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Journal of Chromatography A, 884 (2000) 211–221

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Determination of inorganic and organic anionic arsenic species in water by ion chromatography coupled to hydride generation–inductively coupled plasma atomic emission spectrometry

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Abstract

The development of an analytical methodology for the specific determination of arsenite, arsenate and the organic species monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA), is described. The method is based on an ion chromatographic separation, coupled on-line to post-column generation of the gaseous hydrides by reaction with sodium tetrahydroborate in acidic medium. Detection and measurement were performed by inductively coupled plasma spectrometry operated in the atomic emission mode. Arsenic emission was monitored at 193.7 nm. Different types and sizes of anion-exchange columns, silica and polymeric, were tested using EDTA as eluent. Composition, acidity and flow-rate of the mobile phase were optimized in order to obtain the required resolution. Complete elution and resolution of the four species was achieved in about 6 min. Linear calibration curves were obtained in the 0.05–2 μg ml^{-1} range for As(III), As(V) and MMA, and between 0.1 and 2.0 μg ml^{-1} for DMA. The absolute limits of detection for 200-μl sample injections were in the ng range, with DMA the compound measured with less sensitivity. Results of the analyses of natural samples, such as river and ground waters spiked with the studied species, suggested that analyte recoveries might be dependent on the sample composition.

Keywords: Water analysis; Environmental analysis; Detection, LC; Inorganic cations; Inorganic anions; Organoarsenical compounds; Arsenic

1. Introduction

Interest in arsenic speciation originates from the variable toxicity of its different organic and inorganic species. Inorganic arsenic, present as arsenite and arsenate, is highly toxic. Some methylated species such as monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA), the latter also known as cacodylic acid, are only moderately toxic, and are considered part of some detoxification mechanisms in living organisms. Other quaternary organic compounds as arsenobetaine and arsenocholine are non-toxic. As(III) is regarded as the more toxic form of the element, due to the interference produced on enzymatic processes by bonding to –SH and –OH functional groups [1].

The concentration of total dissolved arsenic in freshwaters depends on the geological and geochemical composition of natural drainage areas. Many geothermal waters and some lakes present relatively high levels of the element. Arsenic distribution is also affected by anthropogenic activities, such as

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0021-9673/00/$ – see front matter
PII: S0021-9673(00)00279-X

mining and smelting operations, coal-fired combustion and the use of agricultural herbicides, pesticides, and medicinal and cosmetic products.

An extensive variation of the arsenic content in natural waters is reported in the literature. Cullen and Reimer [2] have published a very comprehensive monograph on the presence and distribution of inorganic and organic arsenic in the environment. In oxidic waters the arsenate concentration is higher than that of arsenite, which may appear at significant concentrations in deep waters. The synthesis of organoarsenicals requires the presence of living organisms that metabolize the inorganic arsenic precursors. In consequence, methylated compounds are usually found in soils and sediments.

Early studies on arsenic speciation were performed by Braman and Foreback [3] and by Braman et al. [4]. The use of high-performance liquid chromatography (HPLC) for the separation of arsenicals was reported by Brinckman et al. [5], and later applied by numerous authors, mostly employing diverse forms of atomic spectrometry as a mean of specific detection [6–10]. Post-column derivatization of arsenic species by employing formation of the volatile arsenic hydrides, has been coupled with atomic absorption spectrometry (AAS) [7–13], inductively coupled plasma mass spectrometry (ICP-MS) [11,14–17], atomic fluorescence spectrometry (AFS) [18] and ICP-atomic emission spectrometry (AES) [8,19–22]. The chromatographic separation is usually performed by anion-exchange or ion pairing, with phosphate or carbonate buffer solutions as eluents, or by ion exclusion [17].

A method for the determination of two inorganic (arsenite and arsenate) and two organic (MMA and DMA) species by anion-exchange chromatography, was investigated. The suitability of a simple elution system, EDTA at controlled pH, which is extensively employed for the separation of many anions and metal cations, is demonstrated. The optimization of operating conditions aimed to reduce elution times without compromising resolution. Due to the simplicity of interfacing and the sensitivity achievable with radiofrequency (RF) argon plasma atomic emission, on-line hydride generation (HG) followed by ICP-AES was employed for element-selective detection of the separated species.

2. Experimental

2.1. Apparatus and instrumentation

The complete system employed is shown schematically in Fig. 1. ICP instrumentation and hydride generation conditions are listed in Table 1.

