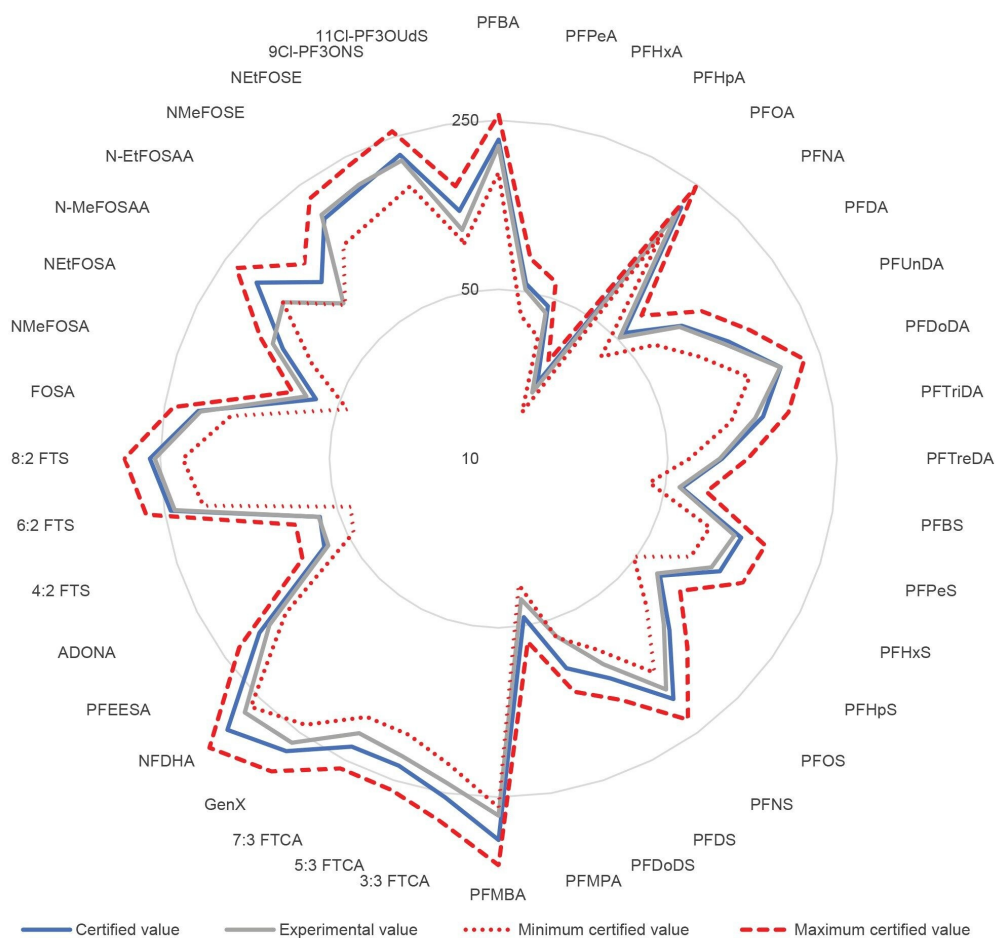
Figure 3. Quantified values of all 40 EPA 1633 target analytes in Waters ERA PFAS in Wastewater CRM. Red lines represent the minimum (dotted) and maximum (dash) certified value range of the CRM. The blue line represents the certified value. The solid gray line represents the average experimental quantitated value (n=3). Note the axis is represented using a log scale.

Analysis of PFAS in Authentic Water Samples

The presented workflow was utilized to detect and quantify the 40 target PFAS analytes in ground water, surface water, influent water, and effluent water. The LC gradient method was designed to provide a minimum of 1 minute separation between potential cholic acid interferences and PFOS.[2] Because cholic acids are produced to aid digestion, they can be present in large amounts in wastewater samples. Figure 3 demonstrates the presence

of cholic acids in the influent and effluent wastewater samples and the successful separation of them from interference with PFOS.

