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Ultra trace determination of bromate in mineral water and table salt by liquid chromatography–tandem mass spectrometry

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ABSTRACT

A liquid chromatography–tandem mass spectrometry method (LC–MS/MS) was developed in order to determine the bromate in mineral water and table salt. The following optimum conditions for the LC–MS/MS detection were established: derivatization reagent (300 mg/L of 2,6-dimethylaniline), acidity (0.2 M HCl), reaction temperature (30 °C) and heating time (20 min). The formed derivative was directly injected in the LC system without extraction or purification procedures. In the established conditions, the method was used to detect bromate in mineral water and table salt. The limit of detection and limit of quantification of bromate in mineral water were 0.02 μg/L and 0.07 μg/L, respectively, and those of table salt were 0.07 μg/kg and 0.23 μg/kg, respectively. The 17 common ions did not interfere even when present in 1,000-fold excess over the bromated ion of 10.0 μg/L. The accuracy was in a range of 92–104% and the assay precision was less than 9% in the table salt. The method was successfully applied to determine bromate in mineral water and table salt.

1. Introduction

Bromate is a disinfection by-product (DBP) that is generated during disinfection processes through the reaction of ozone and bromide in municipal drinking water [1,2]. Bromate is a potential carcinogen, which has been proven by both the US Environmental Protection Agency (EPA) and the International Agency for Research on Cancer [3,4]. Due to these health concerns, the bromated concentration in drinking water is a significant concern among regulatory agencies worldwide [5–8]. Regulatory agencies in the USA [6] and European countries [7] have established a maximum contaminant level of bromate of 10.0 μg/L in drinking water, and Korea [8] has a standard level of the same concentration only in natural mineral water.

Considerable interest has been shown in bromate analysis due to its toxicology; a number of methods have been developed to manage the variety of water matrices using ion chromatography (IC) [9–31]. In fact, the bromate quantity can be determined at sub-μg/L levels using pre-concentration techniques [12,14]. Alternative and sensitive detection techniques include post-column derivatization [10,28,29] and mass detection [17–25,30,31], however, these methods suffer from complex plumbing operations. Gas chromatographic mass spectrometric methods (GC–MS) [32–34] following the redox reaction of bromate and extraction have been developed to detect bromate in complex matrices. These methods can analyze bromate with very low detection limits and without chloride interferences, but they involve multistep reactions including the removal of free bromide [32] and the solvent extraction and concentration before the injection in GC–MS [34], while also suffering from interference in chlorinated waters [33].

A liquid chromatography–tandem triple-quadrupole mass spectrometry (LC–MS/MS) is a common technique in the analytical area and is routinely used to automatically analyze many types of compounds. Several analytical methods for determining the bromate in drinking water or food have been developed using LC–MS/MS [35–37]; however, these methods suffer from interference of ions such as sulfate and carbonate. In particular, it has been difficult to evaluate the occurrence of the chemical in samples containing high concentration levels of ions such as seawater and salt.

The aim of this study is to develop a simple and sensitive bromate determination method using the LC–MS/MS but without the interference of various ions. Several derivatization tests were performed in order to select a reagent with a high sensitivity and low interference in the derivative and to optimize the parameters of LC–MS/MS for automatically analyzing bromate in natural mineral water and table salt. The new method was applied in real sample analyses.

2. Experimental

2.1. Reagents

Sodium chloride (99.5%), potassium iodide (99.9%), potassium bromide (99%), potassium bromate (99.8%), 2,6-dimethylphenol

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(2,6-DMP, 99.0%), 2,6-dimethylaniline (2,6-DMA, 99%), 2,6-diisopropylphenol (2,6-DiPP, 97%), 2,6-di-*tert*-butylphenol (2,6-DtBP, 99%), chlorpromazine hydrochloride (99.9%), trifluoperazine dihydrochloride (99%), *o*-dianisidine (99.9%), acetanilide (99.9%) and 2-naphthol (99%) were obtained from Aldrich (Milwaukee, WI, USA). A stock standard solution of bromate was freshly prepared prior to use by dilution of a 5 mL portion of commercially available potassium bromate solution to 100 mL using water. A known volume of this solution was sequentially diluted in order to obtain a 1.0 mg/L bromate standard solution. This solution was used within 1 h of its preparation.

