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Multielemental determination of arsenic, selenium and chromium(VI) species in water by high-performance liquid chromatography–inductively coupled plasma mass spectrometry

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Abstract

A new method for the simultaneous chromatographic separation and determination of arsenite, arsenate, monomethylarsonic acid, dimethylarsinic acid, selenite, selenate and hexavalent chromium in water is presented. Speciation was achieved by on-line coupling of anion-exchange LC and inductively coupled plasma mass spectrometry (ICP-MS). Optimisation of the chromatographic conditions led to baseline separation of the seven species in 14 min using gradient elution with NH_4NO_3 20 m*M*, pH 8.7–NH_4NO_3 60 m*M*, pH 8.7 as mobile phase. Detection limits are in the range 40–60 ng l^{-1} for arsenic species, around 130 ng l^{-1} for Cr(VI), and higher for Se(IV) and Se(VI) (1.2 and 1.4 μg l^{-1} respectively). The method showed good accuracy and repeatability, and no interference of chloride on ^{75}As, ^{77}Se or ^{53}Cr was observed. The developed method was applied to the analysis of several environmental surface water samples.

Keywords: Water analysis; Arsenic; Selenium; Chromium(VI)

1. Introduction

Chemical speciation is an important topic of research in environmental, toxicological and analytical fields, as the toxicity, availability and reactivity of trace elements depend on the chemical form in which the element is present [1].

Arsenic has a wide range of industrial uses and, as a consequence, anthropogenic emissions greatly exceed natural levels. In surface and groundwater, dissolved arsenic is found in inorganic (arsenite and arsenate) and organic forms such as monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). It is well known that inorganic arsenic exhibits high toxicity levels, while methylated species are less toxic and arsenic compounds such as arsenobetaine and arsenocholine are considered to be non-toxic [2].

Interest in the trace determination of selenium is growing because of its dual role as an essential nutrient for humans at low concentrations and as a toxin at higher concentrations. The narrow concentration range between the two opposing effects requires accurate and precise knowledge of the selenium species present in the environment. In natural waters, selenium exists predominantly in two

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oxidation states: selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}), which are more toxic than organic species [3].

Chromium is a ubiquitous element, not only because of its occurrence in nature, but also due to the many anthropogenic sources resulting from its widespread industrial application. Analytical speciation is required because Cr(III) is essential for humans, whereas Cr(VI) is known to be carcinogenic [3]. Acceptable limits for the element in water differ in almost every country [4,5]. As a guideline, the World Health Organization recommends a maximum level of 10 μg l^{-1} for total As and total Se, and 50 μg l^{-1} for Cr(VI) in drinking water [6]. In Spain, the quality criteria for waste water that could affect surface water have recently been reviewed, establishing a value of 50 μg l^{-1} for total dissolved arsenic, 5 μg l^{-1} for Cr(VI), and 1 μg l^{-1} for dissolved selenium [7].

Hyphenated techniques, such as liquid chromatography with element-specific detection (e.g., AAS, ICP-OES or ICP-MS) are necessary for the proper identification and quantification of trace metal compounds. Ion chromatography mobile phases based on carbonate and phosphate solutions have frequently been used in arsenic speciation. In the case of selenium speciation, phosphate solutions are widely used, and give good chromatographic separations [8,9]. Although a few articles have appeared reporting the use of some of these buffers in the study of chromium, the suitability of carbonate solutions in Cr(VI) separation has been demonstrated [8]. Although good chromatographic results have been obtained using these mobile phases, the tendency of phosphate buffers to clog the sampling and skimmer ICP-MS orifices, and the possible interference of carbonate buffers ($^{40}Ar^{13}C$) with the determination of ^{53}Cr, which increases the detection limits for chromium, suggest the use of mobile phases based on alternative salts. Thus, Magnuson et al. [10] reduced the phosphate buffer concentration and added nitric acid in order to avoid clogging and maintain the ionic strength at a constant value. Pantsar-Kallio and Manninen [11] proposed the simultaneous speciation of As and Cr using a KNO_3-based mobile phase.

