ELSEVIER

Journal of Chromatography A, 912 (2001) 319–327

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Simultaneous determination of arsenic species and chromium(VI) by high-performance liquid chromatography–inductively coupled plasma-mass spectrometry

A.F. Roig-Navarro*, Y. Martinez-Bravo, F.J. López, F. Hernández

Universitat Jaume I, Analytical Chemistry, Experimental Sciences Department, Campus de Riu Sec. ESTCE, 12071 Castello, Spain

Received 16 May 2000; received in revised form 5 January 2001; accepted 15 January 2001

Abstract

The simultaneous determination of As(III), As(V), monomethylarsenic acid (MMA), dimethylarsinic acid (DMA) and Cr(VI) in fresh water has been carried out by coupling an anion-exchange column to an inductively coupled plasma-mass spectrometer. Optimisation of chromatographic conditions led to baseline separation of signals from the five species in approximately 9 min using gradient elution. Detection limits were 0.02–0.05 μg As l^{-1} and 5.5 μg Cr l^{-1}. Repeatability was 2–3% for arsenic species and higher, i.e., 8%, for Cr(VI) due to the higher background for this species. Arsenic species and hexavalent chromium stability in surface water samples was evaluated, and storage conditions were set to 1 day at 4°C in polyethylene flasks (without acidification) in order to avoid As(III)–As(V) conversions. The method was applied to the analysis of surface water.

Keywords: Arsenic; Chromium(VI)

1. Introduction

Several metals are introduced into the environment from natural sources and anthropogenic activity. Many of them, such as arsenic and chromium, undergo chemical transformations in the environment, and their physical and chemical properties, toxicity, mobility and biotransformation, are controlled to a large extent by their physicochemical form. When assessing the hazards of such elements, there is a need for analytical methods that can discriminate between their different chemical forms [1].

Arsenic is widely used in industry and agriculture; as a consequence, anthropogenic emissions greatly exceed natural levels. Speciation of arsenic is of particular interest: whereas arsenite [As(III)] is the most toxic form of the water-soluble species and arsenate [As(V)] is also relatively toxic, the methylated forms, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA), are much less toxic. More complex forms as arsenobetaine (AB) and arsenocholine are considered non-toxic [2,3].

Chromium finds its way into the environment through a variety of industrial wastes. The speciation of chromium has significant importance in the case of environmental samples, because Cr(III) is an

*Corresponding author.

E-mail address: roig@exp.uji.es (A.F. Roig-Navarro).

0021-9673/01/$ – see front matter
PII: S0021-9673(01)00572-6

essential micronutrient for mammals, while Cr(VI) is poisonous to aquatic plants and animal and human life [4,5].

Gas and liquid chromatography (and capillary electrophoresis) coupled to different spectrometric detection systems are generally used for the separation of organometallic species. Numerous papers about As speciation in a large variety of samples, including fresh and sea waters [6,7], sediments and soils [8,9], plants [10], marine organisms [11] and body fluids [12] have been reported. Chromium speciation has been studied mainly in waste water [13,14], solid matrices [15] and industrial wastes [5,16].

The most promising approach for arsenic speciation seems to be the combination of ion chromatography or reversed phase liquid chromatography (LC) on-line hydride generation-atomic adsorption spectrometry (AAS), inductively coupled plasma (ICP)-Atomic emission spectrometry (AES) or, more recently, inductively coupled plasma-mass spectrometry (ICP-MS). Anion-exchange chromatography is the most popular separation technique because of the widely varying first pK_a values of arsenic species [17,18]. Usual methods for Cr(III) and Cr(VI) speciation involve the use of reversed-phase LC, with ion pair creating reagents [19], and ion chromatography with chelating agents [20]. A few studies on Cr speciation use LC without complexing or ion pairing creating agents [21,22].

One of the main benefits of ICP-MS is that it allows multielemental analysis. However, there are few studies on multielemental speciation, probably due to analytical difficulties related to chromatographic separation. Studies on the simultaneous arsenic and selenium [23,24] and arsenic and chromium [25] speciation have been reported, but there is a general lack of information on this subject. The aim of this work is to develop a method for the simultaneous determination of As(III), DMA, MMA, As(V) and Cr(VI) in fresh water, using anion-exchange chromatography hyphenated to ICP-MS. The method has been applied to the analysis of surface water.

