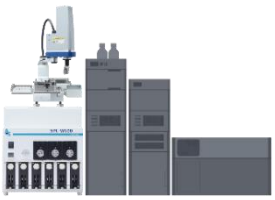
Simultaneous Multi-Component Analysis of PFAS in River Water Using an Online SPE-LC/MS System

Introduction

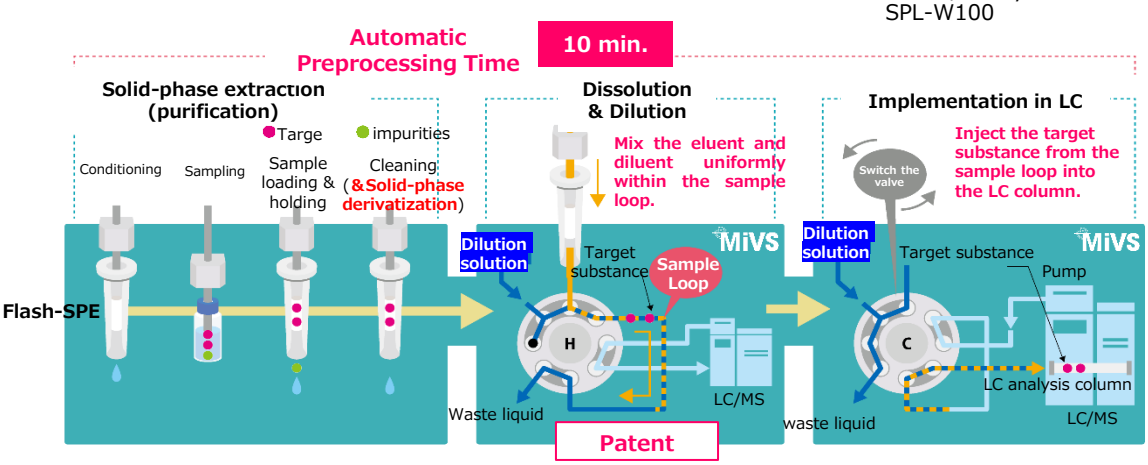
Perfluoroalkyl and polyfluoroalkyl substances (collectively referred to as “PFAS”) are widely used in daily life as processing aids for fluoropolymers, in paints, water repellents, emulsifiers, firefighting agents, and nonstick cookware. However, concerns have been reported regarding environmental pollution and various toxic effects on humans due to their non-volatility and persistence, which cause them to remain in the environment for extended periods.
Currently, perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), and perfluorohexane sulfonic acid (PFHxS) are targeted for testing in water and soil. However, it is anticipated that the number of substances subject to regulation will increase in the future.
This application introduces a multi-component simultaneous analysis method for PFAS in river water using the SPL-W100 online SPE-LC/MS system, which performs fully automated solid-phase extraction and measurement simply by loading the sample.

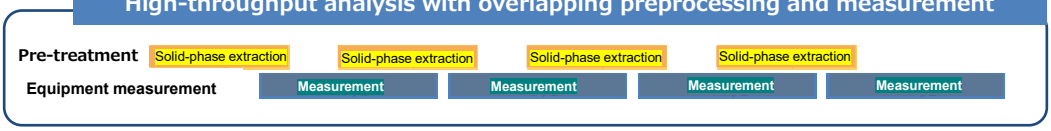
Overview of the Online SPE-LC/MS System

This system achieves “reduced sample volume,” “shortened pretreatment time,” and “online operation” through the use of the dedicated solid-phase cartridge Flash-SPE and the mixed injection valve system [MiVS]. Furthermore, overlapping the pretreatment (solid-phase extraction) and instrument measurement enables more efficient analysis.



