Ion Chromatographic Method with Post-Column Fuchsin Reaction for Measurement of Bromate in Chlorinated Water

***Homer C. Genuino, Maria Pythias B. Espino**
Institute of Chemistry , University of the Philippines, Diliman, Quezon City 1101
*Corresponding author: homer.genuino@uconn.edu
Received: 15 July 2009; Revised: 10 February 2010; Accepted: 10 February 2010

ABSTRACT

An ion chromatographic method that employs a post-column reaction with fuchsin and spectrophotometric detection was optimized for measuring bromate (BrO_3^-) in water. BrO_3^- is converted to Br_2 by sodium metabisulfite and then reacted with acidic fuchsin to form a red-colored product that strongly absorbs at 530 nm. The reaction of BrO_3^- and fuchsin reagent is optimum at pH 3.5 and 65 °C. The method has a limit of quantitation of 4.5 µg L^{-1} and is linear up to 150 µg L^{-1} BrO_3^-. Recoveries from spiked samples were high ranging from 95 to 102 % using external standard calibration and 87 to 103 % using standard addition method. Intra-batch and inter-batch reproducibility studies of the method resulted to RSD values ranging from 0.62 to 2.01 % and percent relative error of 0.12 to 2.94 % for BrO_3^- concentrations of 10 µg L^{-1} and 50 µg L^{-1}. This method is free of interferences from common inorganic anions at levels typically found in chlorinated tap drinking water without preconcentration. The optimized method can be applied to trace analysis of bromate in chlorinated tap drinking water samples.

Keywords: bromate, fuchsin, chlorinated water, post-column reaction, ion chromatography

INTRODUCTION

Bromate (BrO_3^-) may be present in various water types, including those intended for human consumption, either as a major disinfection by-product of the ozonation of water containing naturally occurring bromide ions or as a contaminant of hypochlorite disinfection (Fawell & Walker, 2006; Haag & Hoigné, 1983; Legube, et. al., 2004; von Gunten & Hoigné, 1994; Weinberg, et. al., 2003). Once generated and found in water, BrO_3^- does not easily degrade.

Toxicological studies of BrO_3^- in rats have provided evidence of its possible carcinogenicity (Fuji, et. al., 1984; Kurokawa, et. al., 1990). Acute exposure of rodents to BrO_3^- has been shown to cause neuropathological disorders and induce tumors of the kidney, peritoneum and thyroid (De Borba, et. al., 2005; Kurokawa, et. al., 1990). The lifetime cancer risk determined for BrO_3^- in drinking water for humans was 2×10^{-5} per µg L^{-1} assuming a 2-L daily water consumption (De Borba, et. al., 2005; Fawell & Walker, 2006). Lifetime risks of 10^{-4}, 10^{-5} and 10^{-6} were theoretically associated with exposures to BrO_3^- concentrations of 5, 0.5 and 0.05 µg L^{-1}, respectively. The availability of analytical methods to monitor and determine BrO_3^- in drinking water at sub-µg L^{-1} levels is thus important.

A maximum admissible concentration (MAC) of 10 µg L^{-1} in drinking water is recommended by the US Environmental Protection Agency (US EPA), the European Commission (EC) and the World Health Organization (WHO) (De Borba, et. al., 2005; Fawell & Walker, 2006; Guinamant & Ingrant,