2. Experimental

2.1. Instrumentation

The HPLC system consisted of a Hewlett-Packard 1100 (Hewlett-Packard, Waldbronn, Germany) quaternary pump and an autoinjector with 100-μl sample loop. The separations were performed on an ION 120 (Interaction Chromatography, Mountain View, CA, USA) anion-exchange column (120×4.6 mm, 10 μm) and a Hamilton PRP-X100 (Hamilton, Reno, NV, USA) anion-exchange column (250×4.1 mm, 10 μm).

The HPLC column was connected via 35 cm of PEEK capillary tubing (0.178 mm, I.D.) to a Babington Nebulizer. A Hewlett-Packard 4500 (Yokogawa Analytical Systems, Tokyo, Japan) instrument was used in this work and operational conditions are summarised in Table 1. For data acquisition of HPLC–ICP-MS, the ''time resolved analysis'' mode was used. For the tuning of ICP-MS, previous to each run, a solution containing 10 μg/l of Li, Y, Ce

Table 1
ICP-MS Operational conditions

Instrument	HP 4500
Radio frequency forward power	1250 w
Plasma gas-flow	Ar 15 l min^{-1}
Auxiliary gas-flow	Ar 1 l min^{-1}
Nebulizer gas-flow	Ar 1.15 l min^{-1}
Blend gas	Ar 0 l min^{-1}
Sample depth	7.8 mm
Monitoring mass (TRA)	m/z 75, 53, 35
Integration time/mass	0.5 s
Detector	electron multiplier (voltage 1750 V)
Spray chamber	2°C
Sample introduction flow-rate	1 ml min^{-1}

and Tl was first monitored at m/z 89; the ion intensity was optimised; the ratios of masses $^{156}CeO/^{140}Ce$ and $^{70}Ce^{2+}/^{140}Ce$ maintained; then the oxide ions and doubly charged ions minimised. Finally, resolution and mass axis were optimised monitoring m/z ^{7}Li, ^{89}Y and ^{205}Tl.

The $^{40}Ar^{35}Cl^{+}$ interference on $^{75}As^{+}$ was checked by monitoring of m/z 35. ^{35}Cl gave a chromatographic peak which did not affected arsenic speciation in any of the studied conditions.

2.2. Standards and reagents

K_2CrO_4 (p.a. Merck, Darmstad, Germany), $Na_2CH_3AsO_3 \cdot 6H_2O$ (p.a. Carlo Erba, Milano, Italy), $NaAsO_2$ (p.a. Fluka, Buchs, Switzerland), $Na_2HAsO_4 \cdot 7H_2O$ (p.a. Fluka) and $Na(CH_3)_2AsO_2 \cdot 3H_2O$ (Biochemika, Fluka). Stock solutions of the arsenic and chromium compounds containing about 1000 mg l^{-1} As or Cr, were prepared in water and kept at 4°C. Appropriate dilution by weight of the stock solutions with pure water were prepared fresh daily to the adequate arsenic or chromium compounds concentration. Cr(VI) was the only species of chromium analysed due to its toxicity and in order to avoid the use of the chelating agents needed to avoid Cr(III) precipitation inside the column.

The mobile phases used carbonate buffers prepared from NH_4HCO_3 (Biochemika, Fluka) and phosphate buffers from $NH_4H_2PO_4$ (p.a. Merk). Methanol (HPLC reagent, J.T. Baker, Deventer, The Netherlands) was added yielding 2%. The pH value was adjusted by addition of NH_3 (Trace Selected, Fluka). These solutions were filtered through a 0.45-μm membrane.

Surface water samples from several places from the Castelló and València Provinces (Spain) were analysed. Samples were kept in polyethylene flasks at 4°C and filtered through a 0.45-μm membrane before injection.

All the solutions were prepared with nanopure (Barnstead, Newton, MA, USA) (18.2 MΩ cm) water.

2.3. Recommended procedure

Samples collected in polyethylene bottles were filtered through a 0.45-μm membrane and stored at 4°C without acidification. The analysis was carried out during the 24 h after the collection of the samples.

The water sample was injected into the chromatographic system through a 100-μl loop. The separation was achieved by step gradient of a NH_4HCO_3 based mobile phase at pH 8.0 at 1 ml min^{-1} (see Fig. 4), and the quantitation was carried out by external calibration.