The HPLC module consisted of an Alltech (Deerfield, IL, USA) Model 301 metal-free isocratic pump, a Rheodyne (Cotati, CA, USA) Model 7125 syringe injection valve, fitted with a 200-μl loop, and an analytical column. Three types of columns were tested: (i) Wescan Anion/S silica based, 10 μm particle size (100 mm×4.6 mm I.D.); (ii) Vydac 302 IC 4.6 silica based, 10 μm particle size (250 mm×4.6 mm I.D.); and (iii) Hamilton PRP X-100, polymeric (polystyrene–divinylbenzene), 10 μm particle size (250 mm×4 mm I.D.). The outlet of the column was directly coupled to a laboratory assembled continuous hydride generator, similar to one described elsewhere [23], with some modifications. A U-shaped tube with a bottom drainage outlet replaced the expansion chamber from the original design. Both branches were filled with glass beads, but the outlet portion was left empty. Controlled drainage of the phase separator was carried out by means of a peristaltic pump (Masterflex, Model 7013, Cole Parmer, Chicago, IL, USA). The U-chamber outlet was directly connected to the torch injector to minimize the void volume. A schematic of the separation chamber appears in the insert of Fig. 1. Spectrometer data acquisition and processing were performed with a chromatography software (Konikrom, V 5.2, Konik, Barcelona, Spain) by means of a personal computer coupled to an A/D interface board.

2.2. Reagents

Reagents of analytical-reagent grade were employed throughout. Deionized water (18.3 MΩ) obtained from a NanoPure system (Barnstead, Boston, MA, USA) was used for the preparation of all standard and reagent solutions. Stock solutions 1.0 μg ml^{-1} of As(III) and As(V), were prepared by dissolution of the corresponding oxides in 0.2% (w/v) NaOH solution. Monomethylarsonic acid, sodium

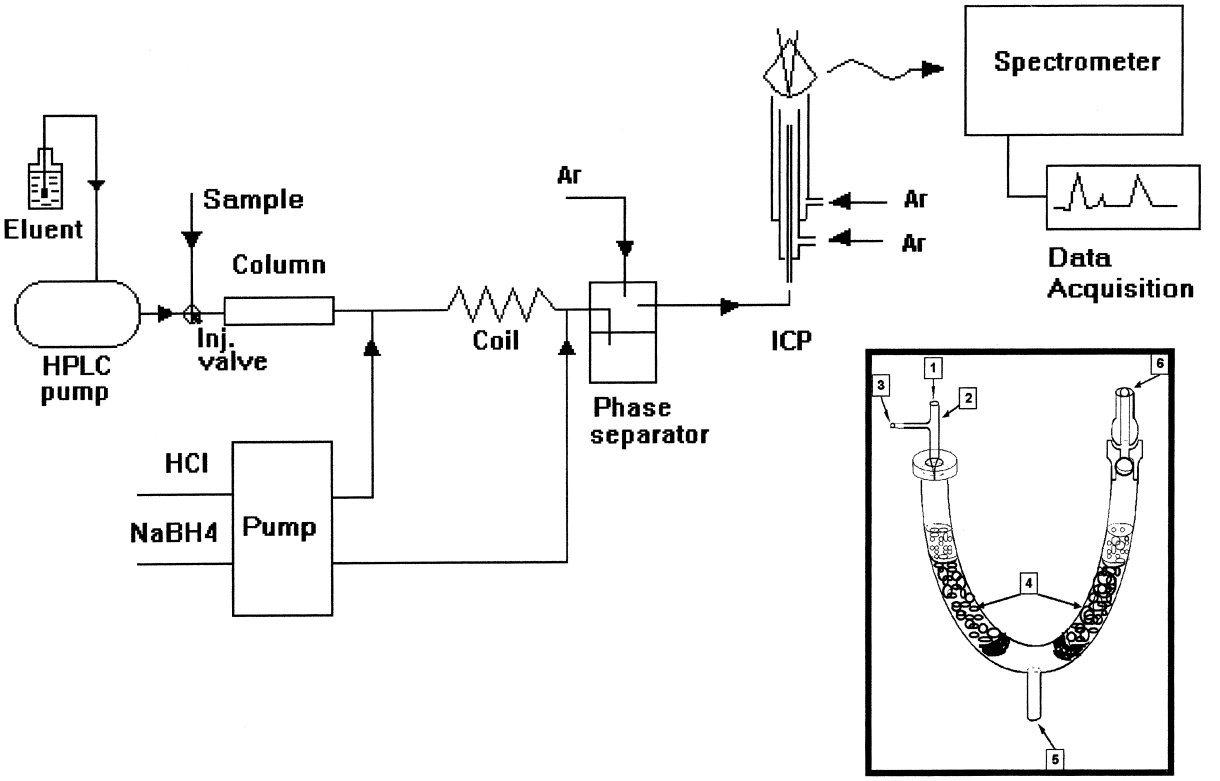

Fig. 1. Schematic of instrumental configuration. Insert: phase separator. 1=AsH_3+liquid inlet; 2=modified Meinhard nebulizer; 3=Ar inlet; 4=glass beads; 5=pumped drainage; 6=to plasma torch.

