

Determination of trace bromate in various water samples by direct-injection ion chromatography and UV/Visible detection using post-column reaction with triiodide

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Abstract: Bromate is a disinfection by-product generated mainly from the oxidation of bromide during the ozonation and disinfection process in order to remove pathogenic microorganism of drinking water, and classified as a possible human carcinogen by International Agency for Research of Cancer (IARC) and World Health Organization (WHO). For the purpose of determining the trace level concentration of bromate, several sensitive techniques are applied mostly based on suppressed conductivity detection and UV/Visible detection after post-column reaction (PCR). In this study, the suppressed conductivity detection method and the PCR-UV/Visible detection method through the triiodide reaction were compared to analyze the trace bromate in water samples and estimated for the availability of these analytical methods. In addition, the state-of-the-art techniques was applied for the determination of trace level bromate in various water matrices, i.e., soft drinking water, hard drinking water, mineral water, swimming pool water, and raw water. In comparison of two analytical methods, it was found that the conductivity detection had the suitable advantage to simultaneously analyze bromate and inorganic anions, however, the bromate might not be precisely quantified due to the matrix effect especially by chloride ion. On the other hand, the trace bromate was analyzed effectively by the method of PCR-UV/Visible detection through triiodide reaction to satisfactorily minimize the matrix interference of chloride ion in various water samples, showing the good linearity and reproducibility. Furthermore, the method detection limit (MDL) and recovery were 0.161 µg/L and 101.0–108.1 %, respectively, with a better availability compared to conductivity detection.

Key words: bromate, drinking water, direct injection ion chromatography, PCR-UV/Visible detection, triiodide reaction

1. Introduction

Disinfection of drinking water is carried out to remove infectious microorganisms and substances

that cause the bad taste or odor of water. Chlorine disinfection is the most common method in public water supplies. However, the by-products of chlorine disinfection such as trihalomethane (THM), a potential

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carcinogen, are produced in addition to inhibiting the taste of water. Furthermore, the generation of chlorine gas in drinking water cause an reluctances for this method, so that the disinfection method is replaced with other methods. A strong oxidants such as potassium permanganate or ozone are available for disinfection to prevent the generation of by-products.¹ Although ozone is widely used as one of the most effective disinfectants, there is a side effect of oxidizing naturally occurring bromide to bromate. The International Agency for Research of Cancer (IARC) specifies that the bromate are potential carcinogens and that the concentration of bromate in drinking water and mineral water must be monitored.² US Environmental Protection Agency (US EPA) and European Union (EU) prescribe concentrations below 10 µg/L in drinking water³ and below 3 µg/L in bottled natural mineral water.⁴

Recently, the disinfection method using hypochlorous acid in each water purification plants has been increasing, based on the onsite hypochlorite generators and onsite generators (OSGs) treatment. However, it has been reported that some components or contaminants, such as BrO_3^- , ClO_2^- , ClO_3^- , and ClO_4^- , be present in the hypochlorite (ClO^-) solution during or after the manufacturing proces.^{1,5-7} Especially, oxyhalides species such as bromate, chlorite, chlorate and perchlorate are contained as impurities in sodium hypochlorite solutions, and still remained in the processed waters of a metropolitan area.

American Water Works Association (AWWA) requires that bromate should be tested in the raw material of hypochlorite. Since January 2018, the periodic monitoring and analysis of bromate was required for all water treatment plants in Korea. For the satisfactory to this requirements, an analytical method with more excellent sensitivity is required.^{8,9} The most widely used analytical method is anion-exchange chromatography (AEC).⁵ Low detection limit of the suppressed conductivity method is in the range of about 0.1–20 µg/L. On the other hand, the low detection limit of IC-MS (ion chromatography-mass spectrometry) is around 6 ng/L with very high sensitivity and detection performance. However, MS detection has difficulties for the instrumental operations

as well as costly high method. Also, contamination might be occurred during the sample pretreatment using the cartridge, moreover involving inconvenient and high-priced processes.

Therefore, in this study, we have examined the method about UV/Visible detection with high sensitivity using post-column reaction (PCR) after anion exchange separation, in order to enhance the detection limit for the analysis of the trace level bromate in various water samples, based on suppressed conductivity detection (EPA 300.1 and ISO 15061) and UV/Visible detection after post-column reaction (EPA 326 and ISO 11206).

