

Application News

Accurate Analysis of PFOA, PFHxS, and PFOS in Drinking Water Using a Triple Quadrupole LC/MS/MS

Yui Higashi, Nami Iwasa

User Benefits

- ◆ PFOA, PFOS, and PFHxS concentrations at 0.2 ng/L (concentration in water sample) can be quantitated using an optimized analytical conditions.
- ◆ The LCMS-8050RX is equipped with CoreSpray technology, which improves consistency and reliability, so concentrations in drinking water can be quantitated with excellent recovery rates and repeatability for recovery tests (1 ng/L in samples).

Introduction

Perfluorooctanoic acid (PFOA), perfluorohexanesulfonic acid (PFHxS), and perfluorooctanesulfonic acid (PFOS) are types of organofluorine compounds that are used for a wide range of applications, such as water repellents, waterproof materials, and surfactants. Due to their chemical stability, there is concern that their environmental persistence could result in harmful accumulations in humans. Therefore, PFOA and PFOS are included in the water quality management goal items, and PFHxS is listed as an item for consideration in Japan.

This article describes the results from analyzing PFOA, PFOS, and PFHxS in drinking water that have been concentrated by a factor of 1000 based on the testing method of the water quality management in Japan.

Sample Preparation

The drinking water samples were pretreated by adding 50 µL of a ¹³C-labelled internal standard solution (a final concentration of 10 ng/L) and then using an anion exchange solid phase column for solid phase extraction. The eluate from the solid phase column was concentrated by drying with nitrogen gas stream, and then bring the volume to 0.5 mL with methanol for analysis. The sample preparation process is shown in Fig. 1. In this case, AquaTrace automatic solid phase extraction system from GL Sciences was used to automate all the steps, from conditioning to concentrating.

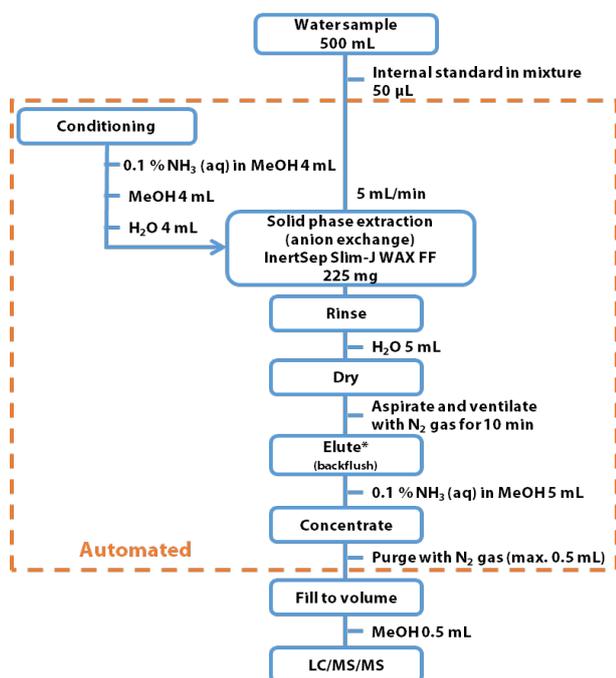


Fig. 1 Sample Preparation Process

(* The solid phase column was manually inverted for elution by backflushing.)

LCMS-8050RX

Samples were analyzed using a triple-quadrupole mass spectrometer, LCMS-8050RX (Fig. 2). The LCMS-TQ8050RX features the new CoreSpray technology, which generates a more uniform nebulizer flow than previous models, and the highly accurate ionization technology enables more consistent measurements.



Fig. 2 LCMS-8050RX

Analytical Conditions

The PFOA, PFHxS, and PFOS were measured based on the HPLC and MS analytical conditions listed in Table 1. Measuring PFAS requires particular care due to the risk of contaminations from the system, the mobile phase, and other sources. For this article, a delay column was installed between the mixer and autosampler to inhibit the effects of PFAS contamination from the system. A reagent intended for PFOS/PFOA analysis was used in the mobile phase.

Table 1 Analytical Conditions

UHPLC (Nexera™-X3 System)	
Analytical Column:	Shim-pack™ GIST-HP C18-AQ (150 mm × 2.1 mm I.D., 3 µm) (P/N: 227-30765-04)
Solvent Delay Column:	Shim-pack XR-ODS II (2 mm × 75 mm, 2.2 µm) (P/N: 228-41623-91)
Mobile Phase A:	10 mM Ammonium Acetate in H ₂ O
Mobile Phase B:	Acetonitrile
Gradient Program:	B 40% – 70% (13 min) – 100% (13.01 – 17 min) – 40% (17.01 – 21 min)
Flowrate:	0.2 mL/min
Column Temp.:	40 °C
Injection Volume:	1 µL
Run Time:	21 min
MS (LCMS-8050RX)	
Ionization:	ESI (Negative mode)
Mode:	MRM
Probe Voltage:	-1 kV
Nebulizing Gas:	3 L/min
Drying Gas Flow:	3 L/min
Heating Gas Flow:	15 L/min
DL Temp.:	150 °C
Block Heater Temp.:	250 °C
Interface Temp.:	300 °C
Probe Position:	+2 mm
MRM Transition:	PFOA <i>m/z</i> 412.90 > 169.10 PFHxS <i>m/z</i> 399.00 > 79.95 PFOS <i>m/z</i> 498.90 > 79.95 ¹³ C ₈ -PFOA <i>m/z</i> 420.90 > 375.85 ¹³ C ₆ -PFHxS <i>m/z</i> 405.00 > 79.95 ¹³ C ₈ -PFOS <i>m/z</i> 506.90 > 80.00

MRM Chromatograms

A standard solution containing 0.2 µg/L each of PFOA, PFHxS, and PFOS (equivalent to 0.2 ng/L in water samples) was measured based on the analytical conditions shown in Table 1. The resulting MRM chromatograms are shown in Fig. 3. With an optimized conditions, good separation from the PFHxS and PFOS branched chains was achieved.