The pure water used in this study was purified using a Milli-Q-Reagent-Grade water system (ZD20) and had a resistivity of >17 MΩ. The table salt samples were purchased from several local supermarkets.

Thirteen mineral water samples and 15 commercially available table salts were purchased from several local supermarkets.

2.2. Derivatization

Water samples of 10 mL were placed into a 20 mL glass-stoppered test tube. For the table salt, samples of 3.0 g were dissolved in 10 mL of pure water and were placed into 20 mL glass-stoppered test tubes.

In order to study the optimal derivatization conditions, the reaction was performed for various amounts of 2,6-DMP, 2,6-DMA, 2,6-DiPP, 2,6-DtBP, chlorpromazine, trifluoperazine, *o*-dianisidine, acetanilide and 2-naphthol (0.10, 0.20, 0.60, 1.0 and 2.0 mg) and reaction times (1, 15, 30, 45, 60, 75 and 90 min). Derivatization efficiencies were calculated at various temperatures (15, 30, 40, 50 and 60 °C) and acidities (in the range of 0.01–0.3 M). The acidity of each sample was controlled using 5 M HCl. The optimum conditions for the bromate derivatization were determined using the areas of the formed derivatives.

The solution was directly transferred into an auto vial, and 10 μL of the solution was injected in the LC system.

2.3. Calibration and quantitation

The calibration curve for the linearity test was established by adding 0.1, 0.5, 1, 5, 10, 50, 100, 250, 500, and 1000 ng of bromate standard to 10 mL of ultra-pure water or 10 mL ultra-pure water dissolved with 3.0 g of NaCl.

The solutions were derivatized with the method selected in the above reaction procedures, and injected into the LC system. The peak area of the bromate standard was used for the construction of the calibration curve.

2.4. Liquid chromatography–mass spectrometry

The liquid chromatography was an Agilent 1200 series (Agilent, Palo Alto, CA, USA) equipped with a binary pump, online vacuum degassing system, and autosampler. The analytes were separated using a 50×2.1 mm^2 Eclipse Plus C18 column with a 1.8 μm pore size (Agilent, USA). A binary gradient with a flow rate of 0.2 mL/min was used. The mobile phase A contained 0.1% formic acid in water and mobile phase B was acetonitrile. The gradient was as follows: at first B=0%, and then increased to 100% after 9 min. All compounds are eluted within 11.0 min.

The MS-MS detection was performed using an Agilent 6460 series Triple Quadruple instrument (Agilent, Palo Alto, CA). The mass spectrometer was operated using the electrospray ionization in the positive ion mode (ESI+). The capillary voltage was set to 4.5 kV. The source temperature was 100 °C and the desolvation temperature was 330 °C. Nitrogen was used as the desolvation gas (flow 480 L/h) and collision gas at a pressure of 3×10^{-3} mbar. Detection was performed in a multiple reaction monitoring (MRM) mode. The MRM transitions were *m*/*z* 200.0 to *m*/*z* 183.0, *m*/*z* 121.1 and *m*/*z* 106.0.

3. Results and discussion

3.1. Selection of derivatization reagent

A derivatization method has been described for the sensitive LC–MS/MS analysis of bromate. In acidic media, bromate is reduced by chloride ion to form bromine, which reacts with the active hydrogen of reagents to form bromo-derivatives through the reaction [32,34]

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

$$Br_2 + \text{reagent} \rightarrow \text{bromo-derivative} + Br^-$$

The formed derivative was designed to be directly injected into the LC system without an extraction procedure. For the direct injection, the derivative must be sensitive by LC–MS/MS. The reagents to be utilized in the above substitution reaction were found from the literature. 2,6-DMP, 2,6-DiPP, 2,6-DtBP, 2,6-DMA, chlorpromazine, trifluoperazine, acetanilide, *o*-dianisidine and 2-naphthol were selected as candidate reagents for the substitution reaction and their molecular structures are shown in Fig. 1. In previous studies, 2,6-DMP, 2,6-DiPP, 2,6-DtBP, and 2,6-DMA have proven to be good reagents for the substitution reaction using halogen [32,34] and chlorpromazine [38], trifluoperazine [39], and *o*-dianisidine [40] have been used as derivatization reagents for the spectrophotometric determination. Acetanilide has also been used for the pre-column derivatization for the HPLC determination [41], and 2-naphthol was used for the fluorescence determination [42].

