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Short communication

Sensitive determination of bromate in ozonated and chlorinated water, and sea water by gas chromatography–mass spectrometry after derivatization

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ABSTRACT

A sensitive gas chromatographic method has been established for the determination of bromate in ozonated and chlorinated water, and in sea water. With acidic conditions, bromate reacts with chloride to form bromine, which reacts with 2,6-dialkylphenol to form 4-bromo-2,6-dialkylphenol. The organic derivative was extracted with ethyl acetate after quenching remaining oxidants with ascorbic acid, and then measured by gas chromatography–mass spectrometry (GC–MS). The lowest detection limit and limit of quantification of bromate in drinking water were 0.02 and 0.07 μg/L, respectively, and the calibration curve showed good linearity with $r^2 = 0.998$. The 32 common ions did not interfere even when present in 100-fold excess over the bromated ion. The accuracy was in a range of 102–106% and the precision of the assay was less than 6% in chlorinated and ozonated tap water, ozonated mineral water, and sea water. The method was sensitive, reproducible and simple enough to permit reliable analysis of bromate to the ng/L level in water.

1. Introduction

Ozone is highly corrosive, toxic and a powerful oxidant [1]. It is accordingly capable of oxidizing many organic and inorganic compounds in water [2,3]. Ozonation of drinking water is the most promising alternative method for the disinfection of water, because the disinfection process does not generate large quantities of halogenated by-products that are common with chlorination [4]. Bromate ions are not normally found in surface water, but if bromide exists in adequate concentrations, some bromide ions are oxidized to bromate during the ozonation process of water [5–7]. Because of health concerns, the concentration of bromate in drinking water is a major concern among regulatory agencies all over the world [8–12].

In Korea, tap water and mineral water are major drinking waters regulated under the Minister of Environment and therefore regulation of contaminants is the responsibility of the Minister of Environment. Because some mineral water products as well as tap water use ozone, the Minister listed bromate as a standard candidate item in the water quality standards for drinking water, and adopted 10 μg/L as a regulatory guideline of bromate [13]. Its analysis is now required at a growing number of laboratories in response to the regulatory guideline and standard. Because of the limitations in the analytical methods used for bromate, it has been difficult, however, to rapidly and sensitively evaluate the occurrence of the chemical in water. The development of simple and sensitive methods for monitoring exposure to bromate in water is of great interest from analytical and toxicological viewpoints.

Many methods based on different principles have been proposed for the determination of bromate in water. Spectrophotometry has been widely employed for the determination of bromate in drinking water through the use of many kinds of dyes [14–18]. Electroanalysis [19,20], X-ray fluorescence analysis [21], flow-injection analysis [22,23], and electrophoresis [24–26] have also been reported as techniques for the determination of bromate, but their sensitivities are not adequate to detect low ng/L. Numerous studies have been devoted to ion chromatographic methods for bromate determination with different detection systems [27–49], and most of these methods have been received in standard methods of analysis [35–38,48]. In fact, bromate can be determined to sub-ppb levels after pre-concentration techniques [30,32]. Alternative and sensitive detection techniques include post-column derivatization [28,37,38] and mass detection [39–49], but these methods suffer from complex plumbing operations or high costs. The major problems for bromate speciation are interferences from other high-concentration ions, including chloride and bromide.

Several authors have reported the determination of bromate by gas chromatography–mass spectrometry (GC–MS) following a bromate reaction and extraction procedure [50,51]. These methods can analyze bromate with very low detection limits and without

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chloride interferences, but involve multistep reactions containing removal of free bromide [50] or suffer from interference in chlorinated waters [51].

The aim of this study is to develop a simple and sensitive analytical method by using the reactivity of bromate with chloride, and formed bromine with 2,6-dialkyl phenols. Our previous paper reported that phenol derivative was formed by a displacement reaction of iodine with active protons at *para*-position of 2,6-dimethylphenol, and the resulting derivative was analyzed by GC–MS [52,53].

