Determination of bromide, bromate and other anions with ion chromatography and an inductively coupled plasma mass spectrometer as element-specific detector ☆

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Abstract

An implementation of the Dionex IonPac AS12A analytical column with an element-specific ICP-MS detection is described for the simultaneous determination of halogen and oxyhalogen anions, sulfate, phosphate, selenite, selenate and arsenate. The chromatographic separation was achieved in less than 4 min with an aqueous 11 mM $(NH_4)_2CO_3$ (pH 11.2, adjusted with aqueous ammonia) as eluent. Special emphasis was given to optimize the ICP-MS detection conditions for the reliable detection (RSD<5%) of bromate and bromide at a bromine concentration level of 1.0 µg l^{-1} with 50 µl sample injection volume. In order to achieve the highest detector response for bromine species an ultrasonic nebulizer equipped with a membrane desolvator had to be employed. The detection limits ($S/N=3$, sample injection volume 50 µl) obtained with the IC–ICP-MS after the optimization were 0.67 µg l^{-1} for BrO_3^-, 0.47 µg l^{-1} for Br^-, 69 µg l^{-1} for ClO_2^-, 4 µg l^{-1} for Cl^-, 47 µg l^{-1} for ClO_3^-, 13 µg l^{-1} for SO_4^{2-}, 36 µg l^{-1} for PO_4^{3-}, 0.4 µg l^{-1} for SeO_3^{2-}, 0.3 µg l^{-1} for SeO_4^{2-}, and 0.4 µg l^{-1} for AsO_4^{3-}. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Waters used for the preparation of drinking waters are frequently contaminated with organic substances and are additionally biologically impure. It is therefore a necessity to purify and disinfect source waters in order to obtain waters of a drinking quality.

Disinfection of source waters is in practice per-formed by chlorination or ozonization procedures. The disinfection of bromide-containing source waters results in the production of bromate (BrO_3^-) [1,2], which was recently shown to be carcinogenic [3] and was therefore classified as a group 2B carcinogen by the International Agency for Research on Cancer (IARC). A lifetime cancer risk based on an average adult's drinking water intake was estimated to be 1 in 10^4 at a 5 µg l^{-1} [4] and 1 in 10^5 at a 3 µg l^{-1} BrO_3^- concentration level [5]. At present, the concentration limits proposed for BrO_3^- in drinking waters by the World Health Organization (WHO) [5], US Environmental Protection Agency (EPA) [6], and the Commission of the European Communities

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[7] are 25 µg l^{-1}, 10 µg l^{-1} and 10 µg l^{-1}, respectively. These relatively high values were set because of the limitations in available analytical techniques and water treatment capabilities in the past. In our opinion the maximum concentration levels for BrO_3^- in drinking waters will be set to lower values in the near future by the responsible environmental protection, governmental and/or health organizations, especially because the analytical techniques capable of simultaneous determination of low-µg l^{-1} BrO_3^- and Br^- concentration levels made a rapid progress in the past few years.

The determination of ionic species is usually performed by means of ion chromatography (IC) coupled to various detectors. Among the detection techniques that were widely used in recent years for the detection of various ions after their chromatographic separation, inductively coupled plasma mass spectrometry (ICP-MS) was shown to offer unique advantages, like element specificity, a wide dynamic linear range and low detection limits [8]. It is noticeable that ICP-MS was mainly applied for the detection of metals and metalloids [8,9]. Among the nonmetallic elements, halogens were periodically investigated [10–17], whereas ICP-MS detection of other nonmetals after their chromatographic separation was reported only by Jiang and Houk for phosphorous and sulfur compounds [18].

The determination of BrO_3^- after its IC separation from iodate and chlorite was performed also with selective post-column reagents with UV–Vis spectrophotometry [19,20], potentiometry [21] and conductometry or direct UV–Vis spectrophotometry [22]. The detection limits for BrO_3^- reported for UV–Vis spectrophotometric detection after its post-column conversion to tribromide ion Br_3^- were in the low-µg l^{-1} range [19,20]. However, these methods possess a substantial drawback, because simultaneous detection of other common anions is not possible. Recently, a simple conductometric detection of bromate after chromatographic separation using a new separation column was reported [23].

