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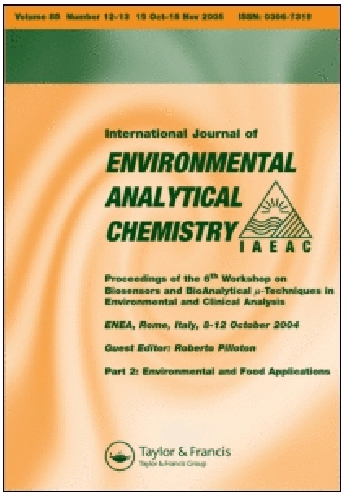

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Optimizing Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry for Speciation Analysis of Arsenic, Chromium and Bromine in Water Samples

Mari Pantsar-kallio[a]; Pentti K. G. Manninen[b]
[a] Department of Ecological and Environmental Sciences, University of Helsinki, Lahti, Finland [b] Lahti Research Laboratory, Lahti, Finland

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OPTIMIZING ION CHROMATOGRAPHY-INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR SPECIATION ANALYSIS OF ARSENIC, CHROMIUM AND BROMINE IN WATER SAMPLES

MARI PANTSAR-KALLIO[a]* and PENTTI K.G. MANNINEN[b]

[a]*University of Helsinki, Department of Ecological and Environmental Sciences, Lahti, Finland and* [b]*Lahti Research Laboratory, Lahti, Finland*

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Inductively coupled plasma mass spectrometry (ICP-MS) was coupled as a multielement detector for ion chromatography (IC) in analysis of chromium, arsenic and bromine species. The efforts were focused on selecting instrumental and operating conditions suitable for IC-ICP-MS. The choice of the eluent for IC was found to be critical. Ammonium buffer and nitric acid were suitable eluents since they did not cause polyatomic interferences or salt deposition on the cone orifices of ICP-MS. Cationic and anionic species could be analyzed simultaneously by coupled column IC-ICP-MS constructed by coupling anion and cation columns in series. This system was applied for speciation of chromium. A method for simultaneous analysis of toxic arsenic and chromium species was developed. Also an on-line preconcentration method allowing extremely low detection limits for bromine species is introduced. By using 5 mL injection volumes bromate and bromide could be analyzed at 0.2 $\mu g\ L^{-1}$ level.

Keywords: Speciation; arsenic; chromium; bromine

INTRODUCTION

To obtain information about the real properties of environmental samples, analytical methods capable of measuring the concentrations of elements in their different physicochemical forms (speciation analysis) are needed. According to IUPAC the term speciation analysis is defined as measurement of the quantities of one or more invividual specific form of a chemical element defined as to molecular, complex, electronic or nuclear structure in a sample. The challenge of

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* Corresponding author. Fax: +358-3-89220289. E-mail: mari.pantsar-kallio@helsinki.fi

speciation analysis is considerable since typically even the total concentrations of the elements in the environment are low. In addition to the need for extreme sensitivity, major problems lie in the potential changes in the elemental forms during sample preparation or analysis.

Hyphenated techniques applying chromatographic separation and element selective detection have proven to be powerful tools in speciation studies.[1–7] The species to be analysed are often in ionized forms, and therefore ion chromatography (IC) is a sensible choice for their separation.[1–2] In addition, also reversed phase chromatography allows separation of ions when complexing eluents are used or complexation of the analytes is applied before analysis.[3–4]

In our research we coupled ICP-MS as a multielement detector for IC. The efforts were focused on selecting instrumental and operating conditions suitable for IC-ICP-MS, so that the analysis times could be kept reasonable and the performance and stability of ICP-MS could be kept constant during analyses. By using hyphenated techniques the eluent must be profitable for separating the analytes and also for the detection technique applied. Salt solutions in high concentrations, and especially the alkaline metals cause salt deposition on cone orifices of ICP-MS thus affecting the sampling process and decreasing the sensitivity.[8] Under optimised conditions, IC-ICP-MS offered the separation power of IC and extremely low detection limits, multielement capability and selectivity of ICP-MS.

