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Application News

LCMS™-8060NX High Performance Liquid Chromatograph Mass Spectrometer

# Direct Analysis of PFOS and PFOA in Tap Water Using Triple Quadrupole LC/MS/MS

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## User Benefits

- Perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) can be analyzed without concentration.
- It is possible to analyze concentrations of less than 1/10 of the target value (50 ng/L) specified in the Complementary Items to Set the Targets for Water Quality Management.
- PFOS and PFOA in tap water can be analyzed with good recovery rate.

## ■ Introduction

Perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are organofluorine compounds which are chemically stable, and there are concerns about health hazards due to their persistence in the body. For this reason, the production of these substances is restricted internationally by the Stockholm Convention.[1), (2)]

For water supply in Japan, the sum of the amounts of these two components, PFOS and PFOA, was set to 0.00005 mg/L (50 ng/L) as the target value (provisional) for the Complementary Items to Set the Targets for Water Quality Management.[(3)] Whereas Application News C224 introduced 1000-fold concentration with solid-phase extraction as a pretreatment process, this article introduces the analysis results obtained by directly injecting tap water without concentration, using the LCMS-8060NX liquid chromatograph mass spectrometer. The results showed that good spike recovery rates were obtained for both components at concentrations 1/10 of the target value, confirming that accurate analysis is possible.

## ■ Analysis Conditions

Table 1 shows the analysis conditions. We installed a delay column between the mixer and the autosampler to separate the PFOA derived from the HPLC system and the PFOA contained in the sample.

Table 1 Analysis Conditions

| | |
|---|---|
| [HPLC conditions] (Nexera™ X3) | |
| Column | : Shim-pack™ Velox SP-C18 (150 mm L × 2.1 mm I.D., 2.7 µm) P/N: 227-32003-04 |
| Delay Column | : Shim-pack XR-ODS II (75 mm × 2.0 mm I.D., 2.2 µm) P/N: 228-41623-91 |
| Mobile phases | : A) 20 mmol/L Ammonium Acetate in $H_2O$ B) Methanol |
| Gradient Program | : B 55% (0.00 min) – 85% (25.00 min) – 95% (25.10 - 30.00 min) – 55% (30.01 – 34.50 min) |
| Flow rate | : 0.25 mL/min |
| Column Temp. | : 40 ˚C |
| Injection volume | : 50 µL |
| [MS conditions] (LCMS™-8060NX) | |
| Ionization | : ESI (Negative mode) |
| Probe Voltage | : -1 kV |
| Focus Voltage | : -3 kV |
| Nebulizing gas flow | : 3 L/min |
| Drying gas flow | : 10 L/min |
| Heating gas flow | : 10 L/min |
| DL temp. | : 200 ˚C |
| Heat Block Temp. | : 300 ˚C |
| Interface Temp. | : 200 ˚C |
| MRM transition (*m/z*) | : PFOS 498.90>79.95 PFOA 412.90>169.10 $^{13}C_8$-PFOS (internal standard) 506.90>80.00 $^{13}C_8$-PFOA (internal standard) 420.90>375.85 |

## ■ Calibration Curves and MRM Chromatograms

Mixed standard samples of 1, 2, 5, 10, 20, and 50 ng/L were prepared with a ratio of water/methanol=90:10, and internal standards ($^{13}C_8$-PFOS, $^{13}C_8$-PFOA) were added as 10 ng/L total concentration for each sample. Using these samples, calibration curves of PFOS and PFOA were created using the internal standard method. Fig. 1 shows the calibration curves obtained. It was confirmed that good calibration curves were obtained for both components, with contribution rate ($r^2$) >0.999, and each calibration point accuracy within the range of 80 to 120%.

