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Journal of Chromatography A, 864 (1999) 263–270

JOURNAL OF CHROMATOGRAPHY A

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Ion chromatography determination of trace level bromate by large volume injection with conductivity and spectrophotometric detection after post column derivatisation

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Received 21 July 1999; received in revised form 17 September 1999; accepted 20 September 1999

Abstract

Bromate is a well known by-product produced by the ozonisation of drinking water; the allowed concentration for human consumption has to be regulated to the low $\mu g\ l^{-1}$ range. A direct injection, ion chromatographic method was developed using a tetraborate eluent with serially connected conductivity and spectrophotometric detection. Bromate was detected after post-column reaction with fuchsin at 520 nm. Sample capacity was investigated by injecting large volumes (up to 6 ml) using a high total hardness and chloride tap water. Linear correlation of bromate response with volumes from 1 ml to 6 ml was demonstrated, the main limitation being the overlapping of the chloride peak with bromate. Up to 1.5 ml sample can be injected without any pre-treatment. With more than 1.5 ml injection volume, a sample pre-treatment with a cartridge in Ag and H form, followed by a 10 min degassing in an ultrasonic bath, was needed. This method was validated by analysing secondary reference materials and real samples from a drinking water treatment plant. The method was linear from the limit of quantification to 20 $\mu g\ l^{-1}$. Reproducibilities in tap water were 18% (5 $\mu g\ l^{-1}$, $n=12$) and 21% (1 $\mu g\ l^{-1}$, $n=4$) respectively for 1.5 and 6 ml injection volumes with conductivity detection, and 17% at 0.5 $\mu g\ l^{-1}$ ($n=9$) with spectrophotometric detection. Calculated detection limits were 0.5 $\mu g\ l^{-1}$ (6 ml) and 2 $\mu g\ l^{-1}$ (1.5 ml) for conductivity detection and 0.3 $\mu g\ l^{-1}$ (1.5 ml) for spectrophotometric detection.

Keywords: Water analysis; Bromate; Inorganic anions

1. Introduction

Bromate, a potential human carcinogen, can be formed by the oxidation of bromide anions during ozonisation and possibly by other oxidants in water treatment [1–4]. In both the USA and the European Union (EU), maximum contaminant levels of 10 $\mu g\ l^{-1}$ have been set [5,6]: the US Environmental Protection Agency (EPA) classified bromate in group B-2 (probable human carcinogen) and established a drinking water maximum contaminant level goal (MCLG) of zero and a maximum contaminant level (MCL) of 10 $\mu g\ l^{-1}$ for bromate in finished water [6]. Toxicological studies have established that the lifetime risks of 10^{-4}, 10^{-5}, 10^{-6} for renal tumours would lead to levels of 5, 0.5 and 0.05 μg of bromate per litre of drinking water. The World Health Organisation (WHO), revising the Guidelines for Drinking Water Quality, proposed for bromate a guideline of 0.5 $\mu g\ l^{-1}$ at a risk level of 10^{-5} [7].

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0021-9673/99/$ – see front matter
PII: S0021-9673(99)01010-9

Depending on results of further research, a risk model could indicate a more definitive guideline value of 3 μg l^{-1} at a 10^{-5} excess risk. The higher limits set by the EU [5] and by the EPA [6] are mainly due to the lack of sensitive analytical methods for routine laboratories. For this reason there is a need for improving the existing methods in terms of sensitivity, cost and reliability. Preconcentration techniques in ion chromatography determination of bromate with conductivity detection [8–10] have been overcome by the introduction of a new high capacity column [11–13] which allows to inject up to 1 ml of water using a carbonate eluent. Nevertheless, our previous work [13] underlined that this approach could be applied without sample pre-treatment only to water characterised by a low total ionic load. An alternative approach to improve sensitivity and selectivity was the use of a different detection system such as inductively coupled plasma mass spectrometry [14–18] or UV–vis and fluorescence detection after post-column derivatisation [19–24]. In this field very promising results were obtained by Achilli and Romele [20,25] using a colorimetric reaction with fuchsin and metabisulphite. Trace levels of bromate were reduced by metabisulphite to form bromine which reacted with reduced fuchsin at pH 3.4 to form a brominated red coloured product.