form (Chem Service, West Chester, PA, USA) and dimethylarsinic acid, sodium form (Sigma, St. Louis, MO, USA) 100 μg ml^{-1} (in arsenic) solutions were prepared by dissolving the appropriate amounts of the reagents in water. These solutions were stored in polyethylene bottles and refrigerated at 4°C. Dilutions were prepared daily.

The solution of EDTA constituting the mobile phase was prepared by dissolving the disodium salt (Merck, Darmstadt, Germany) in water and adjusting the pH with 1 *M* NaOH solution. The 5% (w/v) sodium tetrahydroborate (Riedel-de Haen, Seelze, Germany) was prepared in 0.1% (w/v) NaOH. Both were filtered through 0.22-μm Millipore filters before use. The eluent was also degassed with helium gas before being introduced into the system. Metal solutions for interference studies were prepared from Merck Titrisol.

3. Results and discussion

3.1. Optimization of the hydride generation system

When a continuous hydride generator, based on reaction with $NaBH_4$, is employed on-line as a post-column derivatization reactor, several operational variables may affect the observed ICP emission response. Aside from resolution and retention times, which are strictly dependent on the chromatographic separation characteristics, peak height or integrated peak area signals may undergo variations related to the reaction kinetics and the phase separator design. In order to investigate the optimum conditions for hydride generation, preliminary experiments were carried out without interposing the chromatographic column. A 200-μl loop and the injection valve were used to inject solutions of the different species into

Table 1
Instrumentation and operating conditions

Hydride generation	
5% (w/v) $NaBH_4$ (in 0.1 *M* NaOH)	0.3 ml min^{-1}
4 *M* HCl	1 ml min^{-1}
Sample	1 ml min^{-1}
Gas flow-rate (Ar)	0.3 l min^{-1}
Peristaltic pump	Gilson Minipuls 3, Viton tubing (Gilson Medical Electronics, Middleton, USA)
Plasma	
ICP generation	HFP-2500 D, 27 MHz (Plasma-Therm, Kresson, NJ, USA)
Power	1.25 KW
Ar plasma gas flow	15 l min^{-1}
Ar auxiliary gas flow	1.2 l min^{-1}
Observation height	12 mm above load coil (ALC)
Spectrometer	
Monochromator	VHR 100, 1 m focal length, sequential (Jobin-Yvon, Longjumeau, France)
Grating	Interferographic, 3600 l mm^{-1}
Reciprocal dispersion	0.21 nm mm^{-1} (at 300 nm, first order)
Entrance slit	Width: 50 μm, height: 5 mm
Exit slit	Width: 70 μm, height: 5 mm
Wavelength (nm)	As 193.7
Detector	R-166 type (Hamamatsu)

the hydride generator. The concentration in the HCl channel was varied between 1 *M* and 6 *M*, maintaining the concentration of $NaBH_4$ constant at 5% (w/v). The pH of the eluent (0.1 m*M* EDTA) was 5.9 and the concentration of each species equivalent to 1 μg ml^{-1} in As. Results expressed as integrated peak areas vs. acid concentration are graphically depicted in Fig. 2a. The inorganic species signals increase with acidity. The monomethylated compound gives an almost stable signal, while an abrupt decrease in As emission is observed for the DMA anion. The different behavior of arsenate regarding the less charged inorganic anion may be ascribed to the higher acidity required for the previous reduction of arsenate to arsenite, which is a condition for the subsequent formation of arsine. Kinetic effects that lower the efficiency of reaction in continuous flow may also affect generation of the DMA hydride.

Fig. 2b shows the effect of $NaBH_4$ on As emission when the concentration of that reagent is changed from 1% to 7% (w/v), at a constant concentration of HCl (4 *M*). Significant variations are observed for As(III) and DMA, which decrease, and increase, respectively. As(V) and MMA showed slighter variations. Since quantification of the more toxic As(III) species is considered particularly important, 4 *M* HCl and 5% (w/v) $NaBH_4$ were chosen to ensure high sensitivity for those species, while maintaining an acceptable signal level for the methylated compounds.

