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Evaluation of a fully automated analytical method for PFAS in environmental water

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Introduction

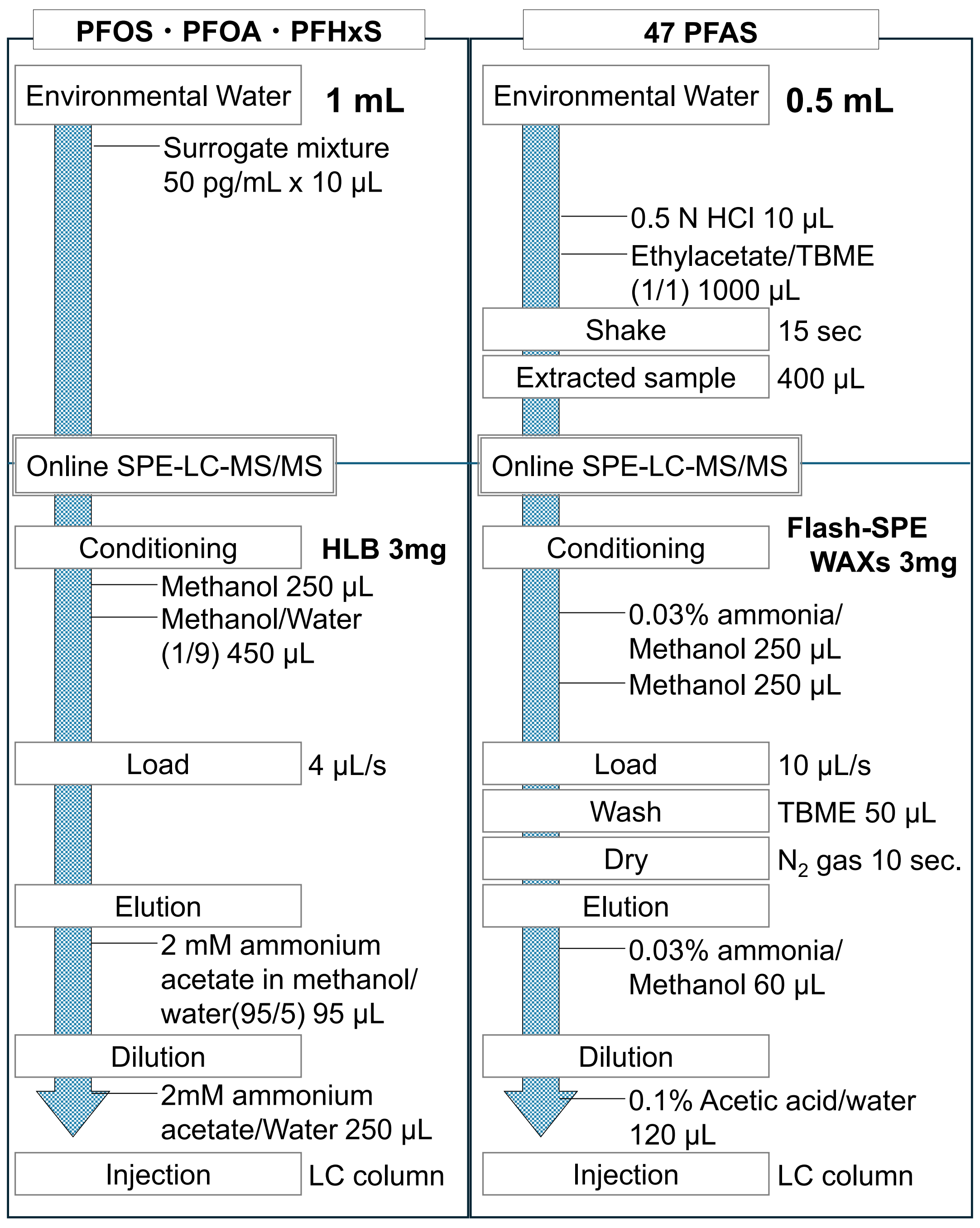
Perfluoroalkyl substances (PFAS) are regarded as a persistent environmental concern on a global scale. In recent years, the technology of fully automated solid-phase extraction (online SPE) has attracted attention due to its potential to reduce costs, save time, and minimize environmental impact. In a previous study, a direct injection was attempted into HLB or WAX (Takazawa, et.al, 2024). However, the method proved inadequate for application to the sample containing high-ion contaminants. The present study proposes a methodology for the removal of ionic contaminants from a sample prior to its loading onto WAX.

Material and Method

The automated analytical method is shown in Fig. 1. Depending on the analytes, several methods were used. These included up to 47 analytes, such as 13 PFCAs, 10 PFSAs, and 24 other PFASs. The analytes were covered by ISO 21675 and EPA methods 533, 537, and 1633. Five picograms of the standard mixture was added to 1 mL of ultrapure water and used as test water. In the case of surface water test, PFOA and PFHxS were not spiked because their concentrations in the surface water were sufficient concentrations for this evaluation. In the 47 PFAS recovery tests, 10 pg of the standard mixture was added; however, the lower limit of detection has not been examined.