In order to select the best reagent from the candidates, they were compared with each other in terms of their reactivity and sensitivity of the derivatives using LC–MS/MS. The reaction rates were determined through the detection of the substituted products at reaction times of 1, 15, 30, 45, 60, 75 and 90 min (Fig. 2). The results indicated that acetanilide and 2,6-DMA exhibited very rapid reactions through the total redox procedure with bromate and high sensitivity according to LC–MS/MS (Fig. 2). Almost the complete reaction occurs in approximately 15 min at 30 °C, provided a sufficiently high concentration of reagent present in the reaction mixture. But the reaction of bromate with acetanilide exhibited two derivative peaks (*ortho*- and *para*-bromo derivatives), which increases the difficulty of the quantification. There was no significant variation in reaction yield noted over this time period. Furthermore, 2,6-DtBP and *o*-dianisidine were converted to bromo-derivatives, which increased until 30–60 min; 2,6-DMP, chlorpromazine, trifluoperazine, and 2-naphthol were not converted to bromo-derivatives nor were they detected using the LC–MS/MS. In order to evaluate the stability of the derivatives, the experiment was repeated by analyzing the extracts stored at room temperature (approximately 20 °C) for two weeks. The mean percentual stability of the 2,6-DMA-derivative after two weeks varied by 2.8% and exhibited very stable properties. As a result, it was decided that 2,6-DMA would be used for the bromate determination due to its sensitivity, reactivity, quantitative properties and stability.

3.2. Optimization of derivatization conditions

In order to obtain the optimal conditions for the bromate determination, the effects of the reagent concentration, acidity, reaction temperature and time were examined.

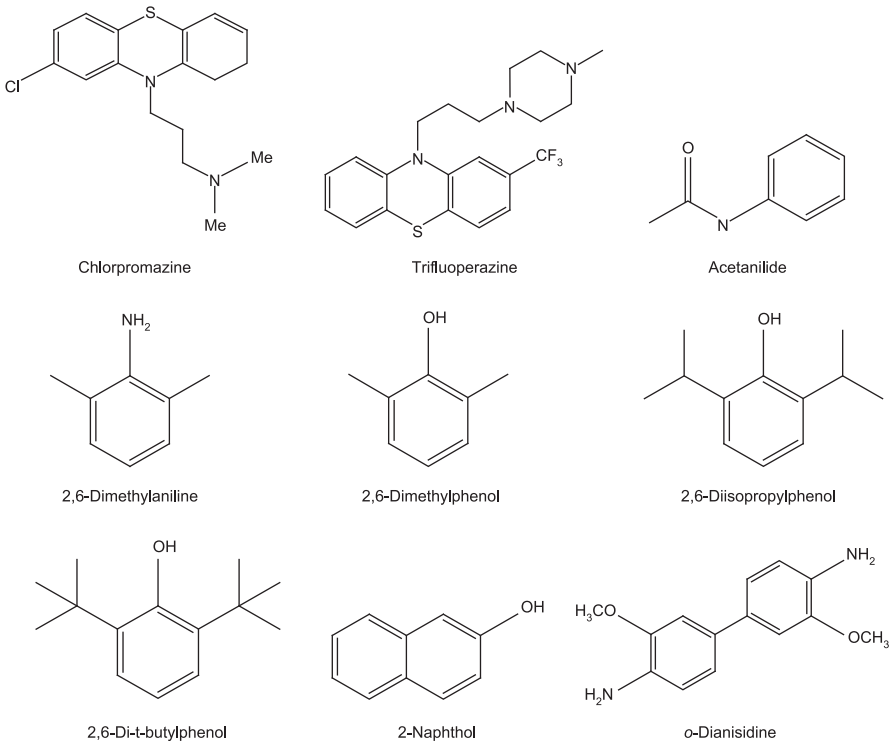

Fig. 1. Reagents used in the substitution reaction and LC–MS/MS detection.

