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Comparison of three post-column reaction methods for the analysis of bromate and nitrite in drinking water

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Abstract

Three post-column ion chromatographic methods (i.e., a sodium bromide–sodium nitrite method, an *o*-dianisidine method, and a potassium iodide–ammonium heptamolybdate method) were compared for bromate and nitrite analysis. Also, the effect of direct mixing of the reagents without ion suppressors for the sodium bromide–sodium nitrite method and the potassium iodide–ammonium heptamolybdate method was investigated. For the analysis of bromate, the three methods showed similar method detection limits (0.17–0.24 µg/l) with pneumatic reagent delivery systems. Direct reagent mixing achieved comparable detection limits to the suppressor configuration. The three methods are also compatible with conductivity detection. When used in combination with conductivity detection, this compatibility allows simultaneous analysis of bromate, nitrite, and other common ions in drinking water, such as bromide. It was found that the *o*-dianisidine method achieves µg/l-level detection of nitrite and bromate with a simpler configuration than the potassium iodide–ammonium heptamolybdate method, while the sodium bromide–sodium nitrite method was not sufficiently sensitive for nitrite analysis at the µg/l level. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the first indication that bromate can be a human carcinogen [1], the formation of the bromate ion has become one of the major concerns for disinfection by-products (DBPs) during ozonation [2]. In 1993, the World Health Organization (WHO) recommended setting a guideline of 25 µg/l for bromate ion in drinking water and estimated the

lifetime cancer risk at 1 in 10⁵ for bromate at 3 µg/l [3]. In the USA, the lifetime cancer risk from exposure to bromate was estimated to be 1 in 10⁴ for 5 µg/l [4], and bromate was regulated at 10 µg/l under Stage 1 of the Disinfectants/Disinfection By-Products (D/DBP) Rule in December 1998 [5].

The current US guidelines and regulations above are higher than the typically acceptable 10⁻⁵ cancer risk level of 0.5 µg/l, and have been set partially based on current analytical limitations with conventional ion chromatographic analysis [6]. The emergence of a high-capacity anion-exchange column expanded the capability of conventional ion chro-

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matographic analysis for bromate with a detection limit of 1 $\mu\text{g}/\text{l}$, but the practical quantification limit (PQL) is still higher than 2 $\mu\text{g}/\text{l}$ [7]. Thus, a more sensitive analytical technique was required for the risk management of the bromate ion based on the 10^{-5} cancer risk level.

Several novel approaches have been developed for the detection of sub- $\mu\text{g}/\text{l}$ levels of bromate during the past few years [8–19]. Those methods employ inductively coupled plasma mass spectrometry (ICP-MS) [8–12], electrospray ionization mass spectrometry (ESI-MS) [13], or post-column derivatizing systems coupled with ion chromatography [14–20]. While ICP-MS and ESI-MS techniques achieve detection limits below 1.0 $\mu\text{g}/\text{l}$, they also possess some drawbacks. For example, ICP-MS and ESI-MS analysis require expensive instruments. Considering this drawback of ICP-MS and ESI-MS analysis, methods based on post-column derivatization and UV-Vis detection are attractive alternatives.

However, it is not easy to select one post-column derivatization method for bromate analysis from the various options because no comparative study has been done on post-column derivatization methods. Each option has its advantages and disadvantages. For example, the method which uses a mixture of nitric acid, potassium bromide and *o*-dianisidine is the simplest method among the post-column derivatization techniques currently proposed [18]. However, the *o*-dianisidine used in this method is a possible carcinogen. That is, this method may require special handling of waste from the system. Alternatively, other post-column systems use less potentially harmful reagents, but those systems are more complicated or require additional cost for anion suppressors for the delivery of reagents [17,19], or an unusual flow cell path length (15 mm) for sufficient sensitivity [14]. The in situ suppression (i.e., acidification) of post-column reagents is a key process for some of these methods because the key reactive compounds such as HBr [17] and HI [19] are not stable under acidic conditions. Also, while the technique by Salhi and Von Gunten [19] has the capability of quantifying nitrite simultaneously at the 1.0 $\mu\text{g}/\text{l}$ level, no information is available on nitrite analysis for the other methods.