In this way, As(III), DMA, MMA and As(V) and Cr(VI) could be satisfactorily analysed in less than 13 min (including 4 min of reequilibration time).

3. Results and discussion

3.1. Chromatographic separation

To obtain the baseline separation of As(III), As(V), DMA, MMA, and Cr(VI) with a single column, two different types of anion-exchange columns were evaluated, and two mobile phases using gradient elution with increasing buffer ion strength were tested at different pH values. A chromatographic study scheme is showed in Fig. 1.

Using an ION 120 column, arsenic species separation was accomplished satisfactorily for the two mobile phases (NH_4HCO_3 and $NH_4H_2PO_4$). However, at the lower pH values tested (pH 8.0 for NH_4HCO_3 and pH 6.0 for $NH_4H_2PO_4$) As(III) — with a pK_a value of 9.2 — was not retained and eluted with void volume. The rest of the species were eluted in the same sequence — DMA, MMA, As(V) — although the total time for each chromatogram was slightly lower with the carbonate buffer rather than with the phosphate buffer.

With $NH_4H_2PO_4$ as the mobile phase, whichever pH was used, or with NH_4HCO_3 at pH 8, Cr(VI) did not elute after 1 h of pumping the more concentrated mobile phase through. Only when the mobile phase was NH_4HCO_3 at pH 10.3, was Cr(VI) resolved and the analysis of arsenic and chromium species completed in less than 16 min using the step gradients showed in Fig. 2.

When the Hamilton PRP-X100 column was used, the phosphate mobile phase could not elute Cr(VI) whichever pH value was used, although the best separation for the arsenic species was obtained at pH

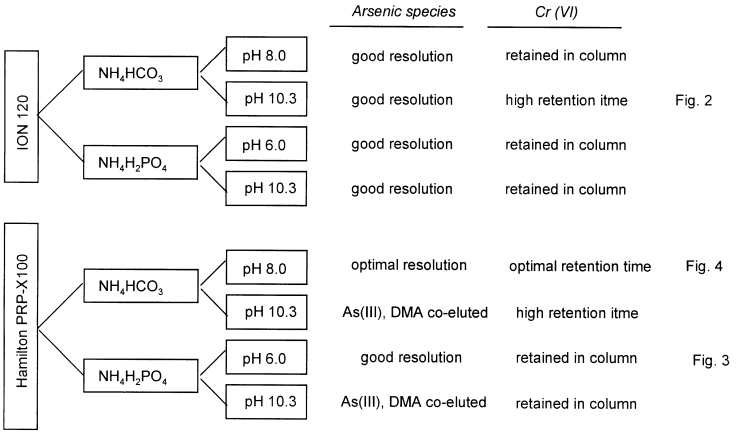
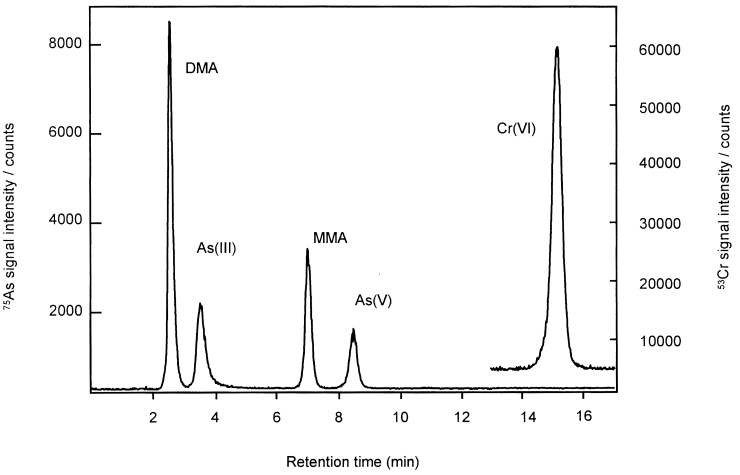


Fig. 1. Scheme of the chromatographic separation study.

6, with a total time for the chromatogram of 7 min (Fig. 3).