The use of ICP-MS detection after chromatographic separation offers excellent detection limits and multi-element capability. However, very few studies have been carried out on the simultaneous speciation of various elements. Thus, multielemental speciation analyses have been carried out by on-line coupling of ion-pair reversed-phase LC to ICP-MS [5,12] or using anion-exchange chromatography in the separation [8,11,13–16]. Guerin et al. [15] reported the simultaneous determination of eight species in standard solutions using isocratic elution with detection limits below 0.23 μg l^{-1} (as the element) for arsenic species, 1.8 μg l^{-1} for Se(IV) and Se(VI), 0.01 μg l^{-1} for Sb(V) and 0.35 μg l^{-1} for Te(VI). Gradient elution was used by Lindermann et al. [16] in the determination of arsenic, selenium and antimony species in standard solutions. Detection limits were below 0.5 μg l^{-1} for arsenic species, around 3 μg l^{-1} for inorganic selenium, and 0.14 and 1.7 μg l^{-1} for Sb(V) and Sb(III), respectively.

In a previous paper [8], we proposed the simultaneous determination of As species and Cr(VI) in environmental fresh water by anion-exchange LC coupled to ICP-MS using carbonate buffer as mobile phase. Good results were obtained for arsenic species (limits of detection around 0.05 μg l^{-1}), but Cr(VI) could only be determined at levels above 5 μg l^{-1}. The aim of this work was to improve the analytical characteristics for Cr(VI) determination and to widen the scope of the method to inorganic selenium in such a way that the method could be applied to the simultaneous determination of As(III), As(V), MMA, DMA, Se(IV), Se(VI), and Cr(VI) in fresh 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 a 100 μl sample loop. The separations were performed on 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 Babing-

ton Nebulizer. A Hewlett-Packard 4500 (Yokogawa Analytical Systems, Tokyo, Japan) instrument was used in this work and the operational conditions and gradient programme are summarized in Tables 1 and 2. For HPLC–ICP-MS data acquisition, ''time resolved analysis '' mode was used. For tuning of ICP-MS, a solution containing 10 μg l^{-1} of Li, Y, Ce and Tl was first monitored at m/z 7, 89, and 205 and the ion intensity optimized. Oxide and doubly charged ions were minimized by measuring the mass ratios $^{140}Ce^{16}O/^{140}Ce$ and $^{140}Ce^{2+}/^{140}Ce^{+}$. Resolution and mass axis were optimized by monitoring m/z ^{7}Li, ^{89}Y and ^{205}Tl.

Interference from chloride was checked by monitoring m/z 53 ($^{37}Cl^{16}O$), 75 ($^{40}Ar^{35}Cl$) and 77 ($^{40}Ar^{37}Cl$).

2.2. Standards and reagents

$NaAsO_2$ (p.a.), $Na_2HAsO_4 \cdot 7H_2O$ (p.a.), $Na(CH_3)_2AsO_2 \cdot 3H_2O$ (Biochemika), $Na_2SeO_3 \cdot 5H_2O$ (Chemika) and Na_2SeO_4 (Chemika) were from Fluka (Buchs, Switzerland), $Na_2CH_3AsO_3 \cdot 6H_2O$ (p.a.) was from Carlo Erba (Milano, Italy), and K_2CrO_4 (p.a.) was from Merck (Darmstad, Germany). Stock solutions of arsenic, selenium and chromium compounds containing about 1000 mg l^{-1} As, Se or Cr were prepared in water and maintained at 4°C. Appropriate dilutions by weight of the stock solutions with pure water were prepared daily to obtain the required concentration.

Table 2
Gradient programme

	Time (min)							
	0	1	1.5	3	3.5	10	10.5	14
% A	100	100	50	50	0	0	100	100
% B	0	0	50	50	100	100	0	0

Mobile phases were prepared from ammonium nitrate (p.a., Scharlau, Barcelona, Spain) and the pH was adjusted by the addition of NH_3 (Trace Select, Fluka). These solutions were filtered through a 0.45 μm membrane before use.

Surface water samples from several locations in Castelló and València Provinces (Spain) were analyzed. Samples were kept in polyethylene flasks at 4°C and filtered through a 0.45 μm membrane before injection [8].

All solutions were prepared with NANOpure (18.2 MΩ cm) water (Barnstead, Newlon, MA, USA).

2.3. Recommended procedure

Samples, collected in 50 ml polyethylene bottles, were stored at 4°C without acidification. Analyses were carried out within 24 h of sample collection.