3.2. Ion chromatographic separation conditions

Due to the different pK_a values of arsenicals (Table 2), varied ionizing species distributions are expected, depending upon the pH of the medium. In fresh water, As(V) and the methylated species are partially ionized, while As(III) is mainly in neutral form. The eluent chosen is able to elute a variety of ions, and has been applied by numerous authors as mobile phase in ion chromatography of both anions and metals [24–27]. A series of experiments were performed to evaluate the influence of the EDTA concentration and pH on retention times and separation efficiency. Fig. 3a shows results obtained at pH 5.9 with various eluent compositions when the 100-mm silica based column was tested. A lowering of retention time was found for both As(V) and MMA when the EDTA concentration is raised. The trend is more noticeable for that of inorganic species, as expected. In addition, some peak overlapping is observed between the methylated species at the

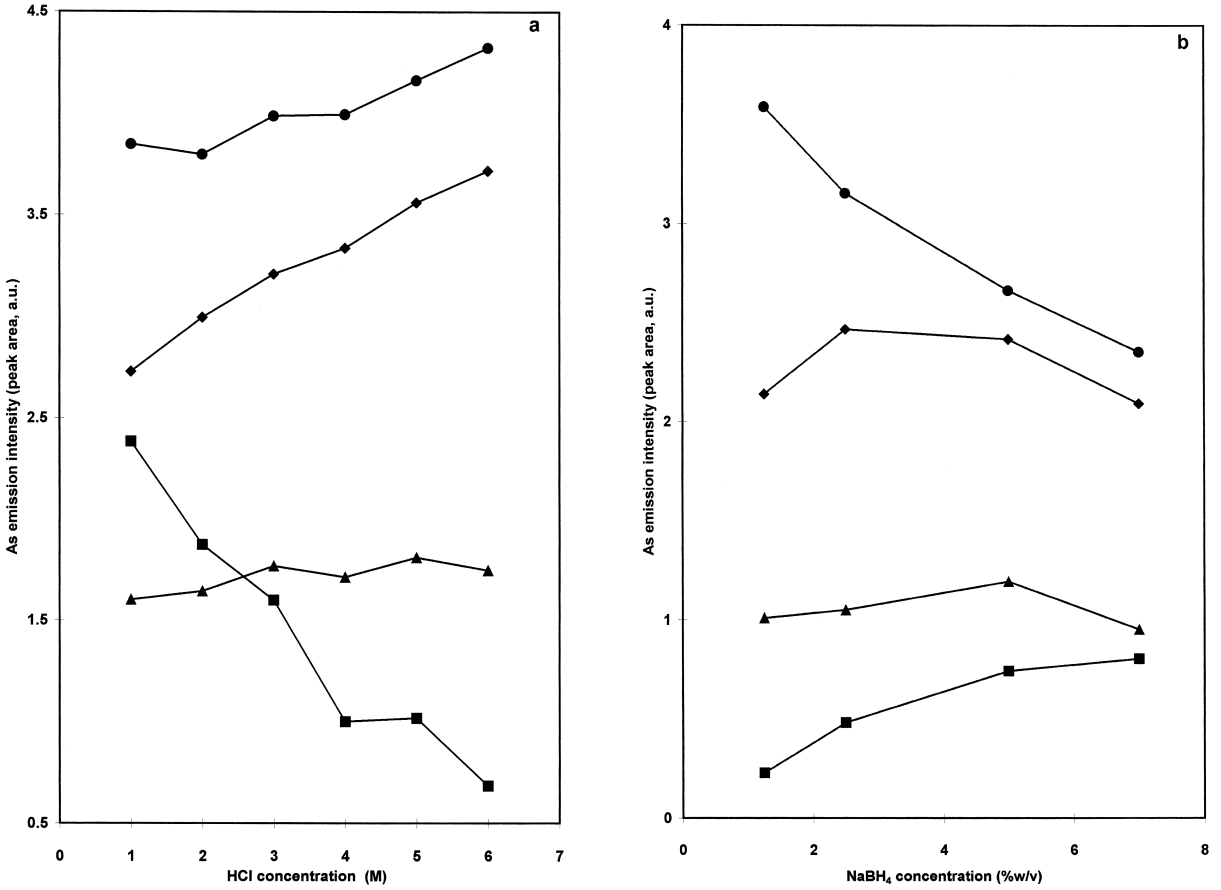

Fig. 2. Variation of arsenic emission intensity with reagent concentrations. (a) HCl; (b) $NaBH_4$. ●=As(III); ♦=As(V); ■=DMA; ▲=MMA.

lower eluent concentration, and between arsenate and DMA from 0.4 to 0.6 m*M* EDTA. A concentration of 0.1 m*M* was chosen for analytical work. A low eluent concentration is expected to increase the lifetime of the silica-based column, but may also present a low buffer capacity.

