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## Matrix effects in the determination of bromate in drinking water by ion chromatography

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### Abstract

Bromate is a well known by-product produced by the ozonation of drinking water; the allowed concentration for human consumption has to be regulated to low  $\mu\text{g l}^{-1}$  range. By using a high-capacity anion-exchange column, it should be possible to determine bromate at this low concentration by direct injection of a very large volume (up to 1 ml) without any sample preconcentration and pretreatment. The feasibility of this technique for the determination of bromate in drinking water has been explored in our work. The experimental results showed that matrix effect, due to inorganic ions contained in drinking water, strongly influenced the chromatographic behaviour of the bromate peak. The increase of the total ion content led to a correlated decrease in the efficiency of the analyte peak so that effective detection limits depended on the matrix composition. In this work chromatographic parameters (efficiency, asymmetry and resolution) of bromate peak are discussed in relation to the concentration of the main inorganic anions, and the injection volume (from 250  $\mu\text{l}$  to 1 ml). © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Water analysis; Matrix effects; Bromate; Inorganic anions

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### 1. Introduction

Bromate can be formed by the oxidation of bromide anions during ozonation and possibly by other oxidants in water treatment [1–4]. Since the bromate ion is a potential human carcinogen, the European Commission has proposed, for the revision of the Drinking Water Directive 80/778/ECC, a bromate limit of  $10 \mu\text{g l}^{-1}$ , defining an analytical determination limit of  $2.5 \mu\text{g l}^{-1}$  [5]; the US Environmental Protection Agency (EPA) established a drinking water maximum contaminant level goal (MCLG) of zero and a maximum contaminant level

(MCL) of  $10 \mu\text{g l}^{-1}$  for bromate in finished water [6]. Bromate analyses can be carried out by direct ion chromatography (IC) with conductivity detection [7–9]. By direct injection with a fixed sample volume of 200  $\mu\text{l}$ , a detection limit of  $7.3 \mu\text{g l}^{-1}$  was claimed [9], but no studies about large volume injection were reported. Preconcentration techniques have been developed in order to improve sensitivity down to sub- $\mu\text{g l}^{-1}$  levels by using gradient elution and a pre-treatment with a silver cation resin to reduce closely eluted chloride anions [10,11]. The improvement of the detection sensitivity was used as an alternative to preconcentration and it was obtained by using post-column derivatisation [12–16] or by hyphenating with inductively coupled plasma mass spectrometry (ICP-MS) [17–20]; these methods suffer of complex plumbing operation or high costs.

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The commercial availability of a new high-capacity anion-exchange column, already introduced in an EPA method [21], suggested us to test this column for the direct determination of bromate in drinking water without any pretreatment using a conventional IC system with conductivity detection. The aim of this work is to discuss the effects of inorganic ion load in the sample on column efficiency and capacity in order to give some practical guidelines to water control laboratories, for the application of this method in bromate monitoring. This work was carried out on synthetic drinking waters prepared dissolving pure inorganic salts in ultra-pure water: the matrix effects from natural organic matter, usually present in every surface drinking water, were not studied in this work.

## 2. Experimental

### 2.1. Materials

All solutions were prepared by dissolving salts of analytical grade in ultra-pure ( $18\text{ M}\Omega\text{ cm}^{-1}$  quality) water produced by a Milli-Q system (Millipore, Bedford, MA, USA). Concentrated standard solutions were prepared from potassium bromate (Carlo Erba, Milan, Italy), sodium chloride (Carlo Erba), potassium sulfate (Carlo Erba), sodium nitrate (Carlo Erba), sodium carbonate (BDH, Poole, UK) and sodium hydrogencarbonate (BDH). Working standard solutions were prepared by dilution of these concentrated solutions with ultra-pure water.

### 2.2. Instruments and chromatographic conditions

A Dionex (Sunnyvale, CA, USA) 4500i ion chromatograph, equipped with a GPM-II gradient pump, an AMMS-II chemical suppressor, a CDM-II conductivity detector and a Rheodyne 9726 (Cotati, CA, USA) injection valve, was used for sample analysis. The chromatographic separation was carried out on a Dionex IonPac AS9-HC ( $250\times 4\text{ mm I.D.}$ ,  $d_p\ 9\ \mu\text{m}$ ) high-capacity anion-exchange analytical column, provided with a Dionex IonPac AG9-HC guard column ( $50\times 4\text{ mm I.D.}$ ,  $d_p\ 9\ \mu\text{m}$ ), using  $9\text{ mM Na}_2\text{CO}_3$  at  $1.0\text{ ml min}^{-1}$  as the eluent solution.  $25\text{ mM H}_2\text{SO}_4$  at  $5\text{ ml min}^{-1}$  was used as regenerat-

ing solution. Eluent was prepared daily, filtered and degassed.

A Dionex AI-450 chromatographic data system was used for instrument control, data collection and processing.

## 3. Results and discussion

### 3.1. Interference from major adjacent peaks (chloride, hydrogencarbonate)

The preliminary injection of tap water spiked with a bromate solution (Fig. 1) showed that the bromate peak can overlap with chloride and hydrogencarbonate neighbouring peaks, present in large amounts in natural waters. By injecting ultra-pure water spiked with a constant amount of bromate ( $40\ \mu\text{g l}^{-1}$ ) and varying concentrations of these interfering ions, the interference limits for these two compounds, at a fixed injection volume of  $250\ \mu\text{l}$ , were determined. When a solution of bromate and hydrogencarbonate ( $200\text{ mg l}^{-1}$ ) was injected, an overlap of these compounds was observed (resolution:  $R_s=0.8$ ) (Fig. 2a). A small addition of chloride ions ( $4\text{ mg l}^{-1}$ ) shifted hydrogencarbonate peak in the tailing of the chloride peak obtaining a good resolution ( $R_s=9$ ) (Fig. 2b). Testing a series of solutions with increasing concentrations of chloride (from 4 to  $400\text{ mg l}^{-1}$ )

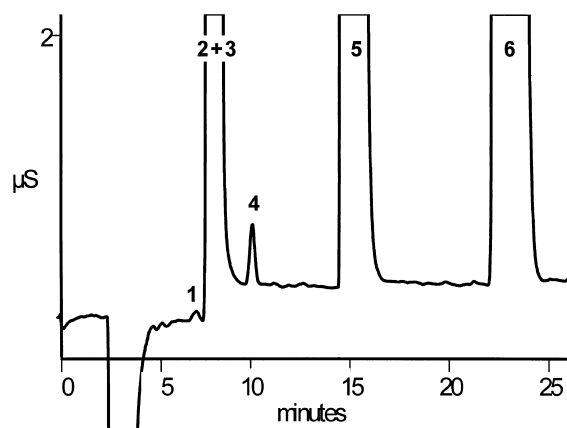


Fig. 1. Chromatogram of a spiked drinking water containing: (1) bromate,  $10\ \mu\text{g l}^{-1}$ ; (2) chloride,  $20\text{ mg l}^{-1}$ ; (3) hydrogencarbonate,  $50\text{ mg l}^{-1}$ ; (4) nitrite, trace; (5) nitrate,  $45\text{ mg l}^{-1}$ ; (6) sulfate,  $30\text{ mg l}^{-1}$ . Sample volume  $1\text{ ml}$ .

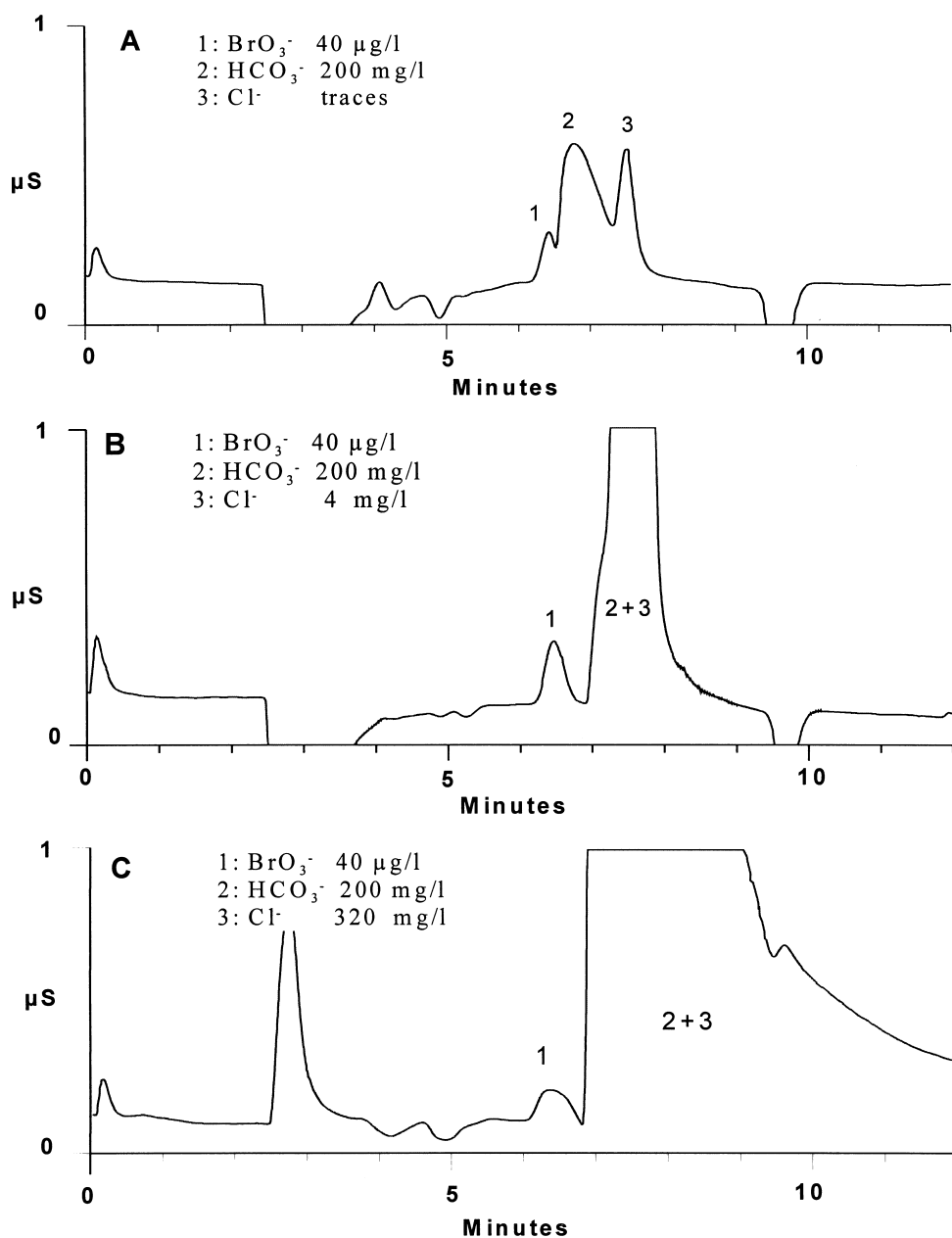


Fig. 2. Interference from chloride and hydrogencarbonate. Sample volume: 250  $\mu\text{l}$ .

$\text{l}^{-1}$ ) and a fixed concentration of hydrogencarbonate (200  $\text{mg l}^{-1}$ ), the maximum chloride concentration to get an acceptable resolution ( $R_s > 1$ ) was 320  $\text{mg l}^{-1}$  (Fig. 2c).

Increasing concentrations of chloride and hydrogencarbonate ions led to a degradation of the bro-

mate peak shape, which was evaluated by calculating efficiency and asymmetry according to the classical chromatographic equations [22]. A first glance at the data showed that peak efficiency was influenced by the sum of anions (chloride, hydrogencarbonate, nitrate and sulfate) present in the solution. Therefore

a systematic study was carried out to infer a relation between efficiency and total anion amount.

### 3.2. Effect of total anion concentration

A series of solutions with different anionic composition but having the same bromate concentration ( $40 \mu\text{g l}^{-1}$ ) was prepared. Two hundred and fifty  $\mu\text{l}$  of each solution were injected and the chromatographic parameters (efficiency, asymmetry and resolution) of bromate peak were calculated. Plotting bromate peak areas and heights vs. total anion content, no evident change (RSD 4.8%) was shown for peak areas, while peak heights showed a marked linear decrease (Fig. 3).

Considering that the efficiency is approximately proportional to the square of the peak height, a second-order polynomial curve between total anion equivalent amount and efficiency was fitted (Fig. 4). The good correlation found ( $R^2=0.986$ ) allows an a priori evaluation of the effect of the total anion amount on the bromate separation efficiency. For example, if a maximum admissible efficiency of 1000 theoretical plates is arbitrarily stated, a capacity limit of  $5 \mu\text{equiv.}$  can be calculated.

### 3.3. Effect of the sample volume

In order to improve the detection limit, we evalu-

ated the effect of increasing the injection volume, while maintaining constant the absolute injected amount of each anion ( $10 \text{ ng BrO}_3^-$ ,  $50 \mu\text{g HCO}_3^-$ ,  $20 \mu\text{g Cl}^-$ ,  $45 \mu\text{g NO}_3^-$  and  $30 \mu\text{g SO}_4^{2-}$ ).

Table 1 shows that this effect is more pronounced on retention time, asymmetry, height and area than on efficiency, which is, in all experiments, of the same order of magnitude of the value calculated by the experimental regression curve (Fig. 4). This is obvious considering that efficiency is only a function of the exchange capacity of the column and must be independent from the injected volume. On the contrary, the large plug of water, injected in the column head, locally diluted the eluent, leading to an increase in the retention time, and in a broadening and fronting of the peak ( $A_s < 1$ ). Therefore, the same polynomial relation, between efficiency and total anion amount (Fig. 4), can be used to forecast the efficiency decrease in the presence of high ionic strength matrices independently from the injected sample volume.

### 3.4. Calibration and detection limits

In order to validate the method for the analysis of bromate at  $\mu\text{g l}^{-1}$  levels, two calibration graphs were generated using, respectively, a 250 and a 1000  $\mu\text{l}$  loop. To evaluate sensitivity changes due to an increase in the sample volume, the two calibrations

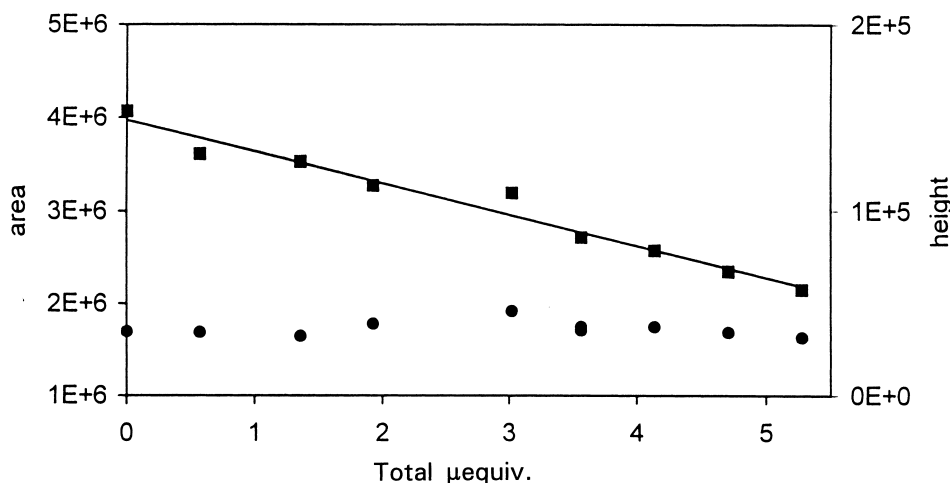


Fig. 3. Plot of bromate peak height (■) (regression equation  $y = -4226.2x + 148548$ ;  $R^2 = 0.9681$ ) and bromate peak area (●) vs. total anion amount (chloride, hydrogencarbonate, nitrate and sulfate;  $\mu\text{equiv.}$ ). Sample volume: 250  $\mu\text{l}$ .

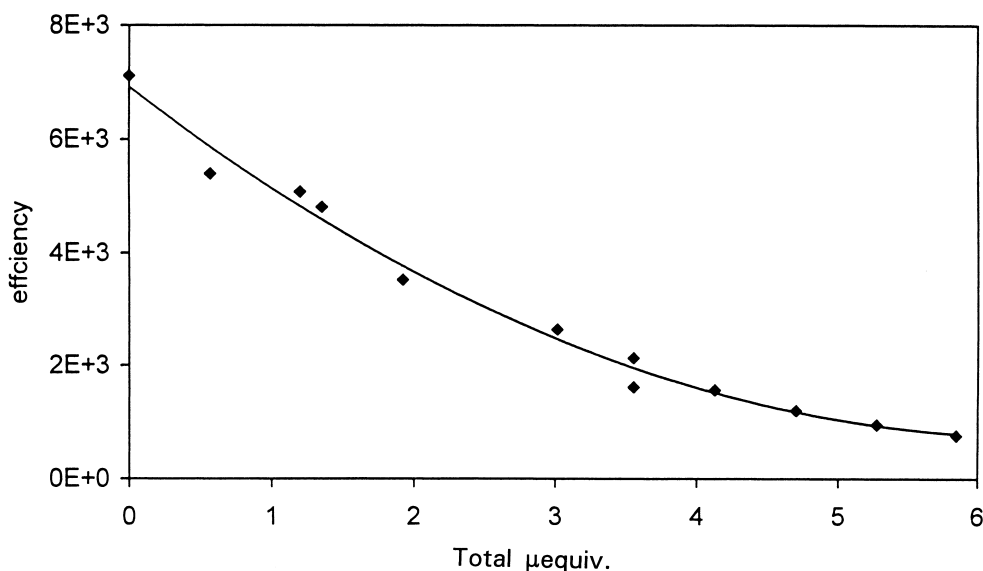


Fig. 4. Plot of bromate peak efficiency vs. total anion amount (chloride, hydrogencarbonate, nitrate and sulfate;  $\mu\text{equiv.}$ ); regression equation  $y=150.59x^2-1932.7x+6933.9$ ;  $R^2=0.9865$ . Sample volume: 250  $\mu\text{l}$ .

were carried out with the same standard solutions prepared by spiking a simulated drinking water matrix containing 20  $\text{mg l}^{-1}$  chloride; 30  $\text{mg l}^{-1}$  nitrate; 22  $\text{mg l}^{-1}$  sulfate and 100  $\text{mg l}^{-1}$  hydrogencarbonate (corresponding to a ionic load of 1.2  $\mu\text{equiv.}$  for 250  $\mu\text{l}$  loop, and 4.8  $\mu\text{equiv.}$  for 1000  $\mu\text{l}$  loop). Bromate solutions ranged from 40 to 4  $\mu\text{g l}^{-1}$  for the 250  $\mu\text{l}$  loop, and from 10 to 1  $\mu\text{g l}^{-1}$  for the 1000  $\mu\text{l}$  loop, corresponding to the same injected absolute masses, from 10 to 1 ng. The examined dynamic range covered only one order of magnitude, because higher bromate concentrations are not found in the environment. The repeatability of the standard peak areas, estimated from RSDs, ranged from 4% at 10 ng to 20% at 1 ng for both the sample volumes.

The weighted regression lines are the following:  $y$  (area units) =  $218\,895x$  (ng) - 25 997 ( $R^2=0.993$ ) for the 250  $\mu\text{l}$  loop and  $y$  (area units) =  $155\,854x$  (ng) - 27 508 ( $R^2=0.998$ ) for the 1000  $\mu\text{l}$  loop.

These data confirm that the use of an increased sample volume leads to a slight decrease in the absolute mass sensitivity. On the contrary the mass detection limit, calculated as three times the standard deviation of the lowest standard peak [23], is the same (about 1 ng injected) for both the sample volumes. This fact suggests that increasing the sample volume from 250  $\mu\text{l}$  to 1 ml is possible without a decrease in the efficiency and with a 4-fold increase in the concentration detection limit (from 4 to 1  $\mu\text{g l}^{-1}$ ).

Table 1

Retention time ( $t_R$ ), asymmetry ( $A_s$ ), efficiency (number of theoretical plates,  $N$ ), peak area and peak height of bromate in function of increasing sample volumes (numbers in parentheses are RSDs, calculated with four replicates)

Sample volume ( $\mu\text{l}$ )	$t_R$ (min)	$A_s$	$N$	Area	Height
250	6.17 (0.7)	1.15 (15)	1613 (4)	1 746 360 (8)	80 413 (6)
500	6.46 (0.8)	1.01 (20)	1689 (15)	1 441 885 (14)	65 847 (11)
750	6.95 (0.7)	0.89 (9)	1448 (3)	1 466 195 (11)	59 050 (11)
1000	7.05 (0.4)	0.87 (8)	1849 (7)	1 418 952 (9)	61 408 (10)

#### 4. Conclusions

The introduction of a high-capacity column for anion analysis in the market needs a detailed study in order to detect actual capacity limits of a similar column. Detection of  $\mu\text{g l}^{-1}$  levels of bromate by direct injection makes necessary to inject large volume of high ionic loading water such as groundwater or surface water subjected to potabilisation treatment. Increasing the sample volume up to 1 ml allows to improve the detection limit up to  $1 \mu\text{g l}^{-1}$ : the large plug of water injected does not greatly influence the efficiency of the separation but has a strong influence on the asymmetry of first eluting peaks such as bromate. The asymmetry is caused by a fronting of the peak which can deteriorate the accuracy in the automated integration. Nevertheless this work demonstrates that this analysis has a sufficient accuracy and reproducibility also with this injection volume. The real capacity limit of the column is determined by the total anion amount which is injected. An anionic load greater than 5  $\mu\text{equiv.}$  leads to an efficiency lower than 1000 theoretical plates (the experimental efficiency of the column for dilute samples is about 7000 theoretical plates) which makes the detection and quantitation of the bromate peak very difficult and inaccurate. Therefore the use of a high volume loop is limited by the total anionic load of the sample and this fact can be considered as the first selection criterion in choosing the right injection volume.

In conclusion, this work gives some aid in the definition of the real application limits of this column in this kind of analysis. The main shortcoming of this approach relates to the selection of matrix used in this study: natural organic matter, usually present in every surface drinking water, and quenching agents, normally added to the sample to prevent column degradation, must be added in a future work for a better matching of our synthetic matrix with a natural one.

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