Concurrent surrogate recovery tests were conducted; however, no surrogate correction was performed to properly evaluate the chemical behavior of each compound.

Online SPE-LC-MS/MS system



PFOS・PFOA・PFHxS		47 PFAS	
Environmental Water	**1 mL**	Environmental Water	**0.5 mL**
Surrogate mixture 50 pg/mL x 10 µL		0.5 N HCl 10 µL Ethylacetate/TBME (1/1) 1000 µL	
		Shake	15 sec
		Extracted sample	400 µL
Online SPE-LC-MS/MS		Online SPE-LC-MS/MS	
Conditioning	**HLB 3mg**	Conditioning	**Flash-SPE WAXs 3mg**
Methanol 250 µL Methanol/Water (1/9) 450 µL		0.03% ammonia/ Methanol 250 µL Methanol 250 µL	
Load	4 µL/s	Load	10 µL/s
		Wash	TBME 50 µL
		Dry	N_2 gas 10 sec.
Elution		Elution	
2 mM ammonium acetate in methanol/ water(95/5) 95 µL		0.03% ammonia/ Methanol 60 µL	
Dilution		Dilution	
2mM ammonium acetate/Water 250 µL		0.1% Acetic acid/water 120 µL	
Injection	LC column	Injection	LC column

Fig. 1 Extraction procedures for PFAS with Online SPE-LC-MS/MS system.

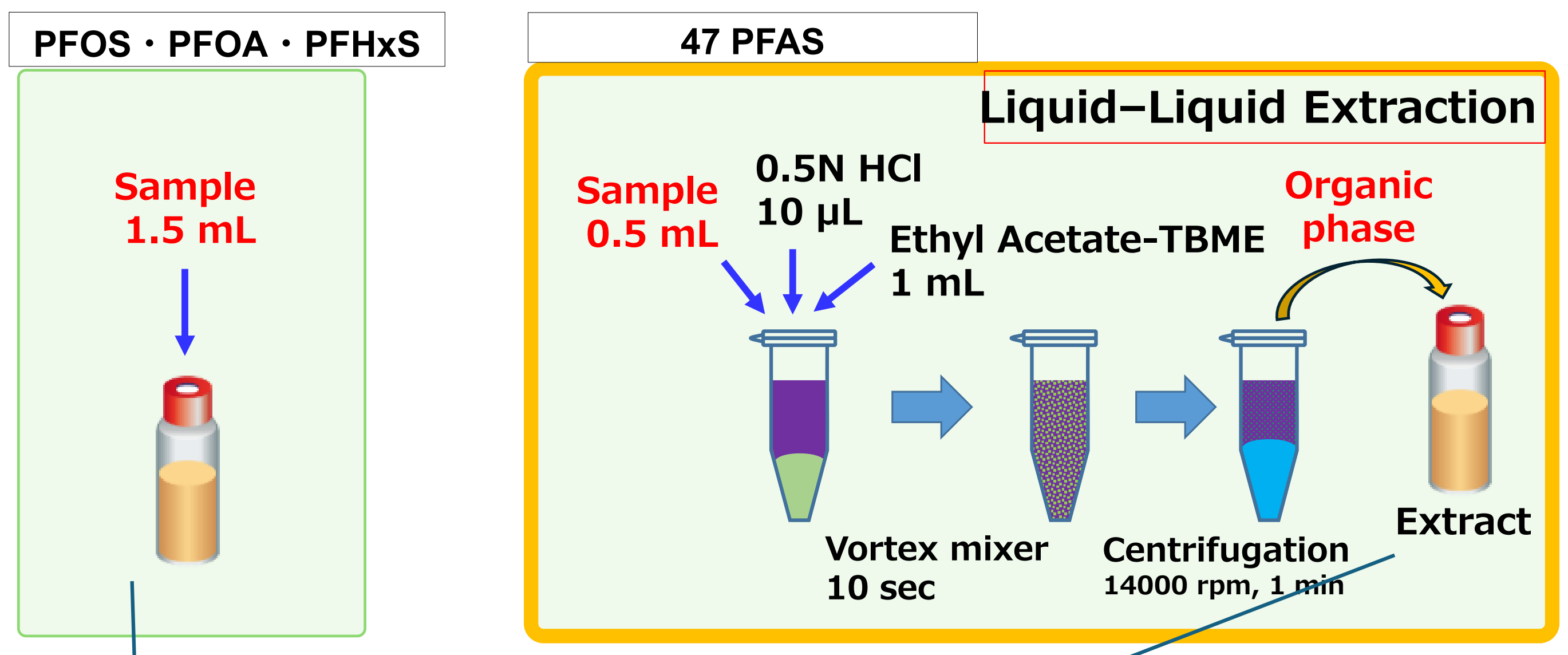


Fig. 2 Pretreatment procedure for PFAS analysis.