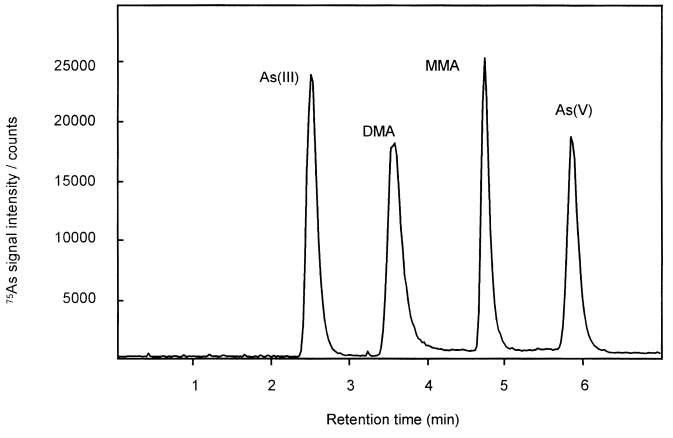
When the NH_4HCO_3 was used as the mobile phase at pH 8.0, arsenic and Cr(VI) speciation was achieved successfully with the Hamilton PRP-X100 column. The concentration gradient was optimized and the analysis was completed within 9 min (Fig. 4). The column was re-equilibrated for 4 min with (4 m*M*) NH_4HCO_3 before the next injection. These chromatographic conditions were accepted as optimal for As(III), DMA, MMA, As(V), and Cr(VI) speciation, and were chosen for the next experiments. As it can be seen in Fig. 4, the mobile phase selected does not allow the analysis of Cr(VI) at



Gradient program

t (min)	0.0	3.0	3.1	8.1	8.2	15.2	15.3	20.3
% A	100	100	75	75	0	0	100	100
% B	0	0	25	25	100	100	0	0

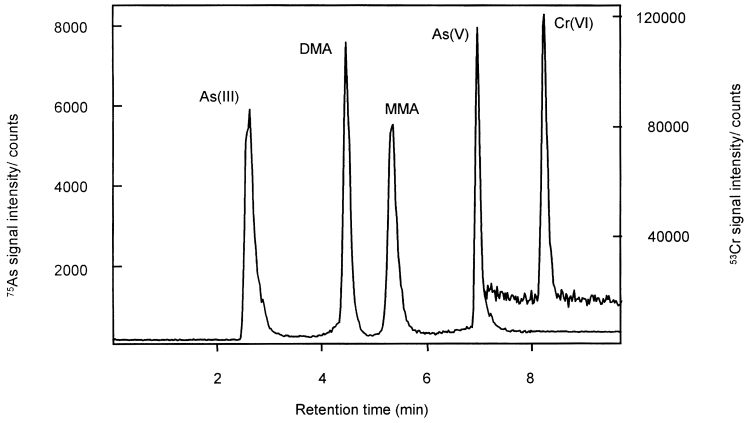
Fig. 2. HPLC–ICP-MS chromatogram of a standard mixture obtained with the ION 120 column. The concentrations were DMA=5 μg l^{-1}, As(III)=1 μg l^{-1}, MMA=2 μg l^{-1}, As(V)=0.3 μg l^{-1} (as As) and Cr(VI)=200 μg Cr l^{-1}. Mobile phase A: 4 m*M* NH_4HCO_3, 2% methanol (pH 10.3); B: 0.3 *M* NH_4HCO_3, 2% methanol (pH 10.3).



Gradient program

t (min)	0.0	1.0	1.1	6.0	6.5	10.0
% A	100	100	0	0	100	100
% B	0	0	100	100	0	0

Fig. 3. HPLC–ICP-MS chromatogram of a standard mixture obtained with the Hamilton PRP-X100 column. Concentration for all arsenic species was As(III), DMA, MMA, As(V)=13 μg l^{-1} (as As). Mobile phase A: 10 m*M* $NH_4H_2PO_4$, 2% methanol (pH 6.0); B: 100 m*M* $NH_4H_2PO_4$, 2% methanol (pH 6.0).



Gradient program

t (min)	0.0	0.5	3.0	4.0	9.0	9.5	13.0
% A	100	75	75	0	0	100	100
% B	0	25	25	100	100	0	0

Fig. 4. HPLC–ICP-MS chromatogram of a standard mixture obtained with the Hamilton PRP-X100 column. Concentrations for all arsenic species was 3.4 μg l^{-1} (as As) and 200 μg l^{-1} for Cr(VI). Mobile phase A: 4 m*M* NH_4HCO_3, 2% methanol (pH 8.0); B: 0.3 *M* NH_4HCO_3, 2% methanol (pH 8.0).

such a low concentration levels as those of the arsenic species, possibly due to the polyatomic interference associated to the ICP-MS analysis of Cr (ArC^+ at m/z 52 and 53) which increased the background noise for this element.