The purpose of this study was to provide comparative information on three post-column derivatization

techniques for bromate ion analysis, i.e., the *o*-dianisidine method based on that of Wagner et al. [18], the NaBr–NaNO₂ method based on that of Weinberg et al. [17], and the KI–(NH₄)₆Mo₇O₂₄ method based on that of Salhi and Von Gunten [19]. These three methods were selected because of their relatively low detection limits and the availability of the details of experimental conditions. We focused on the following four points for comparison. First, method detection limits (MDLs) for bromate were compared among the three methods. Second, the capability of simultaneous nitrite analysis was also examined. Third, chromatograms from the three methods were generated for a spiked sample to compare the performance of the three methods in a natural river water matrix. Lastly, the effect of direct mixing of the reagents without ion suppressors for the NaBr–NaNO₂ and the KI–(NH₄)₆Mo₇O₂₄ methods was investigated to evaluate the possibility of eliminating the cost of the anion suppressors [21].

2. Experimental

2.1. Reagents

For the preparation of the eluent, standards and post-column reagents, 18 M Ω cm water was prepared using a Millipore water purification system (Bedford, MA, USA). A natural river water (pH 7.8 and dissolved organic carbon, 2.0 mg/l) was used for the preparation of a spiked sample of bromate ion and nitrite ion. American Chemical Society (ACS) reagent-grade sodium carbonate (Fisher, Fair Lawn, NJ, USA) was used for the preparation of the 9 mM sodium carbonate eluent. The eluent was degassed with nitrogen gas prior to use. ACS reagent-grade potassium bromate (Fisher) and sodium nitrite (Fisher) were used to prepare standard solutions of bromate and nitrite ions, respectively.

The post-column derivatizing reagent for the NaBr–NaNO₂ method was a 1.0 M NaBr (ACS reagent grade, Fisher)–0.295 mM sodium nitrite (ACS reagent grade, Fisher) solution. For acidification of the reagent in the system, 0.75 M sulfuric acid (ACS reagent grade, Fisher) was prepared. These concentrations were determined based on the values previously reported [16] and the results of

preliminary experiments in our laboratory. The concentrations of the derivatizing reagent and the acid were doubled for the direct mixing configuration to compensate for dilution of reagents.

The post-column derivatizing reagent for the *o*-dianisidine method was prepared in the same manner as described by Wagner et al. [18] with redistilled nitric acid (70%, w/w; Aldrich, Milwaukee, WI, USA), *o*-dianisidine (Sigma, St. Louis, MO, USA), potassium bromide (Sigma), and spectrophotometric-grade methanol (Sigma).

The post-column derivatizing reagent for the KI–(NH₄)₆Mo₇O₂₄ method was a 0.26 M potassium iodide (analytical-reagent grade; Fluka, Buchs, Switzerland)–43 μM ammonium heptamolybdate (Sigma) solution [19]. This solution was prepared daily and degassed with nitrogen gas prior to use. For acidification of the reagent, 0.45 M sulfuric acid (ACS reagent grade, Fisher) was used. These concentrations were again determined based on the values previously reported [19] and the results of preliminary experiments in our laboratory. The concentrations of the derivatizing reagent and the acid were doubled for direct mixing to compensate for the dilution of reagents.

2.2. Instrumentation

Anions were separated by a Dionex (Sunnyvale, CA, USA) DX-300 system with a Dionex IonPac AS9-HC column (250×4 mm I.D.) protected by a Dionex IonPac AG9-HC column (50×4 mm I.D.). The flow-rate of the eluent was 1.0 ml/min throughout this study. Sample loop size was fixed at 500 μl in this study. Except for the experiment to test the compatibility of a conductivity detector with the three methods, a conductivity detector was not connected to the system and eluent was not suppressed to avoid an additional back pressure (i.e., to achieve more stable flow). For this compatibility test, a Dionex PED-2 detector was employed with a Dionex self-regenerating anion suppressor (ASRS-I) operated in the external water mode.

