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Bromate levels in Metro Manila drinking water

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A spectrophotometric method was developed for the analysis of bromate in drinking water. This method requires no sample preconcentration and involves reaction with acidified fuchsin and absorbance measurements at 547 nm. Bromate is detected above 5 μg/L concentration and quantified with the linear range of 50 to 200 μg/L calibration solutions. Drinking water samples in Metro Manila were determined to have high bromate levels, ranging from 17 to 411 μg/L. Bromate, a probable carcinogen, has water quality guideline values of 10 μg/L and 25 μg/L set by the U.S. Environment Protection Agency and the World Health Organization, respectively, as maximum allowable contaminant levels.

Keywords: bromate; drinking water; disinfection by-product; spectrophotometry

INTRODUCTION

Bromate ion, BrO_3^-, is not a natural component of water. Bromate is found in water supplies as a disinfection by-product resulting from treatment by ozonation [1–2]. There is limited information on bromate levels in drinking water following treatment by chlorination. However, there is recent evidence that bromate may be present in water after disinfection using treatment grade sodium hypochlorite solutions containing bromate as contaminant [3–5]. Bromate does not readily adsorb onto suspended particles, is stable in water, and may be stored in municipal supplies for a long time. At present, there is no practical technology available to remove low levels (i.e., 10 μg/L or less) of bromate in drinking water.

Bromate is a very toxic substance in high dosage and has been classified as a probable carcinogen to humans [6–7]. Toxicological studies have estimated a lifetime cancer risk at 1 in 100,000 for 3 μg/L (World Health Organization) and 0.5 μg/L (U.S. Environmental Protection Agency) bromate levels in water [8]. An interim maximum acceptable concentration of 10 μg/L for bromate is established and incorporated in water quality guidelines in Canada and the United States [6, 9–10]. In the United Kingdom, a directive mandatory standard of 25 μg/L is followed until the end of 2003 and 10 μg/L will be followed until the end of 2008 [11]. Other countries such as the Netherlands implement a guideline value of 5 μg/L for bromate [12]. In the Philippines, bromate is not among the inorganic ions being monitored in drinking water for health risks. The Manila Water Company Inc. (MWCI) that operates treatment plants in Balara, Quezon City monitors antimony, arsenic, cadmium, chromium, cyanide, fluoride, lead, total mercury, nitrate, nitrite and selenium in grab samples from the distribution system [13].

Ion chromatography (IC) is the popular method for bromate analysis [14–16]. The U.S. EPA regulatory method for bromate in water (EPA Method 321.8) uses IC/ICP-MS (inductively coupled plasma mass spectrometry). Other methods include IC/post-column derivatization and conductivity detection (EPA Methods 300.0 and 300.1) or detection with UV spectroscopy. These methods claim very low detection limits, as low as 0.2 μg/L. Other researchers employing IC/ICP-MS and using high capacity, high performance, microbore anion exchangers reported lower detection limits at 50 to 65 μg/L.

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To date, no monitoring data on bromate in raw and drinking water supplies in the Philippines were published. The aim of this study was to determine the levels of bromate in Metro Manila drinking water.

In the absence of expensive instrumentation such as the use of IC/ICP-MS, a spectrophotometric method with fuchsin reaction was developed, optimized, and applied for the analysis of bromate in tap water samples from 26 sites, five brands of bottled water and riverwater.

EXPERIMENTAL

Chemicals. All chemicals used were analytical grade. Fuchsin stock solution was prepared by dissolving 100 mg basic fuchsin (Beijing Chemical Works, China) in 100 mL HPLC-water (J. T. Baker, U.S.A.). This solution is stable for several months. The fuchsin developing solution was prepared by adding 0.5 mL HCl (Merck, Germany) to 10 mL of the fuchsin stock solution. This was then diluted to a 100 mL final volume and reduced with 400 mg sodium metabisulfite (Mallinckrodt, USA). A 12 mg/L fuchsin reagent was prepared by dilution of the fuchsin developing solution.

A 1000 μg/L bromate stock solution was prepared by dissolving granular potassium bromate (Mallinckrodt, USA) in HPLC-water.