Speciation of arsenic has been of particular interest, because arsenic is widely distributed in the environment, and the different chemical forms of arsenic exhibit wide-ranging levels of toxicity. Arsenite [As(III)] is the most toxic form of the water-soluble species of arsenic, and a suspected human carcinogen. Arsenate [As(V)] is also relatively toxic; while the methylated forms, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are much less toxic. Arsenobetaine (AB) and arsenocholine (AC), for example, are non-toxic.[9–10] Chromium can also exist in different forms in the environment with different toxicities; Cr(VI) is very toxic and potentially carcinogenic, while Cr(III) is essential for glucose and lipid metabolism of mammals.[11–12]

In Finland compounds of chromium (Cr_2O_3) and arsenic (As_2O_5) have widely been used in wood impregnant solutions and other industrial processes resulting in hundreds of contaminated soils. Soil contamination always posses a risk for contaminating the ground and surface waters, and therefore a single method for determination of the most toxic arsenic and chromium species, As(III), As(V) and Cr(VI) in water samples, is needed. In our research we utilised IC-ICP-MS with anion column for simultaneous determination of these species.

Similar technique was applied also for analysis of bromine species. Bromate can be formed in drinking waters during the disinfecting processes of raw waters,

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especially during ozonation. It's carcinogenic properties were reported in 1990 and thereafter the analysis of bromate has gained interest.[13] Speciation of bromine is challenging because extremely high sensitivity is needed with detection limits of low μg L^{-1}-level. This is difficult to achieve without any preconcentration. Normally the detection limits by IC are in the range of 5 –10 μg L^{-1} which are not sufficient for drinking water analysis. In this paper an on-line preconcentration technique applying large injection volumes (5 mL) is presented for analysis of bromate and bromide in drinking waters.

Many elements like chromium can exist as both anions and cations in the environment. Simultaneous speciation of anionic and cationic chromium species by conventional ion chromatographic methods is difficult because colloidal species or species forming polyatomic interferences in ICP-MS can elute in the void volume through anion and cation exchange columns. Therefore it was important to retain both species: Cr(III) and Cr(VI) in the column before detection. In our research a coupled column system consisting of an anion exchange column and a cation exchange column was used for separating Cr(III) and Cr(VI).[14]

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EXPERIMENTAL

Ion chromatography

The pump for ion chromatography was a dual piston reciprocating gradient pump of PEEK material (Pharmacia LKB, model 2249, Pharmacia Biotech, Uppsala, Sweden) equipped with a Rheodyne-type syringe-loading injector with 0.25 mL or 0.5 mL loop. Waters IC-Pak A HC (150 × 4.6 mm, 10 μm) and IC-Pak A (50 × 4.6 mm, 10 μm) anion columns having trimethyl ammonium functionalized groups on polymethacrylate (Waters Chromatography Division, Millipore Corporation, Milford, MA, USA) were used for separating the anionic species. The cation column used was Guard-Pak CM/D (5 x 3.9 mm, 5 μm) having sulphonic acid groups on polybutadiene maleic anhydride silica. IC was coupled to ICP-MS using 50 cm of 0.5 mm I.D. Teflon capillary tubing.

20 mmol L^{-1} NH_4NO_3 (pro analysi grade, E. Merck, Darmstadt, Germany) adjusted to pH 10.0 with NH_3 was used as mobile phase at flow rate 2 mL min^{-1} for separating AB, As(III), As(V), DMA, MMA and Cr(VI). For analysis of bromine species 10 mmol L^{-1} NH_4NO_3 (2 mL min^{-1}) proved to be effective eluent.

Nitric acid gradient (supra-pure grade, J.T.Baker, Phillipsburg, NJ, USA) was used for coupled column IC to separate both anions and cations. Eluents were filtered through a 0.45 μm filter before use and degassed with sonication. Also the samples were filtered through a 0.45 μm filter before injection into IC.