PFAS were detected in all samples, as highlighted in Table 2. Each sample was collected and extracted in five replicates and the average calculated concentration is reported with associated %RSDs for the replicates. The ground water had the lowest detectable PFAS with nine PFAS detected above the limit of quantitation (LOQ) and ranging from 0.11–7.03 ng/L. The surface water sample had a slightly larger range of PFAS, with 12 detected above the LOQ in a range of 0.17–15.4 ng/L. The wastewater samples had the largest range and concentrations of PFAS detected. A comparison of the detected PFAS in the influent and effluent water is shown in Figure 5. 19 PFAS were quantified in the influent wastewater, whereas 16 were detected in the effluent wastewater, indicating that the water treatment at this site is effective at removing some PFAS. When comparing the concentrations though, most of the PFAS were quantified at approximately the same concentration in both influent and effluent water. NMeFOSE, 3:3 FTCA, and 7:3 FTCA were not present in the effluent water discharged from the treatment plant, and 5:3 FTCA was significantly reduced (from 88.9 ng/L in the influent to 3.9 ng/L in the effluent).
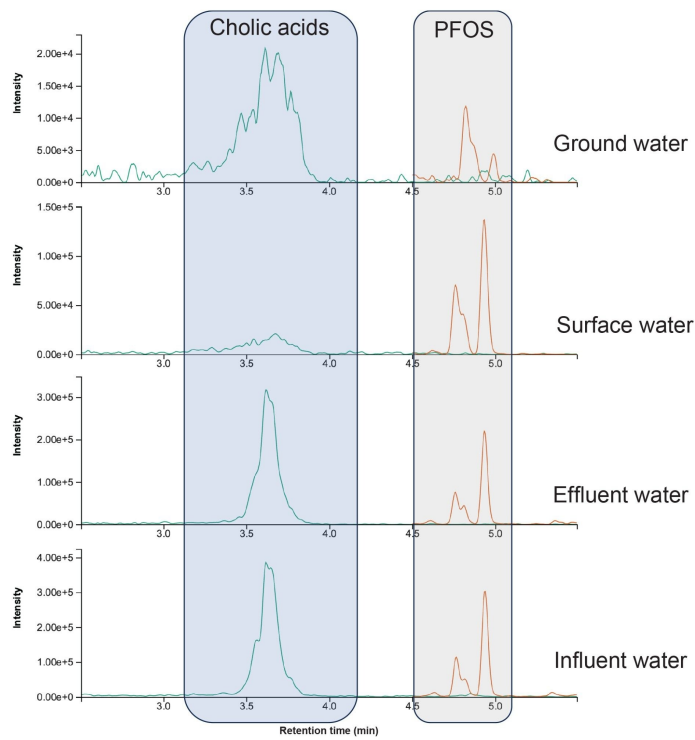
Figure 4. Overlay chromatograms of cholic acids and PFOS MRM channels demonstrating the large cholic acid interference present in wastewater samples.