The effluent from the analytical column was mixed with the post-column reagents in a mixing-T and sent to a 375-μl reaction coil (Dionex) in a water bath. For the NaBr–NaNO₂ method and the KI–(NH₄)₆Mo₇O₂₄ method, the post-column reagents

were acidified with two anion suppressors in series between the mixing-T and a pneumatic reagent delivery system or a Dionex GMP-2 gradient pump. A Linear UVIS 200 system (Reno, NV, USA) with a 10-mm flow cell was used for spectrophotometric detection.

The post-column reaction conditions of the NaBr–NaNO₂ method were as follows: post-column reagent flow-rate, 0.6 ml/min; acidification, 0.75 M sulfuric acid at 3 ml/min with two Dionex ASRS-Ultra anion suppressors in series; reaction temperature, 68°C; detection wavelength, 267 nm. Both the post-column reagent and the acid solution were delivered with Dionex pneumatic reagent delivery systems. For direct mixing, the post-column reagent (0.3 ml/min) and the acid (0.3 ml/min), were delivered using two Dionex pneumatic reagent delivery systems and mixed in another mixing-T. Also, a Dionex advanced gradient piston pump was tested for direct mixing.

The post-column reaction conditions of the *o*-dianisidine method were as follows: post-column reagent flow-rate, 0.5 ml/min; reaction temperature, 60°C; detection, 450 nm. The post-column reagent was delivered with a Dionex pneumatic reagent delivery system.

The post-column reaction conditions of the KI–(NH₄)₆Mo₇O₂₄ method were as follows: post-column reagent flow-rate, 0.3 ml/min; acidification, 0.45 M sulfuric acid at 3.0 ml/min with two Dionex ASRS-Ultra anion suppressors in series; reaction temperature, 25°C; detection wavelength, 352 nm. Both the post-column reagent and the acid solution were delivered with Dionex pneumatic reagent delivery systems. For direct mixing, the post-column reagent (0.15 ml/min) and the acid (0.15 ml/min) were delivered using two Dionex pneumatic reagent delivery systems and mixed in another mixing-T. Also, a Dionex advanced gradient piston pump was again tested for direct mixing.

3. Results and discussion

3.1. Comparison of detection limits

Table 1 summarizes the MDLs of the three post-column methods for bromate analysis. The MDLs

Table 1
Comparison of method detection limits for bromate^a

Method	σ for seven replicates ($\mu\text{g/l}$)	RSD (%)	Calculated MDL ^b ($\mu\text{g/l}$)
NaBr–NaNO ₂	0.053	7.5	0.17
<i>o</i> -Dianisidine	0.075	10.7	0.24
KI–(NH ₄) ₆ Mo ₇ O ₂₄	0.059	8.4	0.19

^a Standard concentration was 0.7 $\mu\text{g/l}$.

^b $\text{MDL} = \sigma \times t_{s,99}$ where $t_{s,99} = 3.14$ for $n = 7$.

were calculated based on US Environmental Protection Agency (EPA) Method 300.1 [7]. Briefly, an MDL was obtained by multiplying the standard deviation for seven replicates of a standard solution by Student's *t*-value for a 99% confidence level (3.14 for $n = 7$).

The order of decreasing bromate MDLs for the three methods were the *o*-dianisidine method > the KI–(NH₄)₆Mo₇O₂₄ method > the NaBr–NaNO₂ method. However, the difference of the MDLs between the three methods was not significantly large. This result suggests that all the three methods have the capability to quantify a bromate level around 0.5 $\mu\text{g/l}$, the 10^{–5} cancer risk level. Also, it is of note that these three methods were all compatible with conductometric analysis, though the MDLs for these methods increased slightly (7–10%) for a configuration with a conductivity detector installed upstream of the post-column reaction systems.