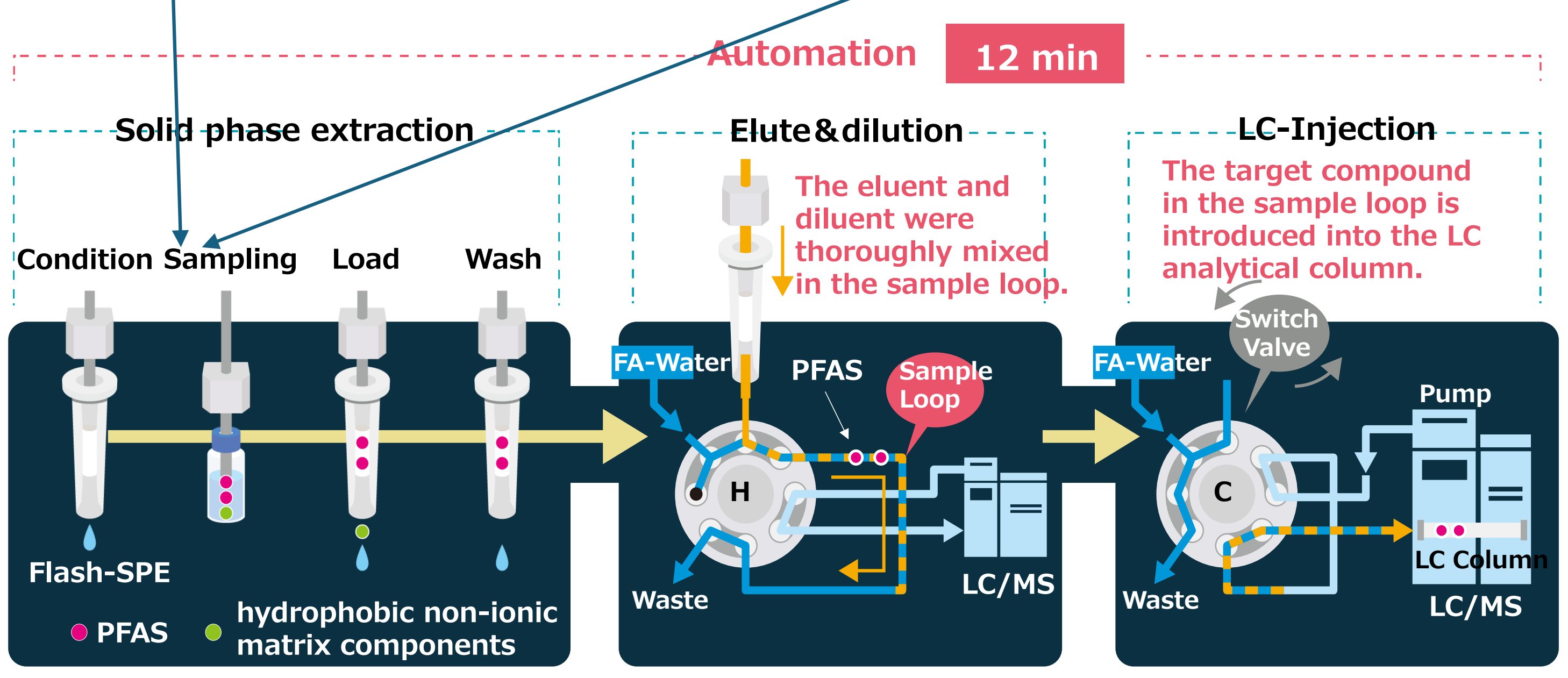
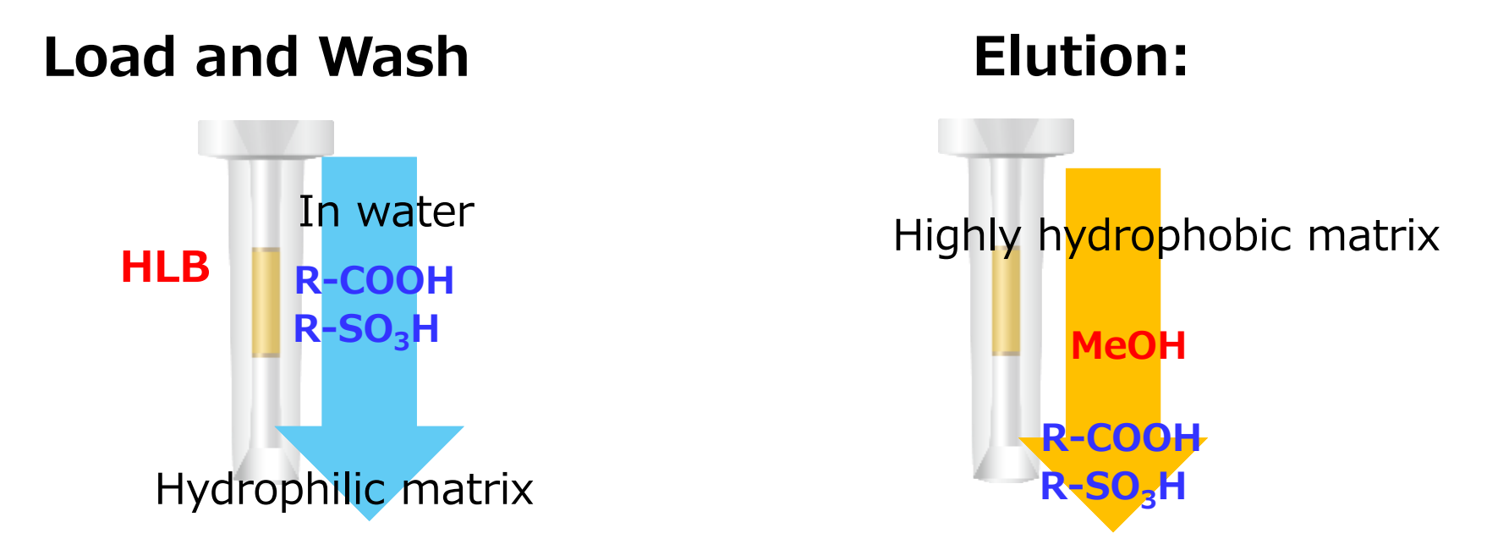


