Specific determination of bromate and iodate in ozonized water by ion chromatography with postcolumn derivatization and inductively-coupled plasma mass spectrometry

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Abstract

A specific determination for bromate, iodate and other halogen anions in drinking water by direct injection using ion chromatography (IC), with either inductively-coupled plasma mass spectrometry (ICP-MS) or postcolumn derivatization, is described. The advantages of ICP-MS as an element-selective detector was evaluated for bromate and iodate by considering the comparison with the postcolumn derivatization. Samples were directly injected into the IC column, and halogen anions were separated. The eluates were directly introduced into ICP-MS and detected at 79 and 127 u. The detection limit ($S/N=3$) for bromate and iodate with injection of 0.5 ml were 0.45 μg/l and 0.034 μg/l, respectively. IC combined with ICP-MS was applied to the simultaneous determination of bromate, bromide and other halogen anions in raw and ozonized water. Good agreement was obtained for the determined values by IC–ICP-MS and postcolumn derivatization. Furthermore, several bromine species different from bromate or bromide were detected by IC–ICP-MS. © 1997 Elsevier Science B.V.

Keywords: Water analysis; Bromate; Iodate; Inorganic anions; Halogen anions

1. Introduction

Bromate can be formed by the oxidation of bromide ions during ozonation and possibly by other oxidants in water treatment [1–4]. Bromate has been estimated as a potential carcinogen, and has been classified in Group 2B by the International Agency of Research on Cancer (IARC). The concentration of bromate in drinking water associated with an excess lifetime cancer risk of 10^{-5} corresponds to 3 μg/l [5]. The World Health Organization (WHO) recommended the provisional guideline value of 25 μg/l which is associated with an excess lifetime cancer risk of 7×10^{-5}, because of limitation in available analytical and treatment methods [5].

Ion chromatography (IC) with a pretreatment method [6] or an on-line preconcentration method [7,8] has been reported for the determination of trace bromate. However, the peak of bromate at the detection limit level will often vanish in that of chloride, which is always present in water at a level of 3 orders of magnitude higher. The authors have developed a sensitive and selective IC determination method for bromate, with postcolumn conversion into tribromide by hydrobromic acid [9]. Sub-microgram per litre levels of bromate in water were determined using the developed postcolumn derivatization. Furthermore, other disinfectant by-products, such as chlorite and iodate, were also detected with similar detection limits.

Inductively-coupled plasma mass spectrometry (ICP-MS) combined with liquid chromatography or IC (LC–ICP-MS or IC–ICP-MS) is an effective technique for the speciation study of metallic and

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organometallic species because of its element selectivity and sensitivity. The combined technique has been also applied to the determination of halogen species, especially iodine, which can be sensitively detected by ICP-MS [10–14].

In the present work, the specific determination of bromate, iodate and other halogen species in drinking water, by direct injection using IC with ICP-MS and postcolumn derivatization, is described. The advantages of ICP-MS as an element-selective detector were evaluated for bromate and iodate, by considering the comparison with postcolumn derivatization. Furthermore, the IC–ICP-MS system was applied to the simultaneous determination of halogen anions in raw and ozonized water.

2. Experimental

2.1. Reagents

All reagents used were purchased from Wako (Osaka, Japan). Stock solutions (1000 mg/l) for each anion were prepared by dissolving with pure water, and were stored in a refrigerator. Analytical solutions were prepared by diluting the stock solution to the required concentration just before use. Pure water was obtained from a Milli-Q system (Nihon Millipore, Tokyo, Japan).

2.2. Instruments

The ion chromatograph used in this experiment was Model IC7000S (Yokogawa Analytical Systems, Japan) equipped with a UV–Vis detector, and the ICP-MS was Model HP4500 (Hewlett-Packard Co., USA). Excelpak ICS-A23 and ICS-A13 (7.6×4.6 mm I.D. each, Yokogawa Analytical Systems) were chosen as separation columns. ICS-A23 and ICS-A13 were packed with hydrophilic and semi-hydrophilic anion-exchange resin with 0.05 mequiv./g of dry, respectively.

2.3. IC–ICP-MS

The IC and ICP-MS systems were connected by a 500×0.3-mm I.D. ETFE tube. Ammonium carbonate was chosen as a mobile phase. Ammonium salt was

Table 1
Operational conditions of ICP-MS

Radio frequency forward power	1300 W
Radio frequency refracted power	<1 W
Plasma gas flow	16.0 l/min
Auxiliary gas flow	1.00 l/min
Carrier gas flow	1.06 l/min
Sampling point	7.5 mm from load coil
Detection mass	79 u (Br), 127 u (I)
Dwell time	0.5 s
Number of scans	1

used to prevent a salt deposition and clogging at the sampling orifice of the ICP-MS system, caused by sodium in a mobile phase. The operating conditions of ICP-MS are described in Table 1.