Results of a study of the effect of eluent pH are summarized in Fig. 3b. The upper pH limit tolerated by a silica column is around 6–7. In consequence we tested the operation of the 100-mm column between pH 4.5 and 5.9. In that range the two inorganic species could be separated from the methylated compounds. Arsenous acid is not ionized and is eluted in the void volume. On the other hand, arsenic acid is ionized ($H_2AsO_4^-$: 89%; AsO_4^{2-}: 11%) and it will be relatively more retained by the column active sites. The elution order of the methylated arsenicals is more dependent of the pH of the mobile phase. At pH 5.9 MMA is fully ionized, but only 31.4% of DMA is in ionic form. Consequently it was expected that DMA should elute with a low retention time, which is opposite to the experimentally observed behavior. It is possible that a retention mechanism

Table 2
Formulae and pK_a values of the four arsenical compounds

Compound	Formula	pK_a
Arsenic acid	$AsO(OH)_3$	2.2, 6.9, 11.5
Arsenous acid	$As(OH)_3$	9.2, 12.1, 13.4
MMA	$CH_3AsO(OH)_2$	3.6, 8.2
DMA	$(CH_3)_2AsO(OH)$	6.2

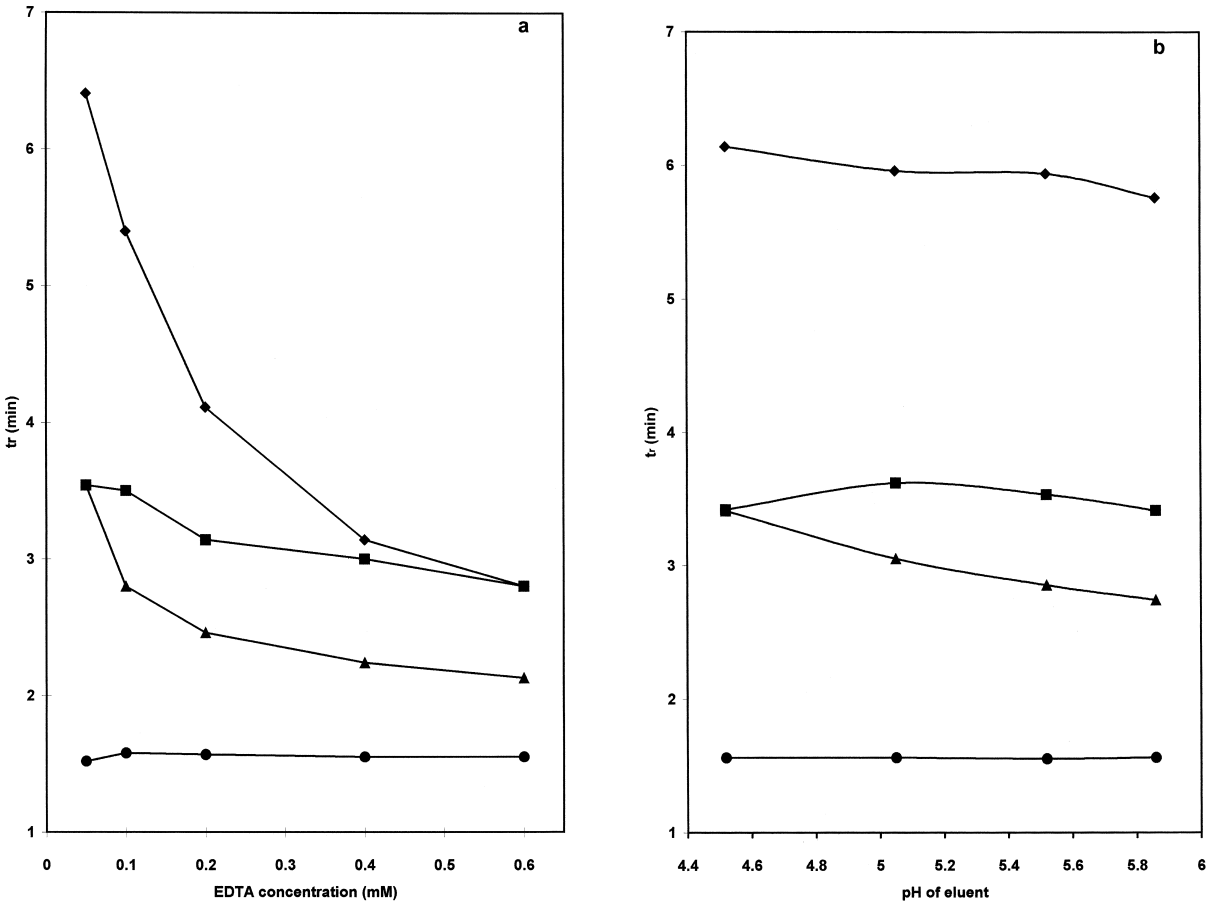

Fig. 3. Variation of the relative retention time with eluent composition and pH. (a) EDTA concentration, (b) pH. ●=As(III); ♦=As(V); ■=DMA; ▲=MMA.