2. Experimental

2.1. Chemicals and samples

Bromate (BrO_3^- , 100 µg/mL) and multi-anion standard (F^- , Cl^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-} 1000 mg/mL) were purchased from High-Purity Standards (USA) without additional purification. Stock standard solution (1 mg/L) was prepared by the dilution of 100 mg/L BrO_3^- 1 mL to 100 mL with ultrapure water. H_2SO_4 , KI and ammonium heptamolybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) were purchased from Sigma-Aldrich (USA) without additional purification. The ultrapure water (18.2 MΩ) was used for the preparation of all experimental reagents.

Eluent solution of 100 mM H_2SO_4 was prepared by dissolving 5.43 mL 98 % H_2SO_4 in 500 mL ultrapure water, and diluted to 1000 mL with ultrapure water. PCR-derivatized solution for the detection of trace bromate was prepared using the mixture of 0.27 M KI and 50 µM ammonium heptamolybdate tetrahydrate, by dissolving 45 g KI and 6.25 mg ammonium heptamolybdate tetrahydrate and diluting it to 1000 mL volume with ultrapure water. KI was stored in brown color bottle wrapped with aluminum foil in order to prevent the interference from light and oxygen, and PCR-derivatized solution was prepared before use to avoid its deteriorations.

In order to evaluate an availability of PCR-UV/Visible detection method, five kinds of real samples were applied to the ion chromatography analysis in

this study. Soft drinking water, hard drinking water, mineral water, swimming pool water, and raw (river) water were used as a test samples. All water samples were used without any purification and pre-concentration, but some samples were doubly diluted with ultrapure water to lower the concentration levels within the range of calibration curve.

2.2 Instruments and operating conditions

The analysis of trace bromate was carried out by ion chromatographic method using 850 Professional IC and 844 UV/VIS Compact IC (Metrohm, Switzerland).

Table 1. Instrumental conditions for the analysis of bromate using IC equipped with PCR-UV/Visible detection system

| Compartment | Operating conditions |
|--------------------------|--|
| Ion Chromatograph | 850 Professional IC and 844 UV/VIS Compact IC |
| Column | Metrosep A Supp 16 100×4 mm (Metrohm) |
| Eluent | 100 mM H ₂ SO ₄ |
| Injection volume | 1000 µL |
| Flow rate | 0.7 mL/min |
| PCR reagent | 0.27 M KI/50 µM (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O |
| PCR reaction coil volume | 400 µL |
| PCR reagent flow | 0.2 mL/min |
| Temperature | 45 °C |
| Detection | UV, λ = 352 nm |

Optimum concentration of PCR reaction: 60 mmol/L KI, 11.1 µmol/L Mo(VI)

The details of ion chromatography conditions for PCR-UV/Visible detection of bromate were described in Table 1, referred to a previous reported method.¹

3. Results and Discussion

3.1. PCR-UV/Visible detection of bromate

One way of the analytical methods for determining bromate is to use an ion chromatograph equipped with suppressed conductivity detection. This method^{5,10} has a disadvantage in that the resolution was lowered due to the influence of chloride ion interferences. Suppressed conductivity detection can be performed for the analysis of bromate simultaneously with other inorganic anions. Therefore, it is necessary to remove the chloride ions in order to exclude the interference of co-elution during the separation process, and use a high-resolution column.

On the other hand, PCR-UV/Visible detection^{3,11,12} using derivatized reagent was recently introduced as a suitable method for selective measurement of bromate, based on ISO 11206 method. In this triiodide method, bromate reacts with potassium iodide with a heptamolybdate catalyst in an acidic environment to finally produce the triiodide as below reaction.¹³

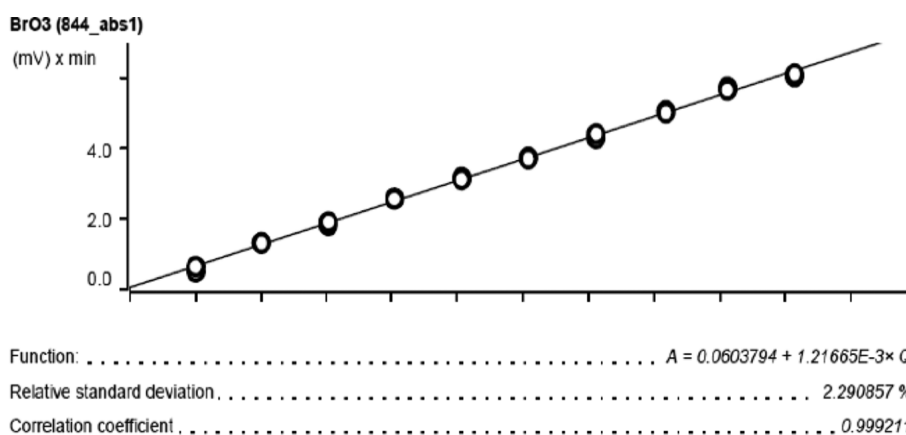
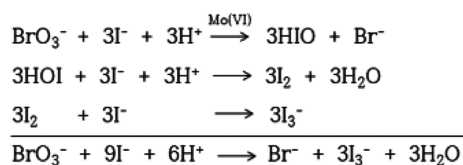