Inductively coupled plasma mass spectrometry

The ICP-MS instrument was a Fisons Plasma Quad PQ II+ (VG Elemental, Winsford, UK) with a V-groove nebulizer, a Scott-type spray chamber and a Fassel-type quartz torch. The ICP-MS operating conditions are presented in Table I. The peak integration was done manually by measuring the raw counts of the peak heights. Single ion monitoring (SIM) with 1000 ms dwell time was used for speciation of bromine at m/z 79 and for speciation of chromium at m/z 52. Time Resolved programme (TRA) in peak jumping mode with dwell time of 250 ms was applied for simultaneous speciation of toxic arsenic (m/z 75) and chromium species (m/z 52). The possible drift in sensitivity of the instrument was monitored with 10 μg $L^{-1}$of In (in 1 % HNO_3) at the end of each analysis.

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TABLE I Typical ICP-MS instrumental parameters used in speciation studies

Parameter	*Value*
RF Power, W	1350
Cool gas flow rate, L min^{-1}	13.5
Intermediate gas flow rate, L min^{-1}	0.90
Nebulizer gas flow rate, L min^{-1}	0.85
Spray chamber temperature, °C	4
Dwell time per m/z, ms	250–1000 ms

Reagents and procedures

Standard solutions of As(III), As(V), DMA, Cr(III), Cr(VI), Br^- and BrO_3^- were prepared from arsenic trioxide (E. Merck, Darmstadt, Germany), sodium arsenate, cacodylic acid sodium salt (Fluka Chemica, Buchs, Switzerland), chromium nitrate, sodium chromate, potassium bromide and potassium bromate (E. Merck, Darmstadt, Germany), respectively. MMA was obtained from Oulu Occupational Health Research Institute, Finland, and both AB and AC from the Pasteur Institute, France. High purity water was from the Milli-Q water purification system (Millipore, Milford, USA).

The calibrants of bromide were verified using IC-MIX2–100 certified reference material (Spex Industries, USA) at concentration of 5 μg L^{-1}. For verifying the speciation of arsenic and chromium in-house reference materials containing 5 μg L^{-1} of As(V), As(III), Cr(III) and Cr(VI) were prepared from arsenic(V) oxide (9939 Titrisol, Merck), sodium meta-arsenite (Riedel de Haën, Germany) chromium chloride (9948 Titrisol, Merck) and potassium chromate (Merck), respectively. The calibrations were accepted if the concentrations of the reference materials were within 20 % accuracy level.

The samples for simultaneous analysis of toxic arsenic and chromium species were each passed through a Sep-pak cartridges (Waters Accell™ Plus CM, Waters Chromatography Division, Millipore Corporation, Milford, MA, USA) before injection into the IC column to eliminate the cationic species AC and Cr(III).

On-line preconcentration of bromine species

Bromide and bromate were concentrated in the analytical column by pumping 5 mL of sample into the column with gradient pump at flow rate of 2 mL min^{-1}. After 2.5 minutes the gradient program was turned to pump 10 mmol L^{-1} NH_4NO_3 to elute the concentrated species from the column to the ICP-MS.

RESULTS AND DISCUSSION

Much attention was paid for selecting eluents suitable for IC-ICP-MS. Solutions with alkaline salts as counterions have often been used as eluents for IC. $Na^+$and K^+, however, even in mmol L^{-1}-level cause salt deposition on the cones orifices of the ICP-MS which affects the sampling process decreasing the sensitivity and repeatability. In this paper three methods used in speciation studies in our laboratory are presented: 1. a speciation method for chromium by coupled column IC-ICP-MS, 2. a method for simultaneous speciation of toxic chromium and arsenic species and 3. a speciation method for bromine utilising large injection volumes. The ICP-MS parameters for all these methods are presented in Table I and ion chromatographic conditions in Table II. The schematic figure for IC-ICP-MS used in studies is presented in Figure 1.

Speciation of chromium by coupled column IC-ICP-MS

The coupled column IC (Figure 1) was constructed by coupling a cation column in series with an anion column to retain both the anionic Cr(VI) and cationic Cr(III). Nitric acid gradient (0–40 mmol L^{-1}) was used to elute the species.