2.4. Postcolumn derivatization

Two Excelpak ICS-A13 columns in series were chosen to separate the halogen species according to the previous paper [9]. The operating conditions of the postcolumn derivatization are described in Table 2.

3. Results and discussions

3.1. Separation of halogen anions

Firstly, the separation of halogen anions using ICS-A13 as the separation column, according to the previous paper [9], was examined to establish appropriate separation conditions. The chromatography behaviour of iodide on anion-exchange resins has been described previously [15]. In this experiment, however, the iodide peak showed a broad and tailing shape, while bromate, bromide and iodate showed good peak shapes. It was also noted that the retention time was long (more than 30 min) and depended on the concentration. It was not drastically improved in spite of a series of change of mobile phase. Therefore, ICS-A23 was used on behalf of ICS-A13 because of the increase of hydrophilicity of packing materials. The use of the ICS-A23 with 0.03 mol/l ammonium carbonate solution (pH 9.2) made it possible to improve the peak shape and retention time of iodide. Fig. 1 shows the chromatograms of

Table 2
Operating conditions of postcolumn derivatization

Ion chromatography	
Column	Excelpak ICS-A13×2
Mobile phase	5×10^{-3} mol/l Na_2CO_3/1×10^{-3} mol/l $NaHCO_3$, 1.0 ml/min
Column temp.	40°C
Injection volume	0.1 ml
Reagent preparation	
Reagent	5 mg/l $NaNO_2$ in 0.5 mol/l NaBr, 1.0 ml/min
Preparation reagent	0.75 mol/l H_2SO_4, 1.0 ml/min
Cation hollow fiber	5 m
Postcolumn derivatization	
Reaction coil	3 m×0.5 mm I.D.
Reaction temp.	40°C
Detection	UV at 268 nm

halogen anion standards by direct injection with a 0.5-ml sample. Four halogen anions were completely separated within 8 min. The analytical time will be reduced by increasing the concentration or pH of mobile phase. For the purpose of this work, that is the simultaneous separation of many halogen species, these separation conditions were a compromise between the number of determinants and analytical time.

3.2. Evaluation of IC–ICP-MS

The linearity, detection limits and repeatability for bromate and iodate were determined. The linear range of bromate and iodate was more than 3 orders of magnitude, from 0.5×10^{-3} to 1 and from 0.1×10^{-3} to 1 mg/l, respectively. Equally, good linearity for bromide and iodide was also obtained. The detection limits ($S/N=3$) for bromate, bromide,
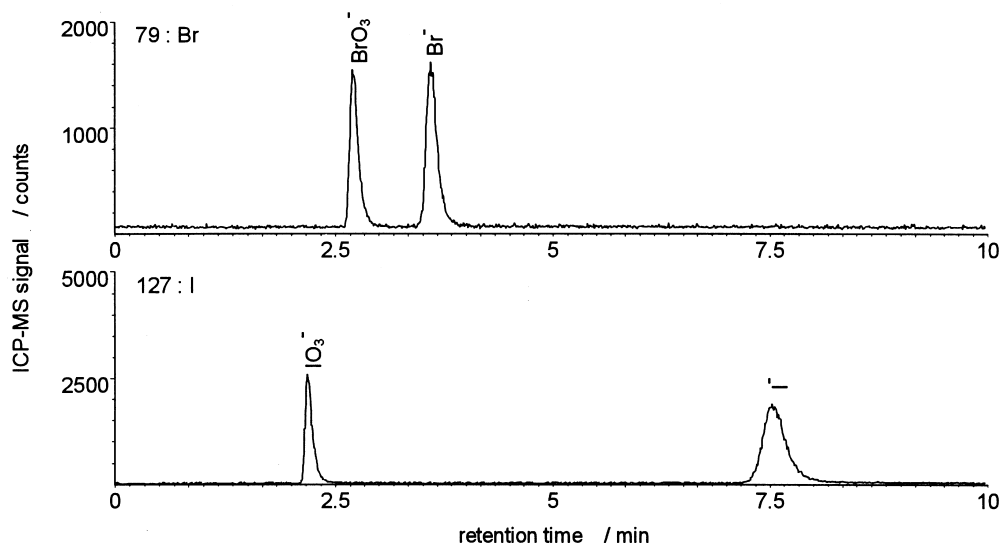