Coupling of IC with ICP-MS for the detection and quantification of bromine species was investigated by several authors [10–17]. Different approaches were used to enable method detection limits (MDLs) for Br^- and/or BrO_3^- in the low-µg l^{-1} range. Creed et al. reported a MDL for bromate of 0.1–0.2 µg l^{-1}

after a pre-concentration of 1.8 ml of sample on a Dionex AG10 column and an additional four-fold improvement of the MDL by implementing preconcentration and an ultrasonic nebulizer [10]. On the other hand, Nowak and Seubert obtained low MDLs by using a custom-made high-capacity ion exchanger and a large injection volume of 885 µl [11]. Recently, Creed and Brockhoff applied isotope dilution analysis for precise determinations of bromate with IC–ICP-MS [17].

In the present work ICP-MS was applied for the detection of BrO_3^-, Br^- and other common anions after their ion chromatographic separation on the Dionex IonPac AS12A analytical column. The work was mainly focussed towards the optimization of the IC–ICP-MS for a reliable detection (RSD<5%) of BrO_3^- and Br^- at a bromine concentration level of 1.0 µg l^{-1} with 50 µl sample injection volume. The optimized IC–ICP-MS conditions for the determination of bromide and bromate were tested also for the simultaneous detection of chlorite (ClO_2^-), chloride (Cl^-), chlorate (ClO_3^-), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), selenite (SeO_3^{2-}), selenate (SeO_4^{2-}) and arsenate (AsO_4^{3-}).

2. Experimental

2.1. Reagents

The reagents used in this study were of analytical-reagent grade from Fluka (Buchs, Switzerland), Merck (Darmstadt, Germany) or LOBA Feinchemie (Fischamend, Austria). Deionized water with a specific resistance of 18.2 MΩ cm (Milli-Q Plus system, Millipore, Bedford, MA, USA) was used for preparing the solutions. All standard stock solutions (except chloride) were prepared daily.

The standard stock solutions of bromate and bromide containing 1.000 g l^{-1} of bromine were prepared by dissolving 188.9 mg of $NaBrO_3$ (Fluka Art. No. 71325) and 128.8 mg of NaBr (Fluka Art. No. 71330) in 100 ml of water, respectively. The chlorite, chloride and chlorate standard stock solutions containing 1.000 g l^{-1} of chlorine were prepared by dissolving 255.1 mg of $NaClO_2$ (Fluka Art. No. 71388), 164.9 mg of NaCl (Merck Art. No.

6404), and 300.3 mg of $NaClO_3$ (Fluka Art. No. 71368) in 100 ml of water, respectively. The standard stock solutions of sulfate and phosphate containing 1.000 g l^{-1} of sulfur and 1.000 g l^{-1} of phosphorous were prepared by dissolving 442.9 mg of Na_2SO_4 (LOBA Art. No. 71768) and 387.4 mg of NaH_2PO_4 (Fluka Art. No. 71496) in 100 ml of water, respectively. The standard stock solutions of arsenate, selenite and selenate containing 1.000 g l^{-1} of arsenic and 1.000 g l^{-1} of selenium were prepared by dissolving 416.5 mg of $Na_2HAsO_4 \cdot 7H_2O$ (Merck Art. No. 6284), 219.0 mg of Na_2SeO_3 (Fluka Art. No. 71950), and 239.3 mg of Na_2SeO_4 (Fluka Art. No. 71947) in 100 ml of water, respectively.

The eluent ammonium carbonate stock solution with 1.10 mol l^{-1} was prepared by dissolving 12.55 g of $(NH_4)_2CO_3 H_2O$ (Fluka Art. No. 9698) in 100 ml of water. Working eluent solution (11.0 mM of total carbonate species, pH 11.2) was prepared by mixing 10 ml of eluent stock solution with 110 ml of conc. ammonia solution (25% NH_3, Suprapur, Merck Art. No. 1.05428) and dilution to 1 l with water. The modified eluent solutions were prepared as the working eluent solution with an appropriate addition of CH_3OH (Fluka Art. No. 65543).