The water sample was filtered through a 0.45 μm

Table 1
Optimised operational conditions for HPLC–ICP-MS

ICP-MS	*HP* 4500
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 (T.R.A.)	m/z 53, 75, 77
Integration time/mass	1 s
Detection	Electron multiplier (voltage −1750 V)
Spray chamber	2°C
HPLC	*HP* 1100
Column	Hamilton PRP-X100 (250×4 mm, 10 μm)
Flow-rate	1 ml min^{-1}
Injected volume	100 μl
Mobile phase	A: 20 m*M* NH_4NO_3, pH 8.7 with ammonia B: 60 m*M* NH_4NO_3, pH 8.7 with ammonia

membrane and then injected into the chromatographic system using a 100 μl loop. Separation is achieved by a step gradient of an NH_4NO_3-based mobile phase at pH 8.7 at 1 ml min^{-1} (see Table 1), and quantification is carried out by external calibration. In this way, As(III), As(V), MMA, DMA, Se(IV), Se(VI) and Cr(VI) can be analysed satisfactorily in 14 min, including re-equilibration time, using the instrumental conditions shown in Tables 1 and 2.

3. Results and discussion

3.1. ICP-MS measurements

High concentrations of chloride can react in the argon plasma and form $^{40}Ar^{35}Cl$ species, with m/z 75. Because arsenic is mono-isotopic and is measured at m/z 75 (^{75}As), Cl^- should be separated chromatographically from arsenic species in order to resolve the $^{40}Ar^{35}Cl$ peak from the analytes.

For the detection of selenium with ICP-MS, six selenium isotopes with natural abundances between 0.96 and 49.96% are available. However, the most abundant isotopes ^{80}Se and ^{78}Se are not accessible for evaluation because of interference from polyatomic argon, $^{40}Ar^{40}Ar$ and $^{40}Ar^{38}Ar$. The usual m/z 82 was not used because of the random presence of ^{82}Kr as a contaminant in the Ar cylinders. Therefore, the ^{77}Se isotope is a good compromise solution for selenium detection. However, the poor efficiency of selenium ionization in the plasma, together with the low isotopic abundance of the ^{77}Se isotope (7.50%), provide higher detection limits for selenium species than those obtained for arsenic and chromium species. Moreover, ^{77}Se can be subject to interference from the formation of the polyatomic species $^{40}Ar^{37}Cl$ in chloride-rich samples. Thus, chloride should also be separated from Se(IV) and Se(VI) to overcome co-elution [5,13].

Chromium was monitored at m/z 53 (^{53}Cr, abundance 9.5%) to avoid interference from $^{40}Ar^{12}C$ at ^{52}Cr (m/z 52), the most abundant isotope of chromium. However, ^{53}Cr is not free from polyatomic interference, because the species $^{37}Cl^{16}O$ can be formed in the plasma when samples with a high chloride content are analysed. Chromatographic separation between Cr(VI) and Cl^- is also required in order to avoid interference. In contrast to selenium, chromium is highly ionized in an argon plasma (>95%) and this provides good detection limits in spite of its low isotopic abundance.

During optimization of chromatographic separation, chloride elution was determined by the presence of three peaks with the same retention time at m/z 53 ($^{37}Cl^{16}O$), 75 ($^{40}Ar^{35}Cl$) and 77 ($^{40}Ar^{37}Cl$).

3.2. Chromatographic separation

3.2.1. Effect of mobile phase composition

Ammonium nitrate was chosen as the eluent in this study because it provides the ionic strength necessary to elute the analytes without the problems related to skimmer clogging and interference in analyte determination, and does not produce a decrease in ionization efficiency of the hot plasma, which is expected when Na is used as the countercation.

Although several authors have reported signal improvements for As and Se [15,17] when 3% methanol is added to the mobile phase, the formation of $^{40}Ar^{13}C$ in plasma led to a substantial degradation of the signal-to-noise ratio and higher limits of detection (LOD) for Cr(VI).

As a first step, isocratic elution was performed at pH 8.20 (adjusted with NH_3) and varying the NH_4NO_3 concentration in the mobile phase from 10 to 60 m*M*. As expected, lower concentrations of NH_4NO_3 led to longer retention times for As(V), Se(VI) and Cr(VI) (>20 min), and higher concentrations resulted in poor resolution for the less-retained species (As(III) and DMA).

Using isocratic elution, it was not feasible to achieve good baseline separation for arsenic species together with a short analysis time. Taking these considerations into account, gradient elution was examined. Thus, two mobile phases, A (20 m*M* NH_4NO_3, pH 8.2) and B (60 m*M* NH_4NO_3, pH 8.2), were used according to the following time programme: 0–2 min, 100% A; 2.0–2.9 min, linear ramp to 100% B; 2.9–9.5 min, 100% B; 9.5–10 min, linear ramp to 100% A; 10–14 min, 100% A. The first step of the gradient programme (2 min) was enough to achieve the resolution of As(III) and DMA. On increasing the ammonium nitrate con-

centration in the second mobile phase, the retention times of As(V), Se(VI) and Cr(VI) were reduced to 7.2, 8.1 and 9.4 min, respectively. The column was ready for the following injection after the last step of the gradient program (total analysis time 14 min).