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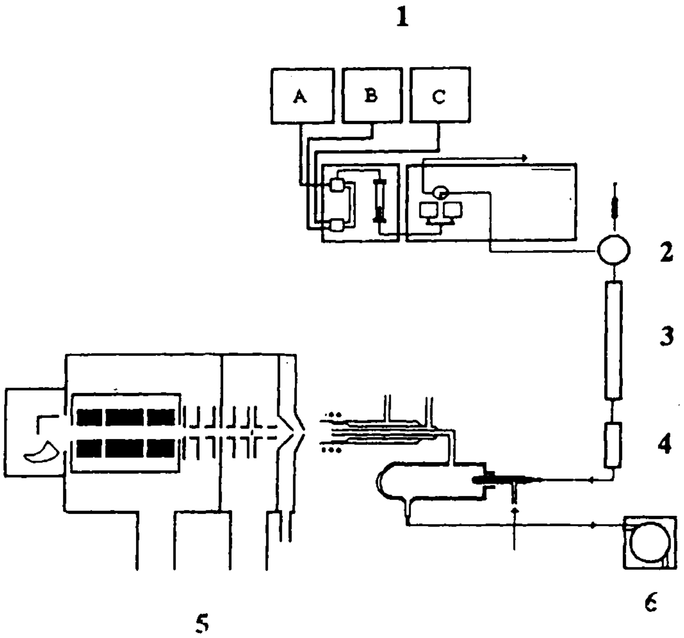

FIGURE 1 The schematic figure of the coupled column IC-ICP-MS used for speciation of chromium. 1. Gradient pump, 2. injector, 3. anion column, 4. cation column, 5. ICP-MS, 6. peristaltic pump. For simultaneous analysis of arsenic and chromium species and for analysis of bromine species the coupled column system was replaced with an anion column

Nitric acid was found to be excellent solvent for IC-ICP-MS, because it did not cause any polyatomic interferences or increase of the baseline since all the elements present in HNO_3 exist in high concentrations in the air. Also no salt deposition on the cone orifices of the ICP-MS took place, but the eluent rather cleaned the instrument during the analysis. The changes in flowrate (in the range 0.5–2.0 mL min^{-1}) did not affect the performance of the ICP-MS. The flowrate of 2 mL min^{-1} was used to get sharp zones and shorter analysis times for the analytes. Using 0–40 mmol $L^{-1}HNO_3$ gradient chromium species could be analyzed in 10 minutes. Carbonate ions in the sample, which can cause polyatomic interferences m/z 52 eluted in the void volume and thus did not interfere the analysis. The chromatogram for speciation of chromium in a lake water sample is presented in Figure 2. Details for the method are described elsewhere.[14] The method has been applied for analysis of chromium species in drinking waters, lake waters and waste waters. The detection limits for the method are presented in Table II.

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TABLE II Ion chromatographic conditions used for different methods

Speciation method	*Column*	*Elution*	*Detection limits (6 σ- criterion)injection volume*
Cr(III), Cr(VI)	Anion (IC-Pak A) and cation column (Guard-Pak CM/D) in series	Gradient 0–40 mmol L^{-1}	Cr(III) 0.3 μg L^{-1}
		HNO_3	Cr(VI) 0.5 μg L^{-1}
			inj. 0.5 mL
As(III), As(V), MMA, DMA, AB, Cr(VI)	Anion (IC-Pak A) HC		AB, Cr(VI) 0.3 μg L^{-1}
		Isocratic 20 mmol L^{-1}	As(III), DMA 0.4 μg L^{-1}
		NH_4NO_3, pH 10.0	MMA, As(V) 0.5 μg L^{-1}
			inj. 0.5 mL
Br^-, BrO_3^-	Anion (IC-Pak A) HC	Isocratic 10 mmol L^{-1}	Br^-, BrO_3^- 0.2 μg L^{-1}
		NH_4NO_3	inj. 5.0 mL

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Simultaneous speciation of arsenic and chromium

NH_4NO_3 proved to be effective eluent for IC-ICP-MS in the analysis of anionic species. NH_4NO_3 did not cause any salt deposition on the ICP-MS cones and no polyatomic interferences. Nitric acid, which was used as eluent for speciation of chromium by coupled column system was also tested. However, baseline separation of As(III) and DMA could not be achieved.