2.2. Chromatographic conditions

A Hewlett-Packard HP1100 liquid chromatography module equipped with a Dionex (Sunnyvale, CA, USA) IonPac AG12A (4 mm) guard column and IonPac AS12A (4 mm) separation column was used. The samples were injected using an HP1100 autosampler (injection volume was 50 μl). The eluent flow-rate was 2.0 ml min^{-1}. The outlet of the separation column was directly connected to the ultrasonic nebulizer equipped with membrane desolvator. The data were evaluated with the Hewlett-Packard chromatographic software and with Microcal Origin (Microcal Software, USA) software package.

2.3. ICP-MS system

The HP4500 ICP-MS (Hewlett-Packard, Waldbronn, Germany), which served as an element-specific detector, was equipped with an ultrasonic nebulizer and a membrane desolvator U-6000AT$^+$

(CETAC Technologies, Omaha, NE, USA). On its way to the plasma, the aerosol produced by the vibration of the membrane was first heated (140°C), afterwards cooled (0°C), and finally directed to the membrane desolvator. The heating parameter of the membrane desolvator was set to 150°C and the sweep gas (argon) flow-rate adjusted to 2.0 l min^{-1}. The ICP-MS detector was tuned with a 100 μg l^{-1} Br^- solution. The operating parameters were adjusted by monitoring the bromine isotope ^{79}Br with the sampling time of 0.1 s. The optimum operating conditions producing the highest signal intensity for ^{79}Br (4.4 10^4 counts per second per 1 μg l^{-1} Br^-) were: radio frequency (RF) power 1230 W, reflected power <2 W, plasma gas 14.8 l min^{-1}, auxiliary gas 0.93 l min^{-1}, carrier gas 0.57 l min^{-1}, blend gas (argon) 0.15 l min^{-1}. Other inorganic anions ClO_2^-, Cl^-, ClO_3^-, SO_4^{2-}, PO_4^{3-}, SeO_3^{2-}, SeO_4^{2-}, and AsO_4^{3-} were monitored at $m/z=35$, 34, 31, 78 and 75 for chlorine, sulfur, phosphor, selenium and arsenic, respectively.

3. Results and discussion

Direct comparison of the MDLs reported in the literature is troubled due to the different approaches. It is therefore plausible to compare the detection limits for direct sample injection (DL) in order to allow direct comparison of the analytical systems used. The reported DLs were re-calculated on an element basis for the 50 μl sample injection to be able to compare the results also with the analytical performance of the system used in our work. The MDLs and the DLs are summarized in Table 1. It can be seen that detection limits (sample injection volume 50 μl, calculated on bromine basis) below 1.0 μg l^{-1} for BrO_3^- and Br^- have not been readily achieved.

Bromine has a high first ionization potential (11.84 eV) [24]. Its incomplete ionization in the argon plasma (less than 5%) [25] leads to higher detection limits compared to the fully ionized elements. Thus a reliable detection of low-μg l^{-1} or sub-μg l^{-1} concentrations of bromine species with ICP-MS after chromatographic separation is difficult to achieve (without including a preconcentration step) (Table 1). The detection of both bromine

Table 1
Comparison of BrO_3^- and Br^- MDLs and calculated DLs as reported in the literature

Ref.	BrO_3^-		Br^-	
	MDL (ng l^{-1})	DL*[f] (μg l^{-1} Br)	MDL (ng l^{-1})	DL*[f] (μg l^{-1} Br)
[10]	100–200[a]	3.2	NA[g]	NA
	50[b]			
[11]	50–65[c]	0.6	NA	NA
[12]	–	1.7	NA	NA
[13]	–	31	–	50
[14]	–	0.8	–	2.0
[15]	450[d]	1.4	440[d]	2.2
[16]	70[d]	44	80[d]	80
[17]	300[e]	2.2	NA	NA

[a] 1.8 ml sample pre-concentrated on a Dionex AG10.

[b] 1.8 ml sample pre-concentrated on a Dionex AG10 with an ultrasonic nebulizer.

[c] Laboratory-made high-capacity ion exchanger with a sample injection volume of 885 μl.