3.2. Analytical performance characteristics

As a first step, the linearity and matrix effects were checked in some fresh waters. The slopes obtained for normal calibrations were compared with those of standard additions. The concentration range studied was 0.05–1000 μg l^{-1} As for arsenic species and 20–1000 μg l^{-1} Cr for Cr(VI). The results indicated good linearity (r=0.999) and minor matrix effects in these types of samples.

The detection limit, defined as three times the standard deviation (N=10), were determined in a real sample in which the concentration was near the LOD. A surface water was spiked to a final concentration of 0.1 μg l^{-1} As species and 30 μg l^{-1} Cr(VI). For arsenic species, the LOD varied from 0.018 μg l^{-1} for DMA to 0.046 μg l^{-1} for As(III). The calculated LOD for Cr(VI) was 5.5 μg l^{-1} (Table 2). For Cr(VI), the LOD was checked with one more surface water spiked to 10 μg l^{-1} (Fig. 5).

The experimental detection limits for arsenic are better than those generally obtained in other studies [6,25] and are suitable for the determination of As species in surface water. Regarding Cr(VI), the LOD is much higher than for As species as expected from the use of NH_4HCO_3 as the mobile phase. The acceptable limits for Cr(VI) in soil, waste and water differ in almost every country, and often are 11– 100 μg l^{-1} for water and 2.5 –25 mg kg^{-1} for soil [5]. In Spain, the quality criteria for waste water that could affect surface water have been recently reviewed, establishing a value of 50 μg l^{-1} for total chromium and total arsenic and 5 μg l^{-1} for Cr(VI) [26]. That is, the LOD obtained in this paper can be used to determine Cr(VI) in most fresh waters but should be improved to determine Cr(VI) in, for example, drinking water. Moreover, in a potentially polluted zone with many ceramic or tanning industries (as the Castelló Province, Spain) our method would be suitable for monitoring waste water and polluted surface water.

Other authors [25] also had difficulties with the simultaneous determination of As species and Cr(VI) at sub-ppb levels. Thus, using gradient elution with KNO_3 and decreasing pH, good resolution for As species was achieved, with LODs for As(III) and As(V) of 0.5 (about ten times higher than LODs in the present work), but a high background for Cr(VI) was observed increasing the LOD for this species to 5 μg l^{-1} (similar to the present work). Besides, a reequilibration time of 20 min was required. When more favourable conditions for Cr(VI) were used

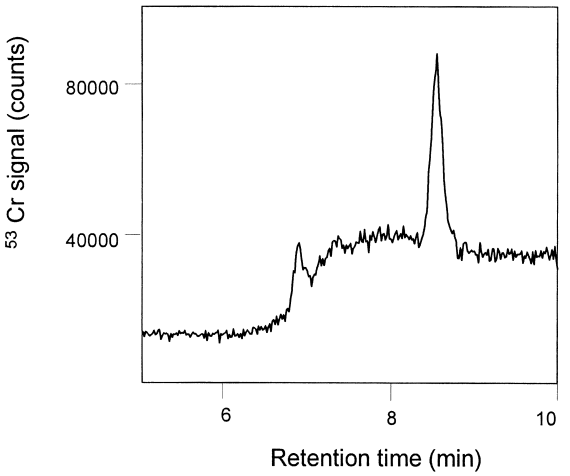


Fig. 5. Anion-exchange HPLC–ICP-MS chromatogram of 10 μg ml^{-1} of Cr(VI) spiked surface water. For experimental conditions see text.

Table 2
Repeatability (N=6), reproducibility (3 days, N=3 each day) and detection limit (N=10) for four As species and Cr(VI)[a]

Species	Repeatability (%)[b]	Reproducibility (%)[b]	Detection limit (ng l^{-1})[c]
As(III)	2.8	3.4	50
DMA	3.2	3.3	20
MMA	1.8	3.5	25
As(V)	1.9	4.9	30
Cr(VI)	7.5	5.9	5500

[a] Experiments carried out with spiked surface water.
[b] Fortification level: 5 μg l^{-1} for As species (as As) and 100 μg l^{-1} for Cr(VI).
[c] Fortification level: 0.1 μg l^{-1} for As species (as As) and 30 μg l^{-1} for Cr(VI).