In the present work we optimised the coupling between the large volume injection technique and the post-column reaction with fuchsin and spectrophotometric detection. We chose to use a tetraborate eluent in order to improve the resolution between bromate and interfering peaks (chloride and carbonate). We validated this simple method applying it to our tap water, characterised by high total hardness (350 mg $CaCO_3$), and to samples collected from drinking water treatment plants of a highly populated city in Italy.

2. Experimental

2.1. Materials

All chemicals were analytical grade reagents. Ultra pure (18 MΩ cm^{-1} quality) water was produced by a Milli-Q system (Millipore, Bedford, MA, USA). Borate eluent was prepared from sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$, Merck, Darmstadt, Germany).

Stock concentrated standard solution (1000 mgl^{-1}) was prepared from potassium bromate ($KBrO_3$, Carlo Erba, Milan, Italy); this solution is stable for several months at 4°C, in dark. Working standard solutions were prepared by dilution of this concentrated solution; these solutions are stable for 1 month at 4°C, in dark.

Stock concentrated fuchsin solution was prepared by dissolving 100 mg of basic fuchsin ($C_{19}H_{18}N_3Cl$, Merck) in 100 ml of ultra pure water in a glass flask; this solution is stable for several months. Fuchsin colour developing reagent was prepared adding 0.5 ml of 6 M hydrochloric acid (HCl, BDH) solution to 10 ml of stock fuchsin solution, followed by reduction with 400 mg of sodium metabisulphite ($Na_2S_2O_5$, Carlo Erba), in 100 ml final volume. This solution is stable for 1 month if stored in glass bottle, at room temperature and in dark. It was further diluted 50 times with ultra pure water before use: the diluted solution must be prepared fresh every day.

2.2. Sample pre-treatment

In order to reduce chloride and carbonate, aqueous samples were filtered through On-Guard Ag and H cation resins (Dionex) at a rate of 1.5 ml min^{-1} and sonicated for 10 min. The cartridges, before application of the sample, were cleaned with 40 ml of ultra pure water and the initial 3 ml of sample were discarded.

Samples from the drinking water treatment plant were stabilised by adding 50 mg of ethylendiamine to 1 l of sample immediately after collection, according to the method of the International Standard Organisation (ISO) [10].

2.3. Instruments and chromatographic conditions

A 4500i ion chromatograph (Dionex, Sunnyvale, CA, USA), equipped with a GPM-II gradient pump, an ASRS-ULTRA electrochemical suppressor, a CDM-II conductivity detector, a UDM-I fixed-wavelength UV–vis 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×

4 mm I.D.; d_p: 9 μm) high-capacity anion-exchange analytical column, provided with a Dionex IonPac AG9-HC guard column (50×4 mm I.D.; d_p: 9 μm), using 25 m*M* $Na_2B_4O_7$ at 1.0 ml min^{-1} as the eluent solution. Soon after the detection of bromate a solution of 50 m*M* $Na_2B_4O_7$ at 1.0 ml min^{-1} was used to purge the column from more retained peaks. Eluents were prepared, filtered and degassed daily.

The spectrophotometry detector, set at 520 nm, was connected in series after the conductivity detector. The diluted fuchsin colour developing reagent, supplied at 1 ml min^{-1} by a pressurised reagent delivery reservoir, was introduced into the column effluent stream by means of a T-junction**.** The 750 μl reaction coil was placed in a thermostated (80°C) water bath (Heto, Birkerød, Danmark).

The electrochemical suppressor was used in auto-suppression recycle mode with a current setting of 300 mA when conductivity detection was applied; when also spectrophotometric detection was employed, the electrochemical suppressor was used in auto-suppression external water mode with a water flow of 5–10 ml min^{-1} and a current setting of 300 mA.

Total analysis time, inclusive of re-equilibration time, was 60–70 min. A Dionex AI-450 chromatographic data system was used for instrument control, data collection and processing.

3. Results and discussion

3.1. Conductivity detection

Inorganic anions, contained in drinking water, strongly influenced the chromatographic behaviour of the bromate peak [13]. Moreover bromate peak can overlap with chloride and carbonate neighbouring peaks, present in large amount in natural waters. Therefore, in order to simulate the matrix effect, we prepared sample solutions spiking with bromate our laboratory tap water, characterised by a high hydrogencarbonate (280 mg l^{-1}) and chloride (31 mg l^{-1}) content with a total hardness of 350 mg $CaCO_3$.