Fig. 3 The process of online SPE-LC-MS/MS.

Results and Discussion

■ PFOS·PFOA·PFHxS

■ Hydrophobic interaction solid-phase extraction.



PFAS in water are retained on the HLB via hydrophobic interactions.
Whereas hydrophilic matrix components are not retained and are removed.

The retained PFAS are eluted from the HLB using methanol and collected.
Whereas hydrophobic matrix components remained in the cartridge.

The method quantification limits for PFOS, PFOA, and PFHxS ranged from 0.1 to 0.2 ng/L by the left method in Fig.1. These values are more than 1/10 less than the target value of 4 ng/L established by the US/EPA. This finding indicates that the method is sufficiently applicable to PFAS research.

Table 2 Determination of limit of quantitation

		PFOS	PFOA	PFHxS
Sample		River water	River water	River water
Sample vol.	(mL)	1	1	1
Sample conc.	(pg/mL)	0.1	0.5	0.07
Injection vol.	(mL)	0.5	0.5	0.05
Operation blank conc. (*n*=3)	(pg/mL)	ND	<0.05	ND
Non-spike conc. (*n*=7)	(pg/mL)	ND	0.50	0.07
Result_001	(pg/mL)	0.09	0.50	0.06
Result_002	(pg/mL)	0.11	0.52	0.07
Result_003	(pg/mL)	0.09	0.50	0.07
Result_004	(pg/mL)	0.07	0.49	0.08
Result_005	(pg/mL)	0.09	0.49	0.07
Result_006	(pg/mL)	0.11	0.50	0.08
Result_007	(pg/mL)	0.08	0.50	0.08
Average	(pg/mL)	0.09	0.50	0.07
CV	(%)	16.3	1.69	7.69
MDL	(pg/mL)	0.1	0.04	0.04
MQL	(pg/mL)	0.2	0.10	0.10

*SD: Standard deviation
**MDL: Method detection limit = 2 x s x t(n-1, 0.05)
***MQL: Method quantification limit = 10 x s

Sample: River water（Saitama prefecture, Japan)

The anion-exchange solid phase was determined to be the most suitable for simultaneous collection of several PFAS components, and Fig.6 shown that good recoveries were obtained by the right method in Fig.1. PFHxA was not calculated correctly due to the confirmation that the surface water contained an amount equivalent to that which was added during this experiment. A recovery of 4:2FTS in both ultrapure water and environmental water was found to be insufficient. A more thorough examination is necessary to gain a comprehensive understanding of the situation. PFOSA, *N*-MeFOSA, and *N*-EtFOSA were found to have been lost in the liquid-liquid extraction process prior to loading to the solid phase cartridge.

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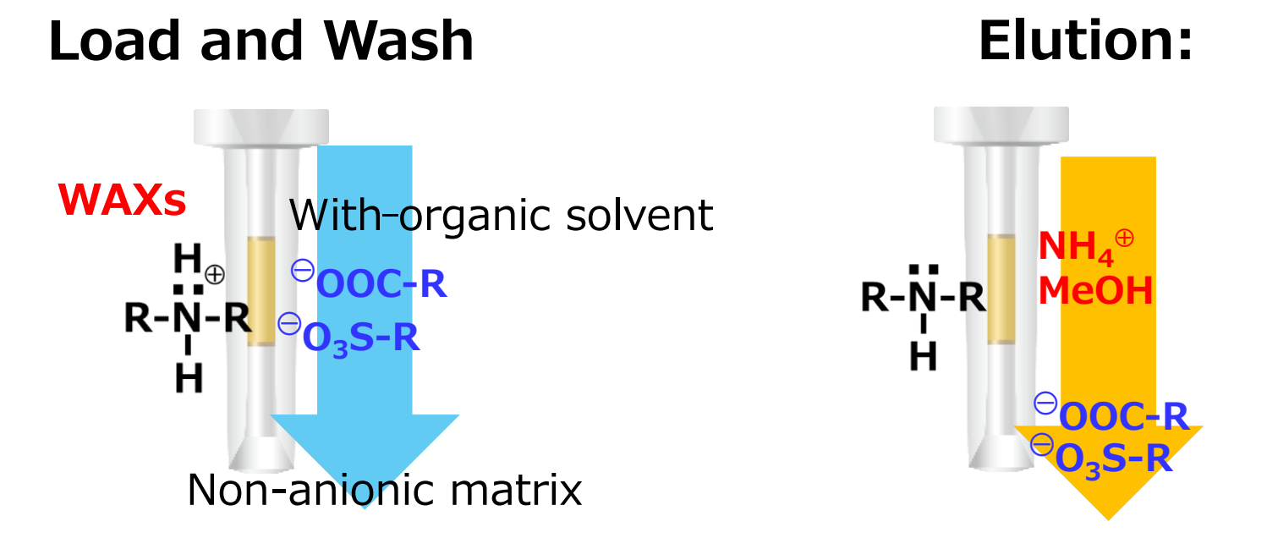
■ 47 PFAS