[d] Sample injection volume of 500 μl.

[e] Sample injection volume of 580 μl.

[f] DL*=MDL normalized for a direct 50 μl sample injection.

[g] NA=Not analyzed.

isotopes ^{81}Br (49.463% relative abundance) and ^{79}Br (50.537%) is additionally troubled by the interference of argon species $^{40}Ar_2^1H^+$ and $^{40}Ar^{38}Ar^1H^+$. The interference of argon species at $m/z=79$ is substantially lower than at $m/z=81$ due to the much lower relative abundance of ^{38}Ar (0.063% relative abundance) compared to ^{40}Ar (99.600%). Thus the ^{79}Br isotope is usually chosen.

3.1. Selection of a mobile phase

Mobile phases containing sodium salts are not desirable when ICP-MS is employed as element-specific chromatographic detector, because a constant sodium ion input changes the plasma conditions and additionally leads to clogging of the cone orifices. These problems can be avoided by either employment of an anionic membrane suppressor after the separation column for the removal of sodium ions prior to the ICP-MS detector or by using eluents in which sodium is replaced by ammonium. Ammonium containing eluents are easily converted to volatile compounds during the passage through the high temperature region of the plasma. Thus, the 10.5 m*M* Na_2CO_3–0.5 m*M* $NaHCO_3$ (pH 11.2) suggested by the column manufacturer [26] was replaced by an aqueous ammonium carbonate solution (11.0 mmol l^{-1} CO_3^{2-}). In order to obtain the

CO_3^{2-}/HCO_3^- ratio of the eluent suggested by the column manufacturer and thus similar chromatographic separation performance, the pH of the 11.0 mmol l^{-1} ammonium carbonate solution was adjusted with $NH_{3(aq)}$ to 11.2.

3.2. Optimization of the IC–ICP-MS system

The optimization procedure of the IC–ICP-MS system was directed towards a reliable detection of BrO_3^- and Br^- at a bromine concentration level of 1.0 μg l^{-1} with 50 μl sample injection volume (equal to absolute detection of 50 pg of bromine). By the term "reliable detection" acquisition of chromatographic peaks for bromine species with a signal-to-noise ratio (S/N) above 3 (based on peak heights) was considered. Two approaches were investigated for the improvement of the ICP-MS detection of bromine species. The first approach utilizes modification of the mobile phase composition by adding a small quantity of organic modifier and the second uses the increased efficiency of an ultrasonic nebulizer in combination with the first approach.

Ion chromatographic separation of bromine species with the selected 11.0 m*M* $(NH_4)_2CO_3$ (pH 11.2) as the mobile phase and the ICP-MS detector equipped with a standard Babington type nebulizer served as a starting point of the optimization pro-

cedure. The separation column was connected to the Babington nebulizer with a 70 cm polyether ether ketone (PEEK) tubing (I.D.=0.13 mm). The mobile phase composition was changed by adding small quantities of CH_3OH to the mobile phase in order to enhance the ionization of bromine species in the argon plasma. Such an approach was shown to result in a higher detection response and thus lower detection limits [27]. The calibration curves for BrO_3^- and Br^- were recorded in the range from 50 to 200 $\mu g\ l^{-1}$ of bromine for each individual experiment after tuning of the ICP-MS detector with a mobile phase matched solution containing 100 $\mu g\ l^{-1}\ Br^-$. The dependence of the slope of the calibration curves, i.e., detection response, on CH_3OH concentration is presented in Fig. 1.

The highest detector response for BrO_3^- and Br^- was obtained with the mobile phase containing 3% (v/v) of CH_3OH. However, in spite of higher detection response a reliable detection of BrO_3^- and Br^- at a bromine concentration level of 1.0 $\mu g\ l^{-1}$ with the modified mobile phase was not achieved

due to the influence of high effluent ammonia content on the argon plasma resulting in a relatively high background noise (8.3% RSD) and thus low S/N ratio. The lowest bromine concentration level for a reliable detection of BrO_3^- and Br^- using the first approach was 3.0 $\mu g\ l^{-1}\ Br$.