The increased capacity of the AS9-HC column allowed the introduction of relatively large sample volume that led to a sensitivity improvement but also to an increase in the interfering peak concentration. To achieve a better separation between bromate and the interfering peaks, separation was carried out using tetraborate, which is a weaker eluent than carbonate, used in a previous work [13] (Fig. 1, top panel).

The ability of the high-capacity column to tolerate drinking water samples was evaluated by injecting increasing volumes of 10 μg l^{-1} bromate solution prepared both in ultra pure water and tap water (Fig. 2). A very good linear correlation (R^2=0.997) between bromate peak area and sample injection volumes (from 1 to 6 ml) was found, irrespective of the matrix composition. Analysing tap water sam-

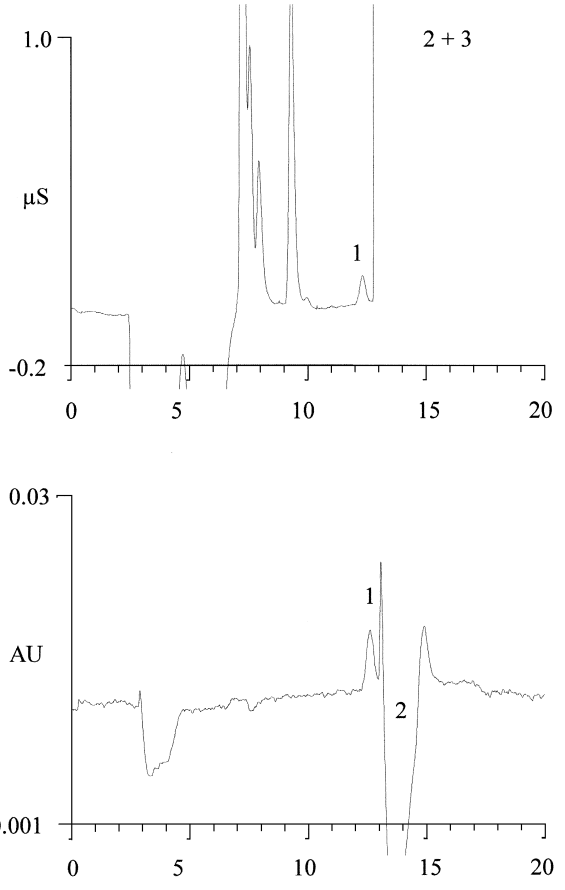

Fig. 1. Chromatograms of tap water spiked with bromate. See text for chromatographic conditions; sample volume, 1.5 ml (time scale in min). Analytes: (1) bromate; (2) chloride; (3) carbonate. Top panel: conductivity detection, bromate 10 μg l^{-1}; Bottom panel: spectrophotometric detection, bromate 2 μg l^{-1}.

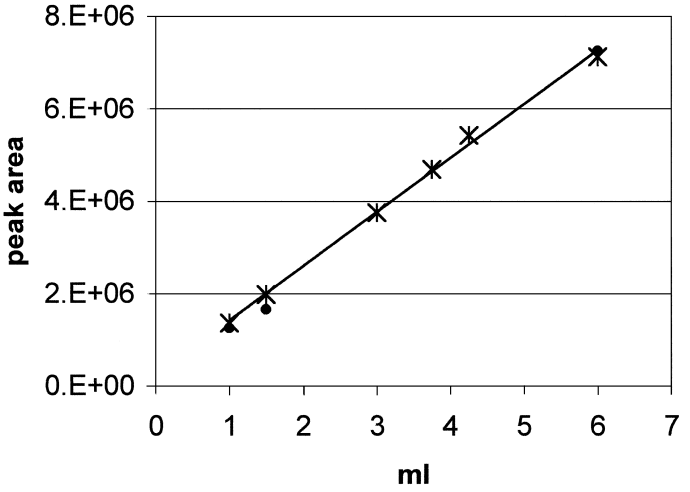

Fig. 2. Plot of bromate peak area vs. loop volume. Bromate concentration: 10 μg l^{-1}; (*) ultra pure water (regression equation $y=1170972x+246836$; $R^2=0.997$); (●) our laboratory tap water.

ples, a total resolution of bromate peak from chloride was achieved until 1.5 ml injection volume, without any sample pre-treatment. Injecting volumes larger than 1.5 ml, a filtration through cartridges in Ag and H form, followed by a 10 min degassing in ultrasonic bath, was needed.