2000; Uraisin, et. al., 2006). This guideline was defined primarily on the basis of the detection capabilities of existing ion chromatographic methodologies. The Philippine National Standards for Drinking Water of 2007 has a maximum guideline level of 10 μg L^{-1} BrO_3^- in drinking water based on the recent risk assessment of the WHO. The proposed detection limit of less than 2.5 μg L^{-1} BrO_3^- by the EC has called for the development of more sensitive analytical methods and alternative techniques (Ingrant & Guinamant, 2002). A number of methods have been developed and adapted to meet the objectives of setting quality standards for BrO_3^- in water. Official methods for BrO_3^- determination include ion chromatography with conductivity detection. Recent studies have shown that the sensitivity of these analytical methods may be improved by coupling the separation using ion chromatography with a specific post-column reaction (Delcomyn, et. al., 2001; Uraisin, et. al., 2006). Three different post-column reaction techniques in ion chromatography have been compared. Post-column reactions with KI-$(NH_4)_6Mo_7O_{24}$, NaBr-$NaNO_2$ and o-dianisidine showed low detection limits ranging from 0.17 to 0.24 μg L^{-1} for BrO_3^- in water (Hautman, et. al., 2001; Salhi & von Gunten, 1999). Performance evaluation of the US EPA method 317.0, which employs both suppressed conductivity and spectrophotometric detection after post-column reaction with o-dianiside, demonstrated specificity and sensitivity for BrO_3^- with a detection limit of 0.042 μg L^{-1} (Wagner, et. al., 2001).

Two similar studies based on the hyphenation of an ion chromatographic system and post-column fuchsin reaction with visible absorbance detection showed the pH and temperature dependence of the BrO_3^--fuchsin reaction (Archilli, et. al., 1999; Valsecchi, et. al., 1999). Using a standard carbonate-bicarbonate mobile phase, a linear range of 0.1 to 100 μg L^{-1} and a detection limit of 0.1 μg L^{-1} BrO_3^- were reported by Archilli, et. al. (1999). Valsecchi, et. al. (1999), on the other hand, used a tetraborate mobile phase and obtained a linear range of 0.5 to 10 μg L^{-1} and detection limit of 0.4 μg L^{-1} BrO_3^-. Their methods were successfully used in quantifying trace levels of BrO_3^- in actual drinking water samples.

This study aimed to optimize an ion chromatographic method involving post-column fuchsin reaction followed by spectrophotometric detection for trace BrO_3^- in chlorinated water as well as provide an alternative analytical technique useful in the strict compliance of water quality standards in the Philippines.

MATERIALS AND METHODS

Reagents and Standard Solutions

All chemicals used were analytical reagent grade. The standards and blank solutions were prepared using ultrapure water at resistance of 18.0 MΩ (Nanopure® Barnstead, USA). Bromate standard solutions were made by dilution of a 1000 μg L^{-1} stock solution of potassium bromate (Merck, Germany). The fuchsin stock solution (FSS) was prepared by dissolving 100 mg basic fuchsin ($C_{19}H_{18}N_3Cl$, Beijing Chemical Works, China) in 100 mL of ultrapure water. Stored at 4 °C in a glass amber bottle, this solution is stable for several months. The color developing solution which acts as post-column reagent was prepared by acidifying 10 mL of FSS with 0.5 mL of 12 M HCl (Merck, Germany) followed by the addition of 350 mg of sodium metabisulfite (Mallinckrodt, USA). The solution was made up to 100 mL with ultrapure water in a glass flask and was left to stand overnight for complete decoloration.

The mobile phase solutions were prepared from 2.5 mM phthalic acid (Merck, Germany) and 2.4 mM tris(hydroxymethyl)aminoethane (Merck, Germany) solutions buffered at pH 3.5. These solutions were filtered through 47 mm×0.2 μm cellulose nitrate membrane filters (Whatman, England) using a filtering apparatus attached to a vacuum source and degassed for several minutes by sonication (Branson Model 8510 Ultrasonic cleaner, USA) prior to use. For the interference studies, inorganic anions (HCO_3^-, Cl^-, SO_4^{2-}, Br^-, F^-, NO_2^-, NO_3^-, PO_4^{3-} and ClO_3^-) of different concentrations (1, 5, 50 and 100 mg L^{-1}) were prepared by dissolving appropriate amounts of the anions in their potassium and sodium salts.

