Analysis of PFAS in river water using on-line SPE-LC/MS system

Introduction

Perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), and perfluorohexane sulfonic acid (PFHxS) are widely used in our daily lives as processing aids for fluoropolymers, paints, water repellents, emulsifiers, fire extinguishing agents, and frying pans. These substances (collectively called “PFAS”) are non-volatile and persistent, and there are concerns about environmental contamination and various toxicities to human health due to their long persistence in the environment.

This application introduces a method for analyzing PFAS in river water using an on-line SPE-LC/MS system that enables fully automated analysis from solid-phase extraction to measurement, aiming at “small sample volume,” “omission of nitrogen gas purge concentration,” “short pretreatment time,” and “automation.

Target

PFOS
PerFluoroOctaneSulfonic acid
MW: 500.1
Logpow = 5 (計算値)

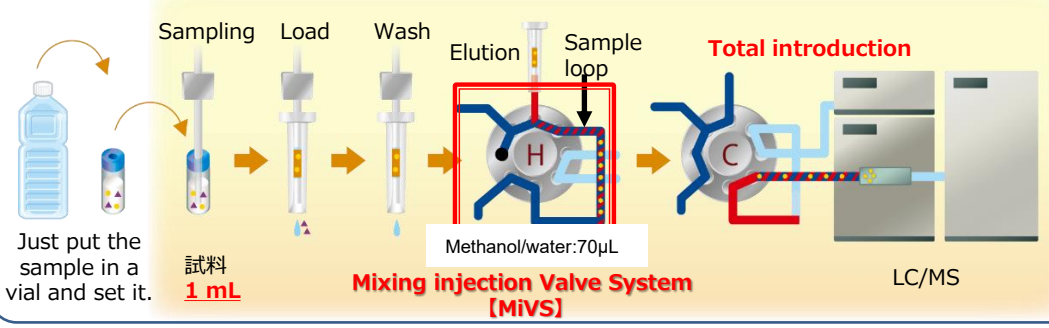
PFOA
PerFluoroOctanoic Acid
MW: 414.1
Logpow = 6.3, 4.9 (計算値)

PFHxS
PerFluoroHexaneSulfonic acid
MW: 400.1
Logpow = 3.7 (計算値)

Online SPE-LC/MS System Overview

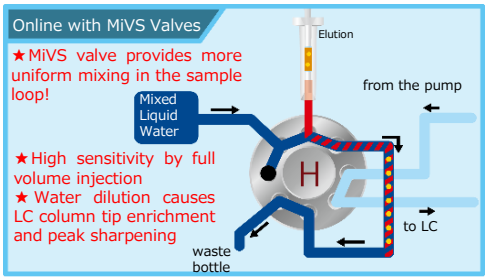
Fully automated from pretreatment to measurement

Pretreatment time : 12 分



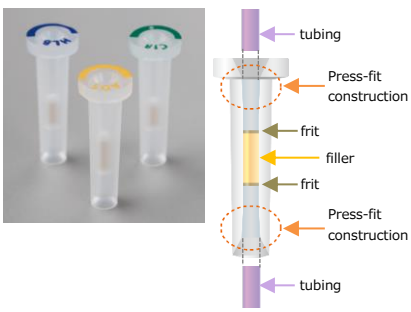
Mixing injection Valve System(Patent)

This is a valve with an ingenious flow path of an eight-way valve. The eluate from the solid phase is mixed with diluent (water) in the valve, and then introduced to the LC column by switching the valve. For example, in reversed-phase mode analysis, the eluent is diluted with water and introduced into the LC to obtain a good peak shape even with a large injection volume. The mixing function in the valve can also be applied to pH adjustment and derivatization of samples.



Flash−SPE(Patent)

The very small filling volume of a few mg allows for small-scale solid-phase extraction and solvent reduction.



SPL-W100
for SPE-LC system

Sample

Information

Key Word
solid-phase extraction
On-line SPE-LC/MS/MS

AiSTI SCIENCE

Product
SPL-W100
Flash-SPE C18

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Experimental Methods

【Standard solution】

3 kinds of organic fluorine compounds mixed standard solution (FUJIFILM Wako Pure Chemical Corporation)

Dispense sample into 1.5mL vials

↓

Set in SPL-W100

SPL-W100

Flash-SPE C18-5 mg : Retention

- Conditioning: Methanol-water (95/5), Methanol-water (1/9)
- **Load[Retention]** **Test solution** 1 mL
- Wash Methanol-water (1/9) 250μL
- Elution Methanol-water (95/5) 70μL

Eluent

- Addition water 70 μL ※Mixed within MiVS

All elution volumes introduced into LC/MS

Measuring conditions

【equipment】

SPL-W100(AiSTI)

LCMS-8045(Shimadzu)

【LC condition】

Analytical Columns : l ODS-3, 3 μm, 2.1 mmID × 75 mm

mobile phase Inertsi

A Liquid : 2mM ammonium acetate-water

B Liquid : 2mM ammonium acetate_MeOH-acetonitrile (1/1)

Velocity : 0.3 mL/min

Gradient : B.Conc. 40 %(0-1 min)→100 %(7-9 min)

Column Temperature : 40 ℃

【MS Conditions】

Ionization mode : ESI Negative

MRM : PFOA 412.9>169, 412.9>368.9

PFOS 499>79.8, 499>98.9

PFHxS 399>79.8, 399>98.9

Result

(1) analytical curve

Figure 1 shows a calibration curve created by measuring a sample prepared by adding mixed standard solution to ultrapure water to achieve a concentration of 0.5-10 ng/L in the sample. Good linearity with correlation coefficients of 0.999 or higher was obtained for all three components.