The eluent for simultaneous analysis of As(III), As(V), MMA, DMA, AB and Cr(VI) was 20 mmol L^{-1} NH_4NO_3 (2 ml/min) adjusted to pH 10 with NH_3. High pH was necessary because of the high pK_a (9.2) of As(III)[15]. All the five arsenic species [As(III), As(V), MMA, DMA, AB] were separated in 6 minutes. Cr(VI) retained more strongly in the anion column eluting in 9 minutes. The chromatogram at m/z 52 and 75 for simultaneous separation of As(III), As(V), MMA, DMA, AB and Cr(VI) is presented in Figure 3. The detection limits for the method are presented in Table II.

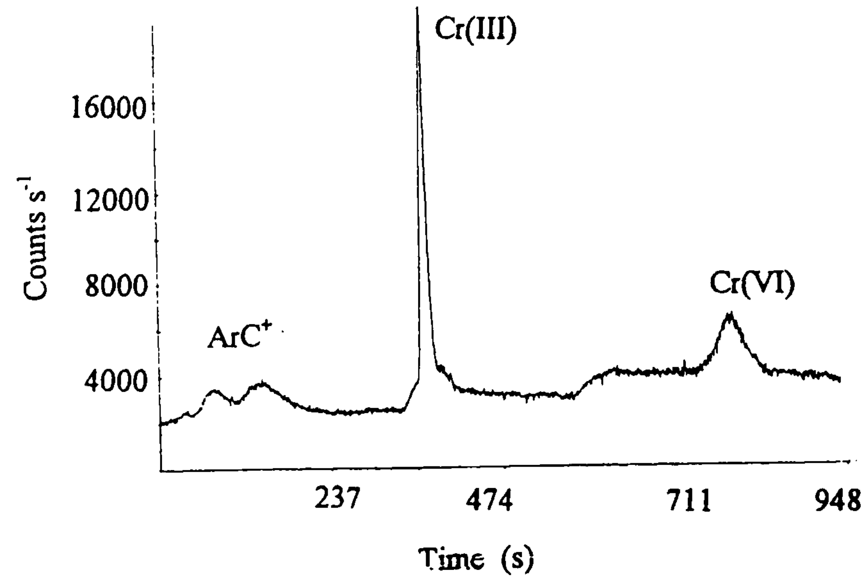

FIGURE 2 The chromatogram for separation 1 μg L^{-1} Cr(III) and 1 μg L^{-1} Cr(VI) spiked in a lake water sample. Nitric acid gradient (0–40 mmol L^{-1} HNO_3). Coupled column IC-ICP-MS; cation column in series with an anion column; flow rate 2 mL min^{-1}. The ICP-MS parameters are presented in Table I and IC parameters in Table II

Elimination of cations

Passing the samples through a cation exchange sep-pak column before analysis eliminated AC and Cr(III) in the samples.[16] This procedure did not affect the recoveries of the anionic species. Removing of cations was necessary, because Cr(III) precipitated as hydroxide at pH 10 causing disturbances in the baseline of the chromatogram at m/z 52. AC, on the other hand, co-eluted in void volume with AB. Since Cr(III) and AC are non-toxic species their analysis is often not so interesting as that of the toxic species.

