Determination of bromide ion in beverage raw water using liquid chromatography/ tandem mass spectrometry (LC/MS/MS)

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Abstract

The bromide ion analysis method in beverage raw water by liquid chromatography/tandem mass spectrometry (LC/MS/MS) was examined, and its validity was evaluated by addition recovery test. As a measurement condition, a multimode column reversed phase + anion exchange resins, into which a quaternary ammonium group was introduced, were used for the purpose of appropriately separating for high–polarity bromide ion and other ionic compounds on the chromatogram. The calibration curve of bromide ion showed good linearity in the concentration range of 0.5 to 10 µg/L, and the repeatability (RSD) of the 1.0 µg/L bromic acid standard solution was good (2.4 %). Furthermore, as a result of the addition recovery test ($n = 7$) of ground water, the results for bromide ion in tap water showed that the recovery efficiency was 90 % and the RSD was 1.4 %, and satisfied results were obtained for the real samples.

Key words

bromide ion, liquid chromatography, tandem mass spectrometry, LC/MS/MS, groundwater

1. Introduction

When bromide ions are contained in the raw water of drinking, ozone treatment may generate bromate in the drinking water (Pantsar–Kallio and Manninen, 1999). This bromate is classified as Group 2 (possibility of carcinogenesis) at the International Agency for Research on Cancer (IARC), and their carcinogenicities has been pointed out (IARC, 1999). For this reason, the tap water standard item of bromate is specified in the Japan Water Supply Law, and its standard value is set at 0.01 mg/L (10 µg/L) (Ministry of Health, Labor and Welfare Japan, 2003).

It is known that the production amount of bromate in ozone treatment of drink raw water is proportional to ozone injection rate, reaction time, bromide ion concentration in raw water, and so on. Kumar and colleagues showed a strong correlation between bromate concentration in bottled water and bromide ion, as bromide ion (µg/L) = 0.31 × bromide ion (µg/L) + 2.37 ($r = 0.78$) (Kumar et al., 2011). Therefore, in order to control the bromate concentration of ozone–treated water from drink raw solution to 1/10 of the standard value, it is important to estimate the concentration of bromide ion in beverage raw water up to approximately 1 µg/L.

Generally, an ion chromatographic method (hereinafter referred to as "IC") is used for bromide ion analysis (JIS, 2003). However, the lower limit of determination of bromide ion concentration by IC is around 100 µg/L, and quantitative analysis with bromide ion concentration around 1 µg/L is impossible. IC/MS/MS combining ion chromatography method (IC) and tandem mass spectrometry (MS/MS) as an analysis method is capable of quantitative analysis up to 1 µg/L of bromide ion concentration in beverage raw water (Asami et al., 2007). The researches on IC combined with inductively coupled plasma mass spectrometry (ICP-MS) have been reported (Kurata et al., 2010). However, these analytical methods are not widely used as a general analytical method, because they need complex devices which are very expensive and low in versatility.

Liquid chromatography/tandem mass spectrometry (hereinafter referred to as "LC/MS/MS") can be mentioned as an alternative and more versatile method compared with IC–MS/MS and IC/ICP-MS methods. LC/MS/MS has been studied in various compound analysis such as haloacetic acid (Tahara et al., 2010; 2012), pesticide (Sugimoto et al., 2015), organic tin (Furukawa et al., 2013), PFOS/PFOA (Saito et al., 2003) and anionic surfactant (Furukawa et al., 2017). Although LC/MS/MS devices are classified as expensive devices, there are also wide range of applicable analytical applications, and the penetration rate in domestic inspection agencies is high. The authors previously studied the determination of bromide in drinking water combining this LC/MS/MS with multimode column (reversed phase + anion exchange) capable of adequate separation of highly polar compounds, and it was confirmed that it is effective as drinking water quality inspection method (Furukawa et al. 2016).

In the present study, with reference to LC/MS/MS using a multimode column capable of appropriately separating and quantitatively analyzing the highly polar compound, analysis method of bromide ion in beverage raw water was investigated, in which the quantification limit became very low (1.0 µg/L).

2. Experimental

2.1 Reagent

One mL of a bromide ion standard stock solution (1000 mg/L) manufactured by Wako Pure Chemical Industries, Ltd. was made up to 100 mL with Milli-Q water. Thereafter, it was gradually diluted to 0.5, 1, 2, 5, 10 μg/L with Milli-Q water in a timely manner.

