Chloride interference in the determination of bromate in drinking water by reagent free ion chromatography with mass spectrometry detection

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Abstract

Bromate, a well known by-product of the ozonation of drinking water, has been included among the substances which have to be monitored in the drinking water according to the last EC Directive 251/98 on potable water with a regulated limit of $10\,\mu g\,l^{-1}$. The need of performing routine analysis at this limit is a driving force for the developing of new simple and sensitive methods of detection, which should be also able to overcome the effect of matrix composition. This work explored the use of mass spectrometry detection with electrospray ionisation hyphenated to a reagent free ion chromatograph with hydroxide gradient elution for the determination of bromate in drinking water. The use of a high capacity hydroxide selective column operated in gradient mode allowed to avoid the interference by carbonate peak, which moved to longer retention times. The effect of increasing chloride concentrations from 0 to $250\,mg\,l^{-1}$, which is the guideline limit for drinking water in Directive 251/98/EC, was to decrease absolute mass spectrometric response and chromatographic efficiency and, on the consequence, to increase the effective detection limits. The effect of the chloride concentration on the detection of bromate is discussed.

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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]. Bromate has been regulated in EC countries by the EC 98/83 Drinking Water Directive that stated a bromate limit of $10\,\mu g\,l^{-1}$, defining an analytical determination limit of $2.5\,\mu g\,l^{-1}$ [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 $10\,\mu g\,l^{-1}$ for bromate in finished water [6]. A lot of literature has been devoted to the ion chromatographic methods for bromate determination with different detection systems [4,7] and most of these methods have been received in standard methods of analysis. In fact, bromate can be determined by suppressed conductivity detection [8], and

preconcentration techniques have been developed in order to improve sensitivity down to sub-ppb levels [9]. Alternative and more sensitive detection techniques were post-column derivatisation [10,11] or ICP–MS [12], but these methods suffer of complex plumbing operation or high costs. An interesting comparison among these detection techniques was published by Schminke and Seubert [13] who concluded that sample pre-treatment with silver cation resin is necessary when conductivity detection is used.

Our previous works have been devoted to the exploration of large volume injection as an alternative and simpler tool for improving sensitivity using a high capacity anion exchange column with carbonate/bicarbonate eluent and conductivity [14] or spectrophotometric detection after post-column derivatisation [15]. The main drawback of these methods was the negative effect of matrix composition on the bromate peak efficiency [14] that influences also the effective method detection limit. To overcome matrix problems we explored in this work the use of mass spectrometry detection

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with electrospray ionisation hyphenated to a reagent free ion chromatograph with hydroxide gradient elution.

API-MS hyphenated to a suppressed ion chromatography system was used by different research groups [16–22] to determine bromate in drinking water with satisfactory sensitivity. Real water samples were analysed up to 41 mg l^{-1} of chloride without sample pre-treatment [16], but it is evident from Fig. 2 of reference [16] that bromate peak was not immune from matrix interference. The aim of our work is to explore the feasibility of large volume direct injection of sample characterised by chloride concentrations from 0 to 250 mg l^{-1}, which is the guideline limit for drinking water in Directive 251/98/EC, without sample pre-treatment.

2. Experimental

2.1. Materials and chemicals

All solutions were prepared by dissolving salts of analytical grade in ultra pure (18 MΩ cm^{-1} quality) water produced by a Milli-Q system (Millipore, Bedford, MA, USA). Concentrated standard solutions were prepared from potassium bromate (Carlo Erba, Milano, Italy), sodium chloride (Carlo Erba), potassium sulphate (Carlo Erba), sodium nitrate (Carlo Erba), sodium carbonate (BDH Chemicals Ltd, Poole, England) and sodium hydrogen carbonate (BDH Chemicals Ltd). Working standard solutions were prepared by dilution of these concentrated solutions with ultra pure water. Water for chromatography was also purified (18 MΩ cm^{-1} quality) by a Milli-Q system.

2.2. Chromatographic separation

Chromatographic analyses were performed on a DX-600 Ion Chromatograph (Dionex, Sunnyvale, CA, USA) equipped with AS50 Autosampler, GS50 Gradient Pump, LC25 column compartment, ED50 conductivity detector and single quadrupole mass spectrometer. Separations were carried out using a Dionex IonPac AS11-HC (250 mm × 2.0 mm) analytical column and an IonPac AG11-HC (50 mm × 2.0 mm) guard column. Anions were detected by serially connected suppressed conductivity detection and MS spectrometry. Suppression was achieved using a ASRS-UltraII electrochemical suppressor, supplied with external water. KOH eluent was electrolytically on-line generated using an EG40 Eluent Generator equipped with EluGen-OH cartridge at a constant flow rate of 0.3 ml min^{-1}. The KOH gradient program was composed of three steps: (1) 6 mM isocratic elution from 0 to 8 min; (2) linear gradient up to 30 mM from 8 to 20 min; (3) 30 mM isocratic elution for 5 min. All separations were carried out at 30 °C and samples were filtered through 0.45-μm filters before injection.

