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Application News

LCMS™-8050 High Performance Liquid Chromatograph Mass Spectrometer

Analysis of PFOA, PFHxS, and PFOS in Tap Water Using Triple Quadrupole LC/MS/MS

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User Benefits

- In addition to PFOA and PFOS included in the Complementary Items to Set the Targets for Water Quality Management, PFHxS, newly added as an Item for Further Study, can be quantified down to a concentration of 5 ng/L, less than 1/10 of the target value.
- All of the above components can be quantified in tap water with good recovery rates.

■ Introduction

Perfluorooctanoic acid (PFOA), perfluorohexane sulfonic acid (PFHxS), and perfluorooctane sulfonic acid (PFOS) are organofluorine compounds which are chemically stable, and there are concerns about health hazards due to their persistence in the body.

For water supply in Japan, the 1st Study Group on the FY 2020 Sequential Revision of Water Quality Standards held in January, 2021 has decided to designate PFHxS as an Item for Further Study as of April, 2021, in addition to PFOA and PFOS already specified as the Complementary Items to Set the Targets for Water Quality Management.

This article introduces the results of analyzing 1000-fold concentrated tap water samples with the LCMS-8050 liquid chromatograph mass spectrometer, according to the test method for the Complementary Items to Set the Targets for Water Quality Management (Target 31).[(1)]

The results confirmed that all three components, PFOA, PFHxS, and PFOS, can be accurately analyzed at a concentration (5 ng/L) less than 1/10 of 0.00005 mg/L (50 ng/L), the target value for PFOS and PFOA.

■ Pretreatment

As a pretreatment of tap water samples, the internal standard labeled with ^{13}C was added to the sample water to obtain a concentration of 5 ng/L, followed by solid phase extraction using an anion exchange solid phase column. The eluate from the column was concentrated by using N_2 gas and the volume was then fixed with methanol for analysis.

Fig. 1 shows the pretreatment flow for tap water.

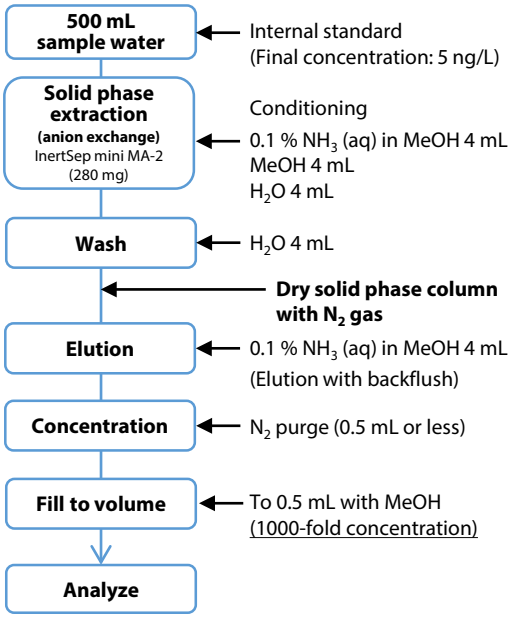


Fig. 1 Pretreatment Flow

■ Analysis Conditions

PFOA, PFHxS, and PFOS were measured according to the HPLC and MS analysis conditions shown in Table 1.

Table 1 Analysis Conditions

[HPLC conditions] (Nexera™ X3)		
Column	:	Shim-pack™ GIST C18-AQ HP (150 mm × 2.1 mm I.D., 3 µm) (Shimadzu GLC, P/N: 227-30765-04)
Mobile phases	:	A) 10 mmol/L Ammonium acetate in H_2O B) Acetonitrile
Gradient Program	:	B 25% (0-1 min) – 100% (26-30 min) – 25% (30.01-34 min)
Flow rate	:	0.2 mL/min
Column Temp.	:	40 °C
Injection volume	:	5 µL
[MS conditions] (LCMS-8050)		
Ionization	:	ESI (Negative mode)
Probe Voltage	:	-1 kV
Nebulizing gas flow	:	3 L/min
Drying gas flow	:	5 L/min
Heating gas flow	:	15 L/min
DL Temp.	:	200 °C
Heat Block Temp.	:	300 °C
Interface Temp.	:	300 °C
MRM transition	:	PFOA *m/z* 412.95>168.95
		PFHxS *m/z* 398.95>79.95
		PFOS *m/z* 498.95>79.95
		$^{13}C_8$-PFOA *m/z* 420.95>375.95
		$^{13}C_3$-PFHxS *m/z* 401.95>79.95
		$^{13}C_8$-PFOS *m/z* 506.95>79.95

■ MRM Chromatogram of Each Component

A mixed standard solution containing 5 ng/L each of PFOA, PFHxS, and PFOS (equivalent to 1000-fold concentration) was measured using the analysis conditions in Table 1, and Fig. 2 shows the respective MRM chromatograms obtained. All three components were found to be sufficiently detectable at concentrations less than 1/10 of the target value (50 ng/L).