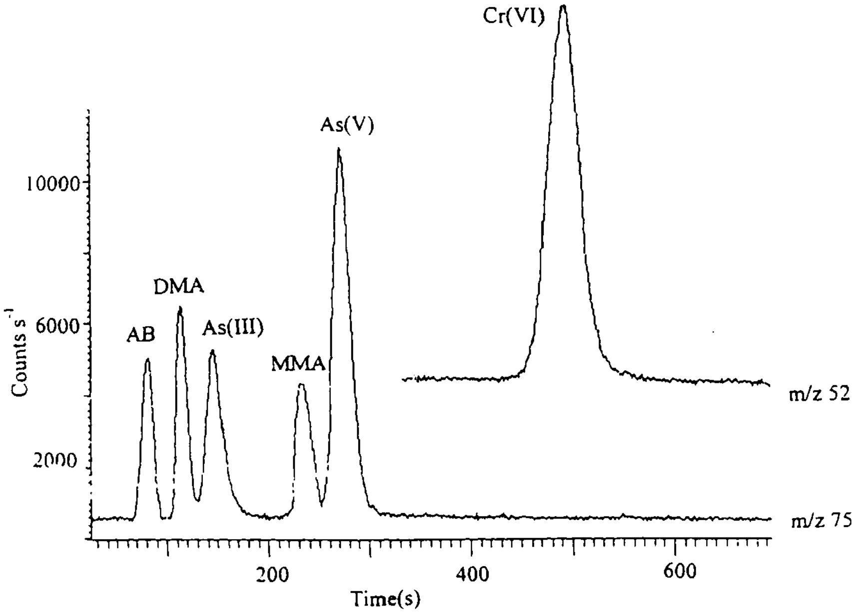

FIGURE 3 The chromatogram for simultaneous separation of 5 μg L^{-1} of As(III), MMA, DMA, AB and 10 μg L^{-1} of As(V), Cr(VI). Isocratic elution with 20 mmol L^{-1} NH_4NO_3 at pH 10.0, flow rate 2 mL min^{-1}. The ICP-MS parameters are presented in Table I and IC parameters in Table II

Polyatomic interferences

Chloride can cause polyatomic interferences at m/z 75 as $ArCl^+$ if present in high concentrations. With the proposed method even 500 mg L^{-1} of chloride in the sample did not cause any additional peaks in the chromatogram, but prevented the separation of DMA and As(III). On the other hand, this high concentration is not very likely to be present in water samples. But if the concentration of chloride is over 500 mg/l dilution of the sample is necessary.

Application of the method

The method has been applied for analysis of ground water and drill water samples and industrial effluents. Only two ground water samples studied this far have contained Cr(VI). Concentrations of Cr(VI) in these samples were only 1

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$\mu g\ L^{-1}$. In industrial effluents from galvanizing plants high concentrations of Cr(VI) (even 174 mg L^{-1}) have been measured.

Inorganic arsenic species are widely distributed in soils and ground waters in Finland. Natural arsenic concentration in soil is quite high in some areas, even 13 mg kg^{-1}.[17] Also wood impregnant industry has caused contamination in many sites. Inorganic forms As(III) and As(V) are the main species in ground waters. Some arsenic has also been present as bound species, which retain in the 0.45 μm filter. No methylated species have been observed in any of the water samples studied.

Speciation of bromide with on-line preconcentration

Recently Diemer and Heumann have reported the advantages of using off-line or on-line IC-ICP-MS for speciation of bromine.[18] Seubert and Nowak presented a self-made high capasity anion exchange column for analysis of bromate by IC-ICP-MS. They used large injection volumes up to 2 mL and obtained detection limits below 0.100 $\mu g\ L^{-1}$, which this far are the lowest reported in literature for bromate.[19]

We have applied an on-line preconcentration (with 1–5 mL injection volume) IC-ICP-MS for analysis of both bromate and bromide in drinking waters. The instrumentation consisted of a commercial high capasity anion exchange column coupled on-line with ICP-MS. 10 mmol L^{-1} NH_4NO_3 was found to be effective eluent. Eluent with potassium as counter ion can not even be used in the analysis of bromine by ICP-MS, because ArK^+ causes polyatomic interferences at bromine isotope 79. This isotope had lower background signal than 81 and was preferred for the analysis.