3.2.2. Effect of pH

The effect of pH was examined in order to optimise the separation of the seven species examined. The chromatographic conditions of the gradient programme were applied using mobile phases with pH ranging from 7.7 to 10.2, adjusted with NH_3. In the same experiment, possible interferences from chloride were studied by adding sodium chloride to standard mixtures of the seven species with the final concentration of NaCl as high as 900 mg l^{-1}. Fig. 1 shows chromatograms obtained at different pH. The signal due to chloride elution was detected simultaneously at m/z 75 ($^{40}Ar^{35}Cl$), 77 ($^{40}Ar^{37}Cl$) and 53 ($^{37}Cl^{16}O$). It can be seen that, when the pH of the mobile phase increased, the retention time of arsenic, selenium and chromium species varied, while chloride interference was not affected.

Se(IV) was subject to interference from $^{40}Ar^{37}Cl$ at pH <8.2 and MMA was subject to interference from $^{40}Ar^{35}Cl$ at pH 8.2. However, at pH >8.7 the resolution decreased for As(III) and DMA, and for MMA and As(V). At pH >9.2, As(III) is present as an anionic compound (pK_a 9.2) and is retained by the stationary phase, resulting in the complete overlapping of arsenite and MMA at pH 10.2.

In contrast to what is expected according to the pK_a values, the retention times of As(V), Se(VI) and Cr(VI) decreased slightly when the pH increased. This behaviour was also observed for selenite and selenate by Li et al. [18] and for arsenate by Vélez et al. [19].

According to the results obtained in our study, pH 8.7 was chosen as a compromise between good peak resolution for the seven species studied and minimum chloride interference.

Finally, an intermediate step was included in order to produce a slight delay in the elution of MMA, thus avoiding partial overlapping between the $^{40}Ar^{35}Cl$ and MMA peaks. The gradient programme was modified as shown in Table 2, resulting in the chromatogram shown in Fig. 2. Baseline separation of As(III), As(V), MMA, DMA, Se(IV), Se(VI) and Cr(VI) was achieved successfully under these conditions and peaks of all species were free from chloride interference. Clearly, the MMA peak was resolved from arsenate and chloride interference.

3.2.3. Effect of ionic strength

In order to investigate whether the ionic strength of the samples affected the chromatographic separation, solutions with NaCl concentrations ranging from 150 to 900 mg l^{-1} were spiked with the seven species under investigation and analysed using the proposed conditions (Tables 1 and 2). Retention times were determined and compared with those calculated as the average of 10 replicate determinations of a standard solution free of chloride. Our results show that there were no significant variations in retention times. Only arsenate, selenium species and Cr(VI) experienced slight variations in retention times (-0.2 min) when samples containing the highest NaCl concentration tested (900 mg l^{-1}) were analysed. Baseline separation between As(V), $^{40}Ar^{35}Cl$ and MMA was achieved in all cases.

Although this test is usually employed by other authors to evaluate the effect of the ionic strength [15,17], the synthetic samples analysed do not have the same matrix as real-world surface waters. Therefore, a new experiment was performed using surface waters instead of sodium chloride solutions. Eight natural waters were spiked with a solution of As(III), As(V), MMA, DMA (4 μg l^{-1} as As), Se(IV), Se(VI) (10 μg l^{-1}) and Cr(VI) (4 μg l^{-1}), analysed in triplicate and the retention times determined. The conductivity of the water samples varied between 1057 μS and 3.34 mS. No peak broadening or significant differences in retention times were observed for any of the species. The retention times obtained in the worst situation assayed — the surface water with the highest conductivity — did not differ considerably from those obtained with standard solutions.

For the three experiments, the assayed retention time was constant to within ±2%. Therefore, the large variations in the ionic strength of the water samples did not affect the chromatographic separation, demonstrating the robustness of the method.