Analyte name	Ground water Concentration (ng/L)	%RSD	Surface water Concentration (ng/L)	%RSD	Influent wastewater Concentration (ng/L)	%RSD	Effluent wastewater Concentration (ng/L)	%RSD
PFBA	7.03	3.0	15.36	8.4	21.93	18.3	21.15	7.7
PFPeA	2.47	2.5	4.30	3.7	11.55	15.5	12.12	3.7
PFHxA	1.67	3.0	3.53	2.7	15.98	17.4	23.81	1.7
PFHpA	1.01	8.0	2.12	5.9	3.33	13.4	3.33	1.6
PFOA	0.69	10.0	4.86	6.7	27.02	14.5	14.89	8.5
PFNA	N.D.	–	0.77	15.0	0.91	11.4	1.28	20.2
PFDA	N.D.	–	0.51	32.1	0.95	4.6	2.44	20.7
PFUnDA	N.D.	–	N.D.	–	N.D.	–	N.D.	–
PFDoDA	N.D.	–	N.D.	–	BLoQ	–	N.D.	–
PFTriDA	N.D.	–	N.D.	–	N.D.	–	N.D.	–
PFTreDA	N.D.	–	N.D.	–	N.D.	–	N.D.	–
PFBS	1.05	7.1	2.83	6.0	41.12	12.6	38.16	3.9
PFPeS	0.11	8.7	0.17	11.8	0.39	23.7	0.34	6.2
PFHxS	0.26	10.3	0.86	5.6	4.72	17.7	4.07	3.5
PFHpS	N.D.	–	N.D.	–	N.D.	–	BLoQ	–
PFOS	0.34	16.4	3.40	22.4	8.17	9.4	6.17	19.9
PFNS	N.D.	–	N.D.	–	N.D.	–	N.D.	–
PFDS	N.D.	–	N.D.	–	N.D.	–	N.D.	–
PFDoDS	N.D.	–	N.D.	–	N.D.	–	N.D.	–
GenX	N.D.	–	0.12	8.8	0.65	15.2	0.59	5.4
ADONA	N.D.	–	N.D.	–	N.D.	–	N.D.	–
9ClPF3ONS	N.D.	–	N.D.	–	N.D.	–	N.D.	–
11ClPF3OUdS	N.D.	–	N.D.	–	N.D.	–	N.D.	–
4_2 FTS	N.D.	–	N.D.	–	N.D.	–	N.D.	–
6_2 FTS	N.D.	–	N.D.	–	4.44	16.2	2.91	18.9
8_2 FTS	N.D.	–	N.D.	–	N.D.	–	N.D.	–
FOSA	BLoQ	–	BLoQ	–	BLoQ	–	BLoQ	–
NMeFOSA	N.D.	–	N.D.	–	N.D.	–	N.D.	–
NEtFOSA	N.D.	–	N.D.	–	N.D.	–	N.D.	–
NMeFOSAA	N.D.	–	N.D.	–	1.16	10.7	1.26	28.1
NEtFOSAA	N.D.	–	N.D.	–	0.90	14.6	0.90	27.6
NMeFOSE	N.D.	–	N.D.	–	2.96	9.8	BLoQ	–
NEtFOSE	N.D.	–	N.D.	–	N.D.	–	N.D.	–
3:3 FTCA	N.D.	–	N.D.	–	4.91	21.4	N.D.	–
5:3 FTCA	N.D.	–	N.D.	–	88.91	18.4	3.91	4.3
7:3 FTCA	N.D.	–	N.D.	–	4.66	16.8	N.D.	–
PFMPA	N.D.	–	N.D.	–	N.D.	–	N.D.	–
PFMBA	N.D.	–	N.D.	–	N.D.	–	N.D.	–
PFEESA	N.D.	–	N.D.	–	N.D.	–	N.D.	–
NFDHA	N.D.	–	N.D.	–	N.D.	–	N.D.	–