Ion Chromatographic Analysis

A Perkin Elmer Lambda 40 UV-Vis spectrophotometer was used for visible spectrum scanning. The Shimadzu HIC-6A ion

chromatograph system used in this study is composed of the following modules: LP-6A delivery pump unit (LC-6A liquid pump with a high-sensitivity noise filter), SPD-6AV UV-Vis spectrophotometric detector, CTO-6AS column oven, SCL-6B system controller, LC-9A liquid pump used for post-column reagent, SIL-6A auto sample injector, and C-R4A integrator and printer/plotter for data processing. Three stainless steel columns (Shimadzu, Japan) were used in the chromatographic system: Shim-pack IC-PC1 pre-column, Shim-pack IC-GA1 guard column and Shim-pack IC-A1 analytical column. The injected samples passed through the preheater before entering the guard column and analytical column inside an oven set at 65 °C. The 4.6 mm (i.d.) × 10 cm (length) × 12.5 µm (particle size) analytical column was packed with an anion exchange resin on a polymethacrylate support incorporating a quaternary ammonium base which is a strong anion-exchange functional group. The ions that elute from the column mix with the fuchsin post-column reagent in the mixing tee. BrO_3^- and fuchsin react completely in the 204-cm reaction coil to form the red-colored product that is directed to the UV-Vis detector. Measurement of BrO_3^- concentration was carried out using external standard calibration and standard addition methods.

RESULTS AND DISCUSSION

Bromate, upon reaction with fuchsin reagent, is detected in the visible region (Espino & Cimatu, 2003; Romele & Achilli, 1998). In this study, a maximum absorbance was obtained at 530 nm when a 10 µg L^{-1} BrO_3^- and acidified fuchsin solution was scanned in the visible range of 400 to 635 nm. The 530 nm wavelength also gave a maximum peak response for the same BrO_3^--fuchsin solution when determined by ion chromatography using different wavelength settings from 520 to 535 nm. The 530 nm wavelength was then used in the subsequent ion chromatographic analyses.

Previous studies revealed that the reaction of BrO_3^- with fuchsin reagent occurs in the acidic range (Achilli & Romele, 1999; Romele & Achilli, 1998; Valsecchi, et. al., 1999). In this study, the optimum pH for the BrO_3^--fuchsin reaction was investigated by varying the pH of the mobile phase from 2.0 to 7.0. Figure 1 shows that a maximum peak response is obtained when the pH of the mobile phase was maintained at 3.5.

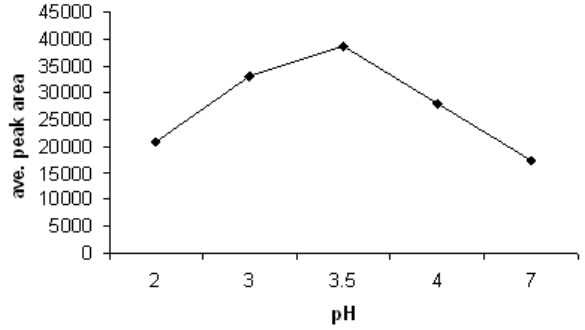

Figure 1. Average peak areas (n=3) for 10 µg L^{-1} BrO_3^- at varying pH of the mobile phase.

Similar to pH, temperature also affects the BrO_3^--fuchsin reaction. Previous ion chromatographic studies found that the BrO_3^- peak response increases as the temperature is raised from ambient to an optimum reaction temperature, e.g., 65 or 80 °C (Achilli & Romele, 1999; Valsecchi, et. al., 1999). In the present study, the optimum temperature is 65 °C as shown in Figure 2.

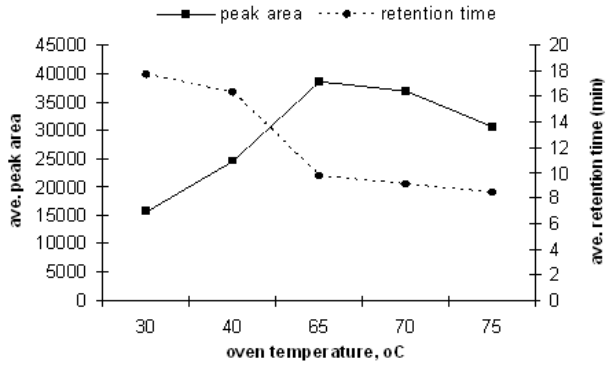

Figure 2. Average peak areas (n=3) and retention times (n=3) for 10 µg L^{-1} BrO_3^- at varying oven temperatures in °C.