2. Experimental

2.1. Reagents

Potassium iodide (99.9%), iodine (99.9%), potassium bromide (99.9%), potassium bromate (99.9%), and sodium hypochlorite (30%) were obtained from Sigma (St. Louis, MO, USA). 2,4,6-Trichlorophenol (TCP), 2,6-dimethylphenol (2,6-DMP), 2,6-diisopropylphenol (2,6-DIPP), and 2,6-di-*tert*-butylphenol (2,6-DTBP) were obtained from Aldrich (Milwaukee, WI, USA). Pentane, ethyl ether, methylene chloride and ethyl acetate and sodium sulfate were used as reagents and solvents. A stock standard solution of bromate was freshly prepared before use by dilution of a 5 mL portion of commercially available potassium bromate solution to 100 mL with water, and standardized iodometrically. A known volume of this solution was sequentially diluted to give a 1.0 mg/L bromated standard solution. This solution was used within 1 h of its preparation. The pure water used in this study was purified by a Milli-Q-Reagent-Grade water system (ZD20) and had a resistivity of over 17 MΩ.

2.2. Derivatization and extraction

10 mL of the water sample was placed into a 20 mL glass-stoppered test tube. 0.7 mL of 5 M HCl was added to the solution and agitated for 1–2 min. A 10 μL of 2,6-DMP solution (5% in MeOH) was then added to the solution and shaken mechanically for 10 min at room temperature. 20 μL of 2,4,6-TCP (10 mg/L in MeOH) as an internal standard was added to the solution. The sample was extracted with 3 mL of ethyl acetate by mechanical shaking for 10 min, and then approximately 10 mg of ascorbic acid was added to the solution to eliminate residual chlorine and bromine following agitation for 30 s. The two phases were separated by centrifugation (5 min at 1500 g) and the organic phase was transferred into a 20 mL glass stoppered test tube and evaporated to 100 μL of residual solvent under a nitrogen stream. The solution was transferred into a V-shape in an auto vial, and a 2 μL sample of the solution was injected in the GC system.

2.3. Calibration and quantitation

The calibration curve for the linearity test was established by adding 1.0, 5.0, 10, 20, 50, 100, 250 and 500 ng (10 mg/L in reagent water) of bromate standard and 20 μL of 2,4,6-TCP (10 mg/L in MeOH) as an internal standard in 10 mL of distilled water. The solutions were extracted with ethyl acetate after the redox reaction with chloride and the substitution reaction with 2,6-DMP, and the extract was injected in the GC system. The ratio of the peak area of the standard to that of the internal standard was used for the construction of the calibration curve.

2.4. Gas chromatography–mass spectrometry

The analytical instruments used were an Agilent 6890 A gas chromatograph with a split/splitless injector (Agilent Technologies, Santa Clara, CA, USA). The analytical column was a 30 m HP-5MS column (cross-linked 5% phenylmethylsilicon, 0.2 mm ID × 0.25 μm FT). The oven temperature program began at 100 °C, was held for 3 min, raised to 250 °C at 10 °C/min and held for 5 min. All mass spectra were obtained with an Agilent 5975 B instrument (Agilent Technologies, Santa Clara, CA, USA). The ion source was operated in the electron ionization mode (EI; 70 eV, 230 °C). Full-scan mass spectra (m/z 45–800) were recorded for the identification of analytes at a high concentration. Confirmation of trace chemicals was completed by three MS characteristic ions, and the ratio of the three MS characteristic ions and the GC-retention time matched the known standard compound. The ions selected for quantification by SIM were m/z 97 and 196 for TCP (internal standard) and m/z 121 and 248 for 4-bromo-2,6-DMP.

3. Results and discussion

3.1. Derivatization

For the GC analysis of bromate, derivatization is necessary. Two major reactions to be considered in the derivatization of bromate are the redox reaction and the substitution reaction.