The second approach to obtain lower detection limits was performed by employing an ultrasonic nebulizer, which excels with a higher nebulization efficiency than the Babington type nebulizer and should therefore lead to lower detection limits. The aerosol formed in the ultrasonic nebulizer was passed through the membrane desolvator to reduce high ammonia input to the argon plasma. To obtain optimum operating conditions argon blend gas had to be added after the membrane desolvator. In this way the signal stability obtained for the 100 $\mu g\ l^{-1}\ Br^-$ tuning solution was 1.2%. It should be mentioned that the addition of 3% CH_3OH to the mobile phase decreased the detector response when the ultrasonic nebulizer together with the membrane desolvator was used. Therefore, 11 mM $(NH_4)_2CO_3$ (pH 11.2)
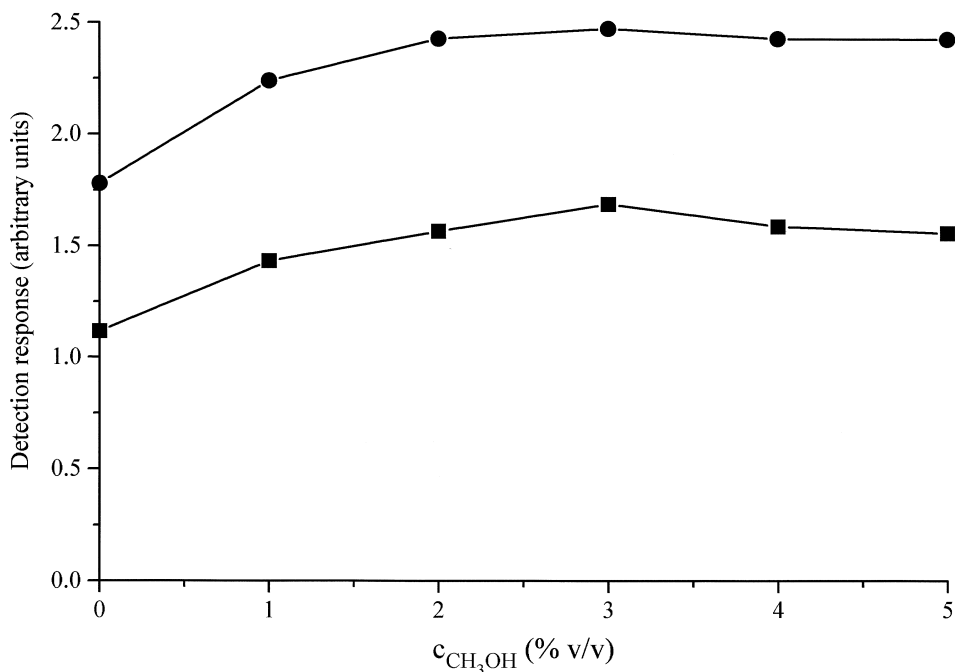

Fig. 1. Dependence of the ICP-MS detection response for bromine-containing anions on the CH_3OH concentration (%, v/v) in 11 mM $(NH_4)_2CO_3$ eluent solution (■ BrO_3^-, ● Br^-). Column, Dionex AS12A; flow-rate, 2.0 ml min^{-1}; injection volume, 50 μl; concentration of bromine anions, 10 $\mu g\ l^{-1}\ Br$; nebulizer, Babington type.

without any CH_3OH was used in all further experiments. The calibrations graphs for BrO_3^- and Br^-, plotted as peak area vs. bromine concentration, were linear in the range from 1.0 to 1000 $\mu g\ l^{-1}$ for each bromine species. The chromatogram of a standard solution of BrO_3^- and Br^- containing 1.0 $\mu g\ l^{-1}$ of bromine of both bromine-containing anions using optimum operating conditions is shown in Fig. 2.