A blank measurement experiment was performed to validate the use of ultrapure water as solvent in preparing calibration or sample solutions. No peak response was observed in the chromatographic measurements of seven replicate blank solutions consisting only of ultrapure water and fuchsin reagent. This confirms that ultrapure water does not contain BrO_3^-. In addition, separate chromatographic measurements were performed on two sets of fortified solutions. The first set of seven replicate solutions were prepared using ultrapure

water spiked with 10 µg L^{-1} BrO_3^-; the second set of seven solutions consisted of bromate-free drinking water spiked with 10 µg L^{-1} BrO_3^-. The average peak areas and % RSD of the two sets of data are in good agreement as shown in Table 1. This further validates the use of ultrapure water in procedural blanks and sample analysis using ion chromatography with post-column fuchsin reaction.

Table 1. Comparison of the average peak areas and percent relative standard deviations of spiked blanks using ultrapure water and bromate-free drinking water as solvents.

Spiked blanks	Average peak area[a] (n=7)	SD	RSD,%
Blank using ultrapure water +10 µg L^{-1} BrO_3^-	38212	708	1.85
Blank using bromate-free bottled water[b] +10 µg L^{-1} BrO_3^-	38010	729	1.92

[a]*Seven replicates with three measurements per replicate.*
[b]*Bottled distilled drinking water (brand:Absolute).*

Inorganic anion interferences in the ion chromatographic determination of BrO_3^- were also investigated. Figure 3 shows the effect of adding common inorganic anions (HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}, Br^-, F^-, NO_2^-, PO_4^{3-}, and ClO_3^-) in four different concentrations to 10 µg L^{-1} BrO_3^- solutions prepared in ultrapure water. A paired t-test was performed to determine whether or not the inorganic anions were interfering at different concentrations. The mean peak area differences of solutions of 10 µg L^{-1} BrO_3^- in ultrapure water were not significantly greater than zero before and after the same solutions were spiked with the inorganic anions at four different concentrations. Student's t-test gave test statistic t values for inorganic anions (HCO_3^- = -0.0392, Cl^- = -3.07, NO_3^- = 0.556, SO_4^{2-} = 1.09, Br^- = 1.55, F^- = -3.93, NO_2^- = -2.32, PO_4^{3-} = 1.00, and ClO_3^- = 1.14) which were lower than the critical t value of 3.18 at 95 % confidence interval from the t-distribution table. These statistical tests proved that the inorganic anions do not interfere in the determination of BrO_3^-. Further, low RSD values ranging from 0.24 to 2.5 % were obtained for the 10 µg L^{-1} BrO_3^- solutions spiked with different concentrations of these anions. It was also observed that in the absence of BrO_3^-, the red-colored product that absorbs at 530 nm was not formed in solutions spiked with the anions. Hence, these anions do not react with the fuchsin reagent which appeared to be BrO_3^--specific.