(isocratic elution with KNO_3 at pH 9.8), a LOD of 0.5 μg l^{-1} was achieved for Cr(VI), but DMA and As(III) were not baseline separated and higher LODs would be expected for As species.

Repeatability and reproducibility were also determined in real-world water samples. A surface water was spiked at 5 μg l^{-1} As of each arsenic species and 100 μg l^{-1} Cr(VI). Six replicates were analysed to determine the repeatability, and additionally three samples per day were analysed in 3 different days to obtain reproducibility. The repeatability for As species, expressed as the coefficient of variation (C.V.), was below 3% and the reproducibility below 6%.

For Cr(VI), the values found were 7.5 and 5.9% for repeatability and reproducibility, respectively. These slightly higher values are a consequence of the worse LOD for Cr(VI) and the higher uncertainty due to the high background for the Cr(VI) determination.

Recovery was tested in a surface water spiked at 0.1, 0.5, 5, and 50 μg l^{-1} As of each arsenic species, and 30, 50, 100 and 500 μg l^{-1} Cr(VI). Six replicates for every one of the four concentration levels were carried out (Table 3). For all fortification levels quantitative recoveries, varying from 87 to 116%, were obtained. Coefficients of variation values were below 5% for all As species at fortification levels above 0.5 μg l^{-1}. At the lowest fortification level assayed (0.1 μg l^{-1} As), which was close to the detection limit, the C.V. exceeded above 5% as corresponded to the greater uncertainty for this low concentration.

For Cr(VI) all C.V.s were near 7% according to the higher background levels for ^{53}Cr detection. However, these values together with recoveries above 90% were regarded as satisfactory.

3.3. Stability of As(III), DMA, MMA, As(V) and Cr(VI) in water samples

The stability of chemical species in environmental or biological samples largely depends on the sample matrix. Some results published show that sample storage at 5°C seems to delay oxidation of As(III) to As(V), and that sample acidification could alter the species distribution [27,28]. In this work, five different surface waters were spiked at 5 μg l^{-1} As of each arsenic species and at 150 μg l^{-1} Cr(VI) and kept in filled polyethylene flasks at 4°C. No acidification was performed in order to prevent changes in the species distribution. The samples were filtered through a 0.45-μm membrane just before injection in the chromatographic system, and analysed periodically over 15 days using the proposed HPLC–ICP-MS multielemental method.

The recoveries for Cr(VI) over 15 days indicated that water samples can be stored in polyethylene flasks at 4°C with no significant losses of Cr(VI) (Fig. 6). Moreover, there was no decrease in total As content and no evidence of any conversion of DMA and MMA into other species over 15 days of storage. However, As(III) spontaneously underwent change to As(V), and about 10% of the As(III) originally present was oxidised after storage after only 24 h in all the samples studied. After 3 days of storage, As(III) oxidation was highly influenced by the sample matrix, and the percentage of As(III) oxi-

Table 3
Recoveries ($N=6$) for all species analyzed in surface water spiked at four fortification levels

Recovery and C.V. (%)				
Species	0.1 μg As l^{-1}	0.5 μg As l^{-1}	5 μg As l^{-1}	50 μg As l^{-1}
As(III)	110(14.6)	112(3.4)	97(2.8)	108(4.8)
DMA	114(5.4)	111(2.7)	99(3.2)	97(1.6)
MMA	99(7.9)	116(2.6)	98(1.8)	97(1.7)
As(V)	114(8.9)	88(4.0)	107(1.9)	87(7.8)
Species	30 μg Cr(VI) l^{-1}	50 μg Cr(VI) l^{-1}	100 μg Cr(VI) l^{-1}	500 μg Cr(VI) l^{-1}
Cr(VI)	92(6.4)	94(7.2)	110(7.9)	94(7.4)