Fig. 1. Standard calibration curve drawn up with 10 bromate solutions between 0.502 – 5.071 µg/L concentrations.

This triiodide product absorbs the light at a wavelength of 352 nm.^{3,11-13} Limit of quantitative analysis of 0.5 µg/L bromate could be available by IC-PCR-UV/Visible method through this triiodide reaction. It is especially useful for the selective determination of bromate in water samples with various matrices.

In this study, we tried to examine that the trace bromate was able to effectively be detected and determined in water samples with high ionic matrix using PCR-UV/Visible method. For the experiments, the calibration range was specified as 0.502–5.071 µg/L according to ISO 11206 regulation. The 10 bromate standard solutions with different concentrations were prepared to make up a standard calibration curve for PCR-UV/Visible method. Fig. 1 shows the standard calibration curve of the linear type based on the concentration of each standard listed in Table 2. From the result, the relative standard deviation

(RSD) of calibration curve was 2.291 % and the correlation coefficient was $r = 0.999211$ with a great linearity, representing a good possibility for the quantitative analysis.

In addition, the method detection limit (MDL) was obtained from the 7-duplicate experiments with 3.00 µg/L bromate standard as shown in Table 3. In result, the measured MDL was 0.161 µg/L with the range of 0.0510 standard deviation. Also, the reproducibility test was carried out using 7.50 µg/L bromate standard. This bromate standard was doubly diluted with ultrapure water in order to fit the concentration within the range of calibration curve. In the result obtained from 10 times repeated experiments, the relative standard deviation was 0.588 %, showing a good reproducibility (Table 4).

The suitability for the PCR-UV/Visible method was examined through the recovery test using bromate standard in order to quantitatively determine

Table 2. Specific concentrations of bromate standard solutions (n=10) to make up a standard calibration curve

| Number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Concentration (µg/L) | 0.502 | 1.003 | 1.514 | 2.018 | 2.531 | 3.040 | 3.556 | 4.090 | 4.560 | 5.071 |

Table 3. Method detection limit (MDL) of bromate analysis measured by PCR-UV/Visible detection method (n=7)

| Repeated No. | Analytical Concentrations (3.00 µg/L) | | | | | | | | S.D. | MDL |
|----------------------|---------------------------------------|------|------|------|------|------|------|--------|-------|-----|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | | | |
| Concentration (µg/L) | 3.08 | 3.10 | 2.97 | 3.10 | 3.05 | 2.99 | 3.03 | 0.0510 | 0.161 | |

Table 4. Reproducibility of bromate analysis measured by PCR-UV/Visible detection method (n=10)

| Repeated No. | Analytical Concentrations (7.50 µg/L) | | | | | | | | | | S.D. | RSD(%) |
|----------------------|---------------------------------------|------|------|------|------|------|------|------|------|------|--------|--------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | | |
| Concentration (µg/L) | 7.58 | 7.58 | 7.60 | 7.55 | 7.56 | 7.57 | 7.47 | 7.49 | 7.49 | 7.56 | 0.0440 | 0.588 |

Table 5. Recovery of bromate analysis for 4-spiked different concentration samples, measured by PCR-UV/Visible detection method

| Statistics | Sample 1 (2.682 µg/L) | | | | | Sample 2 (3.061 µg/L) | | | | |
|-----------------|-----------------------|--------|--------|-------|-------------|-----------------------|--------|--------|-------|-------------|
| | S1 | S2 | Mean | Conc. | Recovery(%) | S1 | S2 | Mean | Conc. | Recovery(%) |
| Spiked (2 µg/L) | 4.669 | 4.736 | 4.703 | 2.021 | 101.0 | 5.178 | 5.267 | 5.223 | 2.162 | 108.1 |
| Statistics | Sample 3 (7.616 µg/L) | | | | | Sample 4 (9.090 µg/L) | | | | |
| | S1 | S2 | Mean | Conc. | Recovery(%) | S1 | S2 | Mean | Conc. | Recovery(%) |
| Spiked (5 µg/L) | 12.693 | 12.838 | 12.766 | 5.100 | 103.0 | 14.331 | 14.118 | 14.225 | 5.135 | 102.7 |