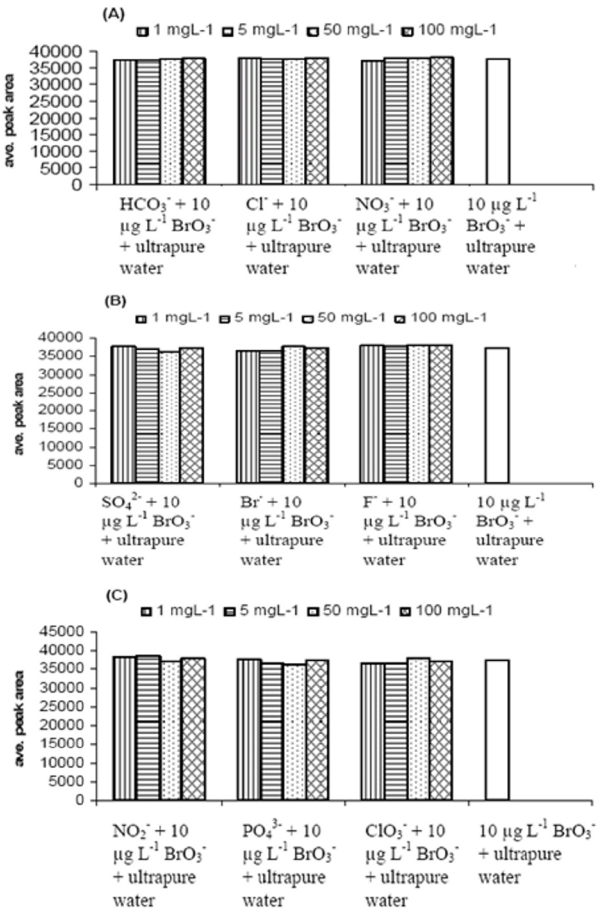

Figure 3. Comparison of inorganic anions [(A): HCO_3^-, Cl^-, NO_3^-; (B): SO_4^{2-}, Br^-, F^-; (C): NO_2^-, PO_4^{3-}, ClO_3^-] at different concentrations spiked in ultrapure water containing 10 µg L^{-1} BrO_3^- and ultrapure water containing 10 µg L^{-1} BrO_3^- only.

Using the optimum conditions, eleven BrO_3^- standard solutions ranging from 2 to 1500 µg L^{-1} were prepared to get the range of concentration from the estimated lowest detectable concentration to a concentration where a departure from linearity will be observed. A linear response was obtained and the limits of the linear dynamic range are presented in Figure 4.

Based on the results of the analysis in wide concentration range (2 to 1500 µg L^{-1}), low-bromate (2 to 150 µg L^{-1}) and high-bromate (150 to 2000 µg L^{-1}) calibration solutions were then measured and compared. Table 2 summarizes the regression and residual analyses for low- and high-bromate concentration calibration curves. Linear (first-order polynomial) and quadratic (second-order polynomial) least square (LS) regression models

were used to assess the degree of goodness of fit of the experimental calibration data. The correlation coefficients and residual values were also derived using these models. The linear and quadratic least squares are polynomials described by a set of coefficients in the following equations:

$$y = a_o + a_1 x \quad (linear, Rdf=2) \qquad (1)$$

$$y = a_o + a_1 x + a_2 x^2 \quad (quadratic, Rdf=3) \qquad (2)$$

where y is the peak area, a_0, a_1 and a_2 are the coefficients of the polynomial, x is the concentration in µg L^{-1}, and Rdf is the required degrees of freedom. The results of the regression and residual analysis showed good agreement between the two LS regression models. This means that the values of x from the linear Equation 1 and quadratic Equation 2 will almost be the same. In this study, the simpler linear LS regression was used to calculate BrO_3^- concentration.

Table 2. Comparison between low-BrO_3^- and high-BrO_3^- calibration data in terms of regression and residual analyses.

Parameters	Low-bromate concentration range 2 to 150 µg L^{-1} (n=3)		High-bromate concentration range 150 to 2000 µg L^{-1} (n=3)	
	Linear least square	**Quadratic least square**	**Linear least square**	**Quadratic least square**
Regression equation	Y=10628 + 2724x	Y=7198 +2985x – 1.80 x^2	Y=45267 0+ 257.9x	Y=396704 + 258x – 0.0855x^2
Correlation Coefficient, r	0.9994	0.9997	0.8402	0.9704
Residuals (absorbance units)	-7.5152 460.991 -483.49 -6824.1 4575.93 8630.05 -6351.8	2907.06 2629.89 514.680 -7897.1 -549.0 3958.0 -1563.4	-56522 -8339.4 29972 30753 33831 4694.8 -34389	-25343 15432.8 18273.4 1247.76 -2798.91 -14132.2 7319.78

The average % RSD (n=3) of the peak areas in the low-bromate concentration curve was 1.47 %, while in high-bromate concentration it was 0.97 %. As expected, the precision improved in high-bromate concentration due to less deviation in replicate analysis that is almost always associated with measurements in higher concentrations. Nevertheless, both values are within the required ± 15 % level.