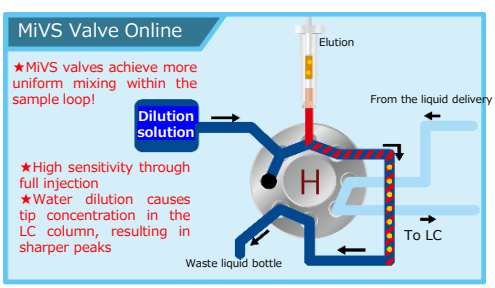
Online SPE-LC/MS System
SPL-W100





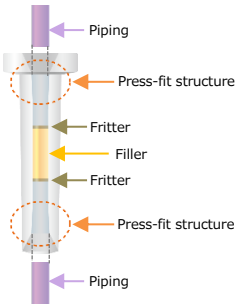
Mixed Injection Valve System [MiVS] (Patent)

This valve features an optimized flow path design. It mixes the eluent from the solid phase with a diluent (such as water) within the valve, then switches the valve to introduce the mixture into the LC column. For example, in reverse-phase mode analysis, it can be used to mix with water to reduce the solvent ratio, adjust the pH of the eluent, or facilitate derivatization.



Dedicated Solid-Phase Cartridge Flash-SPE (Patent)

Since the filling amount is only a few milligrams, small-scale solid-phase extraction is achievable, and it is also effective for reducing solvent usage.



SPL-W100
for SPE-LC system

Sample

Information

This application is the result of a joint research project with the Saitama Prefectural Environmental Science International Center (Mr. Takamine and Mrs. Takazawa).

Key Word

PFAS
Solid-phase extraction
Online SPE-LC/MS/MS

AiSTI SCIENCE

Product

SPL-W100
Flash-SPE WAXs

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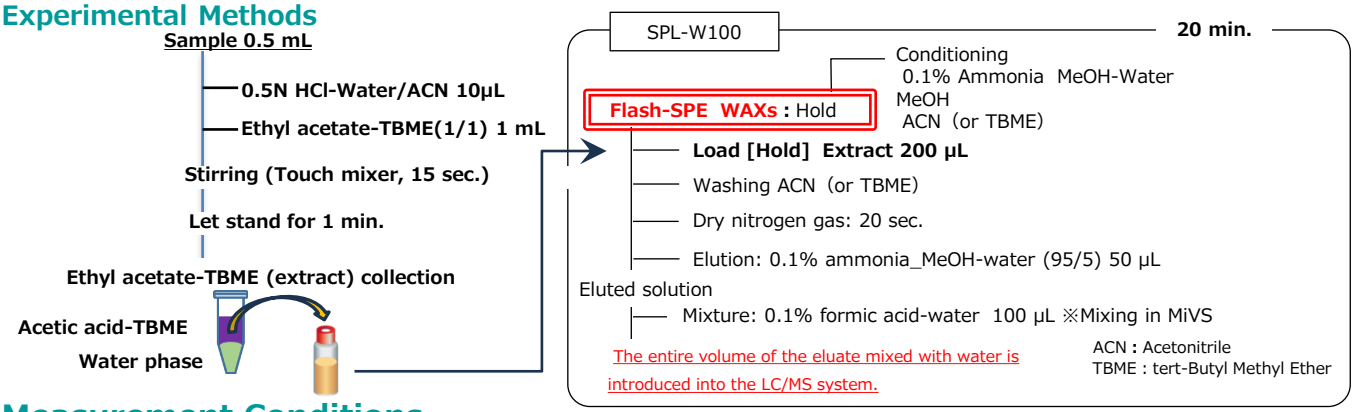
Experimental Methods



Measurement Conditions

【Device】

SPL-W100(AiSTI SCIENCE)、 LCMS-8045(Shimadzu)

【LC Conditions】

Delay Column: Inertsil ODS-3, 3 μm, 3.0 mm ID × 33 mm (UP)
Analytical Column: Inertsil ODS-3, 3 μm, 2.1 mm ID × 75 mm
Mobile Phase A: 2 mM ammonium acetate-water
B: 2 mM ammonium acetate-MeOH-acetonitrile (1/1)
Flow rate: 0.3 mL/min
Gradient: B.Conc. 20% (0 min) → 30% (1-2.5 min) → 40% (3-3.5 min) → 100% (11-15 min) → 20% (16 min)
Column temperature: 40 °C