On the basis of a set of data points obtained after ion chromatographic analysis of a blank solution (Milli-Q water) the average baseline count number N_{base} (solid line, Fig. 2) and standard deviation s were calculated (data points at the void volume were excluded). It can be seen from Fig. 2 that both BrO_3^- and Br^- chromatographic peaks at a bromine concentration of 1.0 $\mu g\ l^{-1}$ are significantly higher than the $N_{base}+3s$ level (dotted line). The signal-to-noise (S/N) ratios (based on peak heights) for BrO_3^- and Br^- (Fig. 2) were 10.8 and 8.9, respectively. The detection limits (sample injection volume 50 μl) obtained were 0.42 $\mu g\ l^{-1}$ Br for BrO_3^- and 0.47 $\mu g\ l^{-1}$ Br for Br^-, what corresponds to the absolute detection limits of 21 pg and 23 pg, respectively. The

detection limits for Br^- and BrO_3^- obtained in this work are among the lowest published so far (see Table 1). It should be mentioned that with the chromatographic conditions used in this work the analysis is finished in 4 min, which is two times faster than that reported by Heitkemper et al. [14] and an important advantage when a large number of samples has to be analyzed.

3.3. Simultaneous separation of other inorganic anions

The optimized chromatographic conditions together with the for detection of bromine containing anions optimized ICP-MS, were additionally investigated for the simultaneous separation and detection of several inorganic anions (BrO_3^-, Br^-, ClO_2^-, Cl^-, ClO_3^-, SO_4^{2-}, PO_4^{3-}, SeO_3^{2-}, SeO_4^{2-} and AsO_4^{3-}). The mentioned anions were monitored at $m/z=79$, 35, 34, 31, 78 and 75 for bromine, chlorine, sulfur, phosphor, selenium and arsenic, respectively. A total ion count chromatogram for a standard solution containing mentioned anions is presented in Fig. 3.
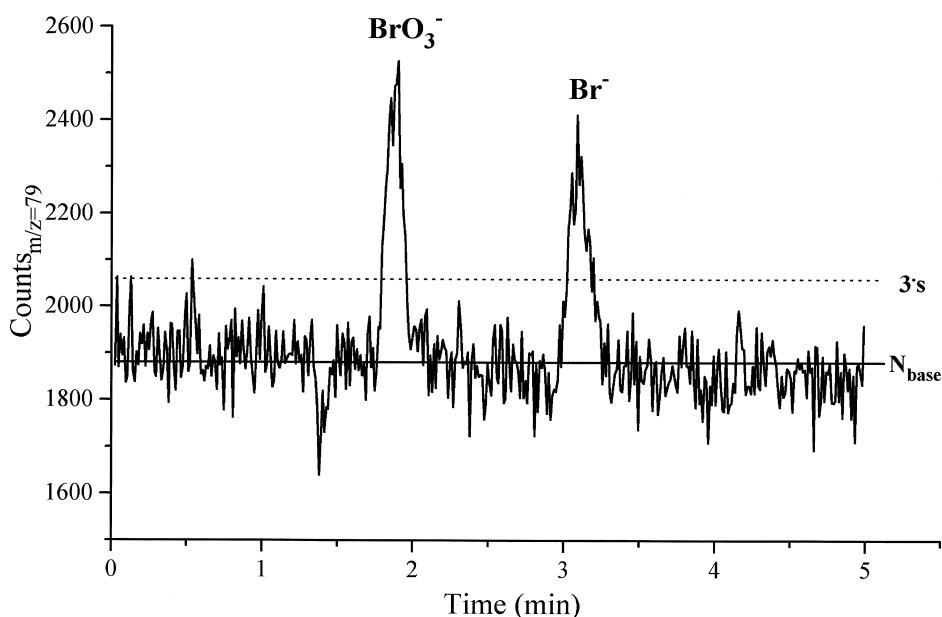