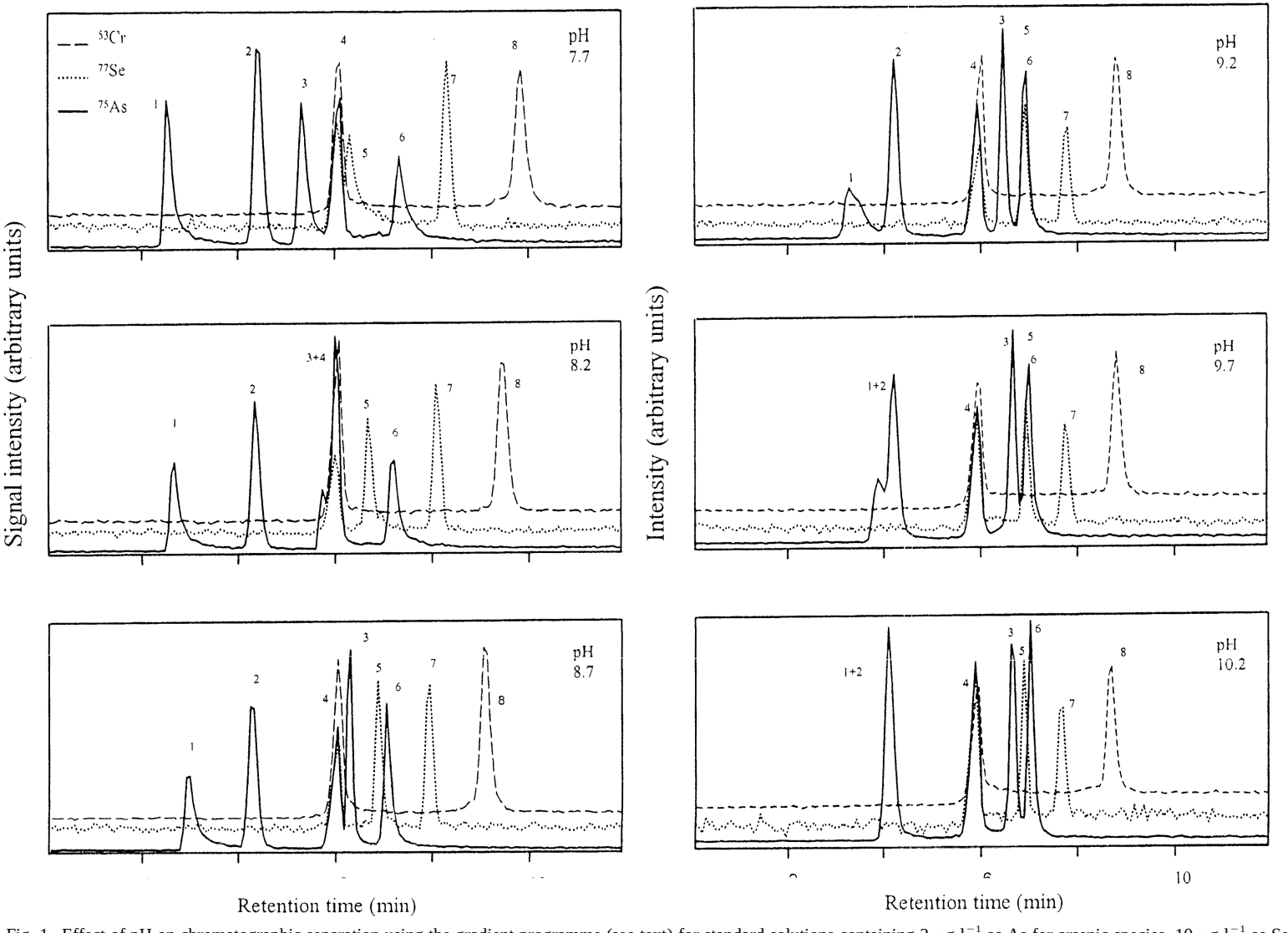

Fig. 1. Effect of pH on chromatographic separation using the gradient programme (see text) for standard solutions containing 2 μg l^{-1} as As for arsenic species, 10 μg l^{-1} as Se for selenium species, 4 μg l^{-1} Cr for Cr(VI), and 900 mg l^{-1} NaCl. Peak identification: (1) As(III), (2) DMA, (3) MMA, (4) chloride interference, (5) Se(IV), (6) As(V), (7) Se(VI), (8) Cr(VI).