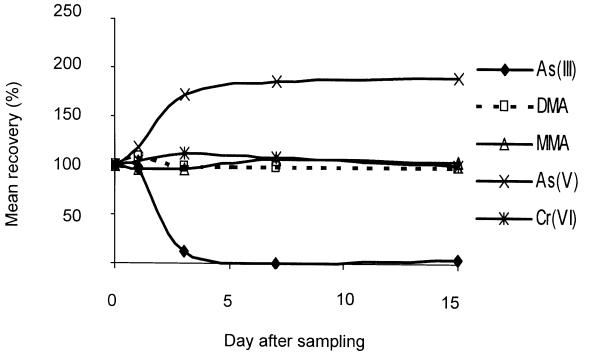


Fig. 6. Stability of As species and Cr(VI) in spiked surface water [5 μg l^{-1} for As species and 150 μg l^{-1} for Cr(VI) maintained at 4°C without acidification]. Mean recoveries for five spiked surface water samples.

dised greatly varied depending upon the sample, with values varying from 10 to 90%. As a cautionary note, sample storage was fixed in 1 day in order to avoid conversions between As(III) and As(V).

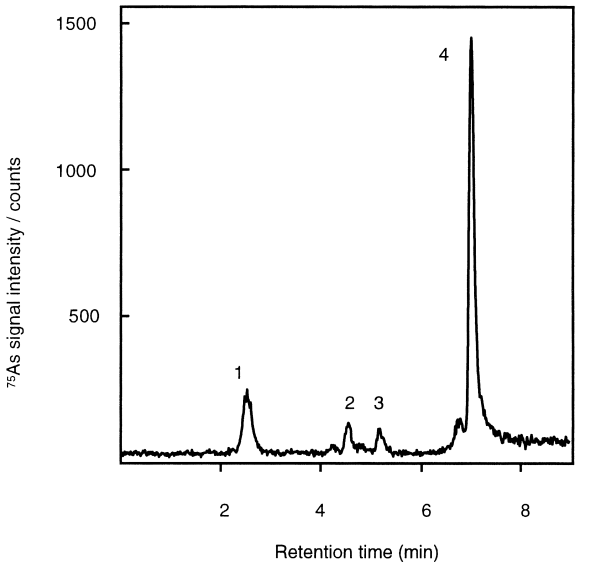


Fig. 7. Anion-exchange HPLC–ICP-MS chromatogram of a surface water sample from ''El Clot'', Castelló province (Spain). Hamilton PRP-X100 column was used and program gradient elution as in Fig. 4. Peaks were identified as 1=As(III); 2=DMA; 3=MMA; 4=As(V).

4. Application of the method to real-world water samples

The HPLC–ICP-MS recommended procedure was applied to the determination of arsenic species and Cr(VI) in 14 surface water samples from different locations of the Castelló and València provinces (Spain). As(V) was found in all of them at concentrations ranging from 0.1 to 5 μg l^{-1}, and was found to be the main compound. As(III) was detected in 11 of the samples analysed, at concentrations ranging from 0.1 to 1 μg l^{-1}. DMA and MMA were found in nine of the samples at lower concentrations than those of inorganic arsenic (between 0.02 and 0.3 μg l^{-1}, as As). As an example Fig. 7 shows the chromatogram for one of the surface water samples. Cr(VI) was not detected in any of the samples analysed.

5. Conclusions

Anion-exchange LC coupled to ICP-MS was used for the rapid determination of As(III), DMA, MMA, As(V) and Cr(VI) in water. Detection limits were lower than 50 μg l^{-1} for the arsenic species and around 5 μg l^{-1} for Cr(VI). The mobile phase selected, which used carbonate solutions, allowed the complete separation of all species in about 9 min, but it produced a baseline increase for Cr(VI) because of polyatomic interferences by ArC^{+}, which caused a higher detection limit for Cr(VI). The possible interference from argon chloride on the detection of arsenic species posed no problem; the chloride was separated chromatographically from the arsenic species, and the argon chloride signal intensity at $m/z=75$ was insignificant. Stability studies in spiked surface waters maintained at 4°C without acidification showed oxidation of As(III) to As(V), but no changes for the other species during 15 days. The maximum storage time under these conditions was set at 1 day in order to avoid changes in the sample composition.

Current research is focused at improving the LOD for Cr(VI), so that the method can be used for the simultaneous sub-ppb determination of both As species and Cr(VI).

Acknowledgements

This work was partially supported by Generalitat Valenciana through the research project GV98-02-130. ICP-MS measurements were made at the Servei Central d'Instrumentació Científica (SCIC, Jaume I University, Spain). Authors thanks Marc Vilano (Universitat de Barcelona, Spain) for providing the MMA standard.

