

Application News

SGLC-LC/MS-052EN

LCMS-8060RX

Analysis of 30 Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in water

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User Benefits

- ◆ Using the SHIMSEN Styra SPE column, two effective and complete sample preparation methods for the analysis of PFAS in water have been established.
- ◆ The methods are applicable to ultrapure water and wastewater, with detection limits as low as 1 ng/L and 10 ng/L, respectively.

■ Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) have become a global concern due to their persistence, bioaccumulation, and endocrine toxicity. PFAS are discharged into the environment through wastewater treatment plants and then enter water sources through material migration or transformation, leading to the contamination of drinking water. Over 4,000 types of PFAS have been reported, and these substances have significant polarity differences. Therefore, if we need to monitor the contamination of PFAS in water, a complete and accurate sample preparation and instrumental analysis method is crucial. In this application, we referred to the methods in ISO 21675-2019 and EPA 1633, used Shimadzu SHIMSEN Styra WAX and SHIMSEN Styra WAX/GCB columns to enrich PFAS in water, Shim-pack Scepter C18-120 column for separation, and Shimadzu LCMS-8060RX for analysis, and established two effective and complete methods for determining the content of 30 types of PFAS in water.

Table 1. LCMS conditions

Equipment	LCMS-8060RX
Guard column	Shim-pack Scepter C18-120 (G), 1.9 μ m, 5 mm $\times$ 2.1 mm I.D. (SGLC, P/N 227-31120-01)
Column	Shim-pack Scepter C18-120, 1.9 μ m, 100 mm $\times$ 2.1 mm I.D. (SGLC, P/N 227-31012-05)
Injection volume	5 μ L
Flow rate	0.3 mL/min(0-19.0 min) $\rightarrow$ 0.6 mL/min(19.01-23.00 min) $\rightarrow$ 0.3 mL/min(23.01-28.00 min)
Mobile Phase	A: 2 mmol/L Ammonium Acetate in H ₂ O B: Methanol
Gradient program (% of B)	5 %(0 min) $\rightarrow$ 50 %(2 min) $\rightarrow$ 100 %(19.0-23.0 min) $\rightarrow$ 5 %(23.01-28.0 min)
Column Oven temp.	40 $^{\circ}$ C
Interface temp.	250 $^{\circ}$ C
Interface voltage	-1.0 kV
Focus voltage	-2.0 kV
Probe position	+3 mm
Nebulizer Gas	3 L/min
Heating Gas	15 L/min
DL temp.	200 $^{\circ}$ C
Heating Block temp.	300 $^{\circ}$ C
Drying Gas	5 L/min

■ Experimental

Materials:

SHIMSEN Styra WAX 150mg/6mL 30pcs (SGLC, P/N 380-00852-06)

SHIMSEN Styra WAX/GCB, 200mg/50mg/6mL, 30pcs (SGLC, P/N 380-05200-05)

■ Sample Preparation:

Sample Collection and Spiking:

Measure 100 mL of water sample (accurate to 1 mL) into a polypropylene bottle. Add 100 μ L of isotopically labeled internal standard (10 ng/mL). Add 10 μ L or 100 μ L of PFAS standard solution (10 ng/mL). Add 500 μ L of acetic acid and mix thoroughly for later use.

SPE Column Preparation:

Attach the SPE column to the SPE apparatus. For the SHIMSEN Styra WAX column, sequentially add 4 mL of 0.1% ammonium hydroxide in methanol, 4 mL of methanol, and 4 mL of ultrapure water to activate and equilibrate the column. For the SHIMSEN Styra WAX/GCB column, due to its higher capacity, increase the volume of solvents used in the SPE process from 4 mL to 5 mL. Keep the column head wet during solvent addition and discard the eluate.

Sample Loading:

Load the entire sample onto the column and pass it through at a flow rate of approximately 3 mL/min (about 1 drop per second). Discard the eluate.