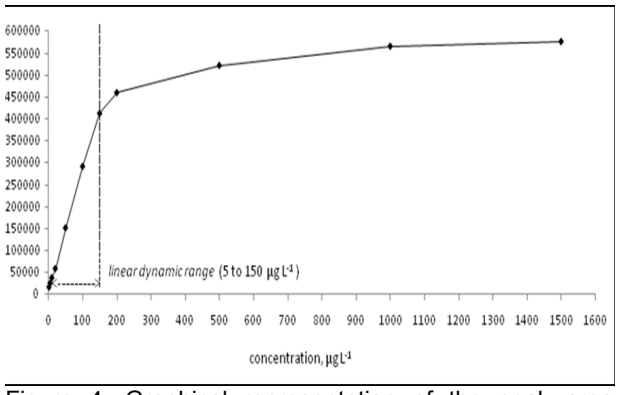

Figure 4. Graphical representation of the peak area response of 2 to 1500 µg L^{-1} BrO_3^- (n=3) in ultrapure water showing linear dynamic range.

Regression analyses given in Table 2 were used to assess the linearity and uncertainty in low- and high-bromate concentration calibration curves. The low-bromate concentration calibration curve has correlation coefficient nearer to unity and residual values that are more random, making it more linear than the high-bromate concentration calibration curve. Figure 5 displays a graphical view of a seven-point regression plot of the low-bromate concentration range showing 95 % confidence interval levels about the regression. This low-bromate concentration range was used in quantifying BrO_3^- in this study.

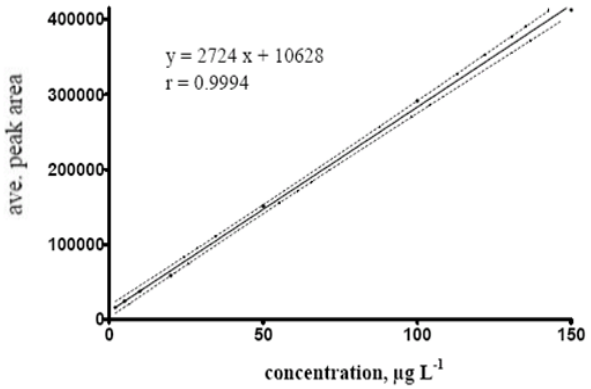

Figure 5. A linear calibration graph for 2 to 150 µg L^{-1} BrO_3^- solutions (n=3) using the optimized ion chromatographic method. [Solid line represents linear regression and dotted lines show 95 % confidence interval levels about the regression.]

Table 3. Intra-batch and inter-batch reproducibility studies for precision and accuracy of the ion chromatographic method.

Average Concentration							
Intra-batch reproducibility				Inter-batch reproducibility			
Concentration[a]	Measured Concentration[b] (SD)[c]	RSD,%	Rel. Error, %	Concentration[a]	Measured Concentration[b] (SD)[d]	RSD,%	Rel. Error, %
10.00	9.988(0.19)	1.93	0.12	10.00	9.900(0.13)	2.01	1.00
50.00	51.47(0.42)	0.81	2.94	50.00	50.88(1.16)	0.62	1.76

[a] *Concentration of prepared BrO_3^- solution in µg L^{-1}.*
[b] *Measured by ion chromatography and calculated using external standard calibration method.*
[c] *Mean for seven replicates with three measurements per replicate in one day.*
[d] *Mean for seven replicates with three measurements per replicate in five days.*

