

Application News

No. C144

Liquid Chromatograph Mass Spectrometry

Analysis of Bromate in Tap Water Using a Triple Quadrupole LC/MS/MS (1)

Bromate in tap water is generated by advanced water treatment processes such as ozone disinfection in the process of water purification. Potassium bromate has been classified by the IARC (1999) as a Group B2 substance which is possibly carcinogenic to humans, and was added to the water quality standards of Japan in 2004. Upon its addition, ion chromatography with post-column absorption spectroscopy was designated as the testing method for bromate. (Annex table 18 of "Method Determined by the Minister of Health, Labour and Welfare on the Basis of the Ordinance Provisions Relating to Water Quality Standards",

Notification No. 261 issued by the Ministry of Health, Labour and Welfare of Japan (MHLW) in 2003)

In December 2016, the MHLW gathered opinions for partial amendment of this method, and as given in annex table 18-2 "Liquid Chromatography-Mass Spectrometry", mass spectrometry was proposed as a new testing method (proposal) for bromate.

This article introduces the results of our examination of LC/MS/MS analysis using an anion exchange column based on this new testing method (proposal).

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■ Examination of Conditions for Analysis Using an Anion Exchange Column

With reversed-phase LC conditions, which are widely used for LC/MS/MS, bromate is difficult to retain because it is a high polarity compound. Therefore in this research, we examined conditions such as mobile phases using the anion exchange column that is given as an example in the new testing method (proposal), and established analysis conditions which enable the retention of bromate (Table 1).

Fig. 1 shows a chromatogram of the standard solution of 0.001 mg/L, which is equivalent to one-tenth the water quality

criterion. With these analysis conditions, bromate was eluted at 3.4 min, exhibiting good retention and a good peak shape.

Fig. 2 shows a five-point calibration curve for concentrations ranging from 0.0005 mg/L to 0.01 mg/L. Favorable linearity was achieved with a correlation coefficient (R) of 0.999 and a coefficient of determination (R²) of 0.998.

Table 1 Analysis Conditions

Column	: GL Sciences SYPRON AX-1 (100 mm L, × 2.1 mm I.D., 5 μm)
Mobile phases	: A) 25 mmol/L Ammonium acetate-water B) Acetonitrile A/B = 70/30 (vol./vol.)
Flow rate	: 0.2 mL/min
Column temp.	: 40 °C
Injection Volume	: 10 μL
Probe Voltage	: -1 kV (ESI-Negative)
DL temp.	: 100 °C
Block Heater temp.	: 300 °C
Interface temp.	: 300 °C
Nebulizing gas flow	: 2 L/min
Drying gas flow	: 10 L/min
Heating gas flow	: 10 L/min
MRM transition	: Bromate ion <i>m/z</i> 129.00>112.95

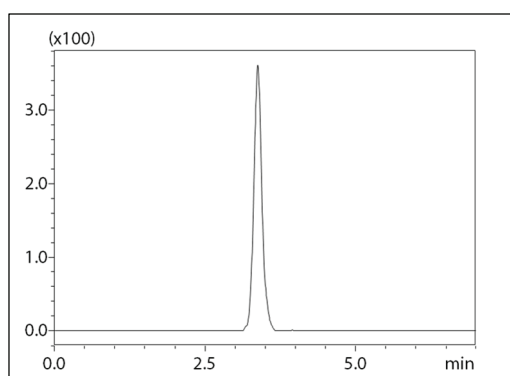


Fig. 1 Chromatogram of Standard Solution of 0.001 mg/L Bromate

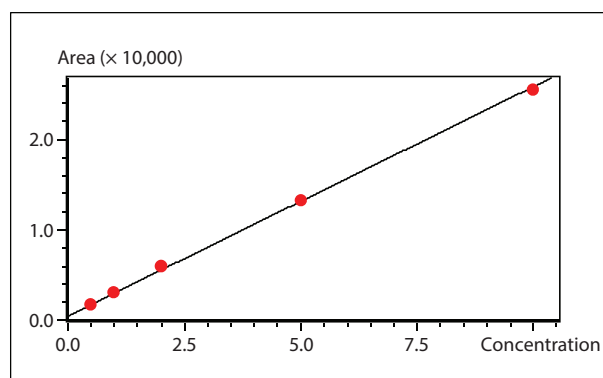


Fig. 2 Calibration Curve of Bromate (0.0005 mg/L to 0.01 mg/L)

Verifying Separation from Anion Impurities in Tap Water

Bromate in tap water can be selectively detected by MRM measurement with LC/MS/MS. However, anions such as sulfate ions also exist in the tap water sample. By separating the chromatograms of such anion impurities from that of bromate, determination precision in tap water analysis is expected to be improved.