Washing:

Sequentially wash the column with 4 mL of ultrapure water and 4 mL of 25 mmol/L ammonium acetate buffer solution (adjust pH to 4.0 with acetic acid). Discard the eluate.

Centrifugation:

Centrifuge the column at 3000 rpm for 2 minutes to remove residual moisture.

Elution:

Sequentially elute the column with 4 mL of methanol and 4 mL of 0.1% ammonium hydroxide in methanol. Collect the eluate and blow down to less than 1 mL under nitrogen at 40 $^{\circ}$ C. Dilute to 1 mL with methanol. Filter through a 0.22 μ m membrane filter and transfer to a PFAS-specific vial for injection.

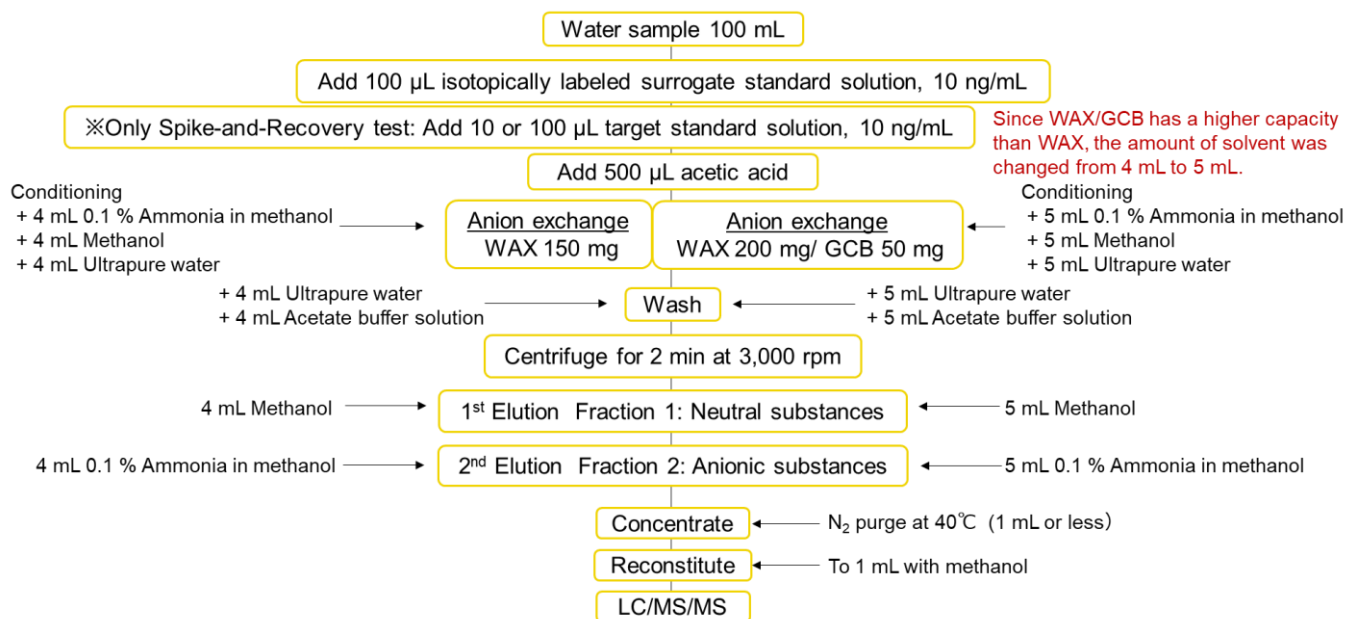


Figure 1. PFAS sample preparation workflow for water.

Table 2. List of MRM used for each PFAS.