References

[1] R. Cornelis, White paper on speciation of trace elements: challenges for chemical analysis into the 21st century, Quim. Anal. 19 (2000), Editorial.
[2] S. Caroli, F. La Torre, F. Petrucci, N. Violante, in: S. Caroli (Ed.), Element Speciation in Bioinorganic Chemistry, Wiley, 1996, Chapter 13.
[3] R. Ritsema, Environmental Applications of Hyphenated Techniques For the Speciation of Tin, Arsenic and Mercury, 1997, Thesis.
[4] D.T. Gjerde, H.C. Mehra, Ion chromatographic speciation of trace metals, in: Trace Metal Analysis and Speciation, Elsevier Science Publishers B.V, 1991, pp. 213–235, Chapter 8.
[5] J. Prokisch, S.A. Katz, B. Kovács, Z. Gyóri, J. Chromatogr. A 774 (1997) 363.
[6] Z. Mester, P. Fodor, J. Chromatogr A 756 (1996) 292.
[7] P. Bermejo-Barrera, J. Moreda-Piñeiro, A. Moreda-Piñeiro, A. Bermejo-Barrera, Anal. Chim. Acta 374 (1998) 231.
[8] P. Thomas, J.K. Finnie, J.G. Williams, J. Anal. Atom. Spectrom. 12 (1997) 1367.
[9] S.H. Hansen, E.H. Larsen, G. Pritzl, C. Cornett, J. Anal. Atom. Spectrom. 7 (1992) 629.
[10] A.R. Byrne, Z. Slejkovec, T. Stijve, L. Fay, W. Gossler, J. Gailer, K.J. Irgolic, Appl. Organomet. Chem. 9 (1995) 305.
[11] J.J. Corr, E.H. Larsen, J. Anal. Atom. Spectrom. 11 (1996) 1215.
[12] R. Ritsema, L. Dukan, T. Roig i Navarro, W. Leeuwen, N. Oliveira, P. Wolfs, E. Lebret, Appl. Organomet. Chem. 12 (1998) 591.
[13] M. Pantsar-Kallio, P.K.G. Manninen, J. Chromatogr. A 750 (1996) 89.
[14] M.J. Powell, U.W. Boomer, Anal. Chem. 67 (1995) 2474.
[15] M.J. Marqués, A. Salvador, A.E. Morales-Rubio, M. de la Guardia, Fresenius J. Anal. Chem. 362 (1998) 239.
[16] K. Vercoutere, R. Cornelis, S. Dyg, L. Mees, J.M. Christensen, K. Byrialsen, B. Aaen, P. Quevauviller, Mikrochim. Acts 123 (1996) 109.
[17] A. Woller, Z. Mester, P. Fodor, J. Anal. Atom. Spectrom. 10 (1995) 609.
[18] S. Saverwyns, X. Zhang, F. Vanhaecke, R. Cornelis, L. Moens, R. Dams, J. Anal. Atom. Spectrom. 12 (1997) 1047.
[19] C.M. Andrle, N. Jakubowski, J.A.C. Broekaert, Spectrochim. Acta 52B (1997) 189.
[20] B. Gammelgaard, O. Jons, B. Nielsen, Analyst 117 (1992) 637.
[21] J. Prokisch, B. Kovács, Z. Gyóri, J. Loch, J. Chromatogr. A 683 (1994) 253.
[22] F.A. Byrdy, L.K. Olson, N.P. Vela, J.A. Caruso, J. Chromatogr. A 712 (1995) 311.
[23] T. Guérin, A. Astruc, M. Astruc, A. Batel, M. Borsier, J. Chromatogr. Sci. 35 (1997) 213.
[24] B.P. Jackson, W.P. Miller, J. Anal. Atom. Spectrom. 13 (1998) 1107.
[25] M. Pantsar-Kallio, P.K.G. Manninen, J. Chromatogr. A 779 (1997) 139.
[26] Real Decreto 995/2000, Ministry of Environment, Spain, June 20, 2000, BOE 147.
[27] G.E.M. Hall, J.C. Pelchat, G. Gauthier, J. Anal. Atom. Spectrom. 14 (1999) 205.
[28] M.A. Palacios, M. Gómez, C. Cámara, M.A. López, Anal. Chim. Acta 340 (1997) 209.