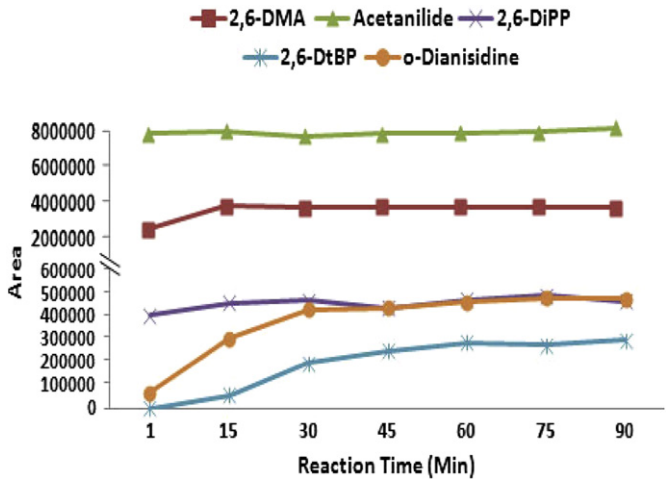

Fig. 2. Bromate reactivity in relation to various derivatization reagents. (This experiment was performed for 20 min at 30 °C.)

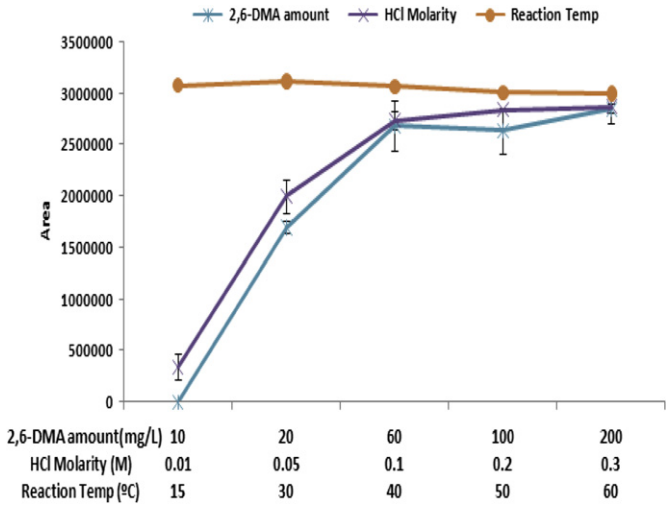

Fig. 3. Bromate reactivity according to various dosages of 2,6-DMA, HCl molarity and reaction temperature. (This experiment was performed for 20 min at 30 °C.)

3.2.1. *Effect of 2,6-DMA concentration*

The effect of the amount of 2,6-DMA in the concentration range of 10–200 mg/L was examined. The strongest peak area enhancement was observed when the amount of added 2,6-DMA was 0.60 mg (60 mg/L in the solution) and maintained persistently beyond that (Fig. 3). Therefore, 3.0 mg (300 mg/L in the solution) was selected as the optimum 2,6-DMA amount considering the substances consuming reagents in the real samples.

3.2.2. *Effect of pH*

Because the reaction occurred in an acidic medium, the effect of various HCl molarities was studied in the range of 0.01–0.3 M. The results demonstrated that the maximum peak area was obtained in 0.1 M HCl, and maintained stability with increasing HCl molarity to 0.3 M (Fig. 3). Thus the 0.2 M HCl solution was chosen for the assay.

3.2.3. *Effect of reaction temperature and time*

The temperature had an important effect on the complete reaction. After controlling the temperature of solution from 15 to 60 °C, the peak intensity values were detected. The experimental results indicated that the peak intensity reached a maximum at 30 °C and decreased constantly to 60 °C (Fig. 3); therefore, a reaction temperature of 30 °C was selected as the optimum value. Here, the heating time was 20 min.