other than ion-exchange, such as adsorption, may be active in the course of the interaction between the methylated species and the stationary phase. This is consistent with the behavior of the longer silica-based column, for which a chromatogram is shown in Fig. 4a. No improvement is observed in the separation of the methylated species, in spite of the higher column length that increases the retention time for the inorganic arsenicals. These are most possibly involved in a pure ion-exchange separation mechanism.

Additional information on the equilibrium mechanism involved in the separation can be obtained from analyte capacity factors [24,28]. By considering data obtained with the 100-mm length silica column, the logarithm of the capacity factors (log k') of the retained As species [As(III) is eluted with the void volume] were plotted as a function of the logarithm of EDTA concentration. Slopes of the obtained straight lines are compared in Table 3 with the corresponding theoretical values. Those were calculated by assuming the ''dominant equilibrium'' and ''the effective charge of the competing anion'' approaches described by Haddad and Jackson [28]. Good agreement was found with results from the first of the mentioned approaches, suggesting that the competing eluent species is $EDTA^{2-}$. At the working pH (5.9) the proportion of that species present in solution is 64.5%.

Finally, flow-rates of the mobile phase between 0.5 and 1.2 ml min^{-1} were tested. A value of 1.0 ml min^{-1} was selected as optimum, allowing a good

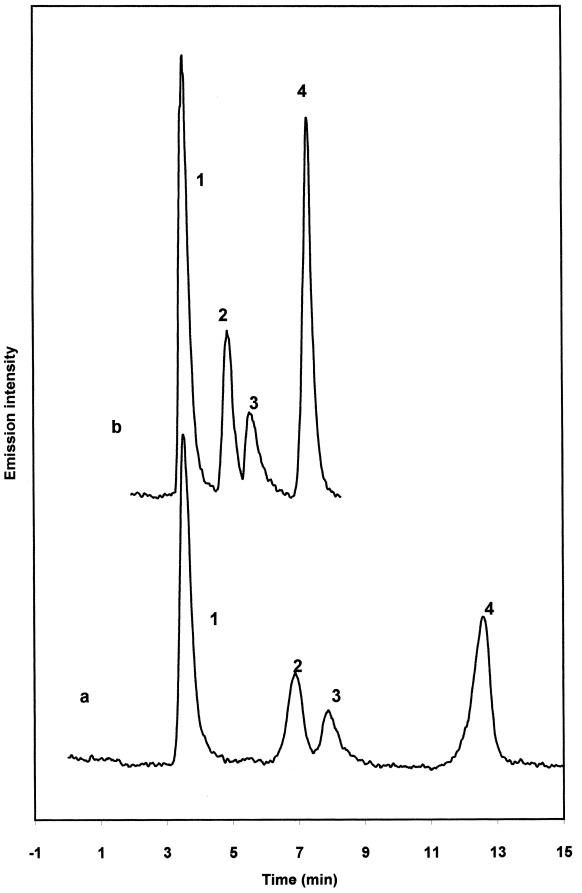

Fig. 4. Chromatograms of arsenic species. Observed peaks: 1=As(III); 2=MMA; 3=DMA; 4=As(V). [EDTA]=0.1 m*M*, pH 5.9, flow-rate=1 ml min^{-1}. Silica-based columns, (a) 250-mm length, (b) 100-mm length.

analyte resolution without significant reduction in peak areas.

A chromatogram of a synthetic sample consisting in a mixture of the four species, equivalent to As 0.2 $\mu g\ ml^{-1}$ each, is depicted in Fig. 4b. The injection loop volume was 200 μl. No significant broadening of the peaks was observed for that volume when compared to 50- and 100-μl injections. This result suggests that, after the optimization of the hydride system, peak broadening arises solely from analyte interaction in the column, with a relatively low contribution from the derivatization reaction and subsequent phase separation step.