S1, S2: number of samples for repeated experiments

the trace bromate. The recovery test was carried out by the analyses of 4-spiked samples (2.00 $\mu\text{g/L}$ and 5.00 $\mu\text{g/L}$) that contained different matrices exist (Table 5).

In case of water samples spiked with 2.00 $\mu\text{g/L}$ bromate standards, the recoveries were 101.0 % and 108.1 %, respectively, for sample 1 and sample 2 (Table 5). When 5.00 $\mu\text{g/L}$ of bromate standard was spiked in water samples, the recoveries were 102.7 % and 103.0 %, respectively, for sample 3 and sample 4, showing a good availability for the quantitative analysis in all four water samples.

3.2. Comparison of conductivity and PCR-UV/Visible detections

In general, two methods, i.e. using suppressed conductivity detection and PCR-UV/Visible detection are applicable to determine the bromate concentration. The conductivity detection method has the advantage to be able to simultaneously analyze bromate and inorganic anions. However, the bromate may not be precisely quantified due to the influence of the other anion matrices. On the other hand, the PCR-UV/Visible detection has the advantage to selectively measure the bromate ion without matrix interference. Fig. 2 shows a ion chromatogram for 0.550 $\mu\text{g/L}$ bromate separated by PCR-UV/Visible detection method. The peak of bromate ion was separated with a retention time of about 8 min without any matrix interferences.

Two ion chromatograms of the bromate standards

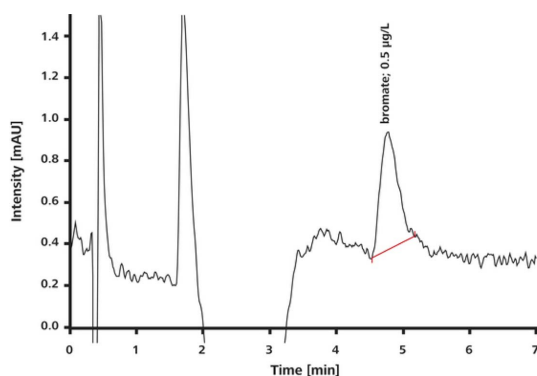


Fig. 2. Ion chromatogram of 0.550 $\mu\text{g/L}$ BrO_3^- standard containing Cl^- , NO_3^- and SO_4^{2-} matrices, obtained with PCR-UV/Visible detection.

(10.0 $\mu\text{g/L}$) were obtained by ion chromatograph equipped with suppressed conductivity detection and PCR-UV/Visible detection from water samples containing other anion matrices, and compared in Fig. 3. Fig. 3(a) shows the ion chromatogram obtained by a conductivity detection method. In the result, all peaks of inorganic anions including bromate (9.40 min retention time) are simultaneously appeared, but a bromate ion peak is almost as closed to chloride ion as it's difficult to differentiate two peaks each other. It means that chloride ions can be acted as a big interference species to quantitatively analyze a trace bromate, due to the influence of the chloride ion peak, especially in case of the high chloride concentration.

However, in case of the PCR-UV/Visible detection method as shown in Fig. 3(b), only one bromate peak appears at the retention time of 10.37 min without any matrix interferences by other inorganic anions. Consequently, as for the water samples with high ionic matrices, especially high concentration of chloride ions, the PCR-UV/Visible detection may be a better application for the IC analysis of trace bromate ion, to be able to replace the suppressed conductivity detection method.