The redox reaction between bromate and chloride ions is described by the following equation. Every mole of bromate in water in acidic media is converted into 0.5 mol of bromine and 2.5 mol chlorine by the redox reaction.

$$2BrO_3^- + 10Cl^- + 12H^+ \rightleftarrows Br_2 + 5Cl_2 + 6H_2O$$

The substitution reaction between bromine or chlorine and 2,6-dialkylphenol is described in Fig. 1. With an acidic condition, halogens (bromine and chlorine) formed by the redox reaction react with 2,6-dialkylphenol to form 4-halo-2,6-dialkylphenol and halide ions. Every mole of bromine or chlorine formed by the redox reaction is converted into a mole of 4-bromo-2,6-dialkylphenol and 4-chloro-2,6-dialkylphenol by the substitution reaction in Fig. 1, respectively. Eventually, 2 mol of bromate in water are converted into a mole of 4-bromo-2,6-dialkylphenol and five moles of 4-chloro-2,6-dialkylphenol by the overall reaction. The final products, 4-bromo-2,6-dialkylphenol or 4-chloro-2,6-dialkylphenol, can be determined by GC–MS. In the current study, the change of the product areas was studied according to increasing concentration of bromate in water, and the responses of two products were very linear and quantitative. Likewise, hypochlorite and hypochloric acid in chlorinated water were converted into 4-chloro-2,6-dialkylphenol by the substitution reaction in Fig. 1. If 4-chloro-2,6-dialkylphenol is used as the final analyte to determine bromate in chlorinated water, the analytical result can be a positive error. Also, 4-bromo-2,6-dialkylphenol was formed from bromate independent of the existence of residual ozone. Therefore, 4-bromo-2,6-dialkylphenol was selected as the final analyte to determine bromate in water. If the sample is not chlorinated water, 4-chloro-2,6-dialkylphenol can be used as final analytes to determine bromate in water by GC–MS.

Phenol derivatives, which are formed by the displacement reaction of active protons at the *para*-position of 2,6-dialkylphenol as a nucleophilic attack of the electronegative halogens, were tested for their utility in the determination of bromate in water. 2,6-DMP, 2,6-DIPP and 2,6-DTBP have an active proton, which can be substituted with halogens. They were compared to each other in terms of reactivity with bromate and stability of the derivatives. The reaction rates were determined by the detection of the substituted products; 4-halo-2,6-dialkylphenols at reaction times of 1.0, 5.0, 10, 20, 30, 40, and 60 min. From the results, 2,6-DMP and 2,6-DIPP showed very rapid reaction with bromate (Fig. 2). Complete reaction took place in about 5 min at room temperature, provided that a

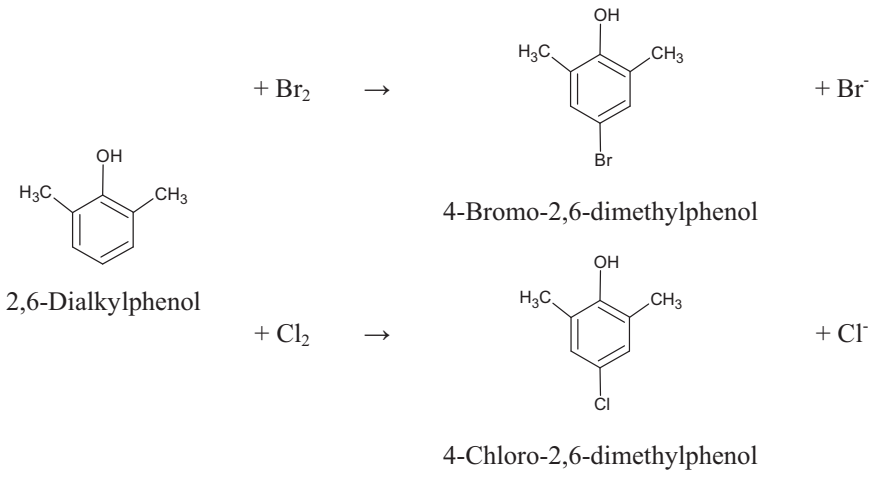

Fig. 1. The substitution reaction between halogens formed from redox reaction with 2,6-dimethylphenol.

sufficiently high concentration of 2,6-DMP or 2,6-DIPP is present in the reaction mixture. No significant variation in reaction yield was noted over this time period. Otherwise, 2,6-DTBP was converted into 4-halo-2,6-di-*t*-butyl phenol, which increased until 30 min.