Ammonium acetate used for mobile phase was reagent grade manufactured by Wako Pure Chemical Industries, Ltd. For acetonitrile by Kanto Kagaku Co., LC/MS analysis, Ltd. was used. Milli-Q water was used as purified water.

2.2 Measurement method and conditions

The sample was directly injected into LC/MS/MS. Table 1 shows the LC/MS/MS measurement conditions used. For these measurement conditions, the results obtained bromate ion analysis by LC/MS/MS were used (Furukawa et al., 2016). In addition, we examined the optimization of LC/MS/MS measurement conditions as follows.

- Confirmation peak separation between bromide ion and coexisting substance
- Calibration curve (confirmation of linearity), calculation of coefficient of variation, lower quantitative limit value and RSD

2.3 Addition recovery test

In order to evaluate the validity of the present analysis method for bromide ion in beverage raw water, the addition recovery test of bromide ion in ground water was carried out ($n = 7$). In the addition of recovery test of bromide ion, a sample obtained by diluting 1 mL of 100 μg/L bromide ion standard solution to 100 mL with the ground water sample was used.

3. Results and discussion

3.1 Confirmation of peak separation between bromide ion and coexisting substance

Figure 1 shows the multiple reaction monitoring (MRM) chromatogram obtained by measuring commercially available mineral water. From this figure, the retention time of measured bromide ion was around 8.3 minutes. On the other hand, a nitrate ion as a coexistent substance was detected at a retention time of 5.4 minutes, a chloride ion at around 9.5 minutes, and a sulfate ion at 19.6 minutes, and these ions could be appropriately separated from the bromide ions. Incidentally, regarding the retention time of coexisting substances, each 100 mg/L standard solutions of bromide ion, nitrate ion, chloride ion, and sulfate ion was individually measured and confirmed beforehand (In all cases, the solution was prepared from 1000 mg/L standard solution of Wako Pure Chemical Industries, Ltd.).

In addition, it was confirmed that sulfate ions with strong holding power eluted from the multimode separation column. As previously discussed, when sulfate ions, which are coexistent substances, remain in the separation column, the retention power of bromide ion in the next measurement deteriorate, and the peak area value of the bromide ion to be measured decreases. The fact of the elution of sulfate ion indicates that most of coexisting substances of inorganic ions contained in beverage raw water could be eluted from the separation column under the measurement conditions in Table 1. For this reason, the coexisting substance may have little influence on the determination of bromide ion in continuous measurement of the present method.

3.2 Selective of quantitative ions of bromide ion

Figure 2 shows the MRM chromatogram obtained by measuring 1.0 μg/L bromide ion standard solution. From this figure, the S/N ratio (57.7) of m/z 81/81 (precursor ion/product ion) monitor ion was larger than the S/N ratio (30.2) of the m/