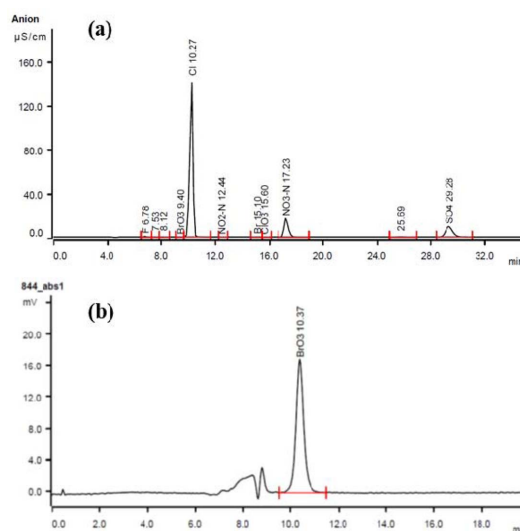


Fig. 3. Ion chromatograms of 10.0 $\mu\text{g/L}$ BrO_3^- standard from water sample containing Cl^- , NO_3^- , SO_4^{2-} and other anions, using a suppressed conductivity detection (a) and PCR-UV/Visible detection (b).

Table 6. Concentrations of trace bromate in various water samples, determined by application of IC-PCR-UV/Visible detection through triiodide reaction

| Statistics | Concentrations ($\mu\text{g/L}$) | | | | | |
|------------|------------------------------------|-------|-------|-------|-------|-------|
| | SD | HD | ML | SP | RW | SS |
| #1 | 2.73 | 9.33 | 3.03 | 7.67 | 7.91 | 1.78 |
| #2 | 2.73 | 9.26 | 2.98 | 7.57 | 7.85 | 1.80 |
| #3 | 2.68 | 9.23 | 3.06 | 7.52 | 7.98 | 1.76 |
| #4 | 2.68 | 9.09 | 3.06 | 7.62 | 7.72 | 1.81 |
| Mean | 2.71 | 9.23 | 3.03 | 7.60 | 7.87 | 1.79 |
| S.D. | 0.030 | 0.102 | 0.036 | 0.064 | 0.112 | 0.020 |
| RSD (%) | 1.09 | 1.11 | 1.20 | 0.85 | 1.42 | 1.11 |

SD = Soft drinking water, HD = Hard Drinking water, ML = Mineral water, SP = Swimming, Pool water, RW = Raw (river) water, SS = Standard solution (1.67 $\mu\text{g/L}$)

3.3. Analysis of real water samples

Analytical method of the IC-PCR-UV/Visible detection through triiodide reaction was applied to determinate the trace level bromate from the real water samples. For the application experiments, five water samples such as soft drinking water, hard drinking water, mineral water, swimming pool water, and raw (river) water, were selected. At the same time, one standard solution (1.67 $\mu\text{g/L}$) was used as for a reproducibility test. Here, the samples of hard drinking water, swimming pool water, and raw (river) water were doubly diluted with ultrapure water to lower the concentrations within the range of standard calibration curve (0.503–5.071 $\mu\text{g/L}$). Quantitative result for the concentrations of trace bromate from the selected five water samples, by ion chromatography analysis equipped with PCR-UV/Visible detection, was shown in *Table 6*. From the analytical data obtained from 4-repeated experiments, the mean concentrations of trace bromate ions were in the range of 2.68–9.33 $\mu\text{g/L}$ with the standard deviation of 0.020–0.112 and the relative standard deviation of 0.85–1.42 %. Based on the experimental results, it was found that the ion chromatography analysis using PCR-UV/Visible detection through triiodide reaction had very good availability for the determination of trace bromate in various water samples. Especially, this system showed the excellent efficiency to decrease the matrix interferences by a lot of chlorine ions.

4. Conclusions

The suppressed conductivity detection method and the PCR-UV/Visible detection method through the triiodide reaction were compared, in order to examine the availability of ion chromatography analysis for the trace level concentration of bromate. Based on the analysis of the trace bromate by suppressed conductivity detection and UV/Visible detection after post-column reaction, it was found that the conductivity detection had the suitable advantage to simultaneously analyze bromate and inorganic anions, besides the bromate might not be precisely quantified due to the matrix interferences especially by chloride ion.

In this study, the IC-UV/Visible detection method with high sensitivity using post-column reaction (PCR) after anion exchange separation, was applied to real water samples with various matrices, in order to enhance the detection limit for the analysis of the trace level bromate. From the experiments, the method detection limit (MDL) and recovery were 0.161 $\mu\text{g/L}$ and 101.0–108.1 %, respectively, with a better availability compared to conductivity detection. In addition, the trace bromate could be analyzed successfully by the method of PCR-UV/Visible detection through triiodide reaction to satisfactorily minimize the matrix interference by chloride ions. Therefore, the trace bromate could be effectively analyzed from the various water samples by this color-development IC method, showing the advantages

of excellent linearity, reproducibility, recovery, and MDL.

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