Fig. 1. Chromatograms of halogen anion standards by IC–ICP-MS. Peaks: BrO_3 (10 µg/l), Br (10 µg/l), IO_3 (1 µg/l), and I (2 µg/l). Experimental conditions: column, Excelpak ICS-A23; mobile phase, 0.03 mol/l $(NH_4)_2CO_3$; flow-rate, 1.0 ml/min; column temperature, 40°C; injection volume, 0.5 ml.

iodate and iodide were 0.45, 0.44, 0.034 and 0.051 μg/l, respectively. The repeatability ($n=6$) for 1.0 μg/l of bromate, 1.0 μg/l of bromide, 0.1 μg/l of iodate and 0.2 μg/l of iodide was 8.1, 8.0, 6.2 and 6.8%, respectively.

In the standard method for water quality, the quantitative limit is determined by the sample concentration which gives 10% of relative standard deviation (R.S.D.) [16]. The quantitative limits of this method were obtained from the R.S.D. values which were calculated for each set of 10 measurements of bromate and iodate solutions at various concentrations. Fig. 2 shows the relationships between the R.S.D. and the sample concentration. The concentrations of bromate and iodate at 10% of R.S.D. were 0.42 and 0.051 μg/l, respectively. Fig. 2 also shows the signal stability in the concentrations which give sufficient sensitivity for bromate and
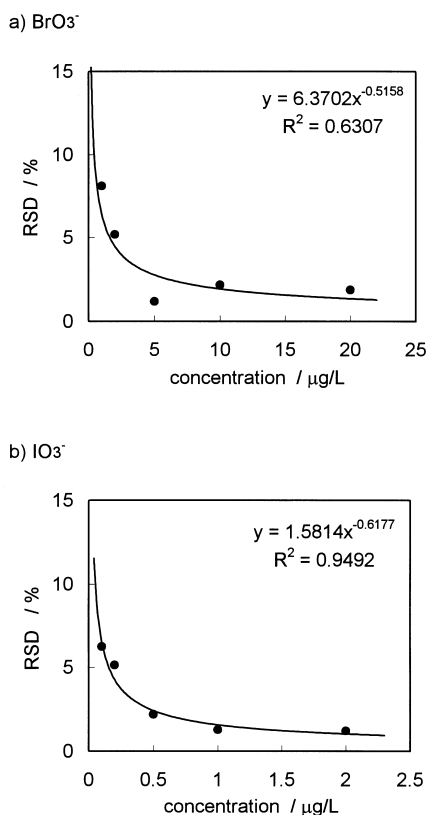
a) BrO3-

b) IO3-

Fig. 2. Relationships between the R.S.D. and sample concentration for bromate (a) and iodate (b). Experimental conditions are same as those given in Fig. 1.

iodate. In both species, R.S.D.s were saturated around 1% even in high concentrations. The saturated R.S.D. is considered to be affected by ICP-MS stability.

3.3. Interference by coexistent substance

Interference from coexistent substances, such as chloride, sulfate and nitrate, has been reported by Creed et al. [14]. They reported that bromate can be determined in a chloride matrix at 5–6 orders of magnitude higher. However, a retention time shift for bromate in 1000 mg/l of chloride matrix was observed. So, the interference from coexistent substances such fluoride, chloride, nitrite, phosphate and sulfate was examined. Mixed anion standard solutions ranging in concentration from 5 to 50 mg/l of anions were injected. Peaks of these anions were not observed on the chromatogram. The retention time shift for halogen anions in a concentration below 50 mg/l of anions matrix was not observed. However, one peak was observed at void volume in a chromatogram at 79 u. This peak was recognized to be a polyatomic ion ($^{40}Ar^{39}K^{+}$) formed by combination of potassium in sample solution with argon as the plasma gas, because it appeared at the retention time of potassium that was observed at 39 u. Conclusively, this peak due to potassium will be neglected on the determination of bromate because it is eluted at the void volume of the anion-exchange column, and completely separated from that of bromate under these separation conditions.

3.4. Application to the determination of halogen anions in water

The present method was applied to the determination of halogen anions in several water samples. The chromatograms of ozonized water using IC–ICP-MS and postcolumn derivatization are shown in Fig. 3. The determined concentrations of halogen anions in raw (river) and ozonized water are listed in Table 3. The concentrations of halogen anions determined by both methods were relatively in agreement. However, some iodate values obtained using ICP-MS were slightly higher than those using postcolumn derivatization. The discrepancy could be due to lack of precision at such a low concentration.
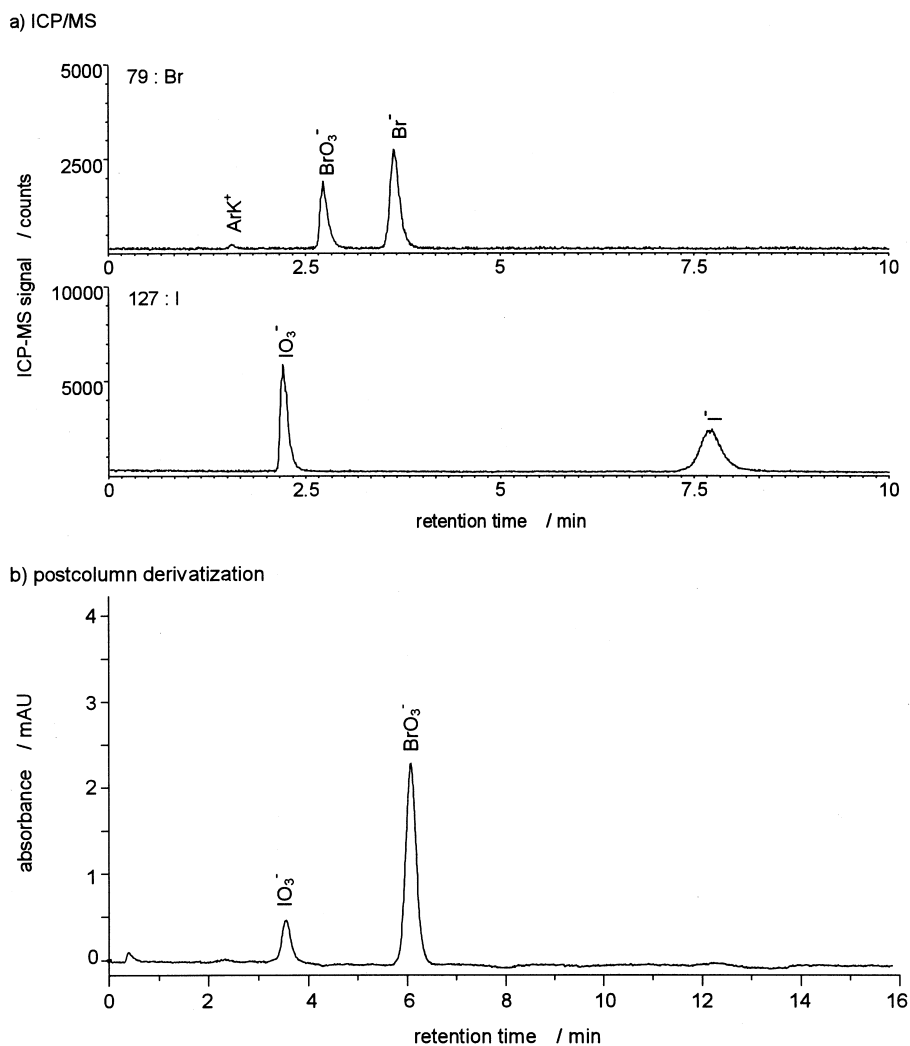
Fig. 3. Chromatograms of ozonized water (sample B) using IC–ICP-MS (a) and postcolumn derivatization (b). Peaks: (a) BrO_3^- (13.0 µg/l), Br (17.8 µg/l), IO_3 (3.57 µg/l), and I (3.56 µg/l); (b) IO_3 (4.13 µg/l), BrO_3 (15.7 µg/l). Experimental conditions are same as those given in Fig. 1 and Table 2.

Furthermore, there could be interference from other iodine-containing species coeluting with iodate, because ICP-MS would detect any species containing iodine, giving a positive error in the iodate values. Bromate values by ICP-MS were a little lower than those using the postcolumn method. The reason is not clear, because bromate values in the postcolumn reaction procedure do not suffer from interference from other oxidants [9].