To evaluate the stability of the derivatives, the experiment was repeated by analyzing extracts stored under dark at 4 °C for 2 weeks. The % losses of 4-bromo-2,6-dialkylphenol after 2 weeks were 3.2% for 2,6-DMP, 3.5% for 2,6-DTBP and 4.5% for DIPP. From the results, 4-bromo-2,6-DMP formed by 2,6-DMP showed superior reactivity and stability compared to those by the other alkylphenols. Therefore, 4-bromo-2,6-DMP was selected as the analyte for the determination of bromate in water.

3.2. Extraction

The derivatives must be extracted from water samples with an organic solvent. Pentane, ethyl ether, methylene chloride and ethyl acetate were tested as the extraction solvent of the derivatives. Among the solvents tested, ethyl acetate was found to yield the highest recovery for extraction of these compounds. The optimum extraction pH of the acidic compounds with ethyl acetate was studied. The extraction was carried out at pH 1.0, 3.0, 5.0, and 7.0. 4-Bromo-2,6-DMP showed maximum recoveries in a range of pH 1–3. For simple extraction conditions, the samples were extracted at reaction pH conditions without pH control. If halogens remain in the sample after the reaction, they can be extracted and, break capillary column during the separation. The residual bromine can also react with ethyl acetate during the extraction to form 1-bromoethyl acetate, as reported by Magnuson [51]. Therefore, the oxidant residues remaining in water after the reaction were removed with ascorbic acid as a scavenger before the extraction. The extract was directly injected into the GC after concentration.

3.3. Interference

The influences of 36 diverse ions and chemical species were examined. The chemicals were added individually to the tested solution. The tolerance limit was defined as the concentration of the added ion causing less than ±3% relative error for bromate determination. The results show that 32 ions and chemical species did not interfere even when present in 100-fold excess over the bromated ion, as shown in Table 1. Otherwise, Fe^{2+}, Mn^{2+}, NO_2^- and As^{3+} interfered with the determination of bromate when present in 10-fold excess over the bromated ion. It is suggested that Fe^{2+}, Mn^{2+}, NO_2^- and As^{3+} react with the liberated Br_2 and Cl_2 to oxidize to Fe^{3+}, Mn^{4+}, NO_3^- and As^{5+}, respectively and may interfere with the determination of bromate in water. When they present under 10-fold than the bromated ion, they do not influence the determination of bromate in water due to rapid substitution reaction between bromine and 2,6-DMP. Also, the 4% NaCl solution and sea water did not influence the determination of bromate in water. The present method allows the determination of bromate without interference in chlorinated water, ozonated water, and sea water.

3.4. Chromatography and mass spectrometry

For the GC separation of the derivative, the use of a nonpolar stationary phase was found to be efficient. The column was stable over more than one thousand injections without notable change of the separation characteristics. Chromatograms are shown in Fig. 2. Separation of the derivatives and the internal standard from the background compounds of water was very good. There were no extraneous peaks observed in a chromatogram of blank water at retention times of 12.7 and 13.5 min.

The mass spectrum of 4-bromo-2,6-DMP shows a molecular ion and base ion at *m*/*z* 200, and the diagnostic ions at *m*/*z* 202, 121, 103, and 91. The ion at *m*/*z* 121 is from the cleavage of bromide from molecular ions, and the ions at 91 and 103 are from the losses of [$2CH_3$+Br] or [H_2O+Br] from the molecular ion.