Table 2. Detected concentrations of PFAS in each type of water sample and associated %RSD of n=5 replicates. (N.D.) not detected. (BLoQ) below limit of quantitation.
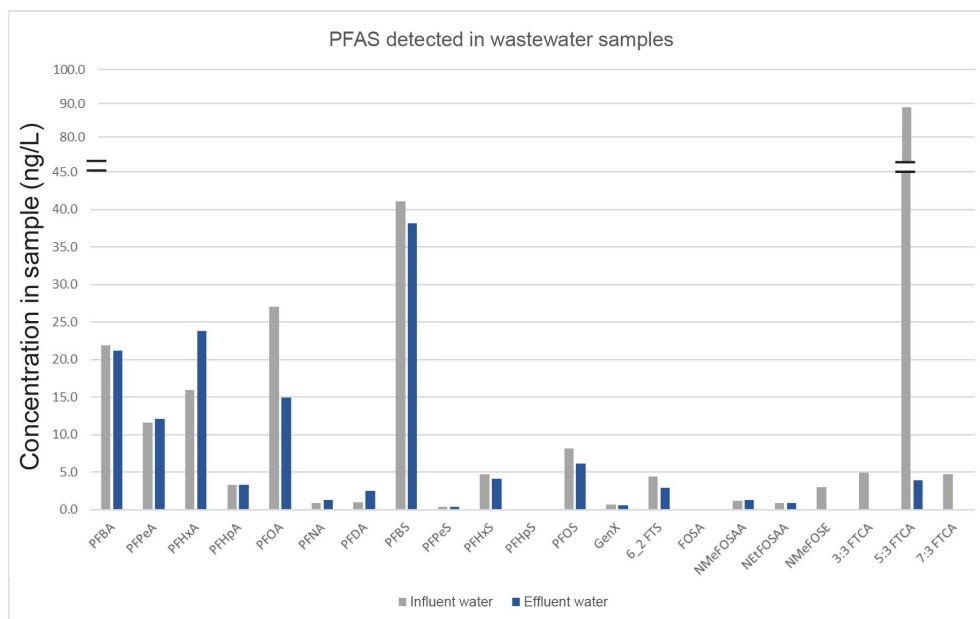
Figure 5. Comparison of the quantified PFAS in influent wastewater (gray) and effluent wastewater (blue). Note the split axis to accommodate the maximum concentration value for 5:3 FTCA.

Conclusion

Sample preparation and analysis was performed for several water samples using EPA 1633 procedures. A prototype bilayer dual-phase SPE cartridge containing both WAX and GCB was utilized for the sample extraction and clean up in place of performing the extraction and clean up in two separate steps with dispersive GCB. This cartridge provides a better user experience and reduces time spent in the sample preparation step. All recoveries were within the acceptance criteria ranges with the mean EIS recovery of 20 extractions (including ground water, surface water, influent water, and effluent water) at 91.2%, with a mean RSD of 9.2%. This demonstrates the equivalence of the bilayer dual-phase SPE cartridge as a suitable single step replacement for the multi-step extraction and clean up presented in EPA 1633. Additionally, a Waters ERA wastewater certified reference material processed and analyzed using the same method was easily within the certified reference value range, giving high confidence in method accuracy. Four types of water samples, varying in complexity, were analyzed

for the 40 PFAS included in EPA 1633 and PFAS were detected in all samples ranging from 0.1 to 88.9 ng/L. The data presented demonstrates that the bilayer dual-phase SPE cartridge in combination with the LC-MS/MS system easily fulfills all requirements for analysis of water samples for EPA 1633.

References

1. US Environmental Protection Agency. Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS, Draft 4. July 2023.

2. US Environmental Protection Agency. Clean Water Act Analytical Methods: CWA Analytical Methods for Per- and Polyfluorinated Alkyl Substances (PFAS). https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas#draft-method-1633 <https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas#draft-method-1633> , Accessed 17 November 2023.

3. K Organtini, K Rosnack, P Hancock. Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Accordance with EPA 1633 Part 1: Establishing and Assessing the Method. Waters Application Note. 720008117. 2023.

Appendix

Compound	Parent	Fragment	CV	CE	Soft transmission	Internal standard	Type of internal standard
PFBA	213.0	169	10	10	No	$^{13}C_3$-PFBA	–
PFPeA	262.9	219	10	5	No	$^{13}C_5$-PFPeA	–
PFHxA	312.9	269	5	10	No	$^{13}C_5$-PFHxA	–
		119	5	20			
PFHpA	362.9	319	15	10	No	$^{13}C_4$-PFHpA	–
		169	15	15			
PFOA	412.9	369	10	10	No	$^{13}C_8$-PFOA	–
		169	10	15			
PFNA	462.9	419	10	10	No	$^{13}C_9$-PFNA	–
		219	10	15			
PFDA	512.9	468.9	15	9	No	$^{13}C_6$-PFDA	–
		219	15	15			
PFUnDA	562.9	518.9	25	10	No	$^{13}C_7$-PFUnDA	–
		269	25	20			
PFDoDA	612.9	568.9	30	10	No	^{13}C-PFDoDA	–
		169	30	25			
PFTriDA	662.9	618.9	5	10	No	^{13}C-PFDoDA + $^{13}C_2$-PFTreDA	–
		169	5	30			
PFTreDA	712.9	668.9	10	25	No	$^{13}C_2$-PFTreDA	–
		169	10	15			
PFBS	298.9	80.1	15	30	No	$^{13}C_3$-PFBS	–
		99.1	15	30			
PFPeS	348.9	79.9	10	30	No	$^{13}C_3$-PFHxS	–
		98.9	10	30			
PFHxS	398.9	80.1	10	35	No	$^{13}C_3$-PFHxS	–
		99.1	10	30			
PFHpS	448.9	80.1	15	35	No	$^{13}C_8$-PFOS	–
		99.1	15	35			
PFOS	498.9	80.1	15	40	No	$^{13}C_8$-PFOS	–
		99.1	15	40			
PFNS	548.9	80.1	20	40	No	$^{13}C_8$-PFOS	–
		99.1	20	40			
PFDS	598.9	80.1	46	46	No	$^{13}C_8$-PFOS	–
		99.1	46	46			
PFDoDS	699.1	80	40	55	No	$^{13}C_8$-PFOS	–
		99	40	55			
GenX (HFPO-DA)	285.0	169	5	7	Yes	$^{13}C_3$-HFPO-DA	–
		GenX	5	35			
ADONA	376.9	251	10	10	No	$^{13}C_3$-HFPO-DA	–
		377.3	10	25			
9Cl-PF3ONS	530.9	350.9	15	25	No	$^{13}C_3$-HFPO-DA	–
		82.9	15	25			
11Cl-PF3OUdS	630.9	450.9	30	30	No	$^{13}C_3$-HFPO-DA	–
		631.2	30	30			
4:2 FTS	326.9	306.9	15	15	No	$^{13}C_2$-4:2 FTS	–
		327.3	15	35			
6:2 FTS	426.9	407	10	20	No	$^{13}C_2$-6:2 FTS	–
		427.3	12	32			
8:2 FTS	526.9	506.8	15	25	No	$^{13}C_2$-8:2 FTS	–
		527.3	15	37			
FOSA	497.9	78	40	30	No	$^{13}C_8$-FOSA	–
N-MeFOSA	511.9	168.9	40	30	No	d_3NMeFOSA	–
		218.9	40	25			
N-EtFOSA	525.9	168.9	5	25	No	d_5NEtFOSA	–
		218.9	5	25			
N-MeFOSAA	569.9	418.9	35	25	No	d_3-N-MeFOSAA	–
		219.1	35	20			
N-EtFOSAA	584.0	418.9	15	20	No	d_5-N-EtFOSAA	–
		525.9	15	20			
N-MeFOSE	616.0	59	15	15	No	d_7-NMeFOSE	–
N-EtFOSE	630.0	59	15	15	No	d_9-NEtFOSE	–

Compound	Parent	Fragment	CV	CE	Soft transmission	Internal standard	Type of internal standard
3:3 FTCA	241.0	116.9	5	40	No	$^{13}C_5$-PFPeA	–
		176.9	5	10			
5:3 FTCA	340.9	216.9	5	25	No	$^{13}C_6$-PFHxA	–
		237	5	10			
7:3 FTCA	440.9	316.9	10	22	No	$^{13}C_5$-PFHxA	–
		337	10	17			
PFMPA	228.9	84.9	23	10	No	$^{13}C_5$-PFPeA	
PFMBA	278.9	84.9	10	10	No	$^{13}C_6$-PFHxA	
PFEESA	314.9	82.9	15	20	No	$^{13}C_5$-PFHxA	–
		134.9	15	20			
NFDHA	295.0	84.9	5	10	No	$^{13}C_5$-PFHxA	–
		200.9	5	10			
$^{13}C_4$-PFBA	216.8	171.9	10	10	No	$^{13}C_3$-PFBA	Extracted IS
$^{13}C_5$-PFPeA	267.9	223	10	5	No	$^{13}C_2$-PFHxA	Extracted IS
$^{13}C_5$-PFHxA	317.9	272.9	10	5	No	$^{13}C_2$-PFHxA	Extracted IS
		119.9	10	20			
$^{13}C_4$-PFHpA	366.9	321.9	15	10	No	$^{13}C_2$-PFHxA	Extracted IS
		169	15	15			
$^{13}C_8$-PFOA	420.9	375.9	5	15	No	$^{13}C_4$-PFOA	Extracted IS
		172	5	10			
$^{13}C_9$-PFNA	471.9	426.9	10	10	No	$^{13}C_5$-PFNA	Extracted IS
		223	10	15			
$^{13}C_6$-PFDA	519	473.9	5	10	No	$^{13}C_2$-PFDA	Extracted IS
		219	5	15			
$^{13}C_7$-PFUnDA	569.9	524.9	5	10	No	$^{13}C_2$-PFDA	Extracted IS
		274	5	15			
^{13}C-PFDoDA	614.9	569.9	10	10	No	$^{13}C_2$-PFDA	Extracted IS
		169	10	25			
$^{13}C_2$-PFTreDA	714.9	169	25	35	No	$^{13}C_2$-PFDA	Extracted IS
		669.9	25	10			
$^{13}C_3$-PFBS	301.9	80.1	10	30	No	18O2-PFHxS	Extracted IS
		99.1	10	25			
$^{13}C_3$-PFHxS	401.9	80.1	10	40	No	18O2-PFHxS	Extracted IS
		99.1	10	35			
$^{13}C_8$-PFOS	506.9	80.1	15	40	No	$^{13}C_4$-PFOS	Extracted IS
		99.1	15	40			
$^{13}C_3$-GenX	287	169	5	12	Yes	$^{13}C_2$-PFHxA	Extracted IS
		119	5	12			
$^{13}C_2$-4:2 FTS	328.9	308.9	40	15	No	18O2-PFHxS	Extracted IS
		81	40	25			
$^{13}C_2$-6:2 FTS	428.9	409	10	20	No	18O2-PFHxS	Extracted IS
		80.9	10	27			
$^{13}C_2$-8:2 FTS	528.9	508.9	10	20	No	18O2-PFHxS	Extracted IS
		81	10	35			
$^{13}C_8$-FOSA	505.9	78.1	35	25	No	$^{13}C_4$-PFOS	Extracted IS
d_3NMeFOSA	514.9	168.9	40	30	No	$^{13}C_4$-PFOS	Extracted IS
d_5NEtFOSA	531	168.9	5	25	No	$^{13}C_4$-PFOS	Extracted IS
D_5-N-EtFOSAA	589	418.9	30	20	No	$^{13}C_4$-PFOS	Extracted IS
		506.9	30	15			
D_3-N-MeFOSAA	572.9	418.9	35	20	No	$^{13}C_4$-PFOS	Extracted IS
		482.7	35	15			
d7-NMeFOSE	623	58.9	15	15	No	$^{13}C_4$-PFOS	Extracted IS
d9-NEtFOSE	639	58.9	15	15	No	$^{13}C_4$-PFOS	Extracted IS
$^{13}C_3$-PFBA	216	172	10	10	No	–	Non-extracted IS
$^{13}C_2$-PFHxA	314.9	119.9	10	20	No	–	Non-extracted IS
		270	10	5			
$^{13}C_4$-PFOA	417	172	10	20	No	–	Non-extracted IS
$^{13}C_5$-PFNA	468	423	10	10	No	–	Non-extracted IS
$^{13}C_2$-PFDA	515	470	20	10	No	–	Non-extracted IS
$^{18}O_2$-PFHxS	403	83.9	10	40	No	–	Non-extracted IS
$^{13}C_4$-PFOS	503	80.2	15	40	No	–	Non-extracted IS
		99.1	15	40			

Appendix Table 1. MS Method conditions used for PFAS analysis of EPA 1633 compounds in water samples on the

Xevo TQ Absolute MS.

Compound	Cal 1 (ng/mL)	Cal 2 (ng/mL)	Cal 3 (ng/mL)	Cal 4 (ng/mL)	Cal 5 (ng/mL)	Cal 6 (ng/mL)	Cal 7 (ng/mL)	Cal 8 (ng/mL)
PFBA	0.02	0.04	0.20	0.40	1.00	2.00	4.0	10.0
PFPeA	0.01	0.02	0.10	0.20	0.50	1.00	2.0	5.0
PFHxA	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFHpA	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFOA	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFNA	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFDA	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFUnDA	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFDoDA	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFTriDA	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFTreDA	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFBS	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFPeS	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFHxS	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFHpS	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFOS	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFNS	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFDS	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
PFDoDS	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
GenX	0.01	0.02	0.10	0.20	0.50	1.00	2.0	5.0
ADONA	0.01	0.02	0.10	0.20	0.50	1.00	2.0	5.0
9ClPF3ONS	0.01	0.02	0.10	0.20	0.50	1.00	2.0	5.0
11ClPF3OUdS	0.01	0.02	0.10	0.20	0.50	1.00	2.0	5.0
4_2 FTS	0.02	0.04	0.20	0.40	1.00	2.00	4.0	10.0
6_2 FTS	0.02	0.04	0.20	0.40	1.00	2.00	4.0	10.0
8_2 FTS	0.02	0.04	0.20	0.40	1.00	2.00	4.0	10.0
FOSA	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
NMeFOSA	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
NEtFOSA	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
NMeFOSAA	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
NEtFOSAA	0.005	0.01	0.05	0.10	0.25	0.50	1.0	2.5
NMeFOSE	0.05	0.10	0.50	1.00	2.50	5.00	10.0	25.0
NEtFOSE	0.05	0.10	0.50	1.00	2.50	5.00	10.0	25.0
3:3 FTCA	0.02	0.04	0.20	0.40	1.00	2.00	4.0	10.0
5:3 FTCA	0.10	0.20	1.00	2.00	5.00	10.0	20.0	50.0
7:3 FTCA	0.10	0.20	1.00	2.00	5.00	10.0	20.0	50.0
PFMPA	0.01	0.02	0.10	0.20	0.50	1.00	2.0	5.0
PFMBA	0.01	0.02	0.10	0.20	0.50	1.00	2.0	5.0
PFEESA	0.01	0.02	0.10	0.20	0.50	1.00	2.0	5.0
NFDHA	0.01	0.02	0.10	0.20	0.50	1.00	2.0	5.0
M4 PFBA	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
M5_PFPeA	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
M5_PFHxA	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
M4_PFHpA	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
M8_PFOA	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
M9_PFNA	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
M6_PFDA	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
M7_PFUnDA	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
M_PFDoDA	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
M2_PFTreDA	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
M3_PFBS	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
M3_PFHxS	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
M8_PFOS	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
M2_42FTS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
M2_62FTS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
M2_82FTS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
M8_FOSA	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
M3_GenX	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
D3_NMeFOSAA	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
D5_NEtFOSAA	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
dNMeFOSA	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
dNEtFOSA	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d7 NMeFOSE	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
d9 NEtFOSE	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
M3 PFBA_NIS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
M2 PFHxA_NIS	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
M4 PFOA_NIS	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
M5 PFNA_NIS	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
M2 PFDA_NIS	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
18O2 PFHxS_NIS	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
M4 PFOS_NIS	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50

Appendix Table 2. Calibration curve range used for PFAS analysis of EPA 1633 compounds in water samples on

the Xevo TQ Absolute MS

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720008143, December 2023

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