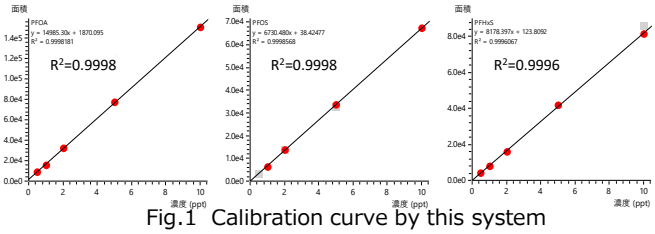

Fig.1 Calibration curve by this system (concentration : 0.5,1,2,5,10 ng/L)

(2) Addition Recovery Rate and Reproducibility

Table 1 shows the recovery rate and reproducibility obtained from the quantitative values obtained by measuring river water as it is with this system and the quantitative values obtained by adding a standard solution to the river water so that the concentration in the sample increases by 5 ng/L. PFOA and PFOS were detected at 5.4 ng/L and 2.9 ng/L (below the limit of quantification), respectively, in the river water in this test.

Figure 2 shows MRM quantitative ion chromatograms obtained with this system for a sample added to ultrapure water (A), river water (B), and ultrapure water (Operation Blank) (C) at 5 ng/L, which is 1/10 of the provisional guideline value of 50 ng/L. The results show that sufficient sensitivity is obtained even at 5 ng/L. On the other hand, 0.17 ng/L of PFOA was detected in the operational blank (C).

Table1 Additive Recovery Test Results and Reproducibility

Sample	No.	PFOA	PFOS	PFHxS
Ultra-pure water STD addition	K-5_1	77,273	28,352	41,675
	K-5_2	77,681	27,862	42,590
	Ave.	*77,477*	*28,107*	*42,133*
Ultrapure water operation blank	BL-1	2,521	N.D.	N.D.
	BL-2	2,690	N.D.	N.D.
	Ave.	*2,606*	—	—
river water	U-1	80,161	20,301	N.D.
	U-2	79,352	19,069	N.D.
	U-3	82,535	18,829	N.D.
	U-4	84,666	19,297	N.D.
	U-5	81,819	18,982	N.D.
	U-6	85,596	20,667	N.D
	Ave.	*82,355*	*19,825*	—
	RSD	***2.2***	***4.2***	**—**
River water STD addition 5 ppt	A-1	148,032	39,325	36,903
	A-2	150,598	36,747	36,387
	A-3	159,889	44,448	38,284
	A-4	154,056	46,589	37,170
	A-5	153,394	43,601	36,956
	A-6	154,785	43,632	36,729
	Ave.	*153,459*	*42,390*	*37,072*
	RSD.%	***2.6***	***8.6***	***1.8***
(A-U)/(K-BL)	recovery rate	**95**	**80**	**88**

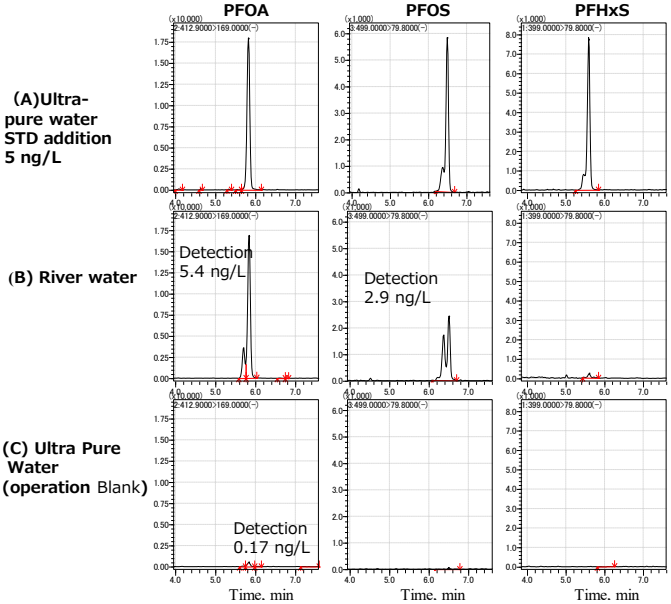

Fig.2 Each MRM ion chromatogram obtained by this system

Summary

This system enables fully automated and rapid analysis of PFAS in river water, from pretreatment to measurement, simply by placing river water in a vial and setting it. This also enables on-site SPE sampling methods, in which samples are loaded onto a solid phase on site and brought back for analysis. We plan to use this system to establish a simultaneous multi-component analysis method for PFAS in addition to PFOA, PFOS, and PFHxS.