■ Ion-Exchange Solid-Phase Extraction.



Anionic PFAS in the organic phase were retained on the positively charged WAXs through ion-exchange interaction. Whereas Non-anionic matrix components are not retained and are removed.

PFAS were eluted by alkaline ammonia in methanol, which neutralized the WAXs functional groups and released the analytes.

■ Effect of Liquid–Liquid Extraction

Organic phase
Ethyl acetate-TBME 1 mL

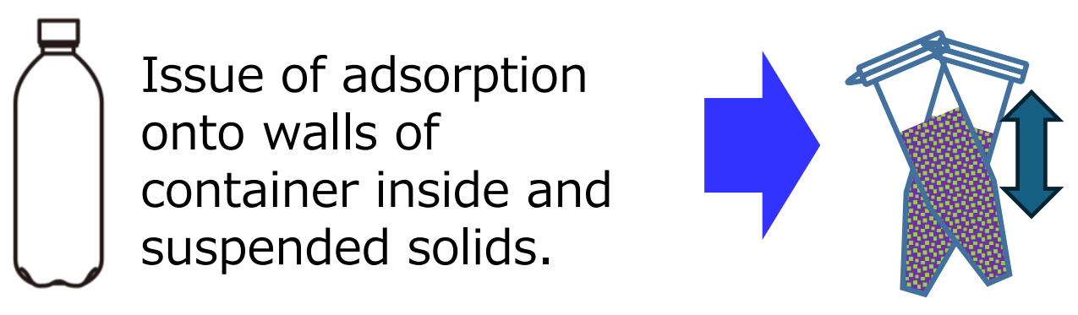
transfer PFAS to the organic phase

Aqueous phase : 0.51 mL
Water 500 µL
HCl-Water 10 µL

Highly polar anionic impurities are transferred to the aqueous phase

For an organic phase, tert-butyl methyl ether (TBME) and ethyl acetate were selected, which were completely separated with a sample water. Ethyl acetate-TBME(1/1) showed the highest recovery efficiency and was selected as the optimal solvent.

■ The conventional method



Issue of adsorption onto walls of container inside and suspended solids.

■ The present method

Via the liquid–liquid extraction process, the organic solvent could be extracted PFAS which was residue to sample containers and suspended solids.

■ Effect of HCl Addition

Addition of HCl improved the recovery of hydrophilic PFAS such as PFBA and PFMPA by suppressing carboxyl group dissociation, increasing hydrophobicity and facilitating transfer to the organic phase.