3.3. LC–MS/MS optimization

The ESI full scan and tandem mass spectra in positive mode were measured for the derivative. As an objective of this study is the detection of a very small amount of bromate residues in the samples, the MRM mode was chosen despite a number of transitions that needed to be programmed in order to undertake a multi compound analysis using the LC–MS/MS. In order to perform the analysis in MRM, the transition ion with the highest abundance and mass was chosen as the quantification ion. The MRM transitions were m/z 200.0 $[M+H]^{+1}$ to m/z 183.0 $[M+H-NH_3]^{+1}$, m/z 121.1 $[M+2H-Br]^{+1}$ and m/z 106.0 $([M+2H-Br-CH_3]^{+1}$.

Fig. 4 presents the MRM ions chromatograms obtained after the derivatization of a standard of bromate and blank. For the LC separation of the derivatives, using of the non-polar stationary phase was found to be efficient. Furthermore, the derivatives did not exhibit adsorption effects in the LC system. The retention time of 4-bromo-2,6-DMA was about 7.65 min. The discrimination by the ion selection was very good. Extraneous peaks were not observed in the chromatogram of the samples at the retention times of the derivative.

3.4. Interference

The effect of foreign substances on the determination of 10 μg/L bromate was investigated using a method with 17 diverse ions and chemical species. The chemicals were added individually to the tested solution. The tolerance limit was defined as the concentration of the added ion, which resulted in less than ±3% relative error for the active species determination. The results demonstrate that the 17 common ions (Cl^-, NO_3^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}, HPO_4^{2-}, $CH_2PO_4^-$, K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Mn^{4+}, Mn^{2+}, Fe^{3+} and Fe^{2+}) did not interfere, even when they were present in 1000-fold (each 10 mg/L) excess over the bromate concentration of 10 μg/L active

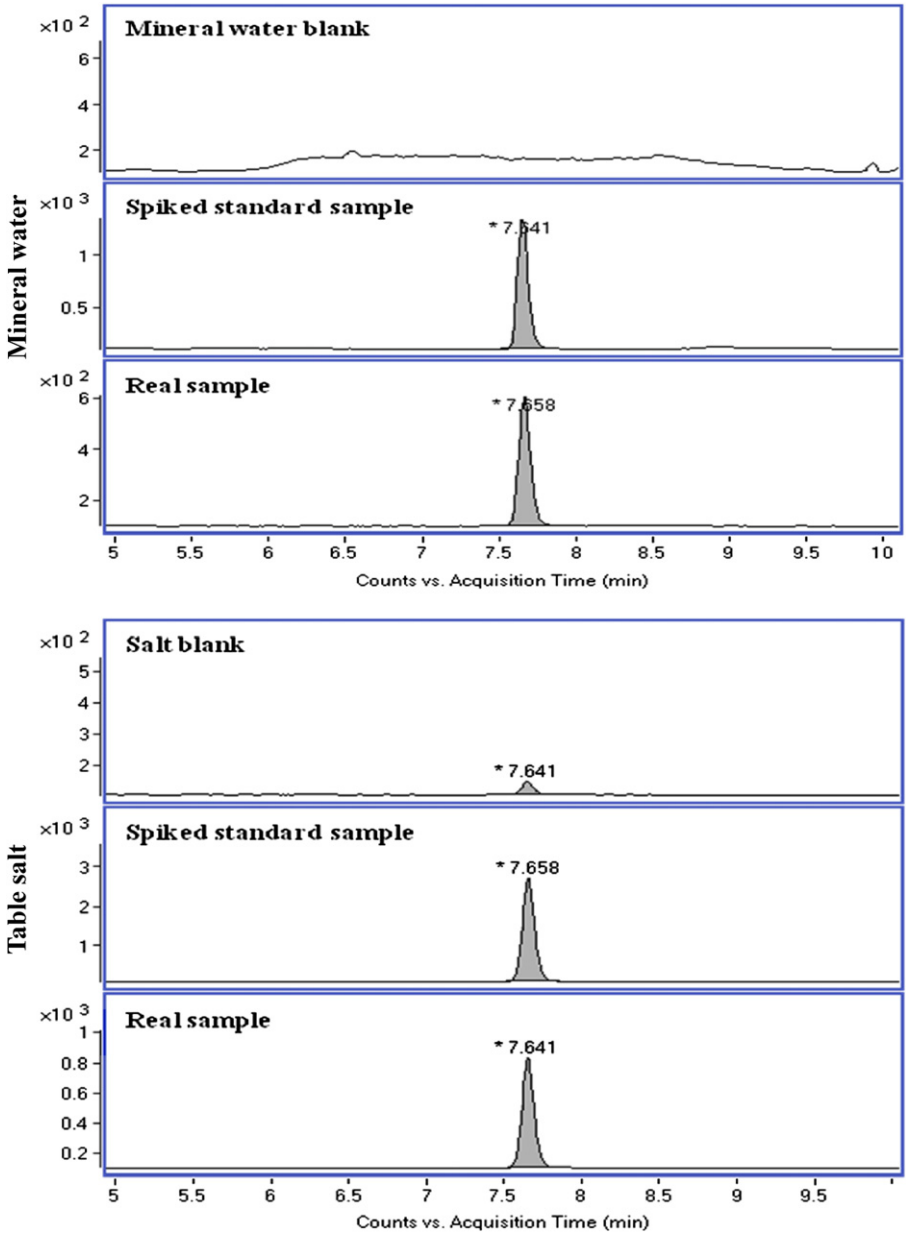

Fig. 4. LC–MS/MS chromatogram of the blank samples, the standard samples spiked in the concentrations of bromate 50.0 μg/L and 83.3 μg/kg, and real samples. (Mineral water and table salt samples were quantified as the concentration of 27.67 μg/L and 37.6 μg/kg, respectively.)

Table 1
Intra- and inter-day laboratory accuracy and precision results for the analysis of bromate in mineral water and table salt ($n=5$).

Matrix	Matrix blank ($\mu g\ L^{-1}$ or $\mu g\ kg^{-1}$)	Spiked conc. ($\mu g\ L^{-1}$ or $\mu g\ kg^{-1}$)	Intra-day measured value		Inter-day measured value			
			Mean ± SD ($\mu g\ L^{-1}$ or $\mu g\ kg^{-1}$)	Accuracy (%)	Precision (%)	Mean ± SD ($\mu g\ L^{-1}$ or $\mu g\ kg^{-1}$)	Accuracy (%)	Precision (%)
Natural mineral water	ND	1.0	1.03 ± 0.03	102.7	2.48	0.99 ± 0.04	98.6	3.61
		10.0	9.90 ± 0.16	99.0	1.64	9.68 ± 0.13	96.8	1.38
Table salt	ND	1.0	1.04 ± 0.03	103.7	2.85	1.01 ± 0.09	101.3	8.68
		10.0	9.23 ± 0.14	92.3	1.47	9.51 ± 0.18	95.1	1.85

species. Also, the 3% NaCl solution did not influence the bromate determination. When Br^- coexists with Cl_2, Br_2, O_3 or ClO_2, it is converted to Br_2, which reacts with 2,6-DMA to form bromo-derivative. To remove the interference of Br^-, it can be eliminated by anion exchange with AgCl before the redox reaction of bromate, as reported by Reddy-Noone et al. [32]. Otherwise, to remove oxidants such as halogens, they can be eliminated by substitution reaction or extraction with ethyl acetate before the redox reaction of bromate, as reported by Magnuson [33]. Therefore, this method can be applicable in drinking water, co-existing residual oxidants and bromide ions.

The LC–MS/MS methods for determining bromate without the derivatization suffer from interference of ions such as sulfate and carbonate, especially in samples containing high ion concentration levels such as seawater or table salt [35–37]. Despite this, the proposed method demonstrated good selectivity, although a derivatization step was necessary.

3.5. Verification of method performance

The method performance was evaluated by determining the detection limit, precision, and accuracy of the method using the new reagent.