Fig. 2. Chromatogram of a standard solution of BrO_3^- and Br^- containing 1.0 $\mu g\ l^{-1}$ Br of each bromine species obtained using optimum operating conditions. Eluent: 11 mM $(NH_4)_2CO_3$; column, Dionex AS12A; flow-rate, 2.0 ml min^{-1}; injection volume, 50 μl; nebulizer, ultrasonic with membrane desolvator.
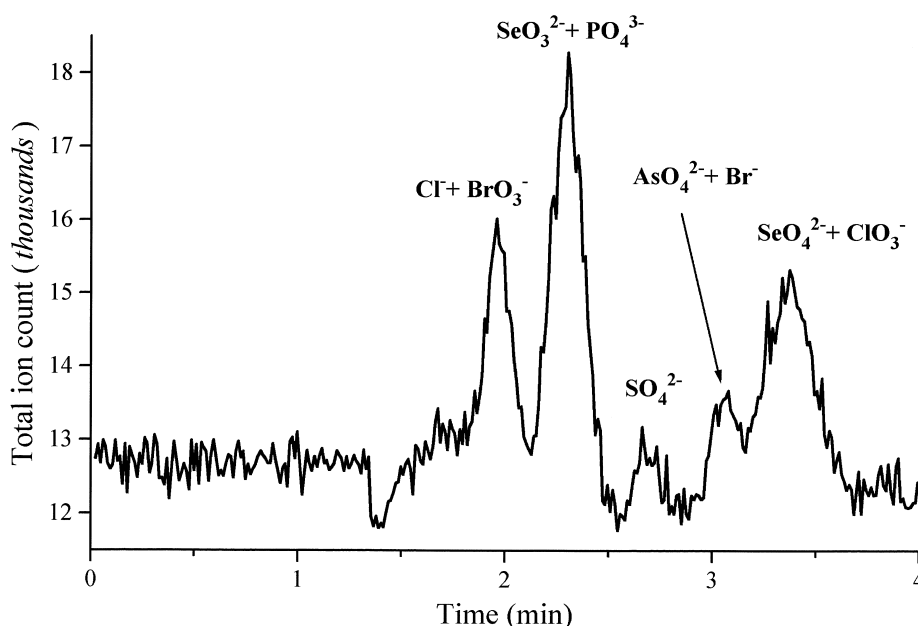
Fig. 3. A total ion count chromatogram for a standard solution containing BrO_3^- and Br^- (each 1.0 µg l^{-1} Br), ClO_2^-, Cl^- and ClO_3^- (each 50 µg l^{-1} Cl), SO_4^{2-} (20 µg l^{-1} S), PO_4^{3-} (20 µg l^{-1} P), SeO_3^{2-} and SeO_4^{2-} (each 1 µg l^{-1} Se), and AsO_4^{3-} (1 µg l^{-1} As) at optimum IC–ICP-MS operating conditions. Eluent: 11 mM (NH$_4$)$_2$CO$_3$; column, Dionex AS12A; flow-rate, 2.0 ml min^{-1}; injection volume, 50 µl; nebulizer, ultrasonic with membrane desolvator.

Instead of 10 individual chromatographic peaks only five can be observed (Fig. 3). Such a chromatogram resembles a theoretical situation, which would be obtained with an equally sensitive detector, but a non-selective one. However, when ICP-MS is used as an element-specific chromatographic detector, the chromatographic separation between different anions is not a prerequisite for their detection, as long as anions containing the same monitored element (for example BrO_3^- and Br^-) are well separated. The extracted chromatograms from the total ion count chromatogram for m/z=79, 35, 34, 31, 78 and 75 are shown in Fig. 4.

The calibration curves (plotted as peak area vs. concentration of the monitored element) were linear (r^2>0.999) in a range from 10.0 µg l^{-1} to 1000 µg l^{-1} for ClO_2^-, Cl^-, ClO_3^-, SO_4^{2-} and PO_4^{3-}, and in a range from 1.0 µg l^{-1} to 10.0 µg l^{-1} for SeO_3^{2-}, SeO_4^{2-} and AsO_4^{3-}. Wider linear responses can be expected but were not investigated in this work. The detection limits calculated on the anion basis (sample injection volume 50 µl) were 69 µg l^{-1}, 4.0 µg l^{-1},

47 µg l^{-1}, 13 µg l^{-1}, 36 µg l^{-1}, 0.4 µg l^{-1}, 0.3 µg l^{-1}, and 0.4 µg l^{-1} for ClO_2^-, Cl^-, ClO_3^-, SO_4^{2-}, PO_4^{3-}, SeO_3^{2-}, SeO_4^{2-} and AsO_4^{3-}.