This necessity can also be verified by the statement in the liquid chromatography-mass spectrometry method (proposal): When the water for testing includes a high concentration of sulfate ions, set analysis conditions under which sulfate ions elute from the separation column.

Fig. 3 shows the chromatograms obtained by adding bromate to a tap water sample (from Kanagawa Prefecture), and monitoring

bromate together with anion impurities. Sulfate ions, chloride ions, nitrate ions, and chlorate ions in the tap water are also retained and eluted, indicating that bromate is separated from these ions.

In general, regarding analysis using an anion exchange column, elution of anion impurities requires adding a high concentration of salt to the mobile phase, thereby requiring more frequent instrument maintenance. However, the ammonium acetate concentration of the aqueous mobile phase used in these analysis conditions is 25 mmol/L, and is therefore about the same level as with regular conditions for reversed-phase LC/MS/MS analysis. This means that these analysis conditions are also robust with regard to instrument maintenance.

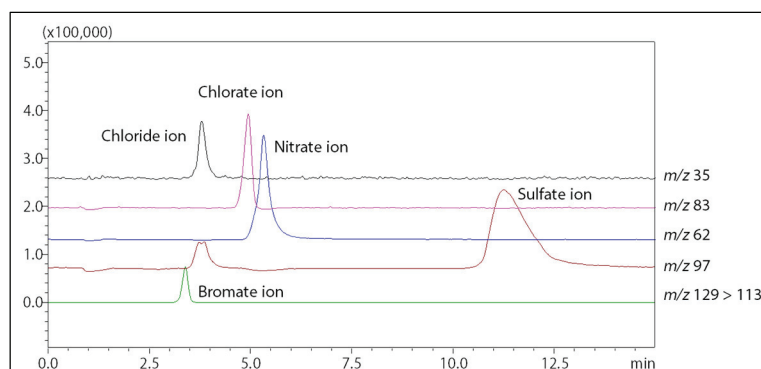


Fig. 3 Chromatograms of Anion Impurities and Bromate in Tap Water

Spike-and-Recovery Test with Tap Water

A spike-and-recovery test of bromate was performed using tap water (from Kanagawa Prefecture). Tap water was measured after being spiked with 0.01 mg/L bromate, which is the water quality criterion, and with 0.001 mg/L bromate, which is a concentration one-tenth the water quality criterion. The obtained chromatograms showed no significant disturbance originating from impurities in tap water (Fig. 4).

Table 2 shows the accuracy and precision calculated from the analysis results of these samples. With both spiking concentrations, the standard given in the validation guideline (notification issued by the MHLW in Sept. 2012) was fulfilled.

In this examination of analysis according to the new testing method (proposal), we confirmed that bromate in a tap water sample can be detected down to a concentration of 0.001 mg/L, which is one-tenth the criterion, without pretreatment.

Unlike the current ion chromatography with post-column absorption spectroscopy method, this analysis method does not require preparation of a reagent, and is therefore expected to improve the efficiency of water quality testing and contribute to reducing the burden of tests.

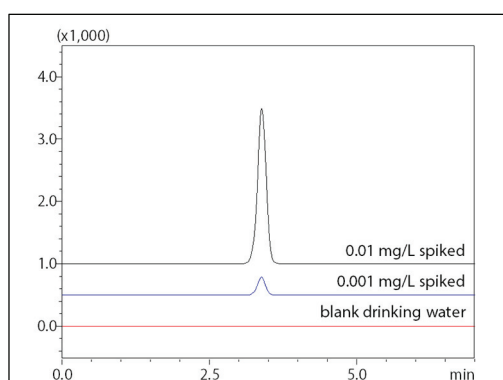


Fig. 4 Chromatograms of Blank Tap Water and Tap Water Spiked with Bromate Standard

Table 2 Spike-and-Recovery Test Results of Bromate (n = 5)

Spiked Conc. mg/L	Accuracy	Precision %RSD
0.01	96.7 %	2.2
0.001	84.6 %	5.2

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