

Application News

Simultaneous Analysis of 40 PFAS Components in Drinking Water Using a Triple Quadrupole LC/MS/MS

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User Benefits

- ◆ Enables analysis of 40 PFAS components within 20 minutes and simultaneous analysis of multiple components without sensitivity loss.
- ◆ Enables quantitative analysis of concentrations as low as 0.2 ng/L (in water samples) for PFOA, PFOS, PFHxS, and others.
- ◆ Consistent and accurate results can be obtained with good recovery rates and reproducibility data for recovery tests.

Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) offer broad versatility for a wide range of applications. Due to their structural stability and resistance to decomposition, they easily accumulate in the environment and are suspected to be harmful for humans. Due to concerns about their environmental impacts, the U.S. Environmental Protection Agency (EPA) and the European Chemicals Agency (ECHA) have been implementing measures to strengthen PFAS-related regulations in recent years. Consequently, efforts to comply with such PFAS regulations have been increasing every year, and the list of compounds governed by such regulations continues to grow. That makes it increasingly useful to apply an analytical method that can reliably analyze all the various PFAS substances at the same time.

This article describes the results from simultaneously analyzing 40 PFAS components (Table 1) as target compounds after automatic sample preparation. Good results were obtained from measuring standard solutions and recovery tests of drinking water samples.

Table 1 List of Compounds

No.	Compound	Type	No.	Compound	Type
1	PFBA	Target	33	11Cl-PF3OUdS	Target
2	PFPeA	Target	34	3:3 FTCA	Target
3	PFHxA	Target	35	5:3 FTCA	Target
4	PFHpA	Target	36	7:3 FTCA	Target
5	PFOA	Target	37	PFEESA	Target
6	PFNA	Target	38	PFMPA	Target
7	PFDA	Target	39	PFMBA	Target
8	PFUnA	Target	40	NFDHA	Target
9	PFDoA	Target	41	13C4-PFBA	EIS
10	PFTeDA	Target	42	13C5-PFPeA	EIS
11	PFTeDA	Target	43	13C5-PFHxA	EIS
12	PFBS	Target	44	13C4-PFHpA	EIS
13	PFPeS	Target	45	13C8-PFOA	EIS
14	PFHxS	Target	46	13C9-PFNA	EIS
15	PFHpS	Target	47	13C6-PFDA	EIS
16	PFOS	Target	48	13C7-PFUnA	EIS
17	PFNS	Target	49	13C2-PFDoA	EIS
18	PFDS	Target	50	13C2-PFTeDA	EIS
19	PFDoS	Target	51	13C3-PFBS	EIS
20	4:2FTS	Target	52	13C3-PFHxS	EIS
21	6:2FTS	Target	53	13C8-PFOS	EIS
22	8:2FTS	Target	54	13C2-4:2FTS	EIS
23	PFOSA	Target	55	13C2-6:2FTS	EIS
24	NMeFOSA	Target	56	13C2-8:2FTS	EIS
25	NEtFOSA	Target	57	13C8-PFOSA	EIS
26	NMeFOSAA	Target	58	D3-NMeFOSA	EIS
27	NEtFOSAA	Target	59	D5-NEtFOSA	EIS
28	NMeFOSE	Target	60	D3-NMeFOSAA	EIS
29	NEtFOSE	Target	61	D5-NEtFOSAA	EIS
30	HFPO-DA	Target	62	D7-NMeFOSE	EIS
31	ADONA	Target	63	D9-NEtFOSE	EIS
32	9Cl-PF3ONS	Target	64	13C3-HFPO-DA	EIS

LCMS-8050RX

Samples were analyzed using a triple-quadrupole mass spectrometer, LCMS-TQ8050RX (Fig. 1). The LCMS-TQ RX series offer the same high sensitivity and high-speed performance achieved by previous models with UF technology, but they also include the new CoreSpray technology, which generates a more uniform nebulizer flow and provides more consistent measurements.



Fig. 1 LCMS-8050RX

Sample Preparation

Drinking water samples were pretreated by adding 20 µL of an internal standard solution (EIS) and then using an anion exchange solid phase column for solid phase extraction. The eluate from the solid phase column was concentrated by a factor of 1000 by drying with nitrogen gas stream and then bring the volume to 0.5 mL with methanol for analysis. The sample preparation process is shown in Fig. 2. In this case, AquaTrace automatic solid phase extraction system from GL Sciences was used to perform all steps, from conditioning to concentrating automatically.

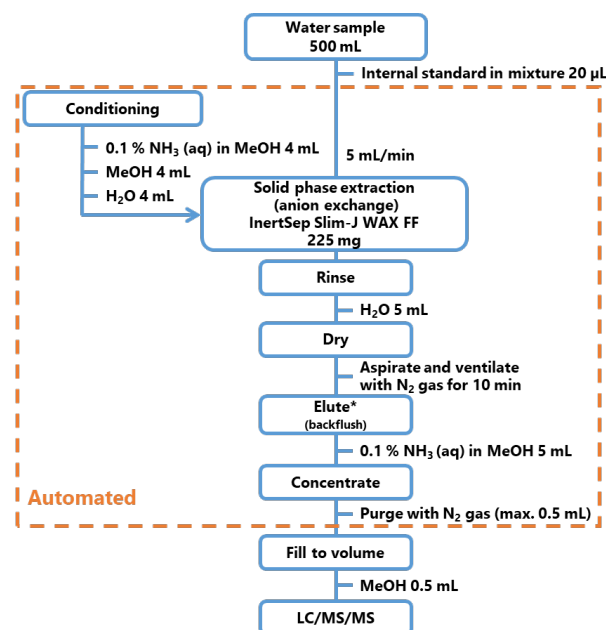


Fig. 2 Pretreatment Process Flow

(* The solid phase column was manually inverted for elution by backflushing.)

Analytical Conditions

The HPLC and MS analytical conditions are shown in Table 2. Measuring PFAS requires particular care due to the risk of contamination from the system, the mobile phase, and other sources.

For this article, a delay column was installed between the mixer and autosampler to inhibit the effects of PFAS contamination from the system. A reagent intended for PFOS/PFOA analysis was used in the mobile phase.

Table 2 Analytical Conditions

UHPLC (Nexera™-X3 System)		MS (LCMS-8050RX)	
Analytical Column:	Shim-pack™ GIST-HP C18 (50 mm × 2.1 mm I.D., 3 μm, P/N: 227-30039-02)	Ionization:	ESI (Negative mode)
Solvent Delay Column:	Shim-pack GIST C18 (50 mm × 3.0 mm I.D., 5 μm, P/N: 227-30015-03)	Mode:	MRM
Mobile Phase A:	2 mM Ammonium Acetate in 5 % (v/v) Acetonitrile in reagent water	Probe Voltage:	-1 kV
Mobile Phase B:	Acetonitrile	Nebulizing Gas:	3 L/min
Gradient Program:	B 5 % – 22 % (2.3 – 5.8 min) – 50 % (8.5 – 10.5 min) – 75 % (12.0 – 13.0 min) – 80 % (13.5 min) – 95 % (13.51 – 16.5 min) – 5 % (16.51 – 20.00 min)	Drying Gas Flow:	5 L/min
Flowrate:	0.4 mL/min	Heating Gas Flow:	15 L/min
Column Temp.:	40 °C	DL Temp.:	200 °C
Injection Volume :	2 μL	Block Heater Temp.:	300 °C
Run Time:	20 min	Interface Temp.:	190 °C
		Probe Position:	+1 mm
		MRM Transition:	Refer to Table 3

Measuring Standard Solutions

The standard solutions that were prepared with CS1 to CS7 concentrations are listed in Table 3 (The equivalent concentrations in water sample). The successive five injections were made per concentration. The MRM chromatograms for CS1 of the 40 target PFAS compounds are shown in Fig. 3, and the CS1 and CS3 area repeatability values are shown in Fig. 4. For CS1, the repeatability was less than 20 % (%RSD of area values) for 87.5 % of the compounds. For CS3, the repeatability decreased to less than 10 % (%RSD of area values) for all compounds.

In this case, calibration curve linearity was evaluated based on the accuracy (%RSD) of the response factor (RF) over the entire calibration curve, as specified in EPA Method 1633.¹⁾ RF values were calculated using Eq. 1, and the results are shown in Fig. 5. The RF accuracy (RF %RSD) values were less than 20 % for all of the 40 PFAS components, which is a good result. Furthermore, RF accuracy (RF %RSD) values were less than 10 % for 34 of the components.

$$RF = \frac{\text{Target Compound Area}}{\text{EIS Area}} \times \frac{\text{EIS Concentration Injected}}{\text{Target Compound Concentration Injected}}$$

Eq. 1 Formula for RF Calculation

Note: The area values for target compounds were calculated as the total of both linear and branched-chain compounds.

Table 3-1 Quantitation Ion, Reference Ion and Concentrations of Standard Solutions (Target)

No.	Compound	Sample Type	ISTD Group	Retention Time	Quantitation Ion m/z	Reference Ion m/z	Concentration (ng/L in water sample)						
							CS1	CS2	CS3	CS4	CS5	CS6	CS7
1	PFBA	Target	1	2.024	213.00 > 169.00	—	0.8	2	5	10	20	50	250
2	PFPeA	Target	2	3.57	263.00 > 219.00	263.00 > 69.00	0.4	1	2.5	5	10	25	125
3	PFHxA	Target	3	4.906	312.95 > 269.00	312.95 > 119.00	0.2	0.5	1.25	2.5	5	12.5	62.5
4	PFHpA	Target	4	7.708	362.95 > 319.00	362.95 > 169.00	0.2	0.5	1.25	2.5	5	12.5	62.5
5	PFOA	Target	5	8.64	412.95 > 369.00	412.95 > 169.00	0.2	0.5	1.25	2.5	5	12.5	62.5
6	PFNA	Target	6	9.119	462.95 > 418.95	462.95 > 219.00	0.2	0.5	1.25	2.5	5	12.5	62.5
7	PFDA	Target	7	9.511	512.95 > 468.95	512.95 > 219.00	0.2	0.5	1.25	2.5	5	12.5	62.5
8	PFUnA	Target	8	9.901	562.95 > 518.95	562.95 > 269.00	0.2	0.5	1.25	2.5	5	12.5	62.5
9	PFDaA	Target	9	10.461	612.95 > 568.95	612.95 > 319.00	0.2	0.5	1.25	2.5	5	12.5	62.5
10	PFTTrDA	Target	Avg. of 9 and 10	11.345	662.95 > 618.95	662.95 > 168.90	0.2	0.5	1.25	2.5	5	12.5	62.5
11	PFTeDA	Target	10	12.237	712.95 > 668.95	712.95 > 168.90	0.2	0.5	1.25	2.5	5	12.5	62.5
12	PFBS	Target	11	4.841	298.95 > 79.95	298.95 > 98.95	0.2	0.5	1.25	2.5	5	12.5	62.5
13	PFPeS	Target	12	7.766	348.95 > 79.95	348.95 > 98.95	0.2	0.5	1.25	2.5	5	12.5	62.5
14	PFHxS	Target	12	8.776	398.95 > 79.95	398.95 > 98.95	0.2	0.5	1.25	2.5	5	12.5	62.5
15	PFHpS	Target	13	9.294	448.95 > 79.95	448.95 > 98.95	0.2	0.5	1.25	2.5	5	12.5	62.5
16	PFOS	Target	13	9.709	498.95 > 79.95	498.95 > 98.95	0.2	0.5	1.25	2.5	5	12.5	62.5
17	PFNS	Target	13	10.2	548.95 > 79.95	548.95 > 98.95	0.2	0.5	1.25	2.5	5	12.5	62.5
18	PFDS	Target	13	10.956	598.90 > 79.95	598.90 > 98.95	0.2	0.5	1.25	2.5	5	12.5	62.5
19	PFDoS	Target	13	12.524	698.90 > 79.95	698.90 > 98.95	0.2	0.5	1.25	2.5	5	12.5	62.5
20	4:2FTS	Target	14	4.404	326.95 > 306.95	326.95 > 80.90	0.8	2	5	10	20	50	250
21	6:2FTS	Target	15	8.398	426.95 > 406.95	426.95 > 80.90	0.8	2	5	10	20	50	250
22	8:2FTS	Target	16	9.323	526.95 > 506.95	526.95 > 80.90	0.8	2	5	10	20	50	250
23	PFOSA	Target	17	11.438	497.95 > 77.95	497.95 > 477.95	0.2	0.5	1.25	2.5	5	12.5	62.5
24	NMeFOSA	Target	18	13.178	511.95 > 219.00	511.95 > 169.00	0.2	0.5	1.25	2.5	5	12.5	62.5
25	NETFOSA	Target	19	13.475	526.00 > 219.00	526.00 > 169.00	0.2	0.5	1.25	2.5	5	12.5	62.5
26	NMeFOSAA	Target	20	9.491	569.95 > 418.95	569.95 > 482.95	0.2	0.5	1.25	2.5	5	12.5	62.5
27	NETFOSAA	Target	21	9.647	584.00 > 418.95	584.00 > 526.00	0.2	0.5	1.25	2.5	5	12.5	62.5
28	NMeFOSE	Target	22	13.016	616.00 > 59.00	—	2	5	12.5	25	50	125	625
29	NETFOSE	Target	23	13.305	630.00 > 59.00	—	2	5	12.5	25	50	125	625
30	HFPO-DA	Target	24	5.693	285.00 > 169.00	285.00 > 185.00	0.8	2	5	10	20	50	250
31	ADONA	Target	24	8.209	376.95 > 251.00	376.95 > 85.00	0.8	2	5	10	20	50	250
32	9Cl-PF3ONS	Target	24	10.032	530.90 > 350.95	532.90 > 352.95	0.8	2	5	10	20	50	250
33	11Cl-PF3OUdS	Target	24	11.728	630.90 > 450.95	632.90 > 452.95	0.8	2	5	10	20	50	250
34	3:3 FTCA	Target	2	2.937	241.00 > 177.00	241.00 > 117.00	1	2.5	6.25	12.5	25	62.5	312.5
35	5:3 FTCA	Target	3	6.076	341.00 > 237.00	341.00 > 217.00	5	12.5	31.25	62.5	125	312.5	1563
36	7:3 FTCA	Target	3	8.952	441.00 > 317.00	441.00 > 337.00	5	12.5	31.25	62.5	125	312.5	1563
37	PFEESA	Target	3	5.943	314.95 > 135.00	314.95 > 82.95	0.4	1	2.5	5	10	25	125
38	PFMPA	Target	2	2.681	228.95 > 85.00	—	0.4	1	2.5	5	10	25	125
39	PFMBA	Target	2	3.916	278.95 > 85.00	—	0.4	1	2.5	5	10	25	125
40	NFDHA	Target	3	4.715	294.95 > 201.00	294.95 > 85.00	0.4	1	2.5	5	10	25	125

Table 3-2 Quantitation Ion, Reference Ion and Concentrations of Standard Solutions (IS)

No.	Compound	Sample Type	ISTD Group	Retention Time	Quantitation Ion m/z	Reference Ion m/z	Concentration (ng/L in water sample)						
							CS1	CS2	CS3	CS4	CS5	CS6	CS7
41	13C4-PFBA	EIS	1	2.025	217.00 > 172.00	217.00 > 172.00	80	80	80	80	80	80	80
42	13C5-PFPeA	EIS	2	3.568	268.00 > 223.00	268.00 > 223.00	40	40	40	40	40	40	40
43	13C5-PFHxA	EIS	3	4.904	318.00 > 273.00	318.00 > 120.00	20	20	20	20	20	20	20
44	13C4-PFHpA	EIS	4	7.707	367.00 > 322.00	367.00 > 322.00	20	20	20	20	20	20	20
45	13C8-PFOA	EIS	5	8.64	421.00 > 376.00	421.00 > 376.00	20	20	20	20	20	20	20
46	13C9-PFNA	EIS	6	9.119	472.00 > 427.00	472.00 > 427.00	10	10	10	10	10	10	10
47	13C6-PFDA	EIS	7	9.51	519.00 > 474.00	519.00 > 474.00	10	10	10	10	10	10	10
48	13C7-PFUnA	EIS	8	9.899	570.00 > 525.00	570.00 > 525.00	10	10	10	10	10	10	10
49	13C2-PFDoA	EIS	9	10.458	615.00 > 569.95	615.00 > 569.95	10	10	10	10	10	10	10
50	13C2-PFTeDA	EIS	10	12.236	714.95 > 669.95	714.95 > 669.95	10	10	10	10	10	10	10
51	13C3-PFBS	EIS	11	4.835	301.95 > 79.95	301.95 > 98.95	20	20	20	20	20	20	20
52	13C3-PFHxS	EIS	12	8.775	401.95 > 79.95	401.95 > 98.95	20	20	20	20	20	20	20
53	13C8-PFOS	EIS	13	9.71	506.95 > 79.95	506.95 > 98.90	20	20	20	20	20	20	20
54	13C2-4:2FTS	EIS	14	4.405	329.00 > 308.95	329.00 > 80.90	40	40	40	40	40	40	40
55	13C2-6:2FTS	EIS	15	8.397	428.95 > 408.95	428.95 > 80.90	40	40	40	40	40	40	40
56	13C2-8:2FTS	EIS	16	9.323	528.95 > 508.95	528.95 > 80.90	40	40	40	40	40	40	40
57	13C8-PFOSA	EIS	17	11.438	505.95 > 77.95	505.95 > 77.95	20	20	20	20	20	20	20
58	D3-NMeFOSA	EIS	18	13.174	515.00 > 219.00	515.00 > 168.90	20	20	20	20	20	20	20
59	D5-NEtFOSA	EIS	19	13.467	531.00 > 219.00	531.00 > 168.90	20	20	20	20	20	20	20
60	D3-NMeFOSAA	EIS	20	9.489	573.00 > 418.95	573.00 > 418.95	40	40	40	40	40	40	40
61	D5-NEtFOSAA	EIS	21	9.645	589.00 > 418.95	589.00 > 418.95	40	40	40	40	40	40	40
62	D7-NMeFOSE	EIS	22	12.997	623.05 > 59.00	623.05 > 59.00	200	200	200	200	200	200	200
63	D9-NEtFOSE	EIS	23	13.282	639.10 > 59.00	639.10 > 59.00	200	200	200	200	200	200	200
64	13C3-HFPO-DA	EIS	24	5.688	287.00 > 169.00	287.00 > 185.00	80	80	80	80	80	80	80

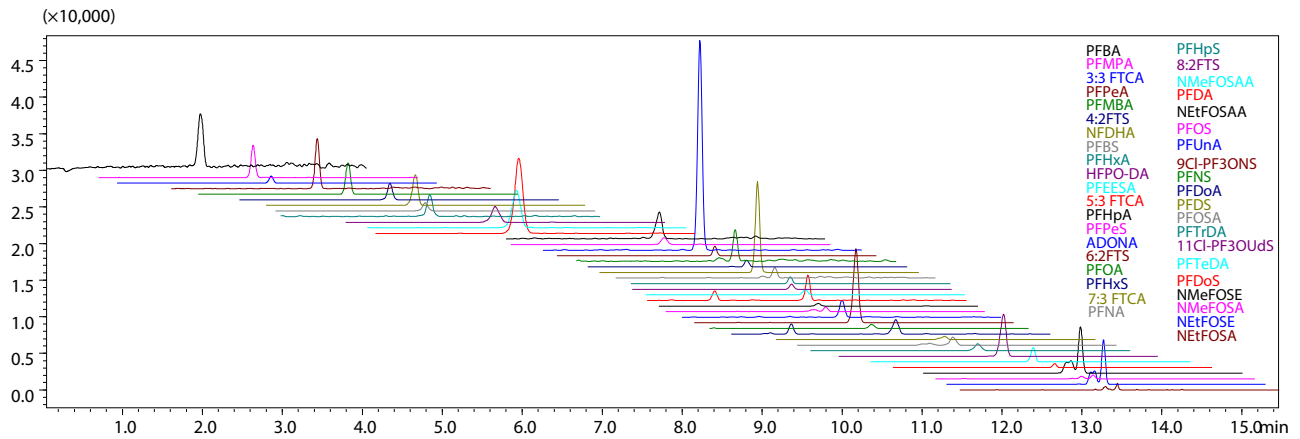


Fig. 3 MRM Chromatogram of PFAS (Target) at CS1

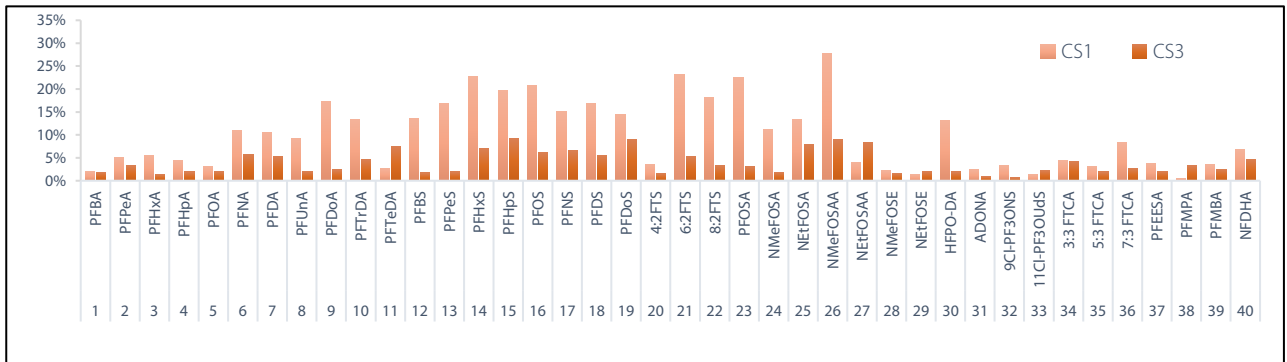


Fig. 4 CS1 and CS3 Area Repeatability (n = 5)

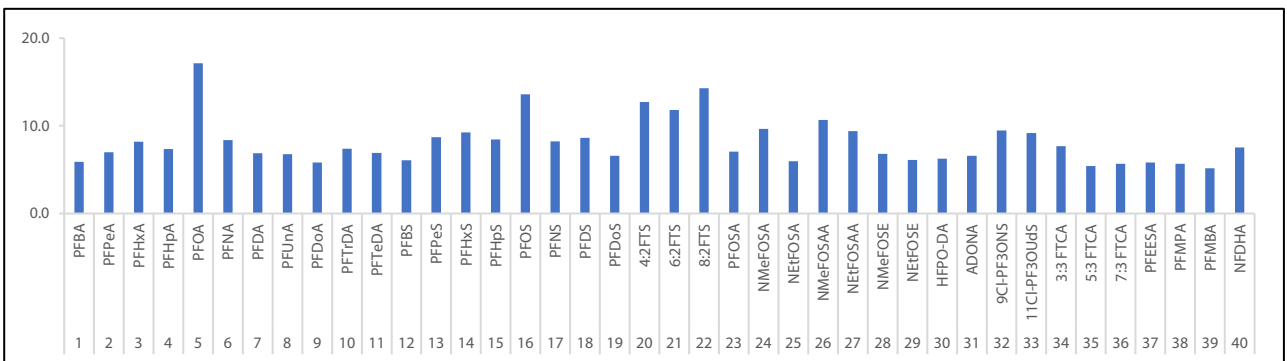


Fig. 5 RF Accuracy for CS1 to CS7 (n = 5 of Each Concentration)

Recovery Test

Target compounds were spiked to the drinking water samples to prepare the respective concentrations. These are shown in Table 4 and are marked as "High" and "Low." Next, the samples were pretreated according to the process in Fig. 2. The quantitation values for PFAS in samples were calculated from Eq. 2. The RF values calculated from Eq. 1 were used for it. As shown in Table 4, for samples with low spike concentrations, recovery rates ranged from 70 to 130 % for 90 % of the compounds, and repeatability was less than 20 %RSD for 95 % of the compounds. For samples with high spike concentrations, recovery rates ranged from 70 to 130 % for 97.5 % of the compounds, and repeatability was less than 13 %RSD for all compounds. These were good results, and they confirmed that drinking water samples can be analyzed accurately.

$$\text{Conc. (ng/L)} = \frac{\text{Area of Target Compounds in Sample}}{\text{EIS Area}} \times \frac{\text{EIS Concentration Injected}}{\text{Avg. RF for Standard Solution}}$$

Eq. 2 Formula for Calculating PFAS Quantitation Values in Sample

Table 4 Recovery Test Results

No.	Compound	Low (n = 3)				High (n = 3)			
		Spiked Concentration (ng/L)	Avg. Concentration (ng/L)	Avg. Recovery Rate (%)	Repeatability (%)	Spiked Concentration (ng/L)	Avg. Concentration (ng/L)	Avg. Recovery Rate (%)	Repeatability (%)
1	PFBA	4	5.2	130	0.7	20	18.9	95	0.8
2	PFPeA	2	2.2	112	3.4	10	10.0	100	1.5
3	PFHxA	1	1.2	121	6.5	5	4.7	93	3.7
4	PFHpA	1	1.2	124	2.6	5	5.1	102	3.3
5	PFOA	1	1.1	113	9.3	5	4.7	95	4.5
6	PFNA	1	1.3	132	5.2	5	5.2	105	5.8
7	PFDA	1	1.3	126	6.7	5	5.4	107	3.0
8	PFUnA	1	1.1	107	4.9	5	4.7	94	0.9
9	PFDoA	1	1.2	115	2.8	5	4.7	94	6.2
10	PFTTrDA	1	1.0	103	5.9	5	4.8	96	1.5
11	PFTeDA	1	1.0	100	4.7	5	4.7	94	4.4
12	PFBS	1	1.2	122	12.1	5	5.3	106	3.7
13	PFPeS	1	0.8	82	6.6	5	3.6	73	4.5
14	PFHxS	1	0.9	90	10.4	5	4.2	85	3.5
15	PFHpS	1	1.0	100	6.2	5	4.6	93	2.6
16	PFOS	1	1.4	140	16.0	5	4.4	88	1.5
17	PFNS	1	0.8	80	20.8	5	3.9	78	5.3
18	PFDS	1	0.7	74	9.7	5	3.5	70	5.6
19	PFDoS	1	0.7	69	7.5	5	2.8	57	2.7
20	4:2FTS	4	4.5	113	5.3	20	20.2	101	0.7
21	6:2FTS	4	4.9	124	8.2	20	20.3	102	1.2
22	8:2FTS	4	4.3	107	13.8	20	19.5	97	5.8
23	PFOSA	1	1.2	120	9.1	5	4.9	98	4.1
24	NMeFOSA	1	1.2	120	6.0	5	5.4	108	11.0
25	NEtFOSA	1	1.0	97	7.5	5	5.0	101	3.1
26	NMeFOSAA	1	1.1	112	1.9	5	5.1	103	6.0
27	NEtFOSAA	1	1.0	98	24.4	5	5.4	108	12.2
28	NMeFOSE	10	11.0	110	5.8	50	48.5	97	1.2
29	NEtFOSE	10	11.1	111	1.3	50	48.1	96	1.8
30	HFPO-DA	4	4.5	112	4.8	20	22.0	110	0.6
31	ADONA	4	4.8	121	2.3	20	21.5	107	1.0
32	9CI-PF3ONS	4	4.9	123	1.0	20	22.0	110	1.6
33	11CI-PF3OUDs	4	3.8	94	6.8	20	15.7	79	3.9
34	3:3 FTCA	5	5.0	101	7.3	25	23.2	93	3.2
35	5:3 FTCA	25	21.8	87	4.0	125	90.1	72	3.2
36	7:3 FTCA	25	20.1	80	3.4	125	87.4	70	1.8
37	PFEESA	2	2.2	111	1.2	10	9.7	97	2.6
38	PFMPA	2	2.5	123	2.2	10	10.6	106	0.6
39	PFMBA	2	2.0	100	3.2	10	8.8	88	1.3
40	NFDHA	2	2.5	124	1.0	10	10.6	106	1.1

Acknowledgments

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Conclusion

LCMS-8050RX provided ample sensitivity for analyzing 40 PFAS components at less than 1/10 of the final maximum contaminant levels (final MCLs) that are specified by the EPA (4 ng/L PFOA, 4 ng/L PFOS, 10 ng/L PFHxS, 10 ng/L PFNA, and 10 ng/L HFPO-DA).

Good recovery rates and reproducibility results were achieved even when evaluating recoveries with 1/4 of the final MCL concentrations.

The above results demonstrate that LCMS-8050RX can be used to simultaneously and accurately analyze 40 PFAS components in drinking water samples.

Reference

- 1) EPA Method 1633
Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS
<https://www.epa.gov/system/files/documents/2024-01/method-1633-final-for-web-posting.pdf>



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