

Application News

No. C173

Liquid Chromatograph Mass Spectrometry

Analysis of Perchlorate in Tap Water Using a Triple Quadrupole LC/MS/MS

Perchlorate is a chemical compound that may occur naturally. It can be found in minerals and is also known to be generated from photochemical reactions in the atmosphere. The compound is highly soluble in water, and after dissociation, exists as stable perchlorate ions. Ingesting large amounts of perchlorate such as from contaminated drinking water may decrease thyroid function, raising human health concerns.

Furthermore, perchlorate is difficult to remove from tap water sources by regular purification processes. In Japan, perchlorate was specified in 2009 as an Item for Further Study in its water quality standards. In 2011, a water quality control criterion of 0.025 mg/L was determined.

Example Analysis Using an Anion Exchange Column

A perchlorate standard solution with a concentration of 0.0025 mg/L, which is a tenth of the criterion concentration, was analyzed using the anion exchange column indicated in Table 1. The obtained MRM chromatogram is shown in Fig. 1 and the absolute calibration curve of the range from 0.001 to 0.025 mg/L is shown in Fig. 2.

Fig. 3 shows the MRM chromatograms obtained by analyzing a mixed standard solution containing chloride ions, sulfate ions, and nitrate ions which exist in tap water at high concentrations. The figure shows that perchlorate is sufficiently separated from these impurity ions.

As of present in 2018, the United States Environmental Protection Agency has designated Method 331 for the analysis of perchlorate in which an LC/ESI/MS method is used. However, no method has been specified in Japan as of yet.

We have already introduced an example analysis of perchlorate using a single quadrupole LC/MS system in Application News No. C85 "Analysis of Perchlorate in Water by Non-Suppressed Ion Chromatography-Mass Spectrometry". This article introduces a high-sensitivity analysis of perchlorate in tap water using the LCMS-8050, which is a triple quadrupole LC/MS/MS, and an analysis using a reversed-phase column.

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Table 1 Analytical Conditions ①

Column	: Shim-pack™ IC-A3(S) (150 mm L. × 2.0 mm I.D., Shimadzu)
Mobile phases	: A) 25 mmol/L Ammonium acetate-water B) Acetonitrile A/B=80/20 (vol/vol)
Flow rate	: 0.4 mL/min
Column temp.	: 40 °C
Injection volume	: 10 µL
Probe voltage	: -3.5 kV (ESI-Negative)
DL temp.	: 100 °C
Block heater temp.	: 300 °C
Interface temp.	: 100 °C
Nebulizing gas flow	: 2 L/min
Drying gas flow	: 10 L/min
Heating gas flow	: 10 L/min
MRM transition	: m/z 99.10>82.95

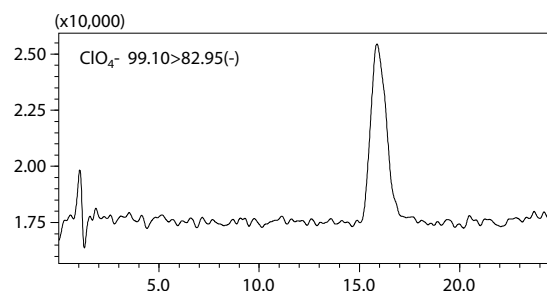


Fig. 1 MRM Chromatogram of Perchlorate (0.0025 mg/L standard solution)

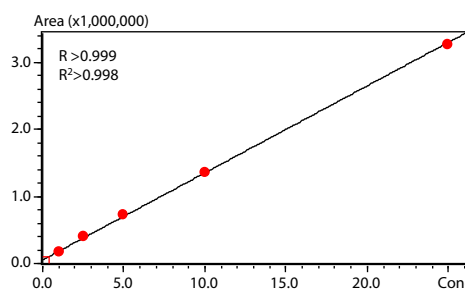


Fig. 2 Five-Point Absolute Calibration Curve of Perchlorate (0.001 to 0.025 mg/L)

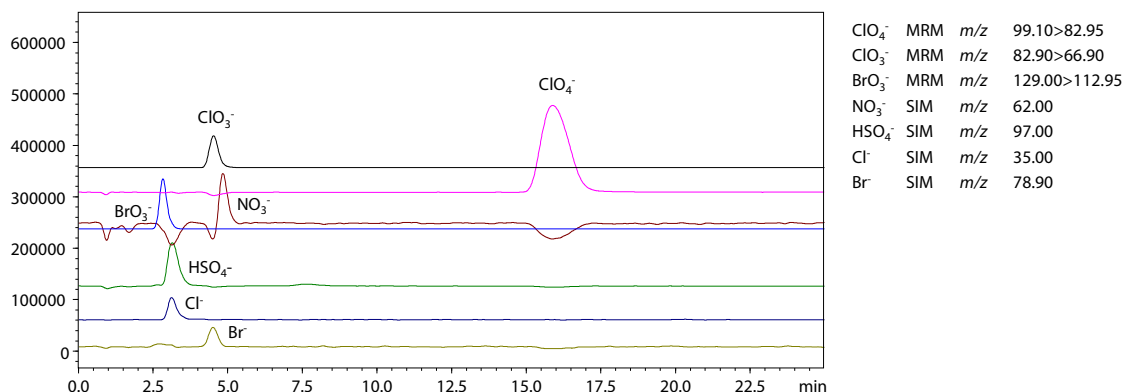


Fig. 3 MRM and SIM Chromatograms of a Mixed Standard Solution with Anions (With scale adjustment)

Example Analysis Using a Reversed-Phase Column

A perchlorate standard solution with a concentration of 0.0025 mg/L, which is a tenth of the criterion concentration, was analyzed using the reversed-phase column indicated in Table 2. The obtained MRM chromatogram is shown in Fig. 4 and the six-point absolute calibration curve of the range from 0.001 to 0.050 mg/L is shown in Fig. 5.