The limit of quantitation of the optimized method was calculated using the following equations:

$$S_{LOQ} = S_{blank} + 10\,s_{blank} \quad (3)$$

$$x_{LOQ} = (S_{LOQ} - S_{blank})/m \quad (4)$$

where S_{LOQ} is the detectable signal, S_{blank} is the mean signal of the blank, s_{blank} is the standard deviation in the blank signal, x_{LOQ} is the limit of quantitation, and m is the slope of the regression line (Loconto, 2006). Baseline absorbance readings in milliabsorbance (mAbs) units of a blank solution flowing through the ion chromatographic system were recorded for 20 min in 30 s intervals. The average values of the absolute difference between two successive absorbance readings were taken. This process was repeated for six more days. An average value of 0.142 mAbs (S_{blank}) and a standard deviation of 0.0727 (s_{blank}) were derived from the resulting seven sets of data. These values were used to solve for S_{LOQ} in Equation 3. Finally, an x_{LOQ} of 4.5 µg L^{-1} BrO_3^- was obtained using Equation 4 and m equal to 0.162. This limit of quantitation is lower than the detection limit of 50 µg L^{-1} previously reported by Espino & Cimatu (2003), making the optimized method more sensitive.Intra-batch and inter-batch (long-term precision) reproducibility studies were performed within one day and five consecutive days, respectively, to determine the accuracy and precision of the optimized method. These were done by carrying out seven replicate analyses of 10.00 and 50.00 µg L^{-1} BrO_3^- solutions. Table 3 presents the calculated RSD and relative error values. Overall, the optimized method showed good repeatability with RSD values within the required ± 15 % for each concentration level. The optimized method is accurate with the relative error of 0.12 to 2.94 %.

Percent recoveries of BrO_3^- spiked in tap drinking water samples in three different concentrations (low, 5.0 µg L^{-1}; medium, 50.0 µg L^{-1}; and high, 100.0 µg L^{-1}) were determined to test the reliability and accuracy of the method using an actual sample matrix. Table 4 gives the % recoveries using external standard calibration and standard addition quantitation methods. Using the external standard calibration method, % recoveries were generally acceptable based on the recommended 80 to 120 % as reported by Lesnik (1992). Low % RSD values were found across the three BrO_3^- concentrations. Notably, better recoveries were obtained for medium and high concentrations when using standard addition method.

Table 4. Percent recovery data for low, medium and high bromate concentrations in tap drinking water[a].

Quantification Method	%Recovery (RSD)[b]		
	Concentration		
	Low 50 µg L^{-1}	Medium 50.0 µg L^{-1}	High 100.0 µg L^{-1}
(using peak area)			
External standard Calibration	99 (1.84)	101 (0.89)	102 (0.77)
Standard addition	89 (1.07)	101 (1.37)	99 (1.08)
(using peak height)			
External standard calibration	97(1.54)	95(0.86)	96(1.40)
Standard addition	87(1.13)	98(1.60)	103(0.77)

[a] *Tap water sample taken from the Faculty Lounge of the Institute of Chemistry, University of the Philippines.*
[b] *Mean for seven replicates with three measurements per replicate.*

The ion chromatographic method described in this study is reproducible, accurate, sensitive and suitable for the analysis of BrO_3^- in chlorinated tap drinking water at trace levels. The method can be used for monitoring BrO_3^- in chlorinated water in the treatment plants as well as in the distribution

lines. This is an available method that can be used to ensure strict compliance of the 10 μg L^{-1} BrO_3^- stipulated in the Philippine National Standards for Drinking Water.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Research and Development Division of the Environmental Management Bureau (RDD-EMB) for the use of their ion chromatograph and laboratory facilities. The Commission on Higher Education (CHED) provided a Master's thesis grant to H. C. Genuino to conduct this study.

REFERENCES

Achilli, M. and Romele, L., 1999, Ion chromatographic determination of bromated in drinking water by post-column reaction with fuchsin, *J. Chromatogr. A.*, 847: 271-277.

De Borba, B. M., Rohrer, J. S., Pohl, C. A. and Saini, C., 2005, A. Determination of trace concentrations of bromate in municipal and bottled drinking waters using a hydroxide-selective column with ion chromatography, *J. Chromatogr. A.*, 1085 (1): 23-32.

Delcomyn, C. A., Weinberg, H. S. and Singer, P. C., 2001, Use of ion chromatography with post-column reaction for the measurement of tribromide to evaluate bromate levels in drinking water,. *J. Chromatogr. A.*, 920: 213-219.