From the MRM chromatogram shown in Fig. 2, it was also confirmed that the delay column can separate the PFOA derived from the HPLC system and that in the sample. Then, Fig. 3 shows each MRM chromatogram obtained from the mixed standard sample, and Table 2 shows the result of the reproducibility test from repeated analyses (n=5). The chromatogram of each component was found satisfactory, and it was also confirmed that the repeatability (%RSD) was <5 %. From these results, we confirmed that the direct injection method can also accurately analyze concentrations less than 1/10 of the target value, 50 ng/L.

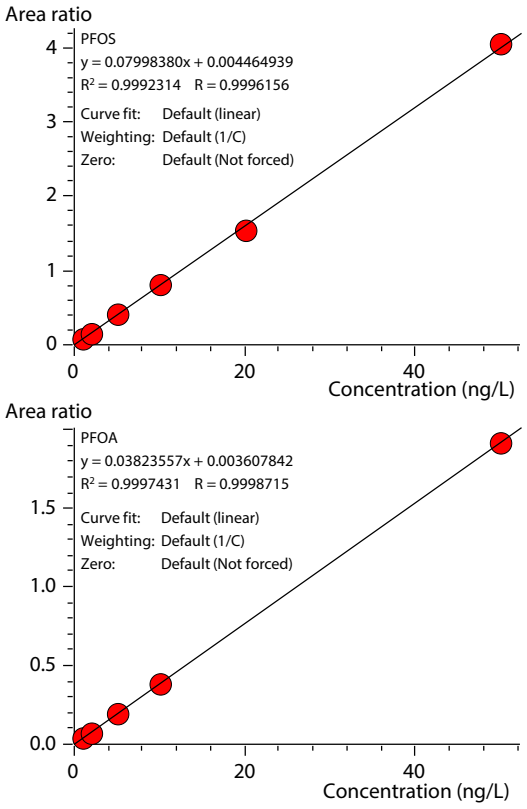


Fig. 1 Calibration Curves of PFOS and PFOA (1-50 ng/L)

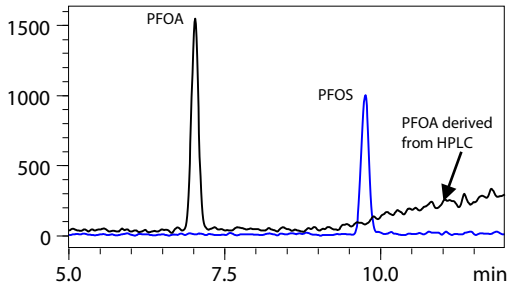


Fig. 2 MRM Chromatogram (1 ng/L mixed standard sample)

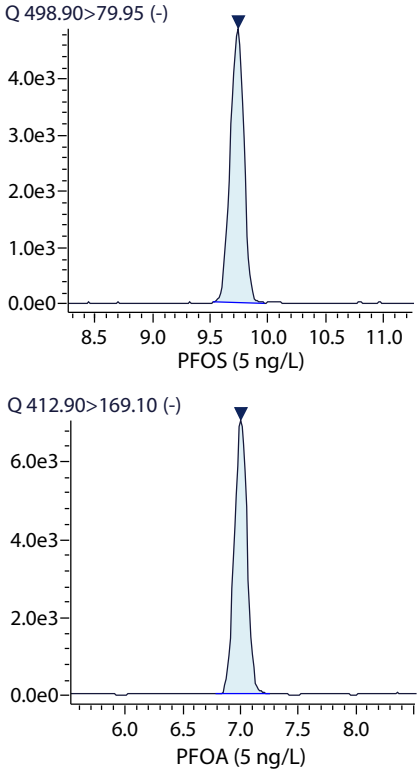


Fig. 3 MRM Chromatograms of PFOS and PFOA

Table 2 Results of Repeated Analyses of Mixed Standard Samples (n=5)

| Component | 1 ng/L | | 5 ng/L | |
|---|---|---|---|---|
| | Accuracy (%) | Repeatability (%RSD) | Accuracy (%) | Repeatability (%RSD) |
| PFOS | 106.8 | 3.3 | 106.2 | 1.9 |
| PFOA | 101.8 | 2.4 | 100.9 | 2.5 |

## ■ Spike-and -Recovery Test on Tap Water

Tap water (from Kanagawa Prefecture) was prepared to obtain the ratio of tap water/methanol=90 : 10 and used as tap water samples. Also, a mixed standard sample was spiked to tap water at a concentration of 5 ng/L for each component, and the spiked tap water was submitted for analysis. When an isomer with a branched chain was detected, the peak area of the isomer was added to that of the linear chain for quantification.