【MS Conditions】

Ionization mode : ESI Negative
Measurement Mode : MRM

Result

Addition recovery tests were conducted using tap water, mineral water, and river water. The recovery rate was calculated from the following equation, using samples added to purified water as the absolute calibration curve (1 point). For the three components PFOSA, NMePFOSA, and NEtPFOSA, recovery was not obtained. This is because they lack anionic charge, resulting in weak retention on the WAX, and because loading with hydrophobic organic solvents likely prevents retention on the WAX. For the other components, good recovery rates and reproducibility were obtained for all samples.

Recovery Rate (%) = (Added Area Value - Blank Area Value) / (Purified Water Added Area Value - Blank Area Value) × 100

Table: Recovery Rates and Reproducibility of PFAS in Each Sample

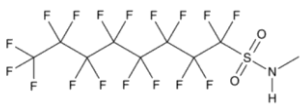
	Sample	Tap water		Mineral water		River water	
		Addition 20 ppt n=5		Addition 20 ppt n=5		Addition 20 ppt n=5	
No.	成分名	Recovery Rate (%)	RSD (%)	Recovery Rate (%)	RSD (%)	Recovery Rate (%)	RSD (%)
1	PFBA	101	4.0	96	2.4	96	4.2
2	PFMPA	92	3.4	92	2.7	85	2.9
3	PFPeA	92	3.7	89	2.6	91	5.9
4	PFMBA	88	5.5	81	1.8	75	3.8
5	PFBS	99	3.3	103	4.5	99	6.0
6	4:2 FTS	99	5.3	94	4.9	84	7.9
7	PFHxA	96	3.5	96	2.7	97	3.4
8	PFEESA	97	3.0	99	4.0	96	3.7
9	HFPO-DA	99	6.6	103	2.1	103	4.2
10	PFPeS	99	6.0	101	2.8	102	4.2
11	PFHpA	97	2.6	95	2.2	97	0.9
12	PFHxS	99	3.9	103	4.2	103	3.1
13	6:2FTSA	96	3.4	97	4.5	99	2.7
14	PFOA	91	6.5	100	3.0	100	3.3
15	PFHpS	100	6.2	102	6.8	105	5.0
16	8:2 FTUCA	99	3.8	102	2.8	104	1.6
17	PFNA	90	3.4	93	2.7	94	2.6
18	PFOS	101	6.8	101	2.9	104	7.2
19	8:2FTSA	94	3.0	98	4.3	98	1.5
20	PFDA	90	3.9	97	3.2	93	2.4
21	FOSA	N.D.	–	N.D.	–	N.D.	–
22	NMeFOSAA	104	7.2	108	4.2	108	6.5
23	NEtFOSAA	101	5.2	106	3.3	108	3.9
24	PFUnA	89	2.2	97	2.2	100	2.6
25	PFDS	101	7.4	102	2.4	109	5.5
26	PFDoA	86	1.9	103	2.7	104	5.3
27	NMeFOSA	N.D.	–	N.D.	–	N.D.	–
28	NEtFOSA	N.D.	–	N.D.	–	N.D.	–
29	PFTrDA	92	2.7	116	1.6	117	3.0
30	PFTeDA	92	5.3	118	1.0	121	4.3
31	PFHxDA	83	2.8	103	1.5	106	7.3
32	8:2 diPAP	96	4.3	113	2.6	118	2.4
33	PFOcDA	80	6.7	91	5.2	89	3.1

※Calculations are based on absolute area values without applying

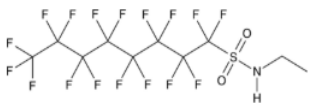
【 Unrecovered components 】

FOSA

NMeFOSA



NEtFOSA



Summary

This system enabled the analysis of approximately 30 PFAS components. Since this system also allows for on-site SPE sampling—where samples are loaded onto solid phases at the site and brought back for analysis—it is considered a useful technique for monitoring analysis.