Sampling and sample preparation. Tap water samples were collected from twenty three households in selected areas in Metro Manila and from three sites inside UP Diliman Campus. Five brands of bottled water (Absolute, Summit, Wilkins, Crystal Spring and Hidden Spring) were bought from the supermarket. Surface water sample was taken from Marikina River. Only the river water sample was filtered prior to analysis.

A 2 mL of 12 mg/L fuchsin developing reagent was added to 10 mL of water samples in duplicates. Some of the water samples were diluted 1.5 times before adding the fuchsin reagent. Blank solutions and standard solutions were prepared with HPLC-water. The solutions were allowed to react for 35 min before analysis.

Spectrophotometric analysis. Spectrophotometric measurements were obtained using a UV-Vis-NIR scanning spectrophotometer (Shimadzu, Japan) and UV-3101 PC. The detection wavelength was 547 nm. Quantitative analysis was carried out with standard calibration curves.

RESULTS AND DISCUSSION

The drinking water supplies in major cities in the Philippines are disinfected by chlorination. Figure 1 shows a general scheme of the treatment processes at the MWCI Balara treatment plants

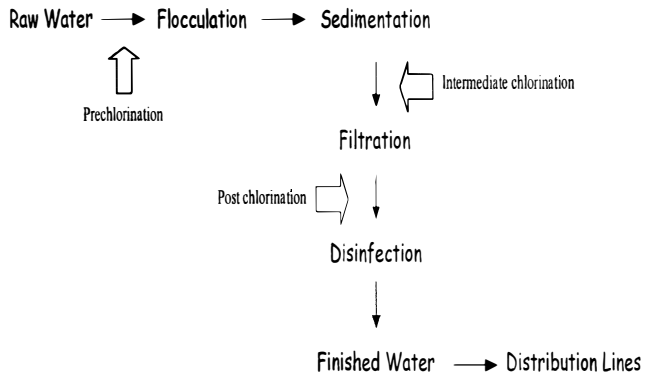

Fig. 1. Basic processes in water treatment.

in Quezon City. Three chlorination steps are performed to inactivate pathogenic microorganisms. During rapid mixing and coagulation, raw water is prechlorinated at a dose level of 0.3 mg/L mainly to remove odor and taste. After flocculation and sedimentation, an intermediate chlorination is carried out at 0.3 mg/L dose level. A final disinfection is done after filtration by injecting gaseous chlorine delivered from high pressure tanks into the finished water before being released to storage or pumping stations and the network of distribution lines in Metro Manila. This final chlorination step assures disinfection at a chlorine level of 1.22 mg/L.

It is widely accepted that bromate is a disinfection by-product of the ozonation of water. Since the Metro Manila drinking water supply is not disinfected with ozone, a possible source of bromate, other than industrial or domestic inputs, is the treatment by chlorination using commercially available sodium hypochlorite. Technical grade hypochlorite that contains bromate may be used during prechlorination and intermediate chlorination in the treatment process.

Bromate reacts with fuchsin reagent, rosanilin ($C_{20}H_{20}N_3Cl$) and pararosanilin ($C_{19}H_{18}N_3Cl$), in acidic conditions to produce a red-colored product that absorbs in the visible region. This reaction was explored to develop a simple spectrophotometric method for the determination of bromate in water.

The UV-Vis scan of a solution containing 100 μg/L BrO_3^- and 19 mg/L acidified fuchsin gave a maximum absorbance at 547 nm. The maximum reaction time of this solution was then obtained by taking the absorbance at 547 nm in regular time intervals for 1 h. The reaction time for the red color to fully develop was 35 min (Fig. 2). Different concentrations of fuchsin reagent (5 to 40 mg/L) were reacted with 100 μg/L BrO_3^- for 35 min. A 12 mg/L fuchsin reagent gave the maximum absorbance at 547 nm (Fig. 3).

Bromate solutions ranging from 1 to 1000 μg/L were reacted with 12 mg/L fuchsin for 35 min. The plot of absorbance vs. concentration showed linear relationships in low BrO_3^- concentrations of 50 to 200 μg/L (Fig. 4) and high BrO_3^-

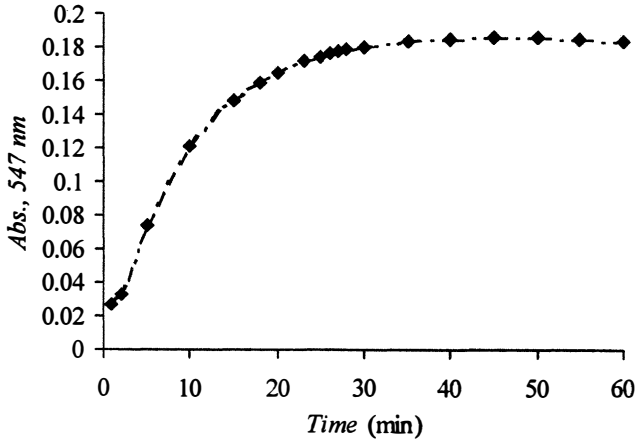

Fig. 2. Optimum reaction time for 100 µg/L BrO_3 and 19 ppm fuchsin reagent.

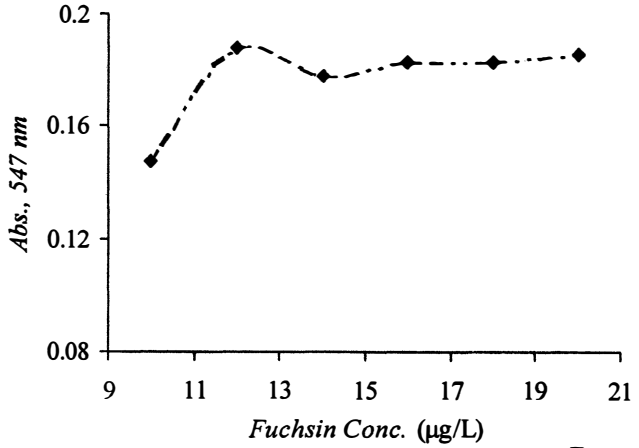

Fig. 3. Optimum fuchsin concentration with 100 µg/L BrO_3^-

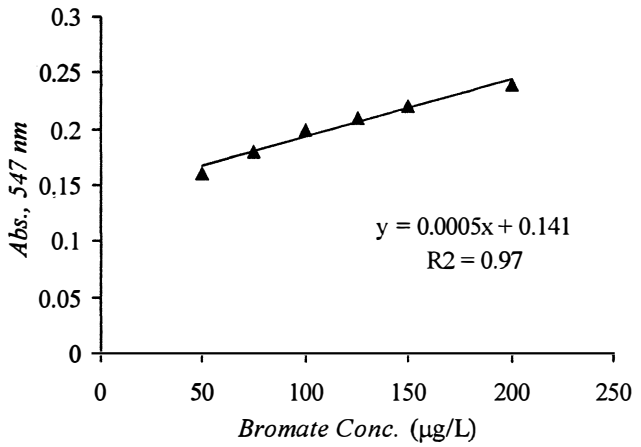

Fig. 4. Low BrO_3 concentration calibration curve.

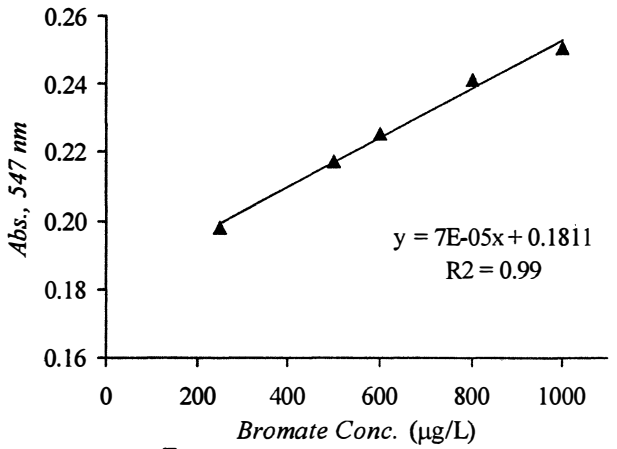

Fig. 5. High BrO_3^- concentration calibration curve.

concentrations of 250 to 1000 µg/L (Fig. 5). Both calibration curves may be used to quantify bromate in actual water samples. The lowest concentration that this method can quantify is 50 µg/L, although BrO_3^- is detected above 5 µg/L. Blank solutions have absorbances almost equal to those of 1 to 5 µg/L BrO_3^- solutions.