Espino, M. P. and Cimatu, K., 2003, Bromate levels in Metro Manila drinking water, *Kimika*, 19 (1): 35-39.

Fawell, J. and Walker, M., 2006, Approaches to determining regulatory values for carcinogens with particular reference to bromate, *Toxicology*, 221 (2-3): 149-153.

Fujii, M., Oikawa, K., Saito, H., Fukuhara, C., Onosaka, S. and Tanaka, T., 1984, Metabolism of potassium bromate in rats I. In vivo studies, *Chemosphere*, 13 (11): 1207–1212.

Guinamant J. and Ingrant, V., 2000, Laboratory and field methods for determination of bromate in drinking water, *EUR Report, EN.*, 19601: 178.

Haag, W.R. and Hoigné, J., 1983, Ozonation of bromide-containing waters: Kinetics of formation of hypobromous acid and bromate, *Environ. Sci. Technol.* 17 (5): 261-267.

Hautman, D. P., Munch, D. J., Frebis, C., Wagner, H. P. and Pepich, B. V., 2001, Review of the methods of the US Environmental Protection Agency for bromate determination and validation of Method 317.0 for disinfection by-product anions and low-level bromated, *J. Chromatogr. A.*, 920 (1-2): 221-229.

Ingrant, V. and Guinamant, J., 2002, Determination of bromate in drinking water: development of lab and field methods, *Trends Anal. Chem.*, 21: 356-365.

Kurokawa, Y., Mackawa, A. and Takahasi, M., 1990, Toxicity and carcinogenicity of potassium bromated—a new renal carcinogen, *Environ. Health Perspect.*, 87, 309-335.

Legube B., Parinet, B., Geliner, K., Berne, F. And Croue, J., 2004, Modeling of bromate formation by ozonation of surface waters in drinking water treatment, *Water Res.*, 38 (8): 2185-2195.

Lesnik, B., 1992. Guidance for Methods Development and Methods Validation for the RCRA Program. Office of Solid Waste, US Environmental Protection Agency, US EPA, Cincinnatti, OH, USA. 1-32.

Loconto, P., 2006. Trace Environmental Quantitative Analysis, Principles, Techniques and Applications, 2nd ed., CRC Press, Taylor & Francis, Inc., OR, USA. 82-83.

Romele, L. and Achilli, M., 1998, Spectrophotometric determination of low levels of bromated in drinking water after reaction with fuchsin, *Analyst*, 123 (2): 291-294.

Salhi, E. and von Gunten, U., 1999, Simultaneous determination of bromide, bromate and nitrite in low μg l−1 levels by ion chromatography without sample pretreatment, *Water Res.*, 33 (15): 3239-3244.

Uraisin, K., Takayanagi, T., Nacapricha, D. and Motomizu, S., 2006, Novel oxidation reaction of prochlorperazine with bromate in the presence of synergistic activators and its application to trace determination by flow injection/spectrophotometric method, *Anal. Chim. Acta.*, 580 (1): 68-74.

Valsecchi, S., Isernia, A., Polesello, S. and Cavalli, S., 1999, Ion chromatography determination of trace level bromate by large volume injection with conductivity and spectrophotometric detection after post column derivatisation, *J. Chromatogr. A.*, 864 (2): 263-270.

von Gunten, U. and Hoigné, J., 1994, Bromate Formation during ozonation of bromide-containing waters: Interaction of ozone and hydroxyl radical reactions, *Environ. Sci. Technol.*, 28: 1234-1242.

Wagner, H. P., Pepich, B. V., Hautman, D. P. and Munch, D. J., 2000, Performance evaluation of a method for the determination of bromate in drinking water by ion chromatography (EPA Method 317.0) and validation of EPA Method 324.0, *J. Chromatogr. A.*, 884 (1-2): 201-210.

Weinberg, H. S., Delcomyn, C. A., and Unnam V., 2003, Bromate in chlorinated drinking waters: Occurrence and implications for future regulation, *Environ. Sci. Technol.*, 37: 3104-3110.