Bromate and iodate, at concentrations of µg/l, were detected even in the raw water. The contamina-

tion of river water with trace bromate was probably caused by waste water. On the other hand, the existence of iodate in mineral water has been also reported [17]. The concentrations of bromate and iodate in the ozonized water were rather increased compared to those in the corresponding raw water, while that of bromide was decreased by ozonation. Apparently, bromate and iodate are formed during ozonation treatment of the water. However, the material balances of bromine and iodine were absolutely incompatible. These results suggest that the

Table 3
Comparison of determined concentrations of halogen anions in raw and ozonized water

Samples	Determined concentrations (μg/l as species)					
	IC–ICP-MS				Postcolumn	
	BrO_3^-	Br^-	IO_3^-	I^-	BrO_3^-	IO_3^-
(A) Raw water	0.26	28.9	0.44	0.63	0.29	0.09
(B) Ozonized sample A	13.0	17.8	3.57	3.56	15.7	4.13
(C) Raw water	1.64	59.1	1.26	2.97	1.65	0.60
(D) Ozonized sample C	1.88	38.5	5.66	0.14	2.31	4.98
(E) Ozonized water	1.87	5.73	5.45	0.05	1.85	4.77

Experimental conditions are same as those given in Fig. 1 and Table 2.

halo-oxyacids are produced by oxidation of the corresponding halides, but that they are not always produced by the same mechanism.

Sample E gave a distinctive chromatogram at 79 u (Fig. 4). Several unidentified species other than bromate or bromide were detected. These species are estimated to be bromine compounds because no interferences from other elements are observed at 79 u. The existence of other bromine species suggests that these species could lead to bromate during ozonation. It could also explain why the sum of bromate and bromide was not constant for ozonized water and raw water (samples D and C) in Table 3. However, the elucidation of the unidentified peaks will be very difficult because of the lower amounts.

Furthermore, a large unidentified peak with a broad peak shape was also detected at a retention

time of about 40 min in the chromatograms of ICP-MS at 127 u. Heumann et al. reported that organoiodide exists in river water, because peaks with exactly the same retention time were obtained in chromatograms of both ICP-MS and UV detection at 254 nm [13].

Therefore, the detection of these unidentified peaks by a simultaneous analysis using ICP-MS at 127 u and UV detection was investigated. No peaks in the UV chromatogram at 254 nm were observed at the retention times of the unidentified iodine peaks in the ICP-MS chromatogram. Furthermore, the retention behaviors of the unidentified peaks were evaluated by adding ethanol to the mobile phase. The retention times were drastically decreased as the concentration of ethanol increased. Clearly, these iodine species were retained because of their hydro-
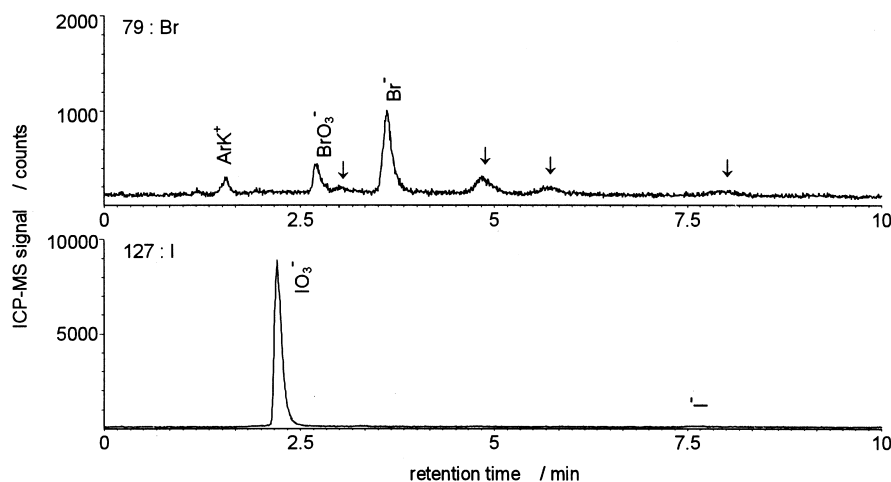

Fig. 4. Chromatograms of ozonized water (sample E). Peaks: BrO_3 (1.87 μg/l), Br (5.73 μg/l), IO_3 (5.45 μg/l), and I (0.05 μg/l). Experimental conditions are same as those given in Fig. 1.

phobicity, not their ionicity, but its chemical structure is still not determined. These unidentified peaks may be related to the production mechanism of the halo-oxyacids by ozonation. A further detailed examination would be necessary to elucidate these unidentified peaks.

4. Conclusions

A specific determination for bromate, iodate and other halogen anions in drinking water by direct injection, using IC with ICP-MS and postcolumn derivatization, is presented. Bromate and iodate were determined in ozonized water at the $\mu g/l$ level without any interference from other anions. The sensitivity of the ICP-MS detector for halogens was also very high (similar to that of metals) and greater than that of other detectors for halogens. The proposed method will be effective for the simultaneous determination of halogen anions.

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