Table 1: LC/MS/MS condition

LC	Apparatus	Agilent1260HPLC
	Column	RSpak JJ-50 2D (Shodex) 2.0 × 150 mm
	Column temperature	40 °C
	Mobile phase A	200 mM CH_3COONH_3 solution contain 0.1 V/V%HCOOH
	Mobile phase B	Acetonitrile
	B: 85 % (0 min) → 85 % (9 min) → 50 % (13 min) → 50 % (21 min) → 85 % (26 min)	
	Flow rate	0.3 mL/min
	Injection volume	10 μL
MS/MS	Apparatus	Agilent 6460
	Ionization method	ESI(Negative)
	Bromide ion (m/z)	Quantitative ion: 81 > 81 Confirmation ion: 79 > 79
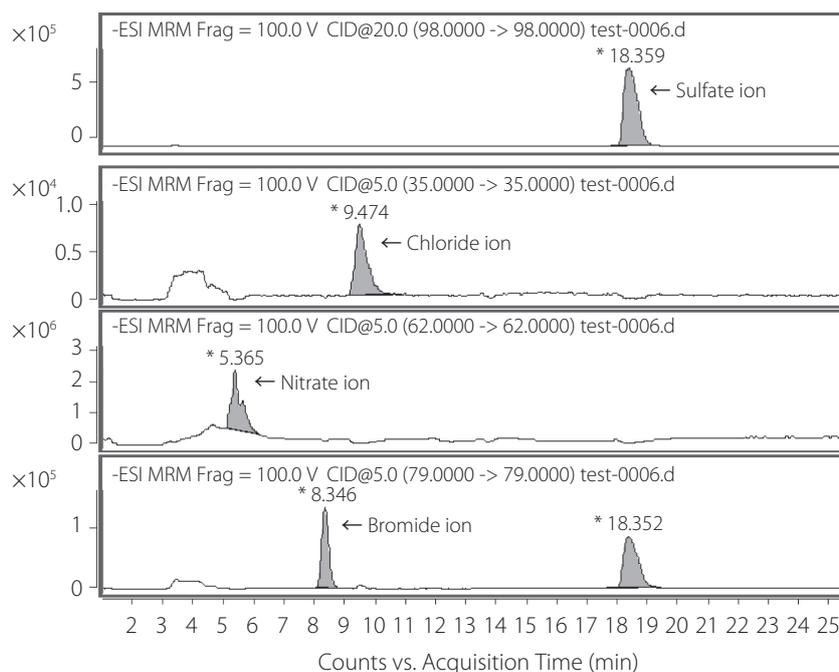
Figure 1: MRM chromatogram of sulfate ion, chloride ion, nitrate ion and bromide ion. Sample was mineral water (Volvic)
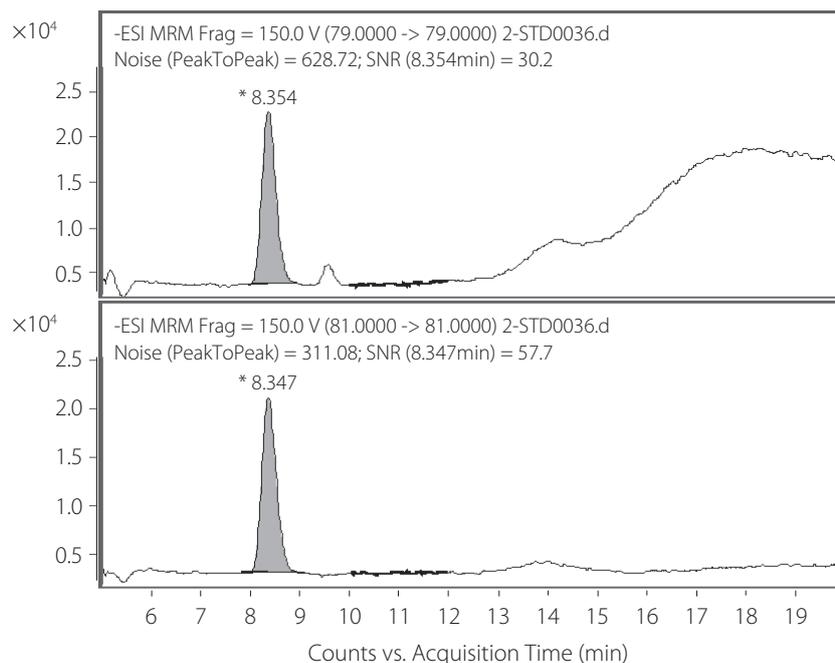
Figure 2: MRM chromatogram of bromide ion standard solution (1.0 μg/L)

z 79/79 monitor ion. Moreover, the MRM chromatogram of m/z 79/79 monitor ion tended to rise in baseline in the latter half of measurement. From the results, it was judged that m/z 81/81 monitor ion is optimal for the quantitative ions of bromide ion.

3.3 Calibration curve, linearity, coefficient of variation, device detection and calculation of lower limit of determination

Figure 3 shows calibration curve of bromide ion standard solution (0.5-10 μg/L) obtained under LC/MS/MS measurement condition in Table 1. From this figure, it was confirmed that the calibration curve of the bromide ion standard solution has a multiple correlation coefficient of more than 0.999, and has good linearity.