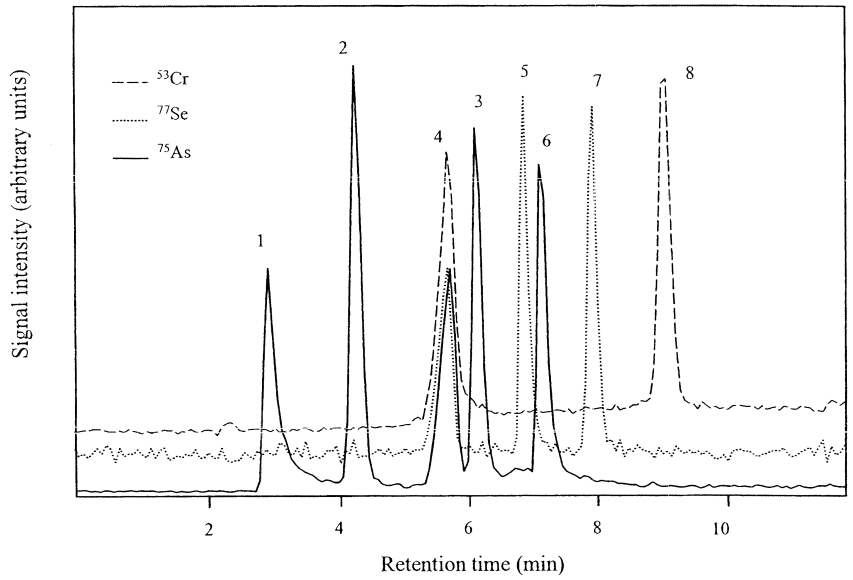

Fig. 2. Anion-exchange HPLC–ICP-MS chromatogram of a standard solution containing 2 μg l^{-1} as As for arsenic species, 10 μg l^{-1} as Se for selenium species, 4 μg l^{-1} as Cr for Cr(VI) and 900 mg l^{-1} NaCl. Peak identification: (1) As(III), (2) DMA, (3) MMA, (4) chloride interference, (5) Se(IV), (6) As(V), (7) Se(VI), (8) Cr(VI). The analysis was performed according to the optimum conditions shown in Tables 1 and 2.

3.3. Analytical performance characteristics

The linearity was checked in the concentration range 0.11–100 μg l^{-1} for arsenic species, 1.5–400 μg l^{-1} for selenium species and 0.45–200 μg l^{-1} for Cr(VI). Correlation coefficients obtained after linear regression were, in all cases, >0.9999.

Additionally, possible matrix effects on the calibration were estimated by the standard additions method for a surface water sample. The slopes were compared with those of external calibrations, as shown in Table 3. It was demonstrated that the surface water matrix did not affect the calibration, and therefore the analysis of surface water can be performed by external calibration.

When the HPLC–ICP-MS procedure was applied to the analysis of six spiked surface water samples (three concentrations), recoveries were satisfactory, with values between 95 and 101% for the medium and highest fortification levels. At the lowest fortification level, which was close to the detection limit, recoveries were in the range 80–97% (Table 4).

Table 3
Calibration curves obtained under the experimental conditions of Tables 1 and 2, using aqueous external standards and the standard additions method for a surface water sample

	Conc. range examined (μg l^{-1})	External calibration		Standard additions	
		r^2	Slope (counts l μg^{-1})	r^2	Slope (counts l μg^{-1})
As(III)	0.11–50	0.99998	12 509	0.99991	12 468
DMA	0.11–50	0.99996	16 096	0.99997	16 427
MMA	0.11–50	0.99998	14 408	0.99999	14 590
As(V)	0.11–50	0.99997	13 622	0.99994	13 630
Se(IV)	1.5–200	0.99998	1041	0.99992	1033
Se(VI)	1.5–200	0.99999	1054	0.99997	1054
Cr(VI)	0.45–100	0.99997	13 249	0.99998	13 419

Table 4
Analytical characteristics of the HPLC–ICP-MS procedure obtained after application to spiked water samples

	Precision ($n = 6$)						Intermediate precision, Level 2 C.V. (%) ($n = 9$)	LOD ($\mu g\ l^{-1}$)
	Level 1[a]		Level 2[b]		Level 3[c]			
	Rec (%)	C.V. (%)	Rec (%)	C.V. (%)	Rec (%)	C.V. (%)		
As(III)	91	4.5	99	1.4	98	1.1	0.6	0.006
DMA	95	5.2	98	0.9	96	0.9	1.9	0.05
MMA	95	3.8	98	2.5	98	0.9	2.9	0.4
As(V)	94	0.8	97	2.9	96	0.6	3.8	0.02
Se(IV)	97	3.7	101	1.7	97	0.9	4.1	1
Se(VI)	94	1.2	95	0.7	97	0.6	3.3	1
Cr(VI)	80	2.6	97	1.6	100	0.6	3.6	0.2