Two additional anion-exchange columns were also examined as possible alternatives to the above-described system. With the longer (250-mm) silica based column, separation was observed, but the resolution of methylated species is not improved and the retention time for As(V) is higher (see Fig. 4a). The 250-mm polymeric column enables one to work in the 2–14 pH range. The elution order for the organoarsenicals differs from that of the silica based column, with DMA eluting before MMA as determined by the pK_a values. However, a noticeable degree of overlapping exists between the two compounds. It can be concluded that the 100-mm silica column appears as the most suitable for arsenic speciation under the selected operating conditions.

Table 3
Equilibrium mechanism approaches – comparison of experimental and theoretical values

Ion	Slope of log k' vs. [EDTA]		
	Observed	Dominant equilibrium (y=2)	Effective charge (y=2.35)
DMA	0.18	0.16	0.13
MMA	0.49	0.50	0.43
As(V)	0.56	0.55	0.47

3.3. Interferences

Although ion chromatography is a powerful separation technique, co-elution of metal species that are not detected at the specific As wavelength can not be ruled out. In particular, when successive sample injections are performed after complete elution of the arsenicals with the purpose of reducing operation times in routine analyses, ionic forms of metals contained in the sample matrix may be co-eluted with any of the analyte species, interfering with the hydride formation reaction.

We selected As(V) to evaluate possible interferences from concomitantly present transition metals in the sample solution. Solutions containing 0.5 $\mu g\ ml^{-1}$ of the analyte and up to 100 $\mu g\ ml^{-1}$ of Mn^{2+}, Mo^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+} and Cr^{3+} were injected into the HG–ICP system by means of the 200-μl loop. The emission from As was recorded and compared with the signal in absence of concomitants. Statistically significant suppression was observed only for Ni^{2+}, even at concentrations as low as 1 $\mu g\ ml^{-1}$. It is possible that EDTA complexation

of most metals reduces potential interferences on the hydride generation reaction. Although the eluent chosen is expected to produce an adequate chromatographic separation of Ni, a significant interference may be envisaged in the case of co-elution with any of the arsenical peaks.

As it has been already mentioned in the previous section, As(III) seems to be totally unretained and elutes with the void volume. This situation could be undesirable in the analysis of real samples due to multiple unretained species potentially co-eluted. Significant effects due to simultaneous elution of metals are not expected, because the complexing capacity of EDTA. As the detector is specific for arsenic atoms, only other arsenic containing compounds potentially able to elute as neutral or cationic species under the method operating conditions should be considered. These include [29] arsenicals containing AsO groups (as trimethylarsine oxide, TMAO) that may become protonated at low pH values, and quaternary arsonium ions of permanent cationic structure. Arsenocholine, arsenobetaine and tetramethyl arsonium ions are included in the second group. These compounds are mostly found in biological samples and do not form volatile hydrides by treatment with sodium tetrahydroborate, and consequently will remain undetected by HG–ICP-AES. The same can be said of arsenosugars [30]. Determination of those species would not be possible with the present system. It would require an appropriate selection and optimization of the chromatographic separation conditions and a subsequent thermal (microwave digestion) or UV radiation treatment to break the organic bounds and to enable the hydride reaction to proceed [31].

3.4. Detection limits and precision

Calibration curves (peak area vs. concentration) were found to be linear between 0.05 and 2.0 μg ml^{-1} for As(III), As(V) and MMA, and between 0.1 and 2.0 μg ml^{-1} for DMA. Higher calibrant concentrations are generally not required for water, soil and sediment analyses, and consequently were not tested. Detection limits were estimated from about 20 replicate peak area measurements as a concentration equivalent to three-times the standard deviation of the background signal corresponding to each peak. Regression data and absolute limits of detection are presented values included in Table 4. These results indicate that the scope of the method regarding its applications to real samples will be limited to natural systems contaminated by natural or anthropogenic causes, and possibly to the determination of arsenicals extracted from sediments or soils that have undergone intensive treatment with arsenic based pesticides. Natural contamination with As of geological origin is of main concern in Argentina. Ground waters belonging to an extended central region of the country, and in many cases employed for human consumption, present abnormally elevated As concentrations. Values higher than 3.8 μg ml^{-1} of total As have been measured in well waters [32].

Table 4
Regression data; fitted equation: $y=a+bx$, where y=peak area (a.u.), x=concentration (μg ml^{-1})

Species	$a \cdot 10^4$	$b \cdot 10^6$	r^{2a}	DL[a] (ng)	n^a
As(III)	4.2	3.0	0.9991	2	21
MMA	1.5	1.0	0.9982	6	21
DMA	−2.3	0.7	0.9881	13	18
As(V)	−0.1	2.0	0.9993	3	21

[a] r^2: Squared correlation coefficient. DL: Detection limit. n: Number of data points.