Calibration curves, limit of detection (LOD) and limit of quantification (LOQ) were calculated for bromate solutions spiked in tap water, both for 1.5 ml injection without sample pre-treatment, and 6 ml injection after cartridge filtration. LODs and LOQs were calculated, according to the IUPAC [26], as respectively three- and ten-fold the standard deviation of bromate solutions at a concentration near the detection limits. The results in Table 1 were calculated from a RSD of 18% at 5 μg l^{-1} ($n=12$) and 21% at 1 μg l^{-1} ($n=4$), for 1.5 and 6 ml injection loop, respectively. The dynamic range was from LOQ to 20 μg l^{-1}, the range of interest in drinking water analysis. The calibrations resulted linear for both the injection volumes [regression equation for 1.5 ml: y (area units)$=167172x$ (μg l^{-1})$+1176$; $R^2=0.998$; regression equation for 6 ml: y (area units)$=696763x$ (μg l^{-1})$+ 59415$; $R^2=0.996$)].

Angular coefficients of calibration curves and detection limits (Table 1) confirm that the use of a 4-fold larger sample volume leads to a direct 4-fold increase in sensitivity. Use of larger volumes is possible if a lower ionic content water is analysed, since the main limiting factor is the concentration of the overlapping peaks.

3.2. Spectrophotometric detection

The coupling of large volume injection with a more sensitive detection system, based on a post-column reaction with fuchsin [20,25] and spectrophotometric detection at 520 nm allowed sub-μg l^{-1} quantification limits to be achieved without any sample pre-treatment. The post column derivatisation method was very simple, because it required only the direct mixing of the reagent solution with the eluent.

Table 1
Limits of detection (LODs) and limits of quantification (LOQs) for bromate analysis

Sample volume (ml)	Cartridge pre-treatment	Detection	LOD (μg l^{-1})	LOQ (μg l^{-1})
1.5	No	Conductivity	2	3
	No	Spectrophotometry	0.3	0.4
6	Yes	Conductivity	0.5	1

pH, a critical parameter, which has to be strictly about 3, was adjusted by flowing the eluent through the electrochemical suppressor, used in the auto-suppression external water mode. Temperature and reagent flow were optimised, by measuring the response of 10 μg l^{-1} bromate spiked tap water (Fig. 3). The temperature resulted the more influencing factor with a plateau over 80°C; higher temperatures can alter the reaction coil and/or generate air bubbles which can cause erratic responses. A reagent flow of 1 ml min^{-1}, with an eluent/reagent ratio of 1, provided the highest bromate peak response, while at higher flows diluting effects prevailed.

Fig. 1b shows the chromatogram of 2 μg l^{-1} bromate spiked tap water, achieved by using these optimised reagent conditions. Since high chloride amount determined a negative peak following the bromate peak, probably due to a change in the eluent refractive index, a good separation between bromate and chloride was needed, as in the case of conductivity detection.

Reproducibility of bromate in tap water, estimated as RSDs, was 17% at 0.5 μg l^{-1} ($n=9$). A good correlation was obtained in the range from 0.5 to 10 μg l^{-1} with the following regression line: y (area units)$=399749x$ (μg l^{-1})$+61936$ ($R^2=0.996$). The detection limits of the method (Table 1) were lower than those obtained by conductivity detection.

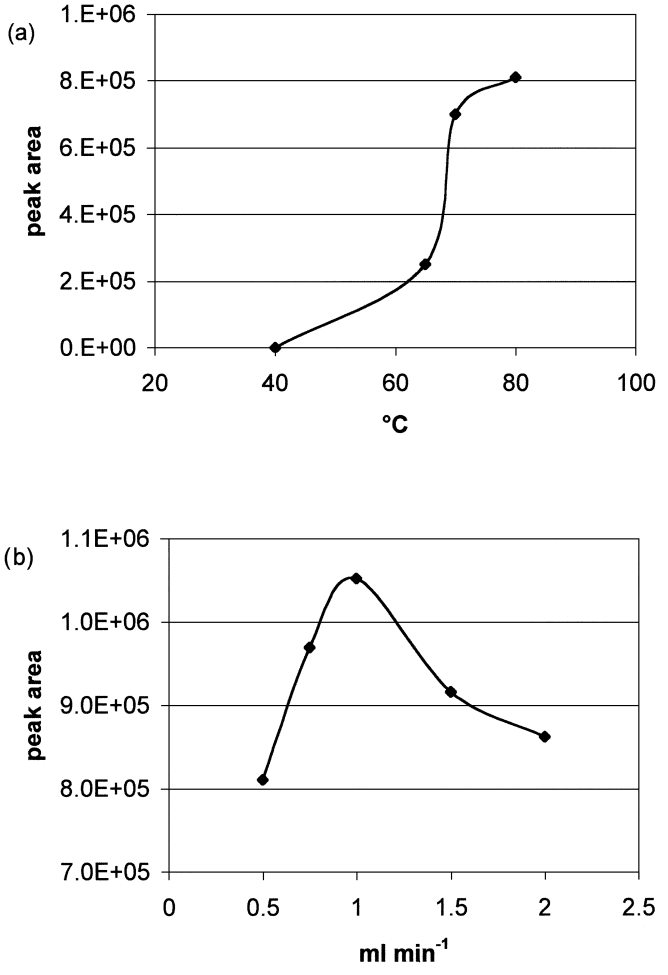

Fig. 3. (a) Effect of the reaction temperature on bromate peak area. Delivery reagent flow: 0.5 ml min^{-1}; 10 μg l^{-1} bromate spiked tap water. (b) Effect of the delivery reagent flow on bromate peak area. Temperature: 80°C; 10 μg l^{-1} bromate spiked tap water.

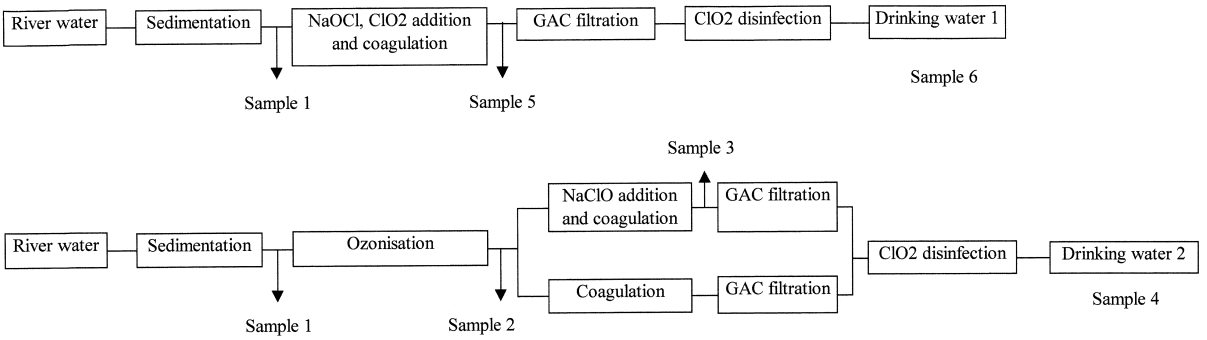

Fig. 4. Scheme of the drinking water treatment plant with the indication of the sampling points. GAC: granular activated carbon.

3.3. Accuracy

Recovery experiments were carried out by spiking with 10 μg l^{-1} bromate real samples from a drinking water treatment plant, whose bromate contents were measured under the detection limits (Fig. 4: samples 1, 2 and 4). The method showed a good recovery, ranging from 86.9 to 109.2% both for conductivity and spectrophotometric detection (Table 2).

Accuracy was established analysing four samples from a recent interlaboratory trial organised by the EU with the cooperation of the (ISO) [27], in order to validate a new ISO method for bromate determination in water [10]. Bromate contents measured by our method, both with conductivity and spectrophotometric detection, (Table 3), are not statistically different (paired *t*-test at 0.05 level) from mean values obtained in the interlaboratory trial.

3.4. Application on real samples

In order to evaluate matrix effects on bromate analysis, water collected from different steps of two drinking water treatment plants were analysed (Fig. 4). Ethylendiamine (EDA) was added to samples immediately after collection, to avoid any further formation of bromate by residual ozone [10]. EDA addition did not affect bromate determination by ion chromatography with tetraborate eluent. During bromate analysis on real samples no interference from

Table 2
Recovery experiments for conductivity and spectrophotometric detection. Direct injection: 1.5 ml

	Amount added (μg l^{-1})	Conductivity (μg $l^{-1)}$	Recovery (%)	Spectrophotometry (μg l^{-1})	Recovery (%)
(1) Sedimented river water	10	10.08	100.8	10.23	102.3
(2) Ozonised water	10	9.56	95.6	10.92	109.2
(4) Drinking water 2	10	8.69	86.9	9.22	92.2

Table 3
Accuracy experiments for conductivity and spectrophotometric detection. Direct injection: 1.5 ml

	Conductivity (μg l^{-1})	Spectrophotometry (μg l^{-1})	Mean value (μg l^{-1})
Standard solution in ultrapure water	5.34	5.18	5.44
High final treated water	2.19	2.61	2.57
Ozonised final treated water	9.06	7.83	8.24
GAC treated water	2.76	3.94	4.00

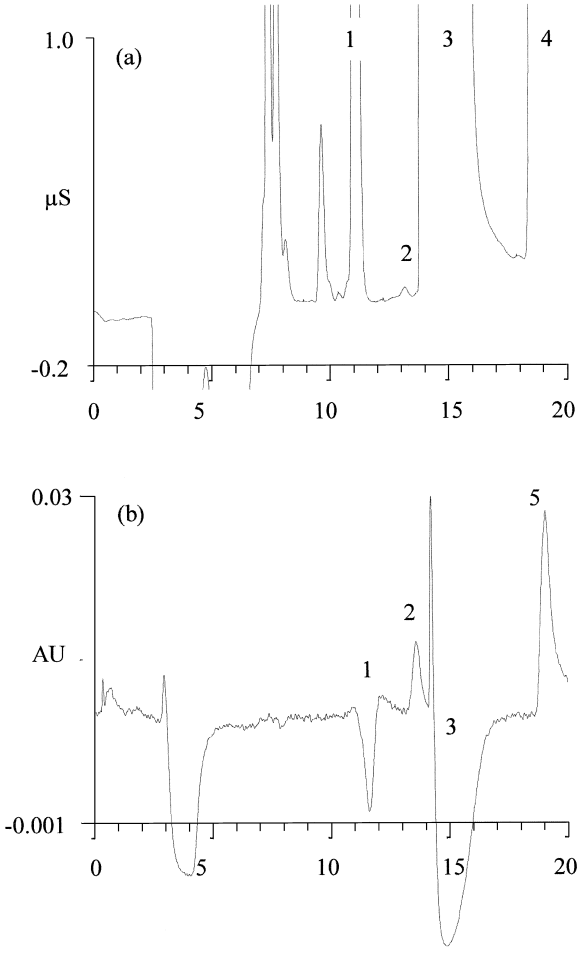

Fig. 5. Chromatograms of ''drinking water 1'' (Sample 6). See text for chromatographic conditions; sample volume: 1.5 ml; (time scale in min). Analytes: (1) chlorite; (2) bromate; (3) chloride; (4) carbonate; (5) nitrite. (a) conductivity detection (b) spectrophotometric detection.

matrix was observed and bromate was totally resolved from other compounds occurring in real samples, as, for example, chlorite (Fig. 5). In the spectrophotometric analysis reactivity of chlorite and nitrite with fuchsin reagent can be clearly observed (Fig. 5b).

Analytical results are shown in Table 4. The river water (sample 1) was free from bromate contamination and the ozonisation treatment (sample 2) did not produce any detectable bromate amount. On the contrary bromate contamination was found after NaOCl treatment (samples 3 and 5). This fact could be due to the presence of bromate as a by-product of the electrolytic preparation of hypochlorite [28]. Filtration with granular activated carbon (GAC), which followed chlorine treatment, reduced the bromate amount [29], but in ''drinking water 1'' (sample 6) it was still present at a detectable level.

4. Conclusions

WHO guidelines proposed that 0.5 $\mu g\ l^{-1}$ of bromate in drinking water represents a risk of 10^{-5}. This value may be very well exceeded in common drinking water practice: for this reason there is a strong need for simple and cost-effective methods to determine bromate at $\mu g\ l^{-1}$ levels. These limits can be achieved by using a high-capacity column with tetraborate eluent. If conductivity detection is used, these limits have been achieved by very-large-volume injection (6 ml), with the drawback of using cartridge pre-treatment with an additive cost. A cheaper solution is to couple large-volume injection with a simple and reliable post-column derivatisation

Table 4
Real sample analysis. Direct injection: 1.5 ml

	Conductivity ($\mu g\ l^{-1}$)	Spectrophotometry ($\mu g\ l^{-1}$)
(1) Sedimented river water	<LOD	<LOD
(2) Ozonised water	<LOD	<LOD
(3) Ozonised and chemical disinfected water	<LOD	1.01
(4) Drinking water 2	<LOD	<LOD
(5) Chemical disinfected water	4.41	5.69
(6) Drinking water 1	3.32	3.35

with fuchsin and colorimetric detection. This method allows to get a LOQ of 0.4 $\mu g\, l^{-1}$ injecting 1.5 ml of water without any sample pre-treatment. Accuracy and reproducibility have been established analysing real samples from a drinking water treatment plant and from an ISO interlaboratory trial. Analysis of the drinking water treatment plant shows that a possible source of bromate is the hypochlorite solution rather than the ozonisation process.

Acknowledgements

The authors thank Dr. Romele (DIIAR, Milan, Italy) for helpful suggestions. We are very grateful to Dr. P. Quevauviller (DGXII, Brussels, Belgium), Professor C. Thompson (Yorkshire Water, Rotherham, UK) and Dr. F. Schmitz (ISO, Germany) who gave us the permission to use unpublished results from the EC Contract SMT4-CT96-2134, coordinated by Anjou Recherche, France.

References

[1] W.R. Haag, J. Hoigné, Environ. Sci. Technol. 17 (1983) 261.
[2] U. von Gunten, J. Hoigné, Environ. Sci. Technol. 28 (1994) 1234.
[3] U. von Gunten, Y. Oliveras, Environ. Sci. Technol. 328 (1998) 63.
[4] I.N. Najm, S.W. Krasner, J. Am. Water Works Assoc. 87 (1995) 106.
[5] CEC, Council Directive Concerning the Quality of Water Intended for Human Consumption, Directive 98/83/CE, Commission of the European Union, Brussels, 1998.
[6] G. Rice, Ozone News 20 (1992) 8.
[7] WHO, Guidelines for Drinking-Water Quality, Vol. 1, Recommendations, World Health Organisation, Geneva, 2nd ed., 1993.
[8] H. Weinberg, J. Chromatogr. A 671 (1994) 141.
[9] R.J. Joyce, H.S. Dhillon, J. Chromatogr. A 671 (1994) 165.
[10] ISO, Water Quality-Determination of Dissolved Bromate using Liquid Chromatography of Ions, Proposal for ISO/DIS 15061, International Standard Organisation, Geneva, 1998.
[11] The Determination of Inorganic Anions in Drinking Water by Ion Chromatography, US Environmental Protection Agency, Cincinnati, OH, 1997, Method 300.1.
[12] L.K. Jackson, R.J. Joyce, M. Laikhtman, P.E. Jackson, J. Chromatogr. A 829 (1998) 187.
[13] S. Colombini, S. Polesello, S. Valsecchi, S. Cavalli, J. Chromatogr. A 847 (1999) 279.
[14] J.T. Creed, M.L. Magnusson, J.D. Pfaff, C. Brockhoff, J. Chromatogr. A 753 (1996) 261.
[15] J.T. Creed, C.A. Brockhoff, Anal. Chem. 71 (1999) 722.
[16] J. Diener, K.G. Heumann, Fresenius J. Anal. Chem. 357 (1997) 74.
[17] M. Yamanaka, T. Sakai, H. Kumagai, Y. Inoue, J. Chromatogr. A 789 (1997) 259.
[18] M. Nowak, A. Seubert, Anal. Chim. Acta 359 (1998) 193.
[19] H.S. Weinberg, H. Yamada, R.J. Joyce, J. Chromatogr. A 804 (1998) 137.
[20] M. Achilli, L. Romele, J. Chromatogr. A 847 (1999) 271.
[21] H.S. Weinberg, H. Yamada, Anal. Chem. 70 (1998) 1.
[22] B.D. Walters, G. Gordon, B. Bubnis, Anal. Chem. 69 (1997) 4275.
[23] Y. Inoue, T. Sakai, H. Kumagai, Y. Hanaoka, Anal. Chim. Acta 346 (1997) 299.
[24] A. Gahr, N. Huber, R. Niessner, Mikrochim. Acta 129 (1998) 281.
[25] L. Romele, M. Achilli, Analyst (London) 123 (1998) 291.
[26] J.D. Winefordner, G.L. Long, Anal. Chem. 55 (1983) 712A.
[27] EC Contract SMT4-CT96-2134, coordinated by Anjou Recherche, France, European Union.
[28] A. Mills, A. Belghazi, D. Rodman, Wat. Res. 30 (1996) 1973.
[29] M. Siddiqui, W. Zhai, G. Amy, C. Mysore, Wat. Res. 30 (1996) 1651.