Table 2 summarizes the detection limits of the three methods for nitrite ion analysis. It was found that not only the KI–(NH₄)₆Mo₇O₂₄ method but also the *o*-dianisidine method can detect nitrite close to 1.0 $\mu\text{g/l}$, while no distinct signal was obtained for nitrite with the NaBr–NaNO₂ method at 100 $\mu\text{g/l}$. Therefore, when performing simultaneous analysis

Table 2
Comparison of method detection limits for nitrite^a

Method	σ for seven replicates ($\mu\text{g/l}$)	RSD (%)	MDL ^b ($\mu\text{g/l}$)
NaBr–NaNO ₂	No distinct signal	–	–
<i>o</i> -Dianisidine	0.42	8.4	1.3
KI–(NH ₄) ₆ Mo ₇ O ₂₄	0.16	6.4	0.5

^a Standard concentrations were 100 $\mu\text{g/l}$ for the NaBr–NaNO₂ method, 5.0 $\mu\text{g/l}$ for the *o*-dianisidine method, and 2.5 $\mu\text{g/l}$ for the KI–(NH₄)₆Mo₇O₂₄ method.

^b $\text{MDL} = \sigma \times t_{s,99}$ where $t_{s,99} = 3.14$ for $n = 7$.

for bromate and nitrite, the KI–(NH₄)₆Mo₇O₂₄ method or the *o*-dianisidine method should be chosen considering that both nitrite and bromate analyses can be subject to interference by chloride on a conventional conductometric detector [19]. Also, it is of note that the configuration of the *o*-dianisidine method is much simpler than that of the KI–(NH₄)₆Mo₇O₂₄ method, though the MDLs of the *o*-dianisidine method were slightly higher than those of the KI–(NH₄)₆Mo₇O₂₄ method for both bromate and nitrite ions.

3.2. Analysis of bromate ion in natural water matrices

Figs. 1–3 compare the performance of the three methods for the analysis of bromate and nitrite ions in a spiked river water sample. For bromate analysis, all the three methods demonstrated sufficient resolution and signal intensity. The recoveries of bromate ion for the spiked sample (1.6 $\mu\text{g/l}$) by the

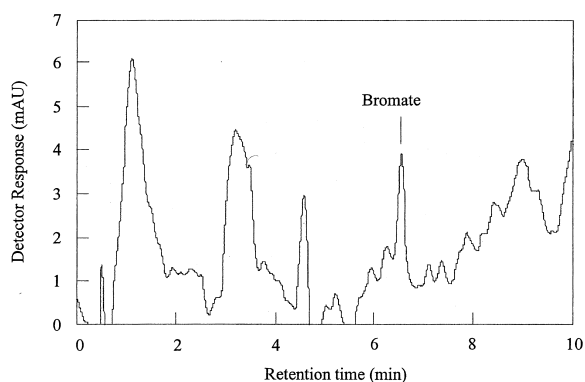


Fig. 1. Sample chromatogram of the simultaneous analysis of bromate and nitrite ions in a river water by the NaBr–NaNO₂ method. Spiked concentrations of bromate and nitrite ions were 1.6 and 25 $\mu\text{g/l}$, respectively.

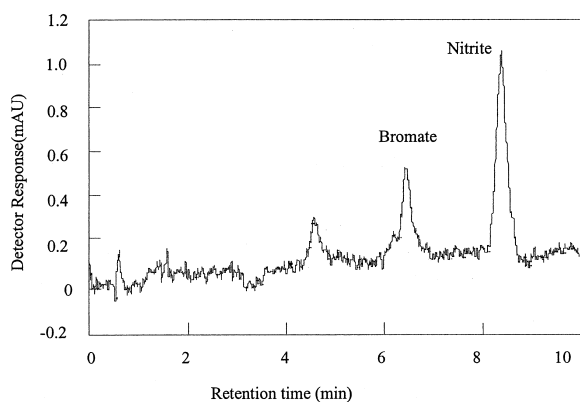


Fig. 2. Sample chromatogram of the simultaneous analysis of bromate and nitrite ions in a river water by the *o*-dianisidine method. Spiked concentrations of bromate and nitrite ions were 1.6 and 25 $\mu\text{g/l}$, respectively.

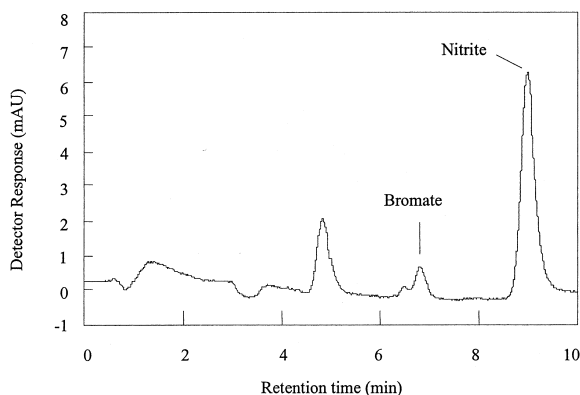


Fig. 3. Sample chromatogram of the simultaneous analysis of bromate and nitrite ions in a river water by the $\text{KI}-(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ method. Spiked concentrations of bromate and nitrite ions were 1.6 and 25 $\mu\text{g/l}$, respectively.

three methods were also acceptable. The recoveries for bromate using the *o*-dianisidine method, the $\text{KI}-(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ method, and the $\text{NaBr}-\text{NaNO}_2$ method were 106, 104, and 94%, respectively ($n=3$ for each). However, more unknown peaks were observed on the chromatogram when using the $\text{NaBr}-\text{NaNO}_2$ method. This may be due to the use of a shorter wavelength for detection. This result would imply that a method with a longer detection wavelength (e.g., *o*-dianisidine method) would be better for bromate analysis in complex water matrices, although further investigation is required to fully evaluate the effect of natural water matrices. Also, further investigation is required to identify the small peak next to bromate peak (around 6.2 min).

The nitrite ion was also well resolved and sufficient detector responses were obtained using the *o*-dianisidine method and the $\text{KI}-(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ method for the spiked sample (25 $\mu\text{g/l}$). The recoveries of nitrite ion by the *o*-dianisidine method and the $\text{KI}-(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ method were 98 and 103%, respectively ($n=3$ for each).

3.3. Direct mixing configuration

The direct mixing configurations of the $\text{KI}-(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ method and the $\text{NaBr}-\text{NaNO}_2$ method were compared with the suppressor configurations to evaluate the possibility of reducing cost by not needing to use the two anion suppressors. The MDLs for the bromate ion by both configurations are summarized in Table 3. The direct mixing configurations achieved comparable MDLs with the suppressor configurations for both the $\text{KI}-(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ method and the $\text{NaBr}-\text{NaNO}_2$ method. Figs. 4 and 5

Table 3

Comparison of method detection limits for bromate between the direct mixing configuration and the suppressor configuration for the $\text{NaBr}-\text{NaNO}_2$ method and the $\text{KI}-(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ method^a

Method	Type of reagent delivery	Calculated MDL ^b for the suppressor configuration ($\mu\text{g/l}$)	Calculated MDL ^b for the direct mixing configuration ($\mu\text{g/l}$)
$\text{NaBr}-\text{NaNO}_2$	Pneumatic	0.17	0.19
$\text{NaBr}-\text{NaNO}_2$	Piston pump	0.14	0.18
$\text{KI}-(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$	Pneumatic	0.19	0.19
$\text{KI}-(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$	Piston pump	— ^c	— ^c

^a Standard concentration was 0.7 $\mu\text{g/l}$.

^b $\text{MDL} = \sigma \times t_{s,99}$ where $t_{s,99} = 3.14$ for $n=7$.

^c No stable baseline was obtained with this configuration. Yellowish color development was observed at the outlet of the pulse damper.

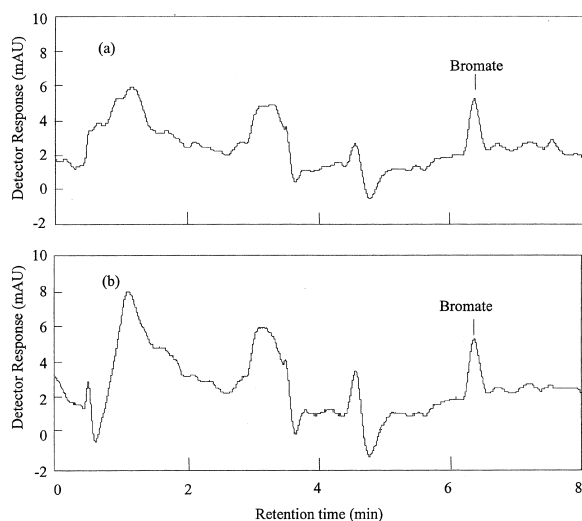


Fig. 4. Comparison between (a) the direct mixing configuration and (b) the suppressor configuration for bromate ion analysis by the NaBr–NaNO₂ method. Standard concentration of bromate ion was 1.6 µg/l.

compare the chromatograms for the standard solution at 1.6 µg/l for the two configurations with the KI–(NH₄)₆Mo₇O₂₄ method and the NaBr–NaNO₂ method, respectively. The broad peaks in the chromatograms before 5 min were considered to be due

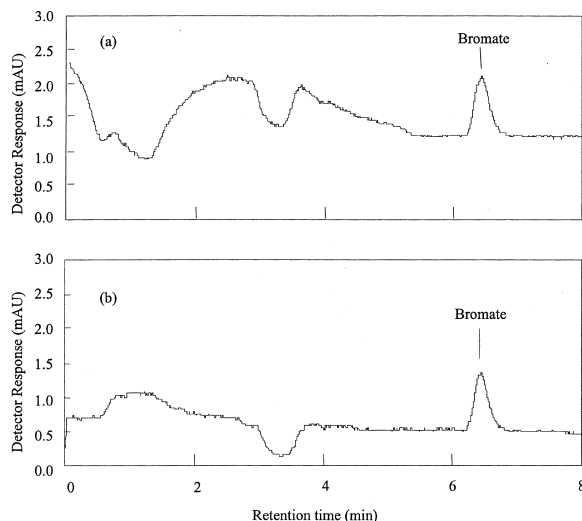


Fig. 5. Comparison between (a) the direct mixing configuration and (b) the suppressor configuration for bromate ion analysis by the KI–(NH₄)₆Mo₇O₂₄ method. Standard concentration of bromate ion was 1.6 µg/l.

to water in the sample (around 3 min) and the noise caused by the movement of the injection port back to the loading position (around 4.5 min for the NaBr–NaNO₂ method). However, none of these peaks interfered with the peak for bromate (around 6.5 min).

A piston pump was also tested as a reagent delivery unit. Table 3 indicates that the piston pump is also applicable for the direct mixing configuration of the NaBr–NaNO₂ method when used with a pulse damper. On the other hand, no stable baseline was obtained for the KI–(NH₄)₆Mo₇O₂₄ method with the piston pump and pulse damper as a yellowish color was observed at the outlet of the pulse damper. Presumably this was due to a reaction between KI and some material inside the pump or pulse damper.

4. Conclusion

The KI–(NH₄)₆Mo₇O₂₄ method, the NaBr–NaNO₂ method, and the *o*-dianisidine method showed similar method detection limits (0.17, 0.19 and 0.24 µg/l) for bromate analysis with pneumatic reagent delivery systems. With respect to the simplicity of the system, the *o*-dianisidine method is the best option of the three. Also, it is of note that the NaBr–NaNO₂ method was considered to be susceptible to the interference by matrix ions because of the use of a lower detection wavelength. It was also found that the *o*-dianisidine method achieves a low-µg/l level detection of nitrite with a simpler configuration (i.e., only one post-column reagent) than the KI–(NH₄)₆Mo₇O₂₄ method, while the sodium bromide–sodium nitrite method was not sensitive enough for nitrite analysis at the µg/l level. The three methods are all compatible with conductivity detection. When used in combination with conductivity detection, this compatibility allows simultaneous analysis of bromate, nitrite, and other common ions in drinking water, such as the bromide ion.

The direct mixing configurations of the reagents without ion suppressors was found to be applicable for use with the NaBr–NaNO₂ method and the KI–(NH₄)₆Mo₇O₂₄ method. The direct mixing configurations can achieve comparable detection limits to those obtained by the suppressor configurations.

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