The perchlorate ion is relatively hydrophobic and exhibits a substantial retention time (approx. 6.3 min) even when using a reversed-phase column. On the contrast, the other anions in the solution have a shorter retention time and thus separation from the perchlorate ion is sufficient as shown in Fig. 6.

Table 2 Analytical Conditions ②

Column	: CAPCELL PAK C18 MG III (150 mm L. × 3.0 mm I.D., SHISEIDO)
Mobile phases	: A) 0.05 % formic acid-water B) Acetonitrile A/B=80/20 (vol/vol)
Flow rate	: 0.4 mL/min
Column temp.	: 35 °C
Injection volume	: 2 µL
Probe voltage	: -3.5 kV (ESI-Negative)
DL temp.	: 100 °C
Block heater temp.	: 300 °C
Interface temp.	: 100 °C
Nebulizing gas flow	: 2 L/min
Drying gas flow	: 10 L/min
Heating gas flow	: 10 L/min
MRM transition	: Perchlorate m/z 99.10>82.95

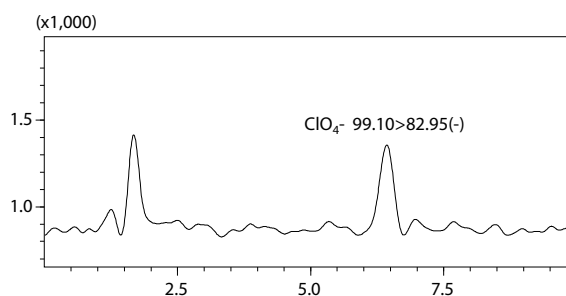


Fig. 4 MRM Chromatogram of Perchlorate (0.0025 mg/L standard solution)

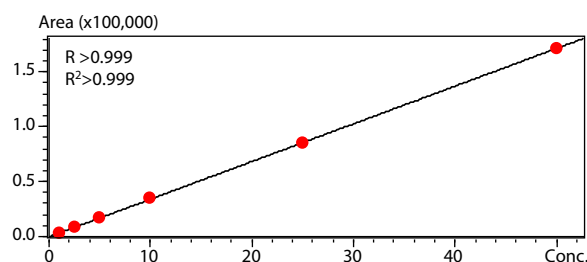


Fig. 5 Six-Point Absolute Calibration Curve of Perchlorate (0.001 to 0.050 mg/L)

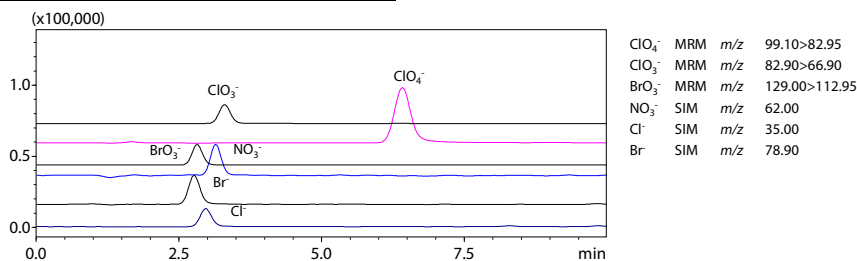


Fig. 6 MRM and SIM Chromatograms of a Mixed Standard Solution with Anions (With scale adjustment)

Spike-and-Recovery Test with Tap Water

Tap water (from Kanagawa Prefecture) was spiked with perchlorate to the water quality criterion of 0.025 mg/L and to a tenth of the criterion at 0.0025 mg/L. The spiked water was analyzed using the analytical conditions ① and ② each. The obtained MRM chromatograms of perchlorate are shown respectively in Figs. 7 and 8. Table 3 summarizes the recovery rate of the perchlorate added to the tap water and the repeatability results. Analyses by both conditions exhibited favorable results.

Table 3 Spike-and-Recovery Test Results for Tap Water (n=6)

Analytical Conditions		Spiking Conc. 0.0025 mg/L	Spiking Conc. 0.025 mg/L
① Ion exchange	Accuracy (%)	105.0	86.7
	Repeatability (%RSD)	2.40	1.69
② Reversed phase	Accuracy (%)	98.7	103.9
	Repeatability (%RSD)	4.08	2.37

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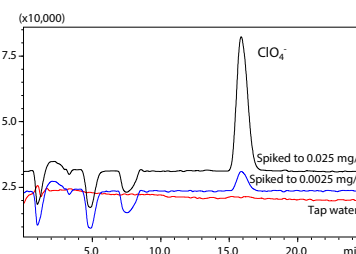


Fig. 7 MRM Chromatograms of Tap Water Spiked with Perchlorate (Analytical conditions ①)

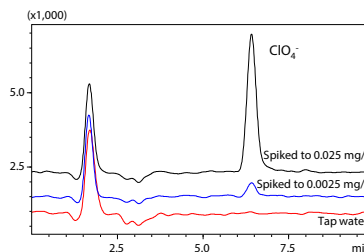


Fig. 8 MRM Chromatograms of Tap Water Spiked with Perchlorate (Analytical conditions ②)

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