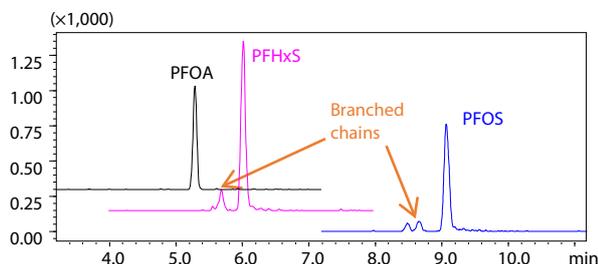


Fig. 3 MRM Chromatograms of Each Component (0.2 µg/L Each)

Calibration Curves

Fig. 4 shows the calibration curves for PFOA, PFHxS, and PFOS that are based on the internal standard method for the concentration range from 0.2 to 20 µg/L (7 points that are equivalent to 0.2 to 20 ng/L in the water samples). The calibration curve correlation coefficient (R) was greater than 0.9996 for all three compounds. Average concentration values at each calibration point (n = 5) were 80 to 120 % of the true value, and repeatability was less than 5 %RSD of the concentration. The area repeatability values (area %RSD value) at 0.2 µg/L, the lowest point of the calibration curves, was also less than 5 %. Excellent calibration performances were confirmed.

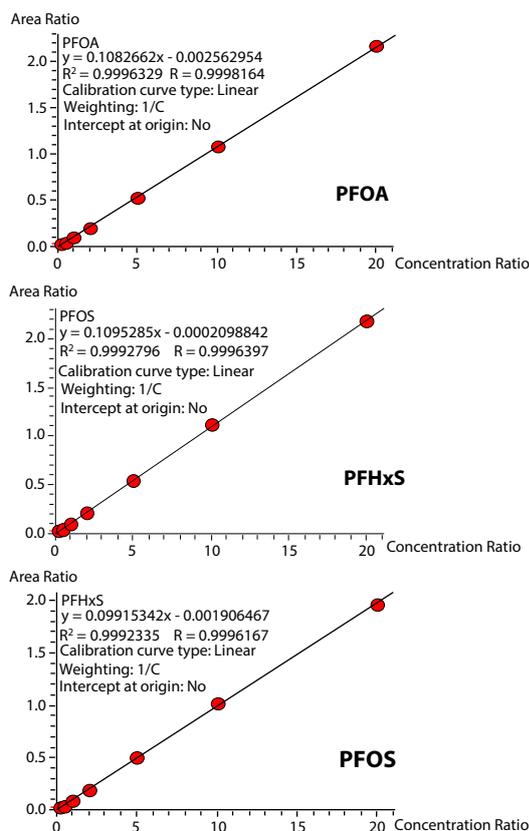


Fig. 4 Calibration Curves for Each Component (0.2 to 20 µg/L)

Recovery Test

Drinking water samples spiked with 1 ng/L or 5 ng/L concentrations of PFOA, PFHxS, or PFOS were prepared and pretreated according to the process indicated in Fig. 2. The results are indicated in Table 2. Recovery rates ranged from 82 to 103 % and repeatability was less than 4 % of concentration, which were both good results that confirmed drinking water samples can be analyzed accurately.

Table 2 Recovery Test Results (n = 5)

Component	1 ng/L Concentration in Water Sample		5 ng/L Concentration in Water Sample	
	Recovery (%)	Repeatability (%RSD)	Recovery (%)	Repeatability (%RSD)
PFOA	82.4	2.5	82.8	2.2
PFHxS	102.9	2.3	94.2	0.9
PFOS	98.6	3.5	92.8	2.0

Conclusion

By using LCMS-8050RX, adequate sensitivity was achieved for analyzing the concentration of 0.2 ng/L (equivalent to 0.2 ng/L in the water samples).

Good recovery rates and reproducibility results were obtained from recovery tests for drinking water with 1 ng/L concentrations using a 1000-fold concentration process. In this case, sample preparation was automated by using the AquaTrace system, which simplified operations and reduced the labor time. LCMS-8050RX system, which is equipped with CoreSpray technology, provided more consistent ionization and ion loading performance, and highly reliable analytical results were achieved.

The above results confirm that LCMS-8050RX system can be used to analyze PFOA, PFHxS, and PFOS in drinking water efficiently and accurately.

Acknowledgments

We are deeply grateful to GL Sciences for their generous help with the sample preparation and other aspects for this article.

Nexera and Shim-pack are trademarks of Shimadzu Corporation in Japan and other countries.