The detection limits obtained with the developed procedure are poorer than those obtained by combination of the chromatographic separation with sensitive detection techniques such as ICP-MS and, in some cases, AAS. Consequently, it is of interest to compare the minimum detectable concentrations obtained in our work with those reported for methods in which different eluent conditions were employed. The detection limits (DLs) obtained with the EDTA elution procedure [2 ng or 10 ng ml^{-1} As for As(III), 3 ng or 15 ng ml^{-1} As for As(V), 6 ng or 30 ng ml^{-1} As for MMA, and 13 ng or 65 ng ml^{-1} As for DMA] are similar or comparable to some of the reported values. For example, in a paper by Bushee et al. [8], arsenite and arsenate were speciated at levels higher than about 50 ng ml^{-1} (as As) by employing HPLC–HG–ICP-AES. The method was applied to the analysis of well water samples. In a comparison of HPLC–flame atomic absorption spectrometry (FAAS) with HPLC–ICP-AES (i.e., without a derivatization step) for the separation of seven

As species carried out by Hansen et al. [11], the detection limits of the former technique laid in the range of As 0.7–1.4 μg ml^{-1} (70–140 ng As) for arsenite, arsenate, MMA and DMA. The method was used for the analysis of aqueous extracts of soil samples from a polluted land site. DLs found for ICP-MS were 7 ng ml^{-1} (0.7 ng As) for arsenite and 3 ng ml^{-1} (0.3 ng As) for arsenate, MMA and DMA. Other compounds whose measurement was included in the same paper were arsenocholine, arsenobetaine and TMA ion. Furuta and Shinofuji [33] reported DLs of 70 ng ml^{-1} for As(III) (3.5 ng As) and 170 ng ml^{-1} (8.5 ng As) for As(V) with ion chromatography–HG–ICP-AES. Even for ICP-MS, the concentration DLs obtained by Feldmann [34] for arsenite and arsenate are of the same magnitude order (As 3.7 ng ml^{-1} and 2.2 ng ml^{-1}, respectively) than those reported in our manuscript for the same species. Woller et al. [10] found absolute limits of detection (as As) of 35 ng for arsenite, 50 ng for arsenate and 20 ng for MMA and DMA, by employing a combination of HPLC–AFS with ultrasonic nebulization (USN). Separation was performed using a phosphate buffer as eluent. The linearity range reported was 250–2500 ng As, compared with 20–240 ng As in our work. Finally, the concentration detection limits reported by Rubio et al. [21] by employing HPLC (anion-exchange)–HG–ICP-AES only differ by a factor of about 3 with our limits for As(III) and DMA, and by a factor of 2 for As(V). The limit for MMA is substantially better for the cited authors: 3.8 ng ml^{-1} against our limit of 30 ng ml^{-1} As for MMA. It must be noticed, however, that the DLs reported in reference [21] are 2σ instead of 3σ as in our work.

Repeatability was estimated from nine successive replicate injections of a standard solution containing a mixture of the four species at the 0.5 μg ml^{-1} As concentration level. Relative standard deviations (RSDs) of peak areas were 5.9% for DMA and 5% for the remaining species.

3.5. Analyses of spiked water samples

Because a certified reference material regarding the studied species was not available to us, speciation of As in real water samples was evaluated through a standard addition procedure. To perform these experiments we selected samples of river and ground waters collected in uncontaminated locations, to assure a possible As content well below the detection limits of the proposed technique. A water sample of drinking quality was also spiked. The composition of those samples regarding common metals and anions was determined by a standard ion chromatographic procedure and is shown in Table 5. Samples were spiked with a standard mixture of the analytes giving an added concentration of As 0.4 μg ml^{-1} each. Fig. 5 shows the obtained chromatograms. Recoveries that appear in Table 6 were calculated by comparison with a pure water standard of the same concentration (Fig. 5a). The four species could be detected in the river sample with good recoveries, with the exception of MMA, which shows a decrease in signal of about 30%. The methylated species signals were almost undetected in the ground water, suggesting an important suppression effect of unclear origin. Besides it, the retention time of As(V) is slightly higher, possibly due to the higher saline concentration of that sample.

The suppression of methylated compound signals observed for the groundwater sample could be originated in a decrease of the hydride generation efficiency for those species due to co-elution effects. The ability of sodium tetrahydroborate to react with arsenic compounds may be impaired by the presence of unknown metal binding ligands or hydrophobic substances [35].

The As(III) peak seems to be absent in the case of the drinking water sample. This could be ascribed to the presence of oxidizing chlorine or chlorine compounds employed during the water purification process. Under these conditