

Analysis of Per- and Polyfluoroalkyl Substances in Wastewater Using EPA Method 1633 with Improved Automated Solid Phase Extraction - Turbo Trace PFC

Application Note

Per- and polyfluoroalkyl substances (PFAS) constitute a group of compounds characterized by perfluorinated or polyfluorinated carbon chain moieties, typically denoted by structures such as $F(CF_2)_n$ or $F(CF_2)_n-(C_2H_4)_n$. Due to their unique properties, these substances have found extensive application in various industrial and consumer products.

Many industrial and consumer applications utilize perfluorooctane sulfonate (PFOS) and other PFAS compounds. These include but are not limited to, stain-resistant coatings for textiles, leather, and carpets; grease-proof coatings for food-contact paper products; firefighting foams; surfactants for mining and oil-well operations; floor polishes; and insecticide formulations. Their widespread usage has led to their ubiquitous presence in the environment.

In recent years, mounting concerns have emerged regarding the widespread distribution and potential adverse effects of PFAS, particularly notable compounds like PFOS and perfluorooctanoic acid (PFOA). These concerns have prompted intensified scrutiny of these substances' environmental occurrence, fate, and potential impacts.

Recent developments in the United States have led to the introduction of EPA method 1633, which addresses the need for robust methodologies to monitor and analyze PFAS. This method, unveiled in early 2024, enables comprehensive analysis across various matrices, including wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue. EPA Method 1633 represents a significant advancement in the analytical toolkit for assessing PFAS contamination and understanding their distribution and behavior in diverse environmental compartments.

Instrumentation

- FMS Turbo Trace PFC™ System The system is modular in nature and can be extended to a total of 4 modules for a total of 8 samples processed in parallel.
- Vacuum pump
- Agilent 6475 TripleQuad LC/MS

Consumables

- Agilent Bond Elut PFAS WAX 150mg cartridges (# 5610-2150)
- Ultrapure DI water
- Methanol pesticide grade
- Ammonium hydroxide

- Formic acid
- Relevant PFAS spiking standards

Method

- Eight synthetic wastewater samples (500 mL) spiked with native PFAS standards and relevant internals
- Load sample bottles onto system and install cartridges
- Rinse bottles are automatically filled during procedure
- Use positive pressure (nitrogen) for pumping solvents and mixes through the system and use vacuum to load the samples
- Condition cartridges with 15 mL 1% methanolic ammonium hydroxide followed by 5 mL of 0.3M formic acid.
- Load samples across the cartridges at 5-10 mL/min (vacuum ~ 8-inch Hg)
- Sample bottles rinsed with 5 mL reagent water (twice) followed by 5 mL of 1:1 0.1M formic acid/methanol and load rinses across the cartridges
- Dry 10 min
- Rinse sample bottles with 5 mL 1% methanolic ammonium hydroxide
- Load rinses across cartridges and collect in polypropylene tubes
- Cleanup over 10 mg of loose carbon
- As per the method no further concentration is carried out.
- Further relevant standards were added prior to LC/MS analysis.



Analysis

- Take aliquot from final 5 mL extract (Method 1633 does not require volume reduction of final extract)
- Agilent 1290 Infinity II LC System
- Agilent 6475 Triple quad LC/MS
- Agilent Zorbax Eclipse Plus C18 column 3.0 x 50 mm, 1.8 μ m
- Column temperature 40 °C
- Injection 5.0 μ L
- Mobile phase 5 mM ammonium acetate in 95% water, 5% acetonitrile (A) and methanol (B)
- Gradient
 - 0 min 98% A 2% B
 - 0.2 min 98% A 2% B
 - 10 min 5% a 95% B
- Stop time 12.2 min
- Dynamic MRM negative electrospray
- T (gas) = 230 °C
- T (sheath) = 355 °C



Turbo Trace PFC System



Compound Name	ECONO-SPE-IDC-1 Final Conc.	ECONO-SPE-IDC-2 Final Conc.	ECONO-SPE-IDC-3 Final Conc.	ECONO-SPE-IDC-4 Final Conc.	Window	RSD(%)
11Cl-PF3OUds	87.1	89.2	82.3	88.9	50-150	3.7
3-3 FTCA	98.1	98.6	85.9	91.2	70-130	6.5
4-2 FTS	90.3	93.6	94.1	91.3	70-135	2.0
5-3 FTCA	99.6	105.2	92.6	95.2	70-130	5.6
6-2 FTS	95.0	104.4	90.0	97.4	70-135	6.2
7-3 FTCA	101.0	102.5	89.1	88.5	55-130	7.9
8-2 FTS	100.2	104.3	87.6	95.2	70-140	7.4
9Cl-PF3ONS	95.2	105.0	93.2	99.5	70-145	5.3
ADONA	96.4	101.4	91.0	95.0	70-135	4.5
EtFOSE	85.1	87.2	86.9	87.4	70-130	1.2
HFPO-DA	106.4	100.1	83.9	96.8	70-135	9.8
MeFOSE	84.7	86.9	89.5	84.8	70-135	2.6
N-EtFOSA	100.3	99.2	102.8	97.2	70-135	2.4
N-EtFOSAA	80.0	87.1	96.0	90.1	70-135	7.6
NFDHA	103.3	103.8	92.9	99.0	65-140	5.0
N-MeFOSA	91.1	112.2	97.7	85.5	70-135	11.9
N-MeFOSAA	91.0	82.2	86.0	94.6	65-140	6.2
PFBA	98.9	99.1	92.9	96.6	70-135	3.0
PFBS	90.2	100.5	90.8	91.4	70-140	5.2
PFDA	90.4	101.5	94.1	88.8	65-140	6.0
PFDoA	80.5	90.3	86.4	91.0	70-130	5.5
PFDoS	80.3	83.7	87.0	92.5	45-135	6.1
PFDS	83.2	93.8	84.4	86.0	70-135	5.5
PFEESA	102.2	105.7	91.9	97.2	70-135	6.1
PFHpA	95.6	105.2	89.8	91.4	70-135	7.3
PFHpS	111.3	104.6	101.5	94.2	70-140	6.9
PFHxA	105.0	106.6	94.7	97.4	70-135	5.7
PFHxS	91.7	89.5	91.7	89.1	70-135	1.6
PFMBA	96.9	100.6	91.6	95.4	65-145	3.9
PFMPA	97.9	102.4	91.8	96.1	60-140	4.5
PFNA	100.6	107.0	93.3	93.9	70-140	6.5
PFNS	96.1	105.2	101.9	87.0	70-135	8.2
PFOA	90.2	102.4	89.9	89.9	65-155	6.6
PFOS	90.9	90.3	91.6	86.2	70-140	2.7
PFOSA	84.8	96.9	83.0	86.8	70-135	7.1
PFPeA	99.0	102.4	94.8	97.6	70-135	3.2
PFPeS	87.3	97.6	96.6	97.7	70-135	5.3
PFTDA	88.6	89.2	90.3	82.5	70-145	4.0
PFTTrDA	83.2	89.0	81.1	93.0	60-145	6.3
PFUnA	94.5	107.7	95.8	86.1	70-135	7.2

Table 1. Recoveries (%) and RSDs (%) for 40 native PFAS in synthetic wastewater (1633) using Turbo Trace PFC (spiked with 1-38 ng/L).



Compound		ECONO-SPE-IDC-1	ECONO-SPE-IDC-2	ECONO-SPE-IDC-3	ECONO-SPE-IDC-4	
Name	Percent	% Recoveries	% Recoveries	% Recoveries	% Recoveries	Window
13C2-4-2 FTSA		104.2	105.1	92.3	93.7	40-200
13C2-6-2 FTS		105.1	96.7	101.1	97.7	40-200
13C2-8-2 FTSA		93.7	94.8	91.5	90.2	40-300
13C2-PFDoDA		111.6	98.3	99.8	104.2	10-130
13C2-PFTDA		104.8	101.3	100.0	94.9	10-130
13C3-HFPO-DA		95.4	93.8	96.6	91.8	40-130
13C3-PFBS		101.3	96.5	93.4	91.7	40-135
13C3-PFHxS		110.2	108.9	100.8	101.6	40-130
13C4-PFBA		94.1	90.3	96.7	94.3	5-130
13C4-PFHpA		94.8	94.9	99.6	93.9	40-130
13C5-PFHxA		93.3	96.5	97.7	92.0	40-130
13C5-PFPeA		95.7	97.4	97.6	93.7	40-130
13C6-PFDA		109.1	97.1	97.5	111.9	40-130
13C7-PFUnA		95.7	88.5	86.5	103.1	30-130
13C8-PFOA		88.8	87.7	90.1	90.8	50-200
13C8-PFOS		82.3	85.3	84.3	100.5	50-200
13C8-PFOSA		90.1	94.6	88.2	96.0	40-130
13C9-PFNA		87.9	86.1	87.3	87.3	40-130
2H3-N-MeFOSAA		88.0	91.5	85.0	95.5	10-130
2H3-N-MeFOSAA		89.3	90.3	85.2	91.3	40-170
2H5-N-EtFOSA		96.0	97.0	89.5	80.5	10-130
2H5-N-EtFOSAA		89.3	84.5	83.9	98.1	25-135
2H7-MeFOSE		80.0	88.4	80.5	81.8	10-130
2H9-EtFOSE		83.2	87.5	83.8	81.1	10-130

Table 2. Recoveries (%) and acceptance windows (%) for 24 surrogate PFAS in synthetic wastewater (1633) using Turbo Trace PFC.

Compound	ECONO-MDL-1	ECONO-MDL-2	ECONO-MDL-3	ECONO-MDL-4	ECONO-MDL-5	ECONO-MDL-6	ECONO-MDL-7	STDEV	MDL
Name In ng/L	Final Conc.	Final Conc.	Final Conc.	Final Conc.	Final Conc.	Final Conc.	Final Conc.		
11Cl-PF3OUdS	0.35	0.36	0.41	0.43	0.43	0.37	0.45	0.04	0.13
3-3 FTCA	0.76	0.87	1.07	0.84	0.86	0.87	1.10	0.13	0.40
4-2 FTS	2.21	2.16	2.40	2.14	1.99	2.33	2.31	0.14	0.44
5-3 FTCA	4.73	5.04	4.36	4.34	4.85	4.76	5.99	0.56	1.75
6-2 FTS	1.07	1.07	1.41	1.39	1.24	1.44	1.29	0.16	0.49
7-3 FTCA	3.29	3.28	4.07	3.09	3.46	3.39	4.72	0.58	1.81
8-2 FTS	1.86	1.72	1.91	2.01	2.04	1.94	2.98	0.42	1.31
9Cl-PF3ONS	0.53	0.60	0.65	0.61	0.67	0.59	0.74	0.07	0.21
ADONA	0.70	0.69	0.78	0.73	0.74	0.72	1.08	0.14	0.42
EtFOSE	6.34	6.29	6.58	5.77	5.24	5.40	5.88	0.50	1.58
HFPO-DA	0.95	1.06	1.15	0.96	1.15	0.87	1.04	0.11	0.33
MeFOSE	5.40	5.55	5.57	4.85	5.10	4.83	4.77	0.35	1.11
N-EtFOSA	0.53	0.47	0.54	0.45	0.53	0.57	0.47	0.05	0.15
N-EtFOSAA	0.26	0.27	0.33	0.32	0.28	0.23	0.37	0.05	0.15
NFDHA	0.40	0.40	0.48	0.36	0.45	0.43	0.61	0.08	0.26
N-MeFOSAA	0.52	0.56	0.52	0.56	0.47	0.45	0.45	0.05	0.15
N-MeFOSAA	0.24	0.28	0.25	0.24	0.23	0.17	0.22	0.03	0.10
PFBA	0.81	0.86	0.87	0.82	0.88	0.88	1.26	0.16	0.49
PFBS	0.22	0.24	0.28	0.24	0.28	0.24	0.32	0.03	0.11
PFDA	0.19	0.24	0.26	0.17	0.22	0.24	0.30	0.04	0.13
PFDoA	0.31	0.38	0.44	0.43	0.31	0.33	0.46	0.06	0.20
PFDoS	0.18	0.19	0.18	0.18	0.19	0.18	0.23	0.02	0.06
PFDS	0.16	0.20	0.26	0.16	0.23	0.23	0.28	0.05	0.15
PFEEESA	0.43	0.45	0.55	0.48	0.48	0.43	0.62	0.07	0.22
PFHpA	0.21	0.21	0.25	0.21	0.24	0.24	0.31	0.04	0.11
PFHpS	0.19	0.27	0.29	0.22	0.25	0.26	0.24	0.03	0.10
PFHxA	0.21	0.22	0.25	0.20	0.24	0.20	0.34	0.05	0.16
PFHxS	0.20	0.20	0.28	0.27	0.22	0.22	0.31	0.04	0.14
PFMBA	0.30	0.31	0.38	0.31	0.33	0.34	0.50	0.07	0.22
PFMPA	0.29	0.31	0.33	0.31	0.34	0.33	0.48	0.07	0.20
PFNA	0.22	0.20	0.30	0.24	0.20	0.22	0.29	0.04	0.13
PFNS	0.18	0.16	0.23	0.18	0.19	0.18	0.17	0.02	0.07
PFOA	0.18	0.18	0.25	0.19	0.23	0.27	0.26	0.04	0.13
PFOS	0.21	0.25	0.24	0.25	0.28	0.26	0.34	0.04	0.13
PFOSA	0.34	0.37	0.36	0.32	0.36	0.33	0.47	0.05	0.16
PFPeA	0.39	0.40	0.45	0.39	0.42	0.42	0.47	0.03	0.10
PFPeS	0.22	0.21	0.28	0.19	0.24	0.18	0.31	0.05	0.14
PFTDA	0.51	0.60	0.39	0.52	0.48	0.41	0.39	0.08	0.25
PFTTrDA	0.57	0.53	0.52	0.44	0.39	0.43	0.40	0.07	0.22
PFUnA	0.24	0.25	0.29	0.26	0.23	0.26	0.32	0.03	0.11

Table 3. Method Detection Limit values for 40 native PFAS in synthetic wastewater (1633) using Turbo Trace PFC (spiked with 0.2-6 ng/L).



Native PFAS background Turbo Trace PFC (ng/L)

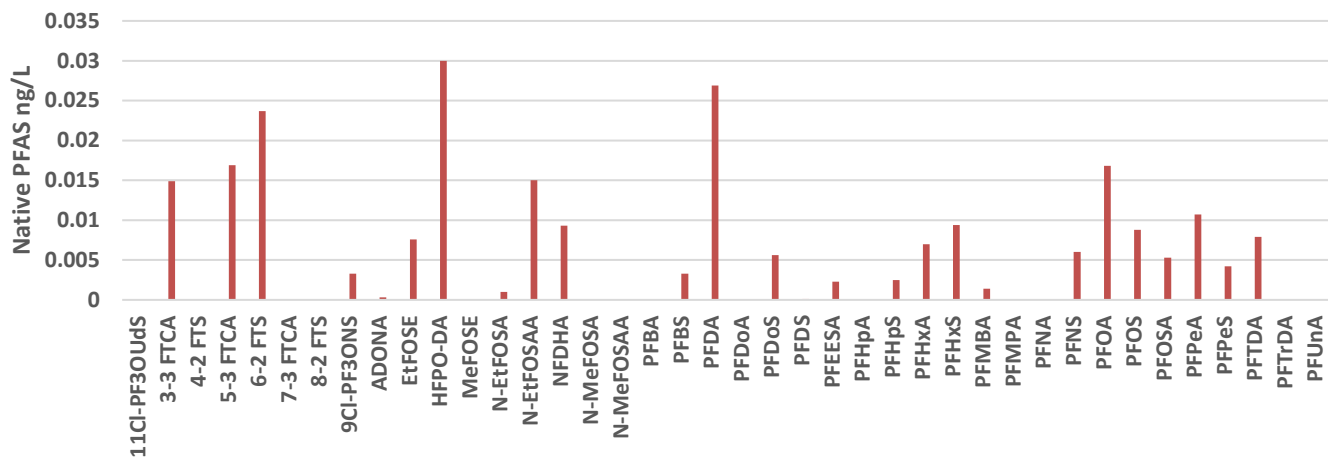


Table 4. Native PFAS background with Turbo Trace PFC for method 1633 (in ng/L).

Compound Name	Sample-Lake-1 Final Conc.	Sample-Lake-2 Final Conc.	Sample-Lake-3 Final Conc.	Sample-Well-1 Final Conc.	Sample-Well-2 Final Conc.	Sample-Well-3 Final Conc.	Sample-tap-water-1 Final Conc.	Sample-tap-water-2 Final Conc.	Sample-tap-water-3 Final Conc.
11Cl-PF3OUds	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-3 FTCA	0.01	0.02	0.02	0.01	0.01	0.02	0.00	0.02	0.00
4-2 FTS	0.00	0.00	0.00	0.06	0.09	0.06	0.00	0.00	0.00
5-3 FTCA	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.03
6-2 FTS	0.04	0.02	0.04	0.01	0.01	0.04	0.06	0.05	0.07
7-3 FTCA	0.04	0.09	0.05	0.03	0.00	0.00	0.00	0.00	0.00
8-2 FTS	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00
9Cl-PF3ONS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ADONA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
EtFOSE	0.11	0.07	0.09	0.15	0.17	0.10	0.00	0.00	0.00
HFPO-DA	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.11	0.05
MeFOSE	0.07	0.02	0.09	0.14	0.07	0.09	0.00	0.00	0.00
N-EtFOSA	0.01	0.00	0.02	0.00	0.00	0.00	0.01	0.02	0.00
N-EtFOSAA	0.00	0.00	0.00	0.03	0.02	0.00	0.02	0.00	0.00
NFDHA	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.00	0.01
N-MeFOSA	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.00
N-MeFOSAA	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
PFBA	0.23	0.32	0.39	1.50	1.59	1.79	0.54	0.65	0.65
PFBS	0.11	0.09	0.14	1.69	1.86	1.69	0.60	0.53	0.55
PFDA	0.03	0.02	0.04	0.05	0.06	0.04	0.00	0.00	0.00
PFDoA	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00
PFDoS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFDS	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
PFEESA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFHpA	0.15	0.15	0.19	0.79	0.91	0.81	0.41	0.36	0.40
PFHpS	0.00	0.00	0.00	0.04	0.03	0.04	0.03	0.03	0.01
PFHxA	0.17	0.19	0.16	2.01	1.95	2.10	0.67	0.71	0.76
PFHxS	0.08	0.10	0.03	0.96	1.02	1.12	0.21	0.25	0.25
PFMBA	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.01	0.00
PFMPA	0.00	0.02	0.01	0.00	0.01	0.01	0.00	0.01	0.01
PFNA	0.07	0.08	0.20	0.15	0.09	0.09	0.25	0.10	0.20
PFNS	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
PFOA	0.40	0.47	0.49	3.08	3.07	3.30	0.72	0.54	0.79
PFOS	0.17	0.14	0.15	0.55	0.37	0.52	0.45	0.31	0.31
PFOSA	0.01	0.01	0.01	0.00	0.00	0.00	0.02	0.01	0.00
PFPeA	0.12	0.19	0.65	1.58	1.73	1.94	0.66	0.72	0.73
PPFes	0.00	0.00	0.01	0.10	0.13	0.08	0.06	0.05	0.06
PFTDA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFTTrDA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFUnA	0.03	0.05	0.04	0.02	0.02	0.02	0.00	0.00	0.00

Table 5. Native PFAS with Turbo Trace PFC for method 1633 in lake, well, and tap water (in ng/L).



Discussion and Conclusions

40 native PFAS compounds were analyzed using EPA method 1633 (Table 1) with the Turbo Trace PFC and synthetic wastewater. All recoveries were within the acceptance windows of the method with RSDs (%) all < 12%. Run time of the automated system is 70 min. Note that with method 1633 no final concentration step is required. The Turbo Trace PFC produces very good recoveries with low standard deviations.

Surrogate PFAS recoveries (%) and acceptance windows (%) are shown in Table 2. Excellent data were obtained all well within those windows.

Table 3 shows the method detection limits for all 40 native PFAS using synthetic wastewater. Most MDL values are < 0.50 ng/L.

Note that the system has low, non-detect, native background values for PFAS and that the risk of cross-contamination is low (Table 4). Values are < 0.03 ng/L.

Table 5 shows analysis of three different water categories: lake water, well water and tap water. Good reproducibility is seen between the replicates.

The Turbo Trace PFC system produces data that is as good as other more expensive fully automated SPE systems. The system is easy to operate and has fewer valves reducing chance of breakdown and contamination. Cleaning the system between runs is quick and easy.

An important problem with ground and wastewater extraction is the presence of particulate matter which can easily plug up cartridges. Using a vacuum pump to deliver the sample through a minimal pathway to the cartridge prevents clogging. Use of plastic filtration wool in the barrel of the cartridges can eliminate this problem. In this work no clogging of cartridges was observed.

For more information, contact FMS:
FMS Inc.
900 Technology Park Drive
Billerica MA 01821
Phone: (617) 393-2396
Fax: (617) 393-0194
Email: onlineinfo@fms-inc.com

Web site: www.fms-inc.com