Fig. 4 shows each MRM chromatogram obtained, and Table 3 shows the spike recovery rate for 5 ng/L. These results confirmed that the actual sample can also be analyzed with high accuracy.

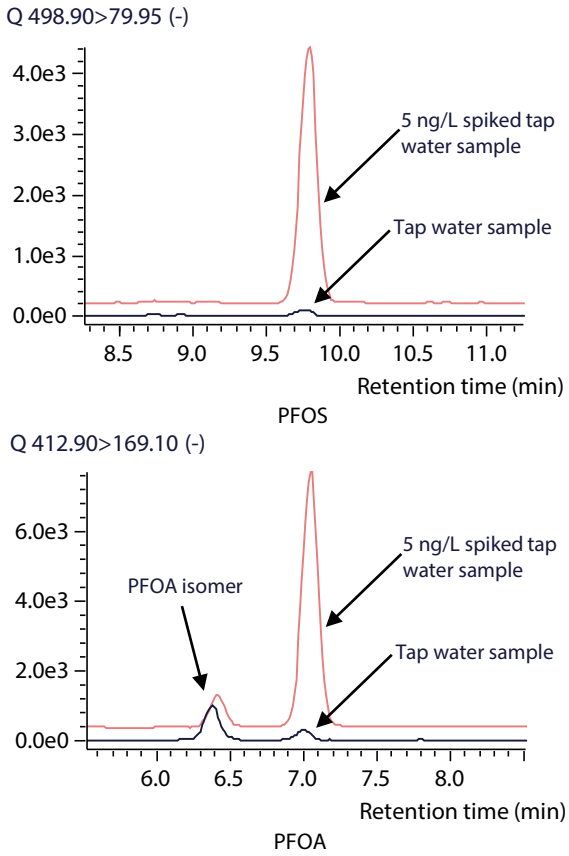


Fig. 4 MRM Chromatograms of Tap Water and Spiked Sample

Table 3 Results of Repeated Analysis of Spiked Tap Water Samples (n=5)

| Component | Spike recovery rate (%) | Repeatability (%RSD) |
|---|---|---|
| PFOS | 109.9 | 1.4 |
| PFOA | 109.5 | 3.9 |

## ■ Conclusion

- In the analysis using the LCMS-8060NX, we confirmed that sufficient sensitivity can be obtained at concentrations below 1/10 of the target value specified in the Complementary Items to Set the Targets for Water Quality Management.
- Good recovery rates and reproducibility obtained in the spike recovery test for tap water samples confirmed that this analysis method can accurately analyze PFOS and PFOA in tap water.

<References>
(1) The Stockholm Convention on Persistent Organic Pollutants (POPs) Annex A (Elimination) as of May, 2019
(2) The Stockholm Convention on Persistent Organic Pollutants (POPs) Annex B (Restriction) as of May, 2019
(3) Notice from the Director of the Health Service Bureau, Ministry of Health, Labour and Welfare
"Enactment of the Ministerial Ordinance on Water Quality Standards and Partial Amendment to the Enforcement Regulations of the Water Supply Act, etc."
(October 10, 2003, No. 1010004, Health Service Bureau [last revision: March 30, 2020, No. 0330-1, Policy Planning Division for Environmental Health and Food Safety)
Appendix 1: Complementary Items to Set the Targets for Water Quality Management



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