Detection limits

Analysis of low concentrations of bromine by ICP-MS is difficult, because bromine has poor detection limits due to its low degree of ionization in the argon plasma.[20] In the analysis of arsenic and chromium, for example, detection limits below $\mu g\ L^{-1}$ -level can easily be achieved with even 0.25 mL injection volume. For bromine the detection limit under these conditions was 10 $\mu g\ L^{-1}$ and preconcentration is required. When using 5 mL injection volume with on-line concentration into the analytical column the detection limits obtained for both bromide and bromate were 0.2 $\mu g\ L^{-1}$ which are usually sufficient for drinking water analysis. The analysis time including concentration was 15 minutes.

Interferences

The possible interference of other anions present in high concentrations was tested for chloride and sulphate. No interferences were observed even with

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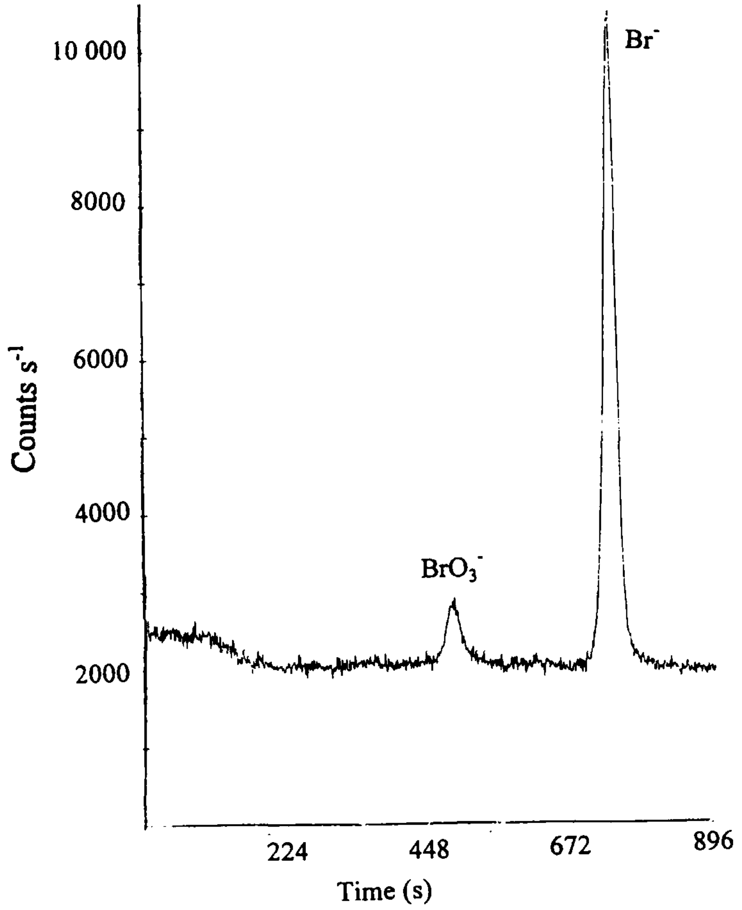

FIGURE 4 The chromatogram for separation of Br$^-$ (3.4 μg L^{-1}) and BrO$_3^-$ (0.3 μg L^{-1}) in a drinking water sample. Isocratic elution with 10 mmol L^{-1} NH$_4$NO$_3$; flow rate 2 mL min^{-1}. The ICP-MS parameters are presented in Table I and IC parameters in Table II

50 mg L^{-1} chloride and 50 mg L^{-1} sulphate. Also no polyatomic interferences caused by ArK$^+$, at bromine isotope 79 were observed.

Applications

The chromatogram for analysis of drinking water is presented in Figure 4. The method has been applied for routine analysis of water samples, for example for analyzing 26 samples collected before and after disinfecting by ozonation.

Bromate was found in only one raw water at concentration of 0.2 μg L^{-1} while the disinfected water samples contained 0.2 μg L^{-1}- 1 μg L^{-1} of bromate. Also total concentrations of bromine increased during disinfecting probably due to bromine impurities in chlorine reagents used in the processes. The concentrations of bromide, however, were decreased. This indicates that bromide converts also other bromine species in addition to bromate during disinfecting.