[a] As(III), DMA, MMA, As(V) 0.11 $\mu g\ l^{-1}$; Se(IV), Se(VI) 1.5 $\mu g\ l^{-1}$; Cr(VI) 0.45 $\mu g\ l^{-1}$.
[b] As(III), DMA, MMA, As(V) 5 $\mu g\ l^{-1}$; Se(IV), Se(VI) 24 $\mu g\ l^{-1}$; Cr(VI) 10 $\mu g\ l^{-1}$.
[c] As(III), DMA, MMA, As(V) 50 $\mu g\ l^{-1}$; Se(IV), Se(VI) 200 $\mu g\ l^{-1}$; Cr(VI) 100 $\mu g\ l^{-1}$.

Coefficients of variation of $<5\%$ were obtained at concentrations close to the detection limit.

Intermediate precision ($n = 9$) was also obtained by analysing replicates of surface water samples spiked at medium concentration on 3 different days. The coefficient of variation was found to be $<4\%$ in all cases.

Detection limits, defined as three times the signal-to-noise ratio (S/N), were determined for a real surface water sample containing As(III) (0.19 $\mu g\ l^{-1}$), DMA (0.16 $\mu g\ l^{-1}$) and MMA (0.067 $\mu g\ l^{-1}$). For As(V), selenium and chromium species it was necessary to spike the water sample to a final concentration near the LOD: As(V) 0.040 $\mu g\ l^{-1}$, Se(IV) 2.1 $\mu g\ l^{-1}$, Se(VI) 2.2 $\mu g\ l^{-1}$ and Cr(VI) 0.5 $\mu g\ l^{-1}$. The experimental detection limits obtained (Table 4) were <0.06 $\mu g\ l^{-1}$ for arsenic species, <1.5 $\mu g\ l^{-1}$ for selenium species and around 0.2 $\mu g\ l^{-1}$ for Cr(VI). These values are satisfactory for the analysis of surface waters at ultra-trace levels and are in agreement with the quality criteria fixed by current legislation for arsenic and chromium. Most selenium legislation does not distinguish between species; however, LODs obtained for selenite and selenate were close to the recommended total Se.

3.4. Application of the method

The recommended HPLC–ICP-MS procedure was applied to the simultaneous determination of As(III), As(V), MMA, DMA, Se(IV), Se(VI) and Cr(VI) in 12 surface water samples from different locations in Castelló and València provinces (Spain). Samples were collected in polyethylene bottles and stored at 4°C without acidification in order to prevent changes in the species distribution [10,20]. Analyses were carried out within 24 h of sample collection to avoid As(III) and As(V) interconversion [8], and samples were filtered through a 0.45 μm membrane before injection.

Arsenite was found in all samples at concentrations <1 $\mu g\ l^{-1}$ (between 0.2 and 0.8 $\mu g\ l^{-1}$), 10 samples analysed contained arsenate at concentrations between 0.1 and 9.0 $\mu g\ l^{-1}$, MMA was detected only in one sample (2.7 $\mu g\ l^{-1}$ as As) and DMA was detected in five samples in the range 0.1–1.5 $\mu g\ l^{-1}$. Selenium species were below the detection limit in all samples analysed. As an example, Fig. 3a shows the chromatogram of a water sample from Sitjar dam (Castelló, Spain), where several arsenic species were detected. Cr(VI) was found at significant concentrations (up to 5.9 $\mu g\ l^{-1}$) in samples from Belcaire river, located in an industrial zone with several tanning industries (Fig. 3b).

4. Conclusions

Anion-exchange LC coupled to ICP-MS was used for the simultaneous multielemental determination of

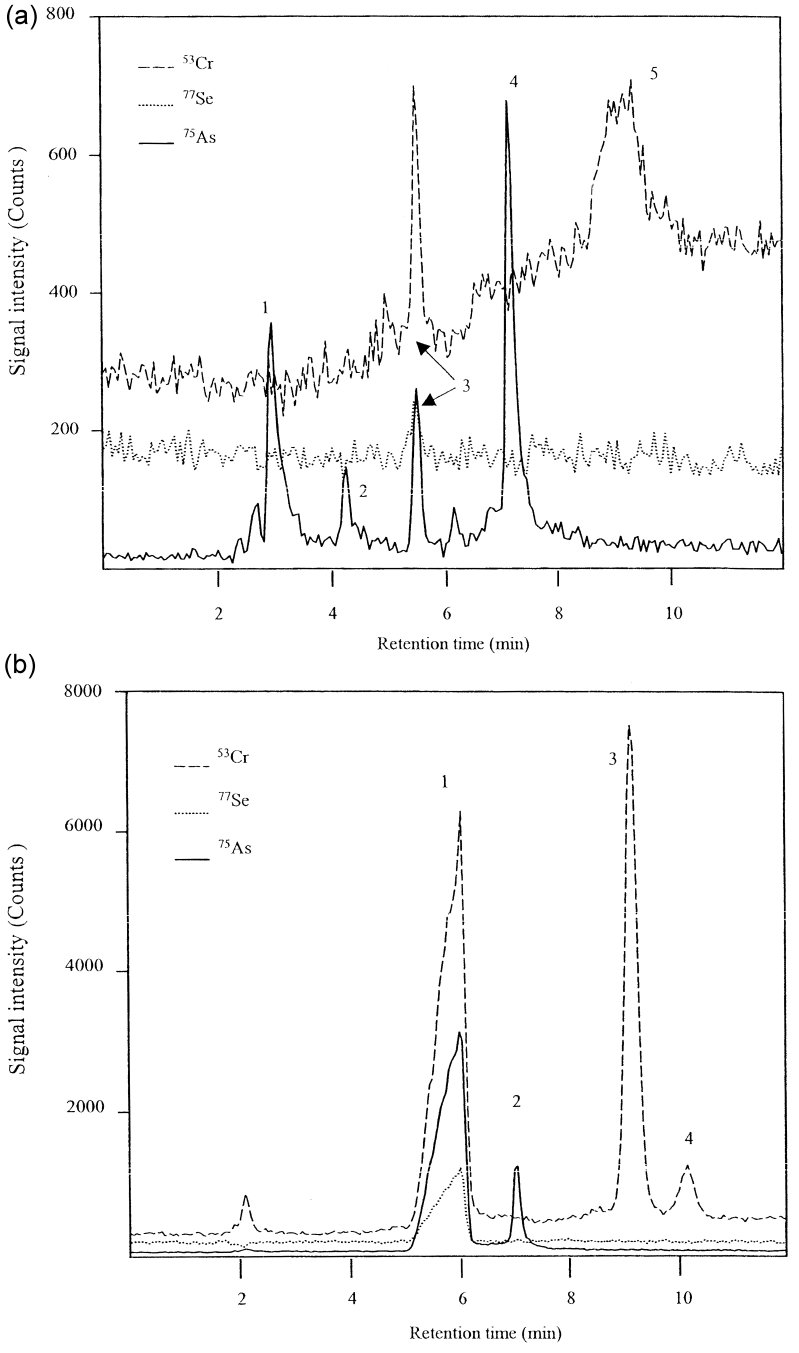

Fig. 3. (a) Anion-exchange HPLC–ICP-MS chromatogram of a surface water sample from Sitjar dam (Castelló). The peaks were identified and quantified as: (1) As (III) 0.66 μg l^{-1}, (2) DMA 0.05 μg l^{-1}, (3) chloride, (4) As (V) 0.50 μg l^{-1}, (5) Cr(VI) 0.44 μg l^{-1}. (b) Anion-exchange HPLC–ICP-MS chromatogram of a surface water sample from Belcaire river (Castelló). The peaks were identified and quantified as: (1) chloride; (2) As(V) 0.9 μg l^{-1}, (3) Cr(VI) 5.9 μg l^{-1}, (4) unknown.

As(III), As(V), MMA, DMA, Se(IV), Se(VI) and Cr(VI) in water. Gradient elution using NH_4NO_3 at pH 8.7 allowed the complete chromatographic separation of all species in less than 10 min (total analysis time 14 min). The use of this mobile phase allowed us to improve the detection limit for Cr(VI) when compared with the carbon-containing mobile phases previously assayed by our group. In addition, chloride interference was separated chromatographically from arsenic, selenium and chromium species. Detection limits were <0.060 μg l^{-1} for As species, <1.5 μg l^{-1} for Se species and 0.18 μg l^{-1} for Cr(VI), and the repeatability was always below 5% at all concentrations tested. The developed method has been demonstrated to be fast, reliable and robust for the analysis of these metal species in fresh waters regardless of the matrix composition.

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