Table 1 shows that the absorbance of tap water samples fortified with 50 µg/L BrO_3^- corresponds to the sum of the absorbance of HPLC-water spiked with 50 µg/L BrO_3^- and the absorbance of tap water samples alone. Common anions do not interfere in the reaction of bromate and fuchsin at this level.

Twenty six tap water samples taken from different sites in Metro Manila, five brands of bottled water and filtered riverwater from Marikina River were analyzed for bromate using the developed spectrophotometric method with fuchsin reaction. No sample preconcentration and cleanup were required in the analysis. A 10-mL sample was reacted with 2 mL of 12 mg/L fuchsin reagent for 35 min before absorbance measurements were obtained at 547 nm. Quantification was carried out using the low BrO_3^- concentration calibration solutions (i.e., 50 to 200 µg/L). Samples with bromate exceeding this range were diluted accordingly and reanalyzed. Samples with bromate detected below this range were quantified by extrapolation using linear regression.

Table 2 shows the bromate levels in Metro Manila drinking water. The bromate concentrations in all samples exceeded the 10 µg/L guideline value set by the U.S. EPA as maximum allowable contaminant level. Bromate was not detected in any of the five bottled water samples. The absorbances of these samples correspond to those of the blank solutions. For bottled water treated by ozonation, it is possible that bromate may be present in very low concentrations that were not detected using this analytical method. Surface water samples from Marikina River gave a 53 µg/L bromate level. Bromate in river systems may be found in relatively low concentrations because of dilution by precipitation and inputs of water from domestic, industrial or commercial structures in the surrounding areas.

Table 1. Absorbance of spiked water samples

Sample [a]	*Absorbance, 547 nm*
50 µg/L BrO_3^- in HPLC-water	0.0727
Pasig water	0.1687
Pasig water + 50 µg/L BrO_3^-	0.2422
50 µg/L BrO_3^- in HPLC-water	0.0714
Barangka water [b]	0.1272
Barangka water + 50 µg/L BrO_3^- [b]	0.1956

[a] n = 2; [b] n = 4

Table 2. Bromate levels in water samples

Water Samples[a]	*Concentration,* (µg/L)
Tap water	
Marikina	110
Barangka-A[b]	170
Barangka-B[b]	78
Loyola Heights	314
Area 14, UP Campus	324
CASAA, UP	186
IC Building, UP	204
UP Village	143
Teachers Village	133
Tandang Sora Avenue	17
Tandang Sora	122
Del Monte, QC	40
San Juan	276
Pandacan	218
Sampaloc-A[c]	168
Sampaloc-B[c]	185
Caloocan-A[d]	144
Caloocan-B[d]	180
Novaliches	161
Sta. Mesa	334
Pasig-A[e]	411
Pasig-B[e]	411
Makati	172
Balintawak	327
Parañaque	211
Valenzuela	161
River water	
Marikina river	53
Bottled mineral water	
Hidden Spring	*nd*
Summit	*nd*
Crystal Spring	*nd*
Bottled distilled water	
Wilkins	*nd*
Absolute	*nd*

[a] collected in Dec 2002; n = 2
[b, c, d, e] different samples from different households
nd = not detected

CONCLUSION

The spectrophotometric procedure that was developed and optimized is a simple method for the analysis of bromate in water that requires no sample preconcentration or cleanup. The preliminary investigation on the drinking water supply of Metro Manila showed high levels of bromate in the range of 17 to 411 µg/L. In the Philippines where there is lack of monitoring and guidelines for bromate in water, this simple method provides a water-quality monitoring tool to establish additional drinking water regulations. In a population where there is high incidence of cancer, the initial results presented in this study offer a baseline data for assessing exposure to bromate in drinking water.

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