3.5. Verification of method performance

A calibration curve was obtained from the extraction after the addition of bromated and ISTD in water. The regression line of peak area ratios of 4-bromo-2,6-DMP to the internal standard on concentration using a least-squares fit demonstrated a linear relationship with $y = 0.302x + 0.015$ and $r^2 = 0.998$, where x is the 4-bromo-2,6-DMP concentration (μg/L) and y is the peak area ratio of bromate to the internal standard.

Table 1
Tolerance limits of various chemicals on the determination of 20 μg/L bromate.

Chemicals	Tolerance limit (×20 μg/L)
K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Mn^{4+}, Al^{3+}, Ag^+, Ba^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Hg^{2+}, Cu^{2+}, F^-, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}, $H_2PO_4^-$, CH_3COO^-, IO_3^-, ClO_3^-, SO_3^{2-}, ClO_2^-	>1000
OCl^-, HOCl, H_2O_2, O_3	>100
Fe^{2+}, Mn^{2+}, NO_2^-, As^{3+}	>10

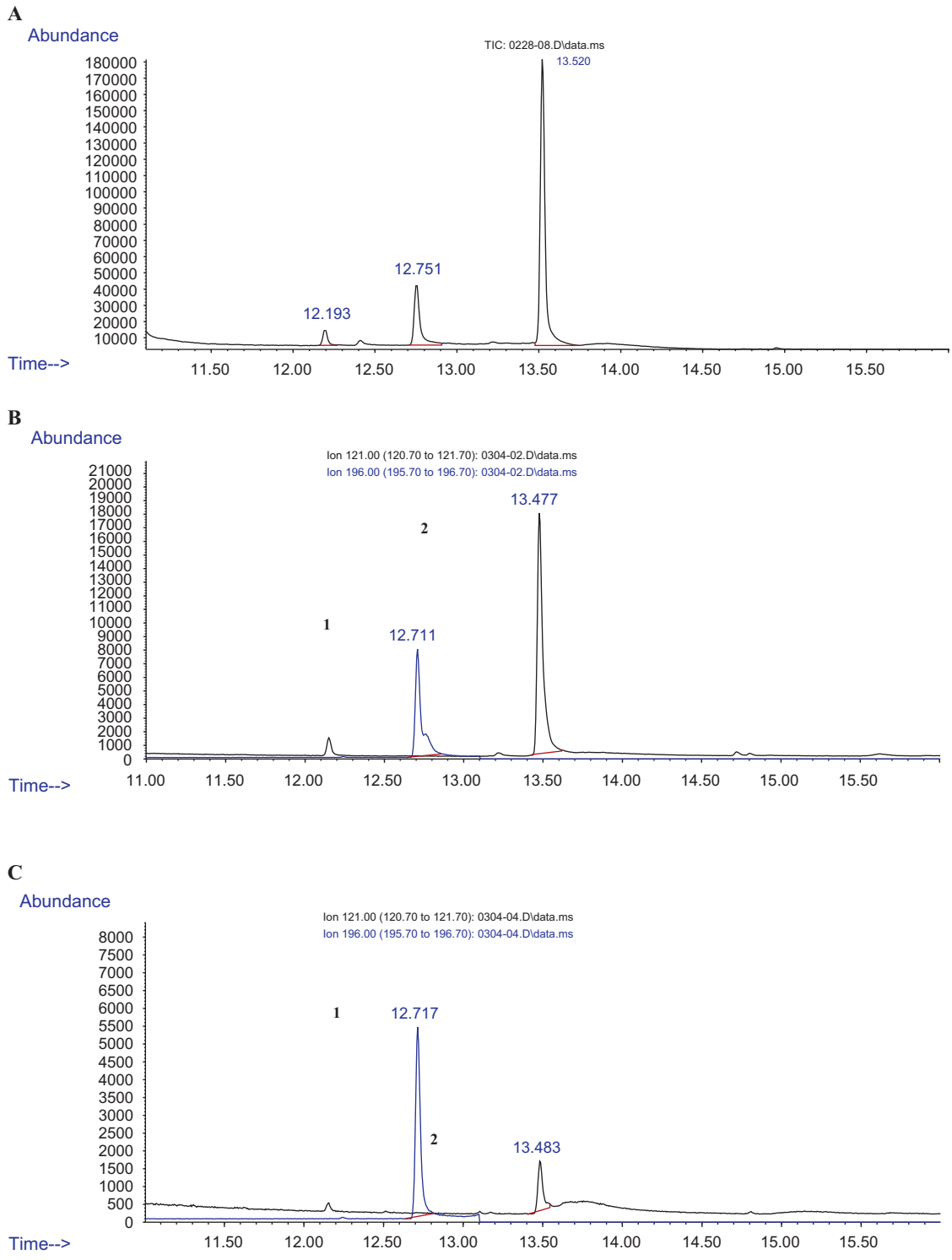

Fig. 2. Chromatogram of the extract of (A) ozonated water spiked with bromate (10.0 μg/L), (B) sea water spiked with bromate (10.0 μg/L) and (C) ozonated mineral water containing bromate of 0.9 μg/L (1 = internal standard (2,4,6-TCP); 2 = 4-bromo-2,6-DMP).

The combination of low background, high derivatization yield, and the high abundance of molecular ions of the derivative permit their determination in water at concentrations well below those reported previously. The limit of detection (LOD) and limit of quantification (LOQ) were defined as the concentration resulting in a minimum signal-to-noise ratio of 3 and 10, coefficients of variation for replicate determinations ($n = 5$) of 15% or less, respectively, from samples spiked in a tab water. LOD and LOQ in this study were calculated as 0.02 and 0.07 μg kg^{-1}, respectively. LOD and LOQ were also estimated in the same matrix, containing 0.01 μg/L, as 3.14 and 10 times of the standard deviation for seven replicates [54]: calculated 0.01 and 0.04 μg/L, respectively.