Dionex Chromeleon 6.40 chromatography software controlled data collection and the operation of all components in the system.

2.3. MS detection

MS detection was carried out by a single stage quadrupole detector (Thermo Finnigan MSQ, Dionex, Sunnyvale, CA, USA). The MS was operated in the negative electrospray (ESI−) ionisation mode at 3.0 kV. Probe temperature was set at 400 °C, cone voltage was −70 V.

Bromate anion has been detected at a mass-to-charge ratio (*m/z*) 127 using isotope ion at *m/z* 129 for peak identity confirmation.

The same MS conditions were also used in Flow Injection experiments carried out using a Valco (Houston, TX, USA) divert valve equipped with a 2 μl loop.

3. Results and discussion

Our previous works [14,15], carried out with an high capacity column (AS9HC) with a carbonate eluent, showed that the interference of chloride and carbonate on bromate determination is due, not only to a simple peak overlapping, but also to a loss in efficiency of bromate peak which lowers the effective limit of determination and peak reproducibility.

The introduction of reagent free chromatography system suggested us to test the feasibility of this kind of approach for bromate determination using a 2 mm AS11HC column with gradient hydroxide eluent and large volume injection (0.85 ml). This choice allows us, on one hand, to shift carbonate peak towards later elution times (Fig. 1), avoiding interference on bromate peak, and on the other hand, by using suppressed hydroxide eluent, to have a less noisy background in MS analysis [19].

The aim of our work was to determine the interference effects due to increasing chloride concentrations from 0 to 250 mg l^{-1}, which is the guideline limit for drinking water in Directive 251/98/EC, when a large volume direct injection is used without sample pre-treatment. The highest chloride
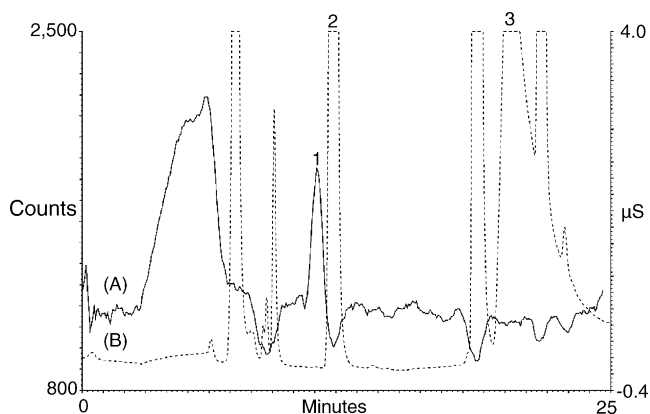

Fig. 1. IC analysis of a low mineral content water spiked with bromate. Chromatographic conditions as in Section 2, injection volume: 850 μl. Peaks: (1) bromate: 0.5 μg l^{-1}; (2) chloride: 1.5 mg l^{-1}; (3) carbonate: 18 mg l^{-1}. (A) MS detection (127 *m/z*); (B) conductivity detection.
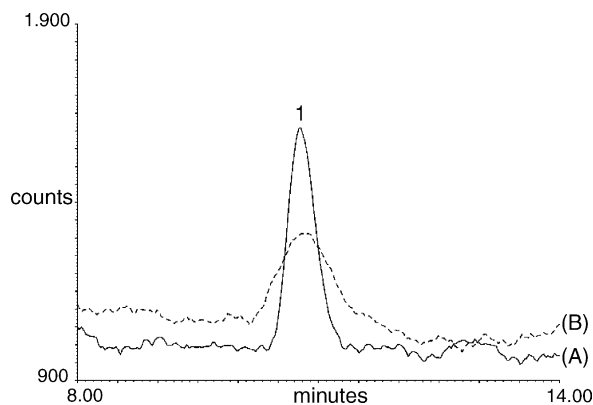
Fig. 2. Influence of chloride concentration on bromate peak shape. IC–MS conditions as in Section 2, MS detection (127 m/z). Injection volume: 850 µl. Peaks: (1) bromate: 0.5 µg l^{-1}. (A) Deionised water; (B) 25 mg l^{-1} chloride solution.

concentration to be tested determined the choice of the maximum injection volume (0.85 ml): at this volume the absolute amount of injected chloride is about 6 µeq, which is less than a tenth of the column capacity (72.5 µeq) and we decided to not overcome this ratio.