Organic phase
Ethyl acetate-TBME

Aqueous phase

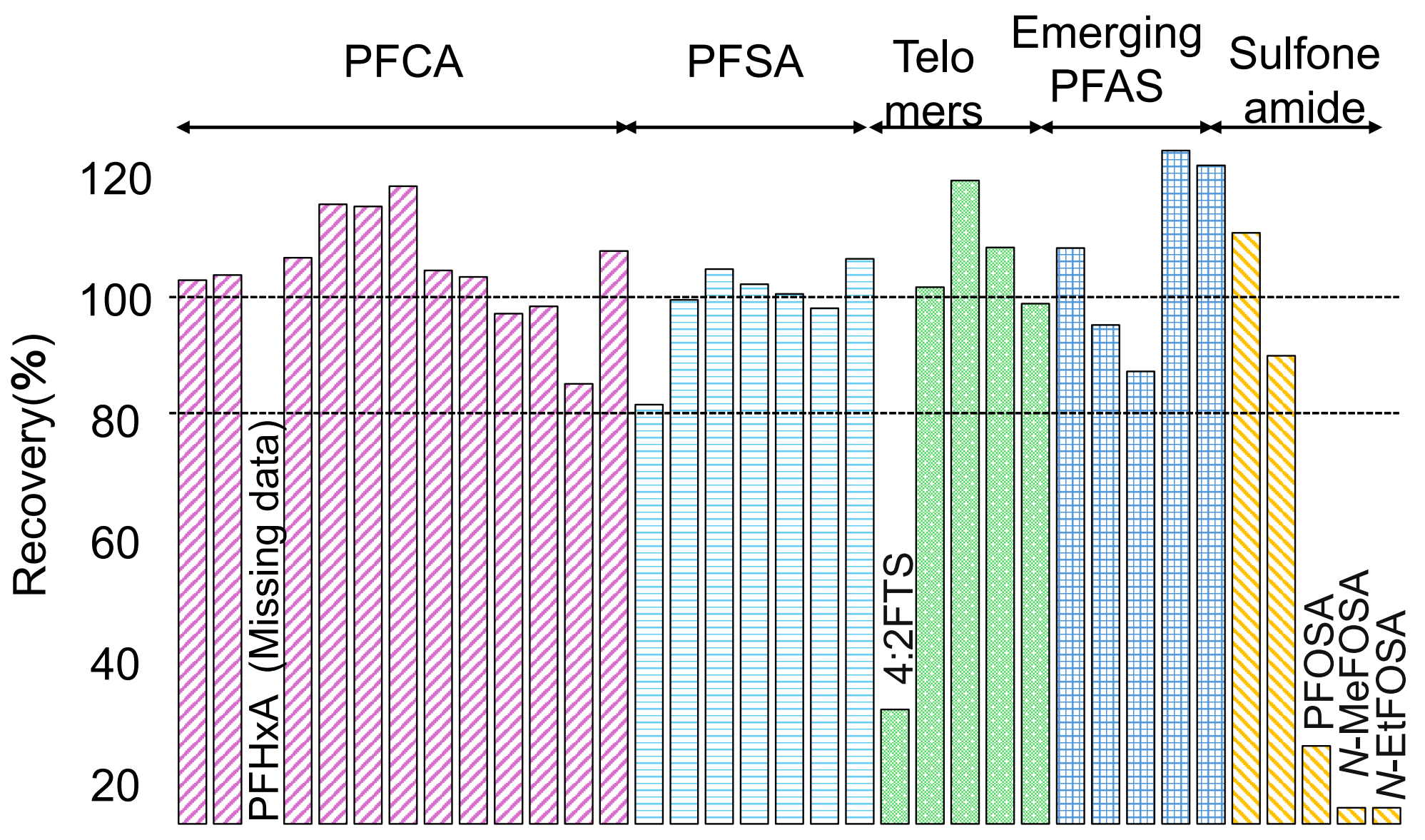


Fig. 6 Recoveries of PFAS in surface water with SPE Cartridges of WAX.

■ Dilution effect in the elution process via online SPE-LC-MS/MS

■ No dilution

Eluent 60 µL
(Speed: 2 µL/sec)

■ Dilution with water

Eluent 60 µL
(Speed: 2 µL/sec)
Diluent 120 µL
(Speed: 4 µL/sec)