The lowest detection limit (LOD) and limit of quantification (LOQ) of bromate in mineral water were approximately 0.02 μg/L and 0.07 μg/L, respectively, and those of table salt were approximately 0.07 μg/kg and 0.23 μg/kg, respectively. The LOD and LOQ were defined as 3.14 and 10 times the standard deviation, respectively for the replicate determinations ($n=7$) from samples spiked at a concentration of 0.01 μg/L or 0.01 μg/kg.

Using a least squares fit technique, an examination of the typical standard curve was undertaken by computing the regression line of a peak area for bromate on the concentration. The regression line of the peak area of bromate on concentration using the least-squares fit demonstrated a linear relationship $y=3603x-34.48$ in a concentration range of 0.1–100 μg/L and $r^2=0.9999$, where x is the bromate concentration (μg/L) and y is the peak area of bromate.

The accuracy and precision were assessed by determining the recovery in samples spiked with pure water. The intra-day accuracy and precision were evaluated using five spiked samples at concentrations of 0.50 and 10.0 μg/L for the liquid sample or 0.50 and 10.0 μg/kg for the solid sample. Furthermore, the 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 1. The accuracy was in a range of 92–104% and precisions of the assay were less than 9%. The results indicate that this method was sufficiently reproducible to permit reliable analysis of the bromate quantity in natural mineral water and table salt.

3.6. Occurrence in mineral water and table salt

The proposed method was used to analyze the bromate quantity in thirteen natural mineral water samples. Bromate was detected in a concentration range of 0.09–27.67 μg/L (mean 2.51 μg/L) in all the samples. Although ozonation for the natural mineral water is prohibited in Korea, bromate detected in the high concentrations is thought to originate from ozonation. If bromide exists in adequate concentrations, some bromide ions are oxidized to bromate during the ozonation process of water [43].

Table 2
Analytical results of bromate formed in salt according to NaBr contents and roast time at 400 °C.

Baking time (h)	NaBr spiked conc. (mg/kg)	Measured conc. (μg/kg)
3	0	1.9
	100	2.7
	200	3.6
	500	4.0
10	0	2.2
	100	3.8
	200	4.3
	500	15.2
24	0	2.6
	100	4.7
	200	8.4
	500	6.6

Fifteen table salts were used to analyze the bromate quantity. Bromate was detected in the concentration range of 1.12–70.02 μg/kg (mean 12.16 μg/kg) in all table salts and in the high concentration of 5.38–70.02 μg/kg (mean 29.55 μg/kg) in the roast table salts. The roast table salts are produced by heating in the furnace of >400 °C, and they are known to be helpful for the human health and salt taste. To confirm the occurrence of bromate during the baking process of table salt, the bromate amount was detected in the samples after spiking of NaBr in reagent sodium chloride and roasting in the furnace of 400 °C. As a result, bromate was formed in the test samples and it increased with prolonging roast time and the increasing NaBr addition amount (Table 2). The roast table salt is taken by many people in Korea, and the hazard effects of bromate formed in the roast table salt should not be neglected. Fortunately, all the normal table salt revealed low bromate concentration levels under 5.0 μg/kg. When taking into account the possibility of a daily consumption of mineral water or table salt, regular monitoring should be considered necessary.

4. Conclusion

Major advantages of this method are as follows: (1) The proposed method sensitively determined bromate without interference from various ions in mineral water and table salts. Acceptable precision and accuracy were obtained in the samples with the complex matrices. (2) Although this method requires a derivatization step in comparison with other LC–MS/MS methods, the procedure is simple and rapid, and is not laborious. (3) This method can be used in drinking water, co-existing residual

oxidants and bromide ions. In this case, Br^- can be eliminated by anion exchange with AgCl before the redox reaction of bromated, or oxidants can be eliminated by substitution reaction or extraction with ethyl acetate before the reaction.

The shortcoming of this method is that the derivatization reaction must be performed before the injection in LC–MS/MS.

The method may provide a suitable alternative to IC–MS or other LC–MS/MS methods for the analysis of trace levels of bromate in complex matrices.

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