Fig. 1 shows the MS ion chromatogram of m/z 127 compared to the conductivity trace of a drinking water low in mineral content spiked with 0.5 µg l^{-1} bromate. It can be observed that, in MS trace, chloride appears as a small negative peak soon after bromate peak and this evidence suggests that chloride can suppress ionisation in electrospray.

Furthermore, the analyses of solutions with fixed bromate concentration (0.5 µg l^{-1}) and different chloride concentrations (from 0 to 25 mg l^{-1}) evidenced that bromate peak shape deteriorated as chloride concentration increased (Fig. 2); this behaviour can be attributed to a strong loss in efficiency due to the chloride competition on column active site. By plotting efficiency, measured as number of theoretical plates (Fig. 3) versus chloride concentration, we verified that efficiency actually decreases from about 4000 to about 1000 theoretical plates passing from 0 to 25 mg l^{-1} chloride solutions. At
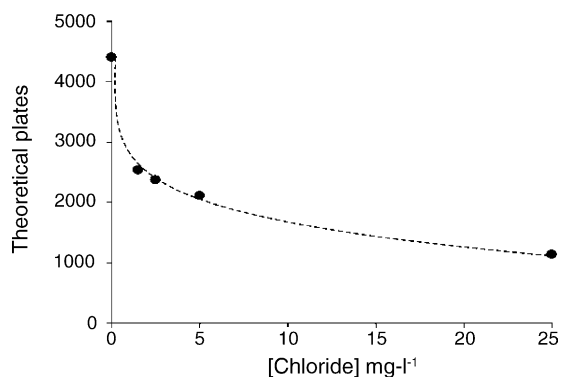
250 mg l^{-1} bromate was not detected. It is worthwhile to note that the efficiency of bromate peak is suddenly halved passing from 0 to 2.5 mg l^{-1} chloride in the solution, showing that also a low chloride concentration drastically influences the bromate peak shape under these chromatographic conditions. This efficiency plot confirms results obtained for conductivity detection and carbonate elution in our previous work [14].

During the same test sequence, we verified that the absolute response of the bromate ion decreases with increasing chloride concentration: this experimental evidence could be attributed either to a chromatographic effect or to an ion suppression in MS detection.

In order to establish at what concentration level chloride influences MS detection of bromate ions, a flow injection experiment was carried out injecting solutions with a fixed bromate concentration (0.5 mg l^{-1}) and increasing chloride concentrations (from 0 to 250 mg l^{-1}). This experimental set up allowed us to discriminate the contribution of MS ionisation and detection on sensitivity from that of chromatographic origin. The plot of responses (expressed in arbitrary units) versus chloride concentration (Fig. 4) showed that chloride actually suppresses bromate response and the response is halved at 10 mg l^{-1} chloride concentration.

These plots (Figs. 3 and 4) suggested that both loss in chromatographic efficiency and ion suppression play a role in the decrease of bromate sensitivity in MS detection when chloride ions are present in the solution. We can suppose that the chromatographic effects prevail at few mg l^{-1} chloride levels, when the two chromatographic peaks are well resolved, while the ion suppression contribution becomes more and more critical as the overlapping between bromate and chloride increases at increasing chloride concentration.

This sensitivity decrease is evident also by comparing calibration curves determined at different chloride concentrations. Angular coefficients of calibration curves ranged from 438 at 2.5 mg l^{-1} Cl$^-$ to 168 at 25 mg l^{-1} Cl$^-$ with an injection volume of 850 µl (Table 1). It was not possible to build a calibration curve for 250 mg l^{-1} Cl$^-$ solutions because no

Fig. 3. Plot of bromate peak efficiency at increasing chloride concentrations. Bromate: 0.5 µg l^{-1}. IC–MS conditions as in Section 2, MS detection (127 m/z). Injection volume: 850 µl.
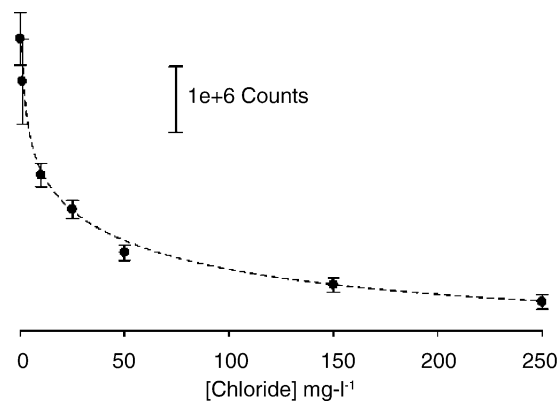

Fig. 4. Plot of bromate MS response (arbitrary units) at increasing chloride concentrations in FIA experiments. Error bars: ±1SD. Bromate: 0.5 mg l^{-1}. MS conditions as in Section 2, MS detection (127 m/z). Injection volume: 2 µl.