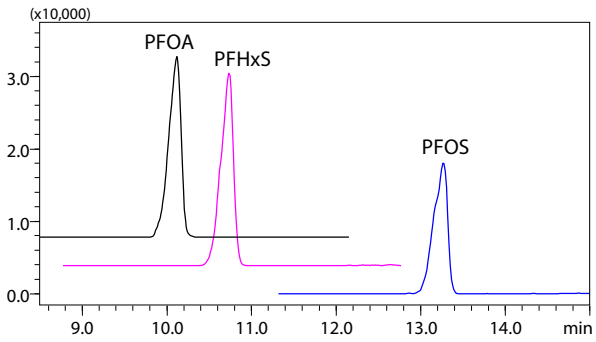
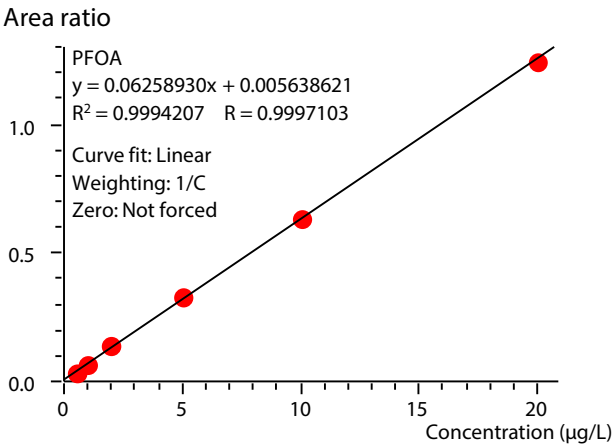


Fig. 2 MRM Chromatogram of Each Component (5 µg/L each)

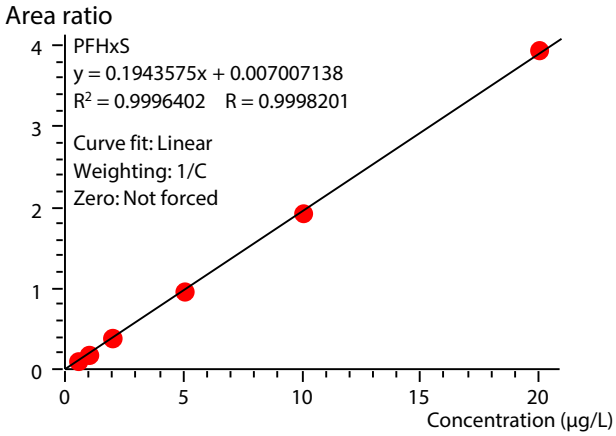
■ Calibration Curve of Each Component

Fig. 3 shows the calibration curves of PFOA, PFHxS, and PFOS in the concentration range of 0.5 to 20 µg/L (6 points) using the internal standard method.

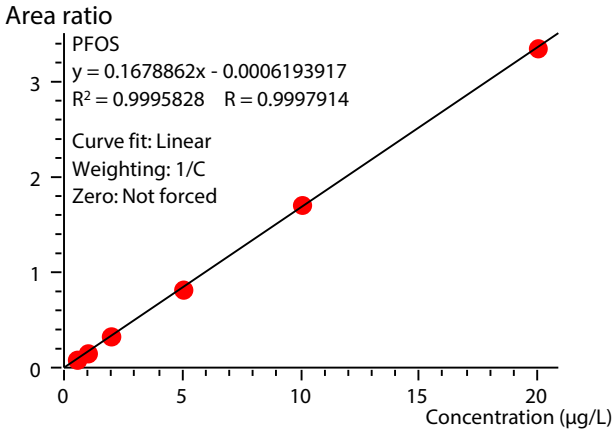
The contribution rate (r^2) of each calibration curve was $r^2 > 0.999$ for all three components, showing good linearity in each curve.



(a) Calibration curve of PFOA



(b) Calibration curve of PFHxS



(c) Calibration curve of PFOS

Fig. 3 Calibration Curve of Each Component

■ Spike-and-Recovery Test on Tap Water

Spike-and-recovery tests were conducted using tap water (from Kyoto Prefecture). Spiked tap water samples were prepared by adding PFOA, PFHxS, and PFOS to the collected tap water to obtain the respective concentration of 5 ng/L, and pretreated according to the flow in Fig. 1.

The obtained spike recovery rate was: 95% for PFOA, 111 % for PFHxS, and 106% for PFOS. Also, the repeatability (%RSD in concentration) was: 3.7% for PFOA, 2.6% for PFHxS, and 7.8% for PFOS (Table 2).

The results showed good spike recovery rate and repeatability, confirming that tap water samples can be analyzed with good accuracy.

Table 2 Spike-and Recovery Test Results (n=6)

Component	Spike recovery rate (%)	Repeatability (%RSD)
PFOA	95	3.7
PFHxS	111	2.6
PFOS	106	7.8

■ Conclusion

- In the analysis using LCMS-8050, sufficient sensitivity was obtained at a concentration less than 1/10 of the target value (5 ng/L) by concentrating the sample 1000 times according to the test method for the Complementary Items to Set the Targets for Water Quality Management (Target 31).
- Good recovery rates and reproducibility were obtained in the spike-and-recovery test for tap water samples, confirming that PFOA, PFHxS, and PFOS in tap water can be analyzed with high accuracy.

<Reference>

(1) Enactment of the Ministerial Ordinance on Water Quality Standards, Partial Amendment to the Enforcement Regulations of the Water Supply Act, etc., and Notes on Water Quality Management (October 10, 2003, No. 1010001, Water Supply Division, Health Bureau [Last Amendment March 30, 2020, No. 0330-1, Water Supply Division, Pharmaceutical Safety and Environmental Health Bureau]) Attachment 4: Inspection Methods for Complementary Items to Set the Targets for Water Quality Management

01-00114 -EN First Edition: Jun. 2021

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