No.	Compound	Precursor M1	Quantifier M2	Qualifier M3
1	PFBS	299	80	99
2	PFHxS	399	80	99
3	PFHpS	449	80	99
4	PFOS	499	80	99
5	PFDS	599	80	99
6	FOSA	498	78	169
7	N-MeFOSA	512	169	219
8	N-EtFOSA	526	169	219
9	N-MeFOSAA	570	419	512
10	N-EtFOSAA	584	419	526
11	6:2 FTSA	427	407	81
12	8:2 FTSA	527	507	81
13	9CI-PF3ONS	531	351	83
14	PFBA	213	169	
15	PFPeA	263	219	69
16	PFHxA	313	269	119
17	PFHpA	363	319	169
18	PFOA	413	369	169
19	PFNA	463	419	219
20	PFDA	513	469	219
21	PFUnDA	563	519	269
22	PFDoDA	613	569	269
23	PFTTrDA	663	619	269
24	PFTeDA	713	669	369
25	PFHxDA	813	769	369
26	PFOcDA	913	869	369
27	8:2 FTUCA	457	393	343
28	8:2 diPAP	989	97	543
29	HFPO-DA	329	169	285
30	DONA	377	251	85

Results and Discussion

Recovery Results of 30 PFAS in Ultrapure Water:

Ultrapure water blank samples were spiked with PFAS standards at concentrations of 1 ng/L and 10 ng/L (equivalent to 0.1 ppb and 1 ppb after concentration), and then processed using the aforementioned sample preparation method and analyzed by LC-MS/MS. The results showed that for the ultrapure water matrix, using the SHIMSEN Styra WAX column, the recovery rates of the 30 PFAS compounds were within the range of 80% to 109% at a spiking concentration of 1 ng/L and within the range of 92% to 116% at a spiking concentration of 10 ng/L, indicating high recovery rates. Using the SHIMSEN Styra WAX/GCB column, except for PFOcDA (which had a recovery rate of 50% at both spiking concentrations), the recovery rates of the other 29 compounds were within the range of 95% to 116% at a spiking concentration of 1 ng/L and within the range of 93% to 114% at a spiking concentration of 10 ng/L, also indicating high recovery rates. The recovery rates of each compound using the different columns are summarized in table 3.

Recovery Results of 30 PFAS in Wastewater Water:

Wastewater blanks were spiked with PFAS standards at concentrations of 1 ng/L and 10 ng/L (equivalent to 0.1 ppb and 1 ppb after concentration), and then processed using the aforementioned sample preparation method and analyzed by LC-MS/MS. The results showed that for the wastewater matrix, using the SHIMSEN Styra WAX column, the recovery rates of the 30 PFAS compounds ranged from 62% to 170% at a spiking concentration of 1 ng/L and from 80% to 113% at a spiking concentration of 10 ng/L, indicating high recovery rates for the higher concentration. Using the SHIMSEN Styra WAX/GCB column, the recovery rates of the 30 PFAS compounds ranged from 81% to 116% at a spiking concentration of 1 ng/L and from 66% to 124% at a spiking concentration of 10 ng/L, also indicating high recovery rates for the higher concentration. The detailed recovery rates for each compound using the different columns are presented in table 4.

Table 3. Recovery Results of 30 PFAS in Ultrapure Water

No.	Compounds	Recovery of Styra WAX (%)		Recovery of Styra WAX/GCB (%)	
		1ng/L	10ng/L	1ng/L	10ng/L
1	PFBA	87	97	100	93
2	PFPeA	96	105	114	103
3	PFBS	94	100	101	95
4	PFHxA	102	97	103	98
5	HFPO-DA	99	103	116	104
6	PFHpA	85	92	95	97
7	DONA	95	93	106	98
8	6:2FTSA	91	112	106	114
9	PFOA	92	96	99	96
10	PFHxS	109	96	106	96
11	8:2 FTUCA	99	100	99	98
12	PFNA	102	97	100	100
13	PFHpS	96	98	107	102
14	8:2FTSA	80	116	112	109
15	NMeFOSAA	88	102	103	98
16	PFDA	91	97	104	97
17	NEtFOSAA	94	105	100	101
18	PFOS	99	96	109	101
19	PFUnA	82	92	103	92
20	9CI-PF3ONS	90	95	106	96
21	PFDoA	96	100	103	98
22	FOSA	95	106	112	99
23	PFDS	94	94	95	95
24	PFTTrDA	95	103	102	96
25	PFTeDA	92	101	102	98
26	NMeFOSA	93	101	114	99
27	8:2 diPAP	93	100	103	101
28	PFHxDA	98	102	115	104
29	NEtFOSA	100	104	110	104
30	PFOcDA	89	99	50	50