Table 1
Regression equations of bromate calibration curves and average efficiency of bromate peaks, expressed as the number of theoretical plates (N), at different chloride concentrations and injection volumes

Bromate range (μg l^{-1})	Chloride concentration (mg l^{-1})	Chloride injected amount (μeq)	Injection volume (μl)	Regression curve	Efficiency (N)
0.05–2.0	2.5	0.06	850	$y = 438x + 82$ ($R^2 = 0.999$)	2207
0.5–2.0	25	0.61	850	$y = 168x + 99$ ($R^2 = 0.998$)	1088
5–20	250	0.61	85	$y = 12.9x + 66$ ($R^2 = 0.999$)	528

signal was detected even at 20 μg l^{-1} bromate. By using a 10-fold lower injection volume (85 μl) a calibration curve with an angular coefficient of 12.9 was interpolated at 250 mg l^{-1} Cl$^-$ for a 5–20 μg l^{-1} bromate range.

As a further consequence, chloride concentration affects also effective limits of detection (LOD). LOD was estimated in a real matrix, containing 1.5 mg l^{-1} Cl$^-$, as threefold the standard deviation for seven replicates of a low concentration (0.5 μg l^{-1}) sample according to [23]: calculated LOD was 0.07 μg l^{-1} with an injection volume of 850 μl. By increasing chloride concentrations, the estimated lower limits of application increased to 0.5 μg l^{-1} at 25 mg l^{-1} Cl$^-$ and to >20 μg l^{-1} at 250 mg l^{-1} Cl$^-$.

At last, how is it possible to analyse bromate in a 250 mg l^{-1} solution? We compared different practical approaches. The first attempt was to reduce the injection volume from 850 to 85 μl, and, under these conditions, we could detect 5 μg l^{-1} of bromate in the 250 mg l^{-1} chloride solution (Table 1), but with a scarce efficiency ($N = 528$, as shown in Table 1). Better efficiency ($N = 1088$) obtained injecting the same absolute chloride amount but with the larger volume suggests that a possible alternative could be the large volume injection of a diluted sample. In fact the use of the larger loop (850 μl) improves the peak efficiency and asymmetry because the relatively huge quantity of water injected into the eluent stream does not elute the anions present in the sample. On the contrary, anions are focalised at the head of the column allowing to get a higher efficiency, as shown in Table 1.

The last tested solution, for the analysis of 250 mg l^{-1} Cl$^-$ water sample, was to apply the reliable and widely used pre-treatment procedure with silver cartridge, according to [24]. The use of OnGuardAgH (Dionex) allows to reduce chloride concentration from 250 mg l^{-1} to few μg l^{-1} with 100% recovery of bromate. After treatment, efficiency of bromate peak was about 2500 plates, that is the same value as that measured in the case of water with low chloride concentration. This simple and more expensive approach assures the best sensitivity without loss in accuracy.

4. Conclusion

The aim of this work was to find a practical solution of the problem of determining bromate in water with high mineral content. The use of hydroxide eluent in a reagent free IC system allows to overcome the problem of carbonate interference in bromate determination, moving carbonate peak towards later elution times.

The hyphenation of mass spectrometry and IC was tested as a selective and sensitive detection method for bromate alternative to post-column derivatisation. Notwithstanding the use of MS spectrometry as detection system for bromate, interference effects of chloride cannot be completely overcome. In fact increasing chloride concentrations lead to a loss in chromatographic efficiency, as previously verified for conductivity detection [14] and a decrease of MS response. In fact chloride ions, also at few mg l^{-1} levels, both induce negative chromatographic effect (i.e. they compete with bromate for the active sites of the column) and acts as an ion suppressor on electrospray ionisation.

On a practical point of view, these observations evidenced that a certain level of chloride in the solution requires a specific calibration curve for that specific matrix. This approach can be adopted only when a laboratory has to monitor the same water source; on the contrary, when waters with different chemism or characterised by chloride concentration of hundreds mg l^{-1} have to be analysed, a pre-treatment with silver cartridge is rather unavoidable in order to allow bromate analysis at low μg l^{-1} levels.

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