Accuracy and precision were assessed by determining the recovery in samples spiked in Milli-Q water due to the impossibility of buying a certified standard material. Intra-day accuracy and precision were evaluated by five spiked samples at concentrations of

Table 2
Intra and inter-day laboratory accuracy and precision results for the analysis of bromate in water ($n = 5$).

Spiked conc (μg/L)	Intra-day measured value			Inter-day measured value		
	Mean ± SD (μg/L)	Trueness (%)	Precision (%)	Mean ± SD (μg/L)	Trueness (%)	Precision (%)
5.0	5.21 ± 0.18	104	3.46	5.36 ± 0.25	107	4.66
10.0	10.3 ± 0.32	103	3.11	10.4 ± 0.42	104	4.04
20.0	21.1 ± 0.76	106	3.60	21.6 ± 0.86	108	3.98

Table 3
Accuracy and precision results for the analysis of bromate spiked in chlorinated or ozonated water matrices.

Matrix	Matrix blank (μg/L)	Spiked conc (μg/L)	Sample no.	Found conc (μg/L)	Accuracy (%)	Precision (%)
Tab water	1.5	5.0	5	6.8 ± 0.4	106	5.88
		10.0	5	11.9 ± 0.5	104	4.20
Mineral water	3.2	5.0	5	8.4 ± 0.4	104	4.76
		10.0	5	13.7 ± 0.6	105	4.38
Sea water	0.4	5.0	5	5.5 ± 0.2	102	3.64
		10.0	5	10.7 ± 0.6	106	5.61

20.0, 10.0, and 5.0 μg/L for bromate, and inter-day accuracy and precision were determined by their recovery in spiked samples on five different days. The reproducibility of the assay was very good, as shown in Table 2. The accuracy was in a range of 103–108% and precisions of the assay were less than 5%.

Generally, an analytical method of bromate is mainly used in ozonated and chlorinated water, and occasionally in sea water, which is utilized as the raw water for drinking water. To test the influence of various matrices on the determination of bromate, accuracy and precision were assessed by determining the recovery in ozonated and chlorinated tap water, ozonated mineral water, and sea water. Those were evaluated by five samples spiked at concentrations of 10.0 and 5.0 μg/L for bromate in above three matrices. The accuracy was in a range of 102–106% and the precision of the assay was less than 6%, as shown in Table 3. The results indicate that this method was reproducible enough to permit reliable analysis of bromate in disinfected tap water, ozonated mineral water, and sea water.