4. Conclusions

One of the main advantages of the element-specific ICP-MS detector coupled to IC is that the chromatographic separation of the analyte ions is not a prerequisite for their detection. Coupling of the Dionex IonPac AS12A analytical column with an ICP-MS as element-specific detector allowed the determination of halogen and oxyhalogen anions, sulfate, phosphate, selenite, selenate and arsenate with an aqueous 11.0 mM (NH$_4$)$_2$CO$_3$ solution at pH 11.2 (adjusted with aqueous ammonia) as an eluent in less than 4 min. The detection limits (S/N= 3, sample injection volume 50 µl), obtained with IC–ICP-MS after the optimization for the highest bromine detection response, were below 1.0 µg l^{-1}

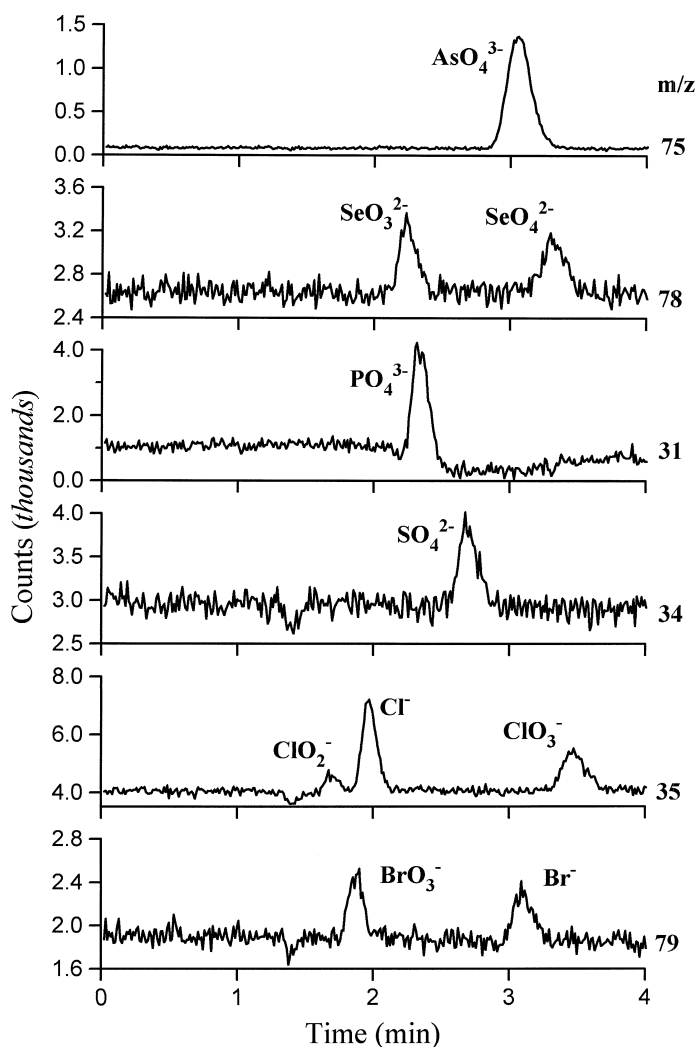Fig. 4. Chromatograms of individual monitored elements for a standard solution of BrO_3^-, Br^-, ClO_2^-, Cl^-, ClO_3^-, SO_4^{2-}, PO_4^{3-}, SeO_3^{2-}, SeO_4^{2-} and AsO_4^{3-} (anion concentrations as in Fig. 3). Eluent: 11 mM $(NH_4)_2CO_3$; column, Dionex AS12A; flow-rate, 2.0 ml min^{-1}; injection volume, 50 μl; nebulizer, ultrasonic with membrane desolvator.

for BrO_3^-, Br^-, SeO_3^{2-}, SeO_4^{2-} and AsO_4^{3-}, below 10 μg l^{-1} for Cl^- and below 100 μg l^{-1} for ClO_2^-, ClO_3^-, SO_4^{2-} and PO_4^{3-}. The detection limits obtained for bromide and bromate are low enough for the practical employment of the described chromatographic set-up in any framework of monitoring of drinking water quality. Finally, it should be mentioned that the MDL of this method can be substantially reduced if larger injection volumes and/or preconcentration step are used.

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