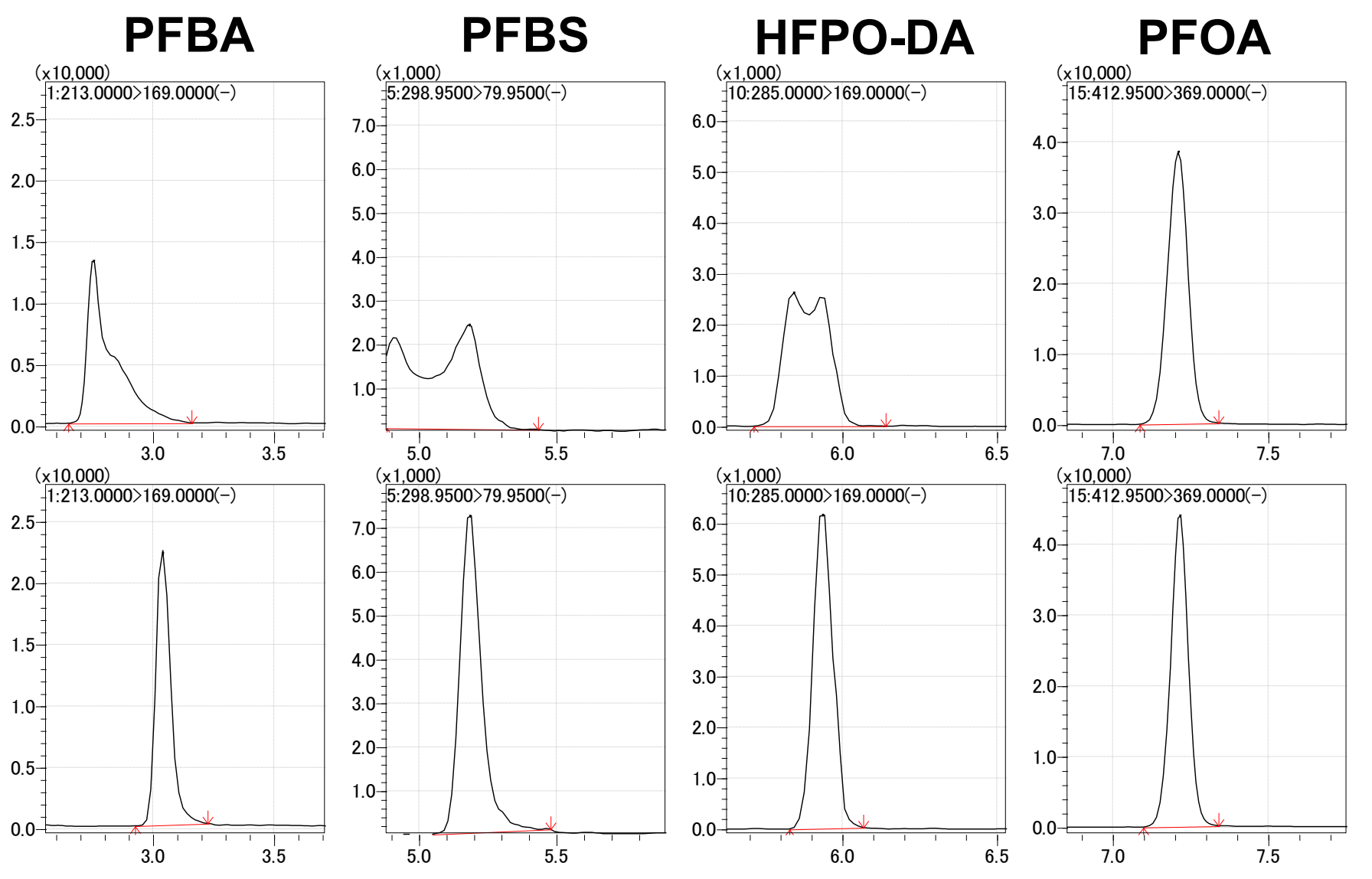


Fig. 4 Peak shape improvement by sample dilution with water after extraction with online SPE system.

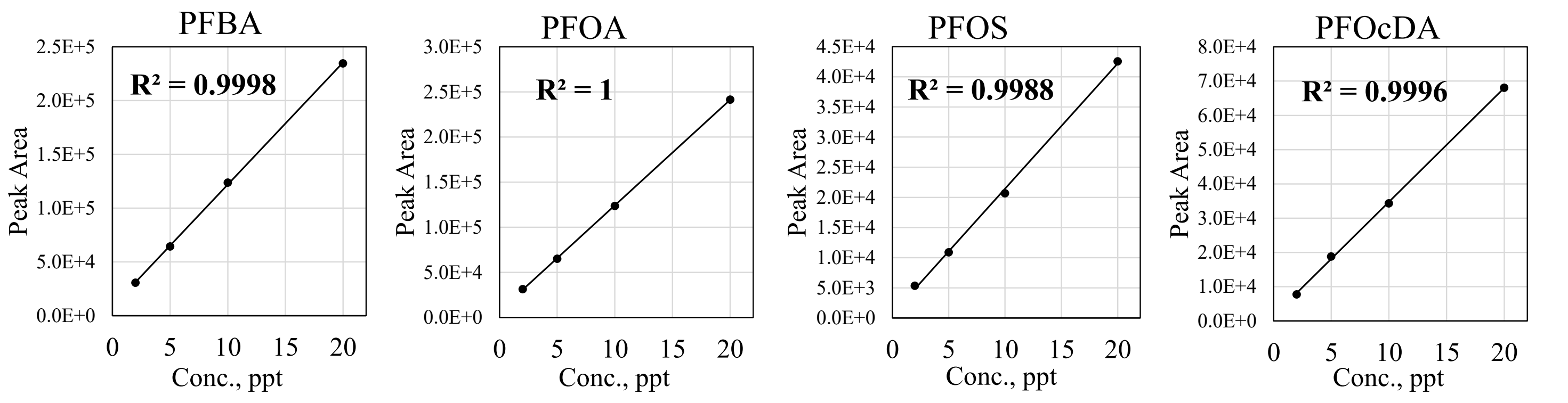


Fig. 5 Absolute calibration curve using the online SPE-LC-MS/MS system.