3.6. Application

We used the proposed method to analyze bromate in fifteen natural mineral water samples, and fifteen ozonated and chlorinated drinking water samples. Bromate was detected in a concentration range of not detected −4.33 μg/L in thirty samples. The maximum concentration of bromate detected in natural mineral water was lower than the EPA guidelines [11].

4. Conclusion

The proposed method very sensitively determines bromate without the interference of oxidant species in chlorinated or ozonated water. The method developed here is also simple, sensitive, and suitable for the determination of low concentrations of bromate ions without the interference of chloride and bromide in sea water. The 36 common ions did not interfere even when present in 100-fold excess over the bromated ion. The accuracy was in a range of 102–106% and the precision of the assay was less than 6% in chlorinated and ozonated tap water, ozonated mineral water, and sea water. Quantification of bromate was excellent, with linear calibration curves over a range of 0.02–100 μg/L. The LOD and LOQ of bromate in drinking water were 0.02 and 0.07 μg/L, roughly meeting the water quality criterion of 1/500 concentration for bromate established by the US EPA. This method can be used in monitoring bromate in tap water and mineral water.

References

[1] Wikipedia Encyclopedia. http://en.wikipedia.org/wiki/Ozone (accessed on 27.10.11).
[2] G. Gordon, R. Kieffer, D.H. Rosenblatt, Progress in Inorganic Chemistry, Wiley-Interscience, New York, 1972, p. 15.
[3] W.R. Haag, J. Hoigne, Environ. Sci. Technol. 17 (1983) 261.
[4] R.J. Joyce, H.S. Dhillon, J. Chromatogr. A 671 (1994) 165.
[5] U. von Gunten, J. Hoignïe, Environ. Sci. Technol. 28 (1994) 1234.
[6] U. von Gunten, Y. Oliveras, Environ. Sci. Technol. 328 (1998) 63.
[7] I.N. Najm, S.W. Krasner, J. Am, Water Works Assoc. 87 (1995) 106.
[8] World Health Organization, Guidelines for Drinking Water Quality, Geneva, Switzerland, 1993.
[9] World Health Organization, Disenfection del'eau, Local Authorities, Health and Environment Briefing Pamphlet Series, vol. 3, Geneva, Switzerland, 1995.
[10] EC, Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, Off. J. Eur. Commun. L330 (1998) 32.
[11] US EPA, Fed. Reg. 63 (241) FR69389, 1998.
[12] World Health Organization, Disinfectants and Disinfection By-Products, International Programme on Chemical Safety Environmental Health Criteria 216, Geneva, Switzerland, 2000.
[13] The Minister of Korea, Drinking Water Act 10154, 2010.
[14] L. Romele, Analyst 123 (1998) 291.
[15] A. Afkhami, T. Madrakian, M. Bahram, J. Hazard. Mater. 123 (2005) 250.
[16] M.G. Mitrakas, J. Anal. Chem. 62 (2007) 1055.
[17] A. Alonso-Mateos, M.J. Almendral-Parra, M.S. Fuentes-Prieto, Talanta 76 (2008) 892.
[18] F. Keiichi, Y. Ryohei, Y. Takeshi, J. Sep. Sci. 32 (2009) 457.
[19] J.F. van Staden, L.V. Mulaudzi, R.I. Stefan, Talanta 64 (2004) 1196.
[20] R. Thangamuthu, Y.-C. Wu, S.-M. Shen, Electroanalysis 21 (2009) 1655.
[21] V.S. Hatzistavros, P.E. Koulouridakis, I.I. Aretaki, Anal. Chem. 79 (2007) 2827.
[22] M. Isawa, T. Yamane, Jpn. Anal. 56 (2007) 745.
[23] O. Hiroki, I. Toshihiko, K. Kiminori, Anal. Sci. 20 (2004) 513.
[24] R. Bodor, D. Kaniansky, M. Masár, K. Silleová, B. Stanislawski, Electrophoresis 23 (2002) 3630.
[25] T. Takayanagi, M. Ishida, J. Mbuna, J. Chromatogr. A 1128 (2006) 298.
[26] K. Himata, C. Warner, D. Currie, J. AOAC Int. 88 (2005) 794.
[27] Y. Liu, S. Mou, Chemosphere 55 (2004) 1253.
[28] Y. Inoue, T. Sakai, H. Kumagai, Anal. Chim. Acta 346 (1997) 299.
[29] Z. Binghui, Z. Zhixiong, Y. Jing, J. Chromatogr. A 1118 (2006) 106.
[30] K. Yuko, T. Toyohide, Anal. Sci. 20 (2004) 1399.
[31] E.T. Urbansky, S.T. Brown, J. Environ. Monit. 2 (2000) 571.
[32] Y. Liu, S. Mou, S. Heberling, J. Chromatogr. A 956 (2002) 85.
[33] Y. Shi, Y. Cai, J. Liu, Microchim. Acta 154 (2006) 213.
[34] B.M. De Borba, J.S. Rohrer, C.A. Pohl, J. Chromatogr. A 1085 (2005) 23.
[35] Method 300.0: The Determination of Inorganic Anions in Water by Ion Chromatography, US Environmental Protection Agency, Cincinnati, OH, 1993.
[36] Method 300: The Determination of Inorganic Anions in Drinking Water by Ion Chromatography, US Environmental Protection Agency, Cincinnati, OH, 1997.
[37] Method 317.0: Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water using Ion Chromatography with the Addition of a Postcolumn Reagent for Trace Bromate Analysis, US Environmental Protection Agency, Cincinnati, OH, 2000.
[38] Method 326.0: Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water using Ion Chromatography Incorporating the Addition of a Suppressor Acidified Postcolumn Reagent for Trace Bromate Analysis, US Environmental Protection Agency, Cincinnati, OH, 2002.
[39] Z.-X. Guo, Q. Cai, C. Yu, J. Anal. Atom. Spectrom. 18 (2003) 1396.
[40] S. Cavalli, S. Polesello, S. Valsecchi, J. Chromatogr. A 1085 (2005) 42.
[41] Q. Cai, Z.-X. Guo, C. Yu, Anal. Bioanal. Chem. 377 (2003) 740.