Table 4. Recovery Results of 30 PFAS in Wastewater Water

No.	Compounds	Recovery of Styra WAX (%)		Recovery of Styra WAX/GCB (%)	
		1ng/L	10ng/L	1ng/L	10ng/L
1	PFBA	127	81	94	92
2	PFPeA	147	111	98	107
3	PFBS	90	96	81	96
4	PFHxA	62	103	153	103
5	HFPO-DA	90	107	98	100
6	PFHpA	69	100	99	97
7	DONA	87	98	92	96
8	6:2FTSA	59	113	137	124
9	PFOA	151	102	73	105
10	PFHxS	95	96	98	100
11	8:2 FTUCA	93	100	94	97
12	PFNA	170	116	101	104
13	PFHpS	100	98	98	99
14	8:2FTSA	84	112	96	114
15	NMeFOSAA	88	106	88	108
16	PFDA	77	99	88	95
17	NEtFOSAA	88	100	108	103
18	PFOS	85	99	94	98
19	PFUnA	82	92	111	96
20	9CI-PF3ONS	92	93	89	95
21	PFDoA	101	104	96	102
22	FOSA	100	110	92	107
23	PFDS	80	85	85	86
24	PFTTrDA	83	85	85	93
25	PFTeDA	93	103	92	104
26	NMeFOSA	96	103	96	103
27	8:2 diPAP	95	98	94	100
28	PFHxDA	100	101	97	102
29	NEtFOSA	92	110	100	107
30	PFOcDA	82	99	65	66

■ Conclusion

This report establishes a method for the determination of 30 perfluoroalkyl and polyfluoroalkyl substances (PFAS) in water. Referring to the methods in ISO 21675-2019 and EPA 1633, SHIMSEN Styra WAX and SHIMSEN Styra WAX/GCB products from Shimadzu were used to enrich PFAS in water, followed by separation using a Shim-pack Scepter C18-120 chromatographic column and detection by Shimadzu LCMS-8060RX. Ultrapure water and wastewater blanks were spiked with PFAS standards at concentrations of 1 ng/L and 10 ng/L, then processed using the aforementioned sample preparation method and analyzed. The results showed that for the ultrapure water matrix, the recovery rates of the 30 PFAS compounds using the SHIMSEN Styra WAX column ranged from 80% to 116%, indicating high recovery rates. Using the SHIMSEN Styra WAX/GCB column, the spike recovery rates for 29 of the PFAS compounds were within the range of 93% to 114%, with the exception of PFOcDA, which had a recovery rate of 50% at both spike concentrations. This method provides a reference for the determination of PFAS content in water.

Appendix: Recommended product collection

Product	P/N from SGLC	Introduction
Sample preparation	380-00852-06	SHIMSEN Styra WAX 150mg/6mL 30pcs
	380-05200-05	SHIMSEN Styra WAX/GCB, 200mg/50mg/6mL, 30pcs
Delay column	227-31015-05	Shim-pack Scepter C18-120, 3um, 3.0 × 33mm
Guard column	227-31120-01	Shim-pack Scepter C18-120 (G), 1.9 um, 5 mm × 2.1 mm
LC column	227-31012-05	Shim-pack Scepter C18-120, 1.9 um, 100 mm × 2.1 mm
Vial	380-06110-01	SHIMSEN PFAS KIT 1.5mL PP Screw Vial with Graduations Transparent. Screw Cap Bonded 100pcs
Syringe filter	380-00301	SHIMSEN Disc PES, 13 mm, 0.22 um 100/box
Safety cap	307019-PP	Safety Cap I, GL45,PFAS-Analytic

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