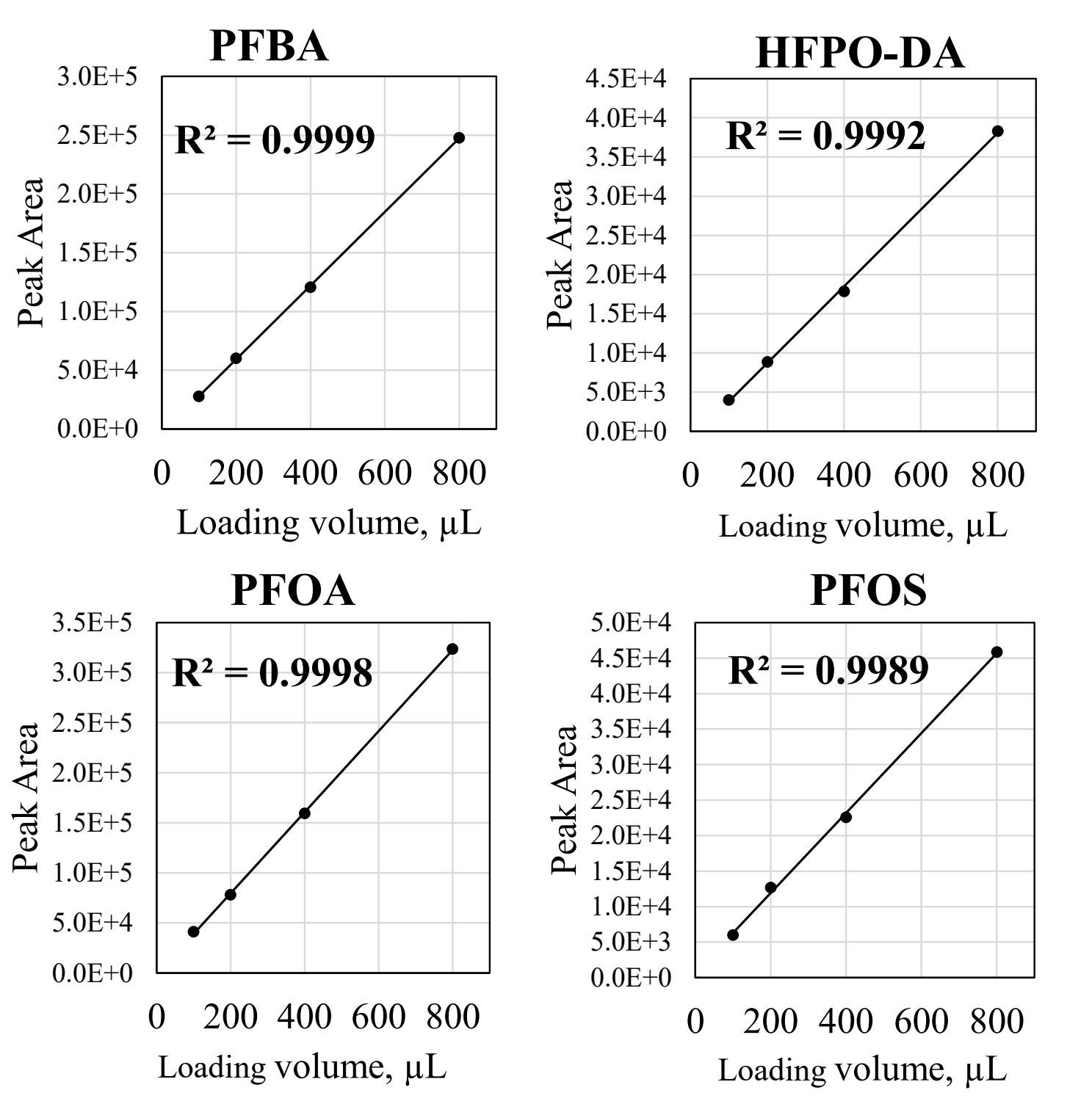
Table 2 Recovery and Reproducibility Test

No.	Analyte	Operation blank	River water	River water + native standard RSD, *n*=6	River water + native standard Rec.
		pg/mL	pg/mL	%	%
1	PFBA	0.2	4.1	*3.2*	92
2	PFPeA	0.2	2.0	*1.8*	95
3	PFHxA	1.0	3.6	*4.2*	96
4	PFHpA	0.2	1.4	*3.4*	99
5	PFOA	0.3	4.2	*2.9*	100
6	PFNA	0.2	1.2	*3.0*	103
7	PFDA	0.2	0.2	*4.3*	102
8	PFUnA	0.2	0.2	*2.8*	98
9	PFDoDA	0.1	0.1	*3.6*	95
10	PFTrDA	0.2	0.0	*2.6*	97
11	PFTeDA	0.1	0.0	*3.3*	96
12	PFHxDA	0.1	0.0	*5.1*	89
13	PFOcDA	0.2	0.0	*12.6*	91
14	8:2 diPAP	N.D.	N.D.	*3.2*	89
15	PFBS	N.D.	1.4	*4.3*	93
16	PFPeS	N.D.	N.D.	*3.0*	94
17	PFHxS	N.D.	0.2	*9.3*	87
18	PFHpS	N.D.	N.D.	*3.2*	89
19	PFOS	N.D.	0.5	*7.1*	84
20	PFNS	N.D.	N.D.	*4.0*	97
21	PFDS	N.D.	N.D.	*8.0*	109
22	8:2 FTUCA	0.1	0.0	*2.4*	110
23	4:2 FTS	N.D.	N.D.	*18.7*	102
24	6:2FTSA	N.D.	N.D.	*5.6*	104
25	8:2FTSA	N.D.	N.D.	*7.8*	103
26	PFMPA	N.D.	N.D.	*2.4*	98
27	PFMBA	N.D.	N.D.	*4.5*	97
28	NFDHA	N.D.	N.D.	*3.0*	88
29	HFPO-DA	N.D.	1.8	*5.0*	104
30	PFEESA	N.D.	N.D.	*2.4*	99
31	NMeFOSAA	N.D.	N.D.	*4.0*	104
32	NEtFOSAA	N.D.	N.D.	*3.3*	110

Sample: Brackish water（Wakayama prefecture, Japan)

※ The recovery rate was calculated from the absolute peak area values (without using stable isotopes).

■ The volume of extract loaded onto the solid phase



■ Optimization of elution volume from SPE cartridge