CONCLUSIONS

IC-ICP-MS proved to be effective technique for speciation of chromium, arsenic and bromine. The coupled column IC-ICP-MS was developed for simultaneous analysis of both anionic and cationic chromium species. The system can also be applied for analysis of cations and anions of other elements. HNO_3 and NH_4NO_3 were suitable eluents for IC-ICP-MS, since they did not cause polyatomic interferences or salt deposition on the cone orifices of ICP-MS. Anion column with NH_4NO_3 could be used for speciation on bromine and for simultaneous speciation of toxic arsenic and chromium species. The detection limits of bromide and bromate were low enough for drinking water analysis by utilizing on-line preconcentration. Similar preconcentration technique can also be used for concentrating Cr(VI) in an anion column before detection. The detection limits (0.5 μg L^{-1}) for Cr(VI), however, are in most cases low enough for drinking water analysis without any precencentration. For analysis of As(III), on the other hand, large injection volumes can not be applied because As(III) has a pK_a value of 9.2 and is not concentrated in the column at pH lower than this.

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References

1. S.H. Hansen, E.H. Larsen, G. Pritzl and C. Cornett, *J. Anal. Atom. Spectrom.* **7** 629–635 (1992).
2. D. Beauchemin, K.W.M. Siu, J.W. McLaren and S.S Berman *J. Anal. Atom. Spectrom.* **4** 285–289 (1989).
3. P. Thomas and K. Sniatecki, *Fresenius J. Anal Chem.* **351** 410–414 (1995).
4. J.J. Thompson and R.S. Houk, *Anal Chem.* **58** 2541–2546 (1986).
5. H. Ding, J. Wang, J.G. Dorsey and J.A. Caruso, *J. Chromatogr. A* **694** 425–431 (1995).
6. R. Lobinski, *Appl. Spectroscopy* **51** 260A-278A (1997).
7. G.K. Zoorob, J.W. McKiernan and J.A. Caruso, *Mikrochim. Acta* **128** 145–168 (1998).
8. D.J. Douglas and L.A. Kerr, *J. Anal. Atom. Spectrom.* **3** 749–752 (1988).

9. J.P. Buchet and R. Lauwerys, in: *Analytical Techniques for Heavy Metals in Biological Fluids* (S. Facchetti, Ed.,, Elsevier, Amsterdam, 1983) pp. 75.
10. A. Léonard, in: *Metals and Their Compounds in the Environment* (E. Merian Ed., VCH, Weinheim, 1991) pp. 751.
11. S.K. Tandon, D.K. Saxena, J.S. Gaur and S.V. Chandra, *Environ. Res.* **15** 90–98 (1978).
12. S. Langård and T. Norseth, in: *Handbook on the Toxicology of Metals* (C. Friberg, G. Nordberg, and V. Vouk, Eds, Elsevier, Amsterdam, 1979) pp. 383.
13. Y. Kurokawa, A. Maekawa, M. Takahashi and Y. Hayashi, *Environ. Health Perspect.* **87** 309–335 (1990).
14. M. Pantsar-Kallio and P.K.G Manninen, *Anal. Chim. Acta* **318** 335–341 (1996).
15. D.R. Lide, (Ed) in: *Handbook of Chemistry and Physics*, (CRC Press, Boca Raton, Florida, 996–1997) 72th ed.
16. M. Pantsar-Kallio and P.K.G. Manninen, *J. Chromatogr. A.*, **779** 139–146 (1997).
17. The Geochemical Atlas of Finland, Part 2, (Geological Survay of Finland, Espoo 1992).
18. J. Diemer and K.G. Heumann, *Fresenius J. Anal. Chem.* **357** 74–79 (1995).
19. A. Seubert and M. Nowak, *Fresenius J. Anal. Chem.* **360** 777–780 (1998).
20. K.E. Jarvis, A.L. Gray and R.S. Houk, *Handbook of Inductively Coupled Plasma mass Spectrometry* (Blackie & Son Ltd. New York, 1992) pp. 248.

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