Table 2 shows the average value, standard deviation (S/N), quantitation lower limit value (10 S/N), and RSD (repeatability) obtained by repeated measurement ($n = 7$) of 1.0 μg/L bromide ion standard solution. From this table, good results
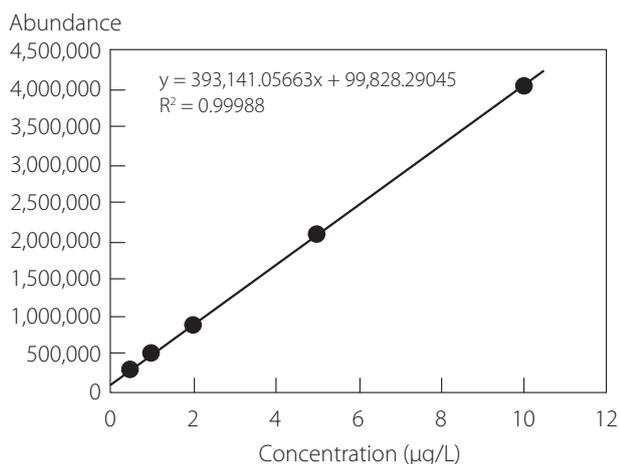
Figure 3: Calibration curve of bromide ion standard solution (0.5-10 µg/L)

$y = 393{,}141.05663x + 99{,}828.29045$
$R^2 = 0.99988$

Table 2 Repeated measurements of bromide ion standard solution(1.0 µg/L)

Average (µg/L)	Standard deviation (σ)	10 σ	RSD
1.1µg/L	0.025	0.25	2.4 %

Note: Number of measurements $n = 7$

were obtained with an average value of 1.1 µg/L, a standard deviation (σ) of 0.025, and RSD (repeatability) of 2.4 %. Furthermore, the limit of quantitation (10S/N) of the present analysis method was very low (0.25 µg/L).

3.3 Addition recovery test and validity evaluation

Table 3 shows the results of the addition recovery test ($n = 7$) for the ground water. From this table, it was confirmed that the collection efficiency of bromide ion in groundwater was 90 %. The RSD was 1.4 %, and good recovery test results were obtained.

Figure 4 shows the MRM chromatogram obtained by the addition recovery test. The bromide ion peak shape obtained

Table 3: Results of the addition of recovery test in groundwater

Sample	Added	Content	RSD	Recovery
Ground water	–	2.3 µg/L	1.7 %	–
	1.0 µg/L	3.2 µg/L	1.4 %	90 %

Note: Number of measurements $n = 7$

in the addition recovery test was excellent for the determinations. In addition, it was confirmed that the present analytical method has high selectivity in the vicinity of the detection time of bromide ion, because it could not affected by coexisting substances contained in groundwater.

Consequently, it was possible for the present analysis method to measure the bromide ion in raw water such as groundwater with a concentration around 1.0 µg/L. The quantitation level was about 100 times better than the conventional IC method (100 µg/L). The present method will become a promising method for the determination of bromide ion.

4. Conclusions

The findings obtained by this research are described as below.

- The calibration curve of bromide ion in the present analysis method showed good linearity in the concentration range of 0.5 to 10 µg L, the repeatability accuracy (RSD) of 1.0 µg /L bromic acid standard solution was 2.4 %. In addition, the lower limit of quantification of quantitative determination of the present analysis method was 0.25 µg/L.
- As a result of the addition test (n = 7) of bromide ion in the groundwater, the collection efficiency of bromide ion in groundwater was 90 %. The RSD was 1.4 %, and good recovery test results were obtained.
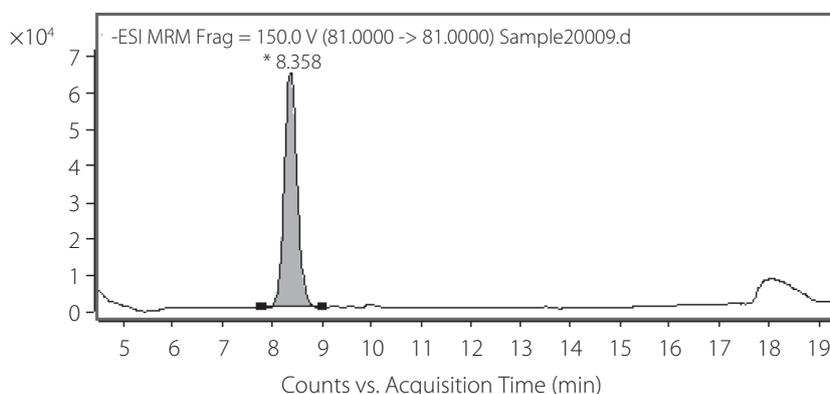
Figure 4: MRM chromatograms of Groundwater sample was added aniline standard solution (1 µg/L)

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