[42] A.R. Elwaer, C.W. McLeod, K.C. Thompson, Anal. Chem. 72 (2000) 5725.
[43] T. Eickhorst, A. Seubert, J. Chromatogr. A 1050 (2004) 103.
[44] G. Schminke, A. Seubert, Fresen. J. Anal. Chem. 366 (2000) 387.
[45] Z.I. Chen, M. Megharaj, R. Naidu, Chromatographia 65 (2006) 115.
[46] A. Seubert, G. Schminke, M. Nowak, J. Chromatogr. A 884 (2000) 191.
[47] H. Shi, C. Adams, Talanta 79 (2009) 523.
[48] Method 321.8: Determination of Bromate in Drinking Waters by Ion Chromatography Inductively Coupled Plasma-Mass Spectrometry, US Environmental Protection Agency, Cincinnati, OH, 1997.
[49] A.A. Othman, S.A. Al-Ansi, M.A. Al-Tufail, Anal. Lett. 43 (2010) 886.
[50] K. Reddy-Noone, A. Jain, K.K. Verma, J. Chromatogr. A 1148 (2007) 145.
[51] M.L. Magnuson, Anal. Chim. Acta 377 (1998) 53–60.
[52] H.S. Shin, Y.S. O-Shin, J.H. Kim, J.K. Ryu, J. Chromatogr. A 732 (1996) 327.
[53] H.S. Shin, Chromatographia 71 (2010) 647.
[54] USEPA Method SW 846, Quality Control, 1992, p. 26 (Chapter 1).