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Application News

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LC-MS

Analysis of Perfluorooctanesulfonic Acid (PFOS) and Perfluorooctanoic Acid (PFOA) in Tap Water Using a Triple Quadrupole LC/MS/MS

Perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), organic fluorine compounds, are known to persist in the environment and are bioaccumulative. PFOS, which was added to Annex B (restriction) of the "Stockholm Convention on Persistent Organic Pollutants" in 2009, has had restrictions placed on its production, use, import and export. Additionally, PFOA was also listed in Annex A (elimination) of the convention at the 9th meeting of the Conference of the Parties to the Stockholm Convention with specific exemptions.

Under the notification issued in March 2020 by the director of the Water Supply Division, Pharmaceutical Safety and Environmental Health Bureau, Ministry of Health, Labour and Welfare (PSEHB/WSD Notification No. 0330-1 to -4), PFOS and PFOA, which had been designated as items for further study have, since April 2020, been added to complementary items with target values. This notification also specifies that 0.00005 mg/L (50 ng/L), which is the total acceptable concentration of these two compounds, has been adopted as the target value.

This article introduces the results of analysis of the 1000-fold condensed tap water using a liquid chromatograph mass spectrometer, LCMS™-8050, in accordance with the analytical method for complementary items with target value (Target 31).

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Pretreatment

Under the analytical method for complementary items with target value (Target 31), tap water samples were pretreated by adding the internal standards ($^{13}C_8$-PFOS and $^{13}C_8$-PFOA) to the sample water to make a concentration of 10 ng/L, followed by solid phase extraction in an anion-exchange solid phase column. The eluate resulting from the solid-phase column was then concentrated under a stream of nitrogen gas, filled to volume with methanol, and then analyzed by LC/MS/MS.

Fig. 1 shows a flowchart of the pretreatment process for tap water.

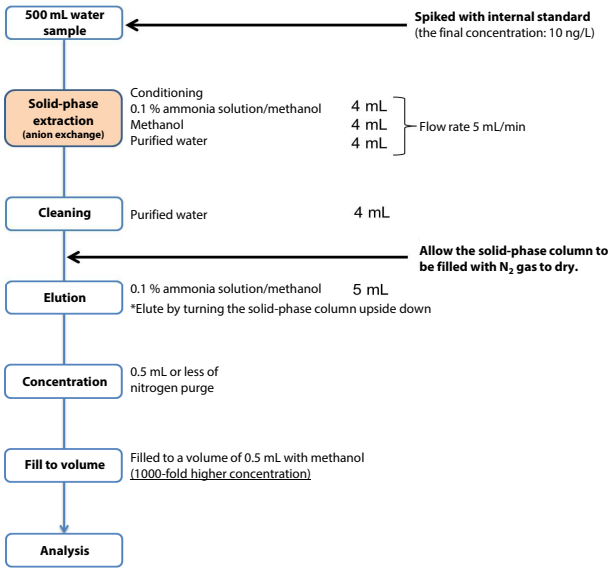

Fig. 1 Flow Chart of Tap Water Pretreatment

MRM Chromatograms of PFOS and PFOA (Measurement of Standard Mixture)

Fig. 2 shows MRM chromatograms of PFOS and PFOA at concentrations of 1 ng/L and 5 ng/L (1000-fold condensed when analyzed) obtained from the analysis of the standard mixture under the analytical conditions shown in Table 1. The chromatograms demonstrated that these compounds can be detected sufficiently even at concentrations of 1/10 or lower than the target value (50 ng/L).

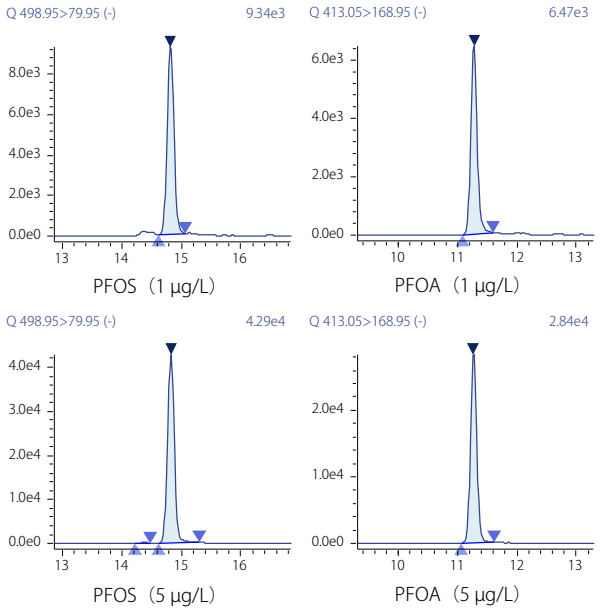

Fig. 2 MRM Chromatograms of PFOS and PFOA (Standard Mixture)

Table 1 Analytical Conditions

Column	:	Shim-pack™ GIST C18-AQ HP (150 mm × 2.1 mm I.D., 3 µm P/N : 227-30765-04)
Mobile phase A	:	10 mmol/L ammonium acetate aqueous solution
Mobile phase B	:	Acetonitrile
Time Program	:	B conc. 25 % (0-1 min) – 100 % (26-30 min) - 25 % (30.01 – 33.5 min)
Flow rate	:	0.2 mL/min
Column Temp.	:	40°C
Injection volume	:	5 µL
Prove Voltage	:	1 kV (ESI-Negative)
DL Temp.	:	200 °C
Block Heater Temp.	:	300 °C
Interface Temp.	:	300 °C
Nebulizing Gas Flow	:	3 L/min
Drying Gas Flow	:	5 L/min
Heating Gas Flow	:	15 L/min
MRM Transition	:	PFOS *m/z* 498.95> 79.95 (-) PFOA *m/z* 413.05>168.95 (-) $^{13}C_8$-PFOS (internal standard) *m/z* 506.90 > 80.00 (-) $^{13}C_8$-PFOA (internal standard) *m/z* 420.90 > 375.85 (-)
Vial	:	1.0 mL disposable vial (P/N : 228-31600-91)

Calibration Curves of PFOS and PFOA (Analysis of Standard Mixture)

Fig. 3 shows calibration curves obtained by the internal standard method for PFOS and PFOA in the concentration ranges of 1 - 20 µg/L (5 points).

Good linearity was obtained with correlation coefficients (R^2) of > 0.999 for all calibration curves of PFOS and PFOA.

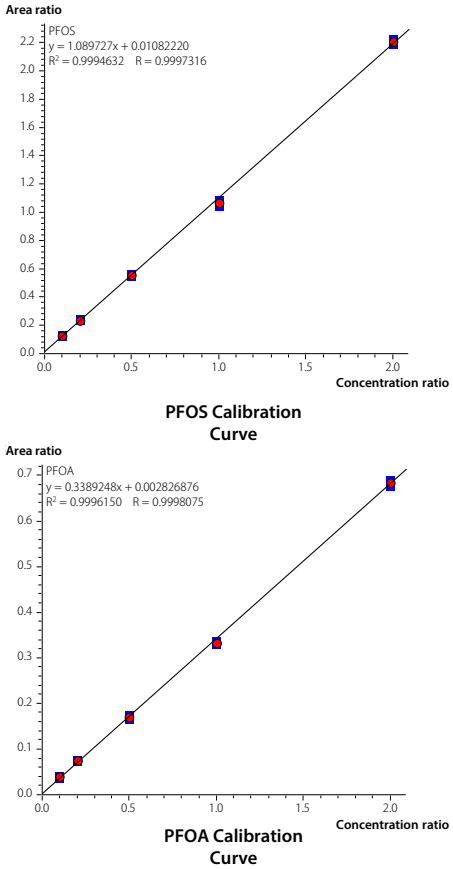

Fig. 3 Calibration Curves of PFOS and PFOA (standard mixture)

Analysis of Tap Water

A spike-and-recovery test was performed using tap water (from Kanagawa Prefecture). Tap water sample was prepared by adding PFOS and PFOA to the collected tap water to make a concentration of 5 ng/L for both compounds. The sample was pretreated in accordance with the flow chart shown in Fig. 1.

Tap water and the tap water sample spiked with the compounds were analyzed and MRM chromatograms of these solutions were obtained, as shown in Fig. 4.

Additionally, Table 2 shows the quantitative results for these compounds. These results demonstrated that the recovery of PFOS and PFOA were 104 % and 79 %, respectively, with a reproducibility (concentration %RSD) of 5 % or lower when repeated 5 times. The accuracy of the control samples after the analysis of tap water was within a range of 80 - 120 %.

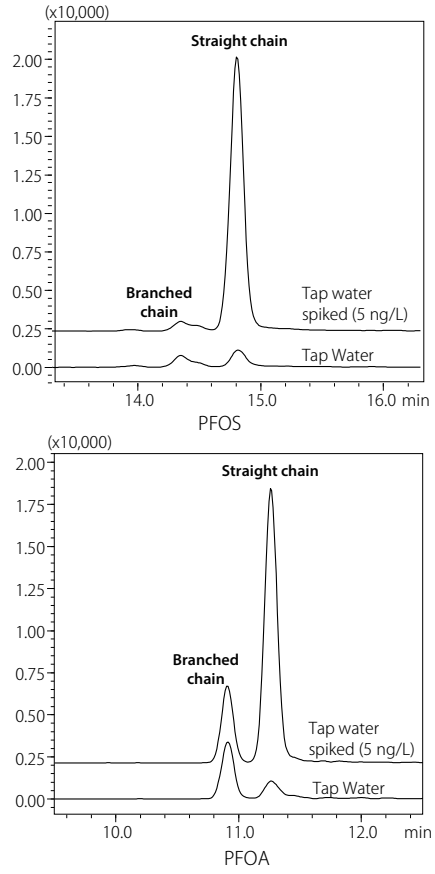

Fig. 4 MRM Chromatograms of Tap Water and Tap Water Samples Spiked with PFOS and PFOA

Conclusion

These results showed that the analytical method using an LCMS-8050 for PFOS/PFOA, complementary items with target value , (Target 31) meets the guidelines for the appropriateness of a tap water quality test, and that the method enables analysis of these compounds with a high degree of accuracy.

Table 2 Results of Spiked-and-Recovery Test with Tap Water

Compound	Quantitative concentration of the compound in tap water (ng/L)	Spike recovery (N=5)	Conc. %RSD (N=5)	Control sample (accuracy) (5 µg/L)
PFOS	N.D.	104 %	1.2 %	101 %
PFOA	1.03	79 %	3.4 %	99 %

*The quantitative values in tap water are determined based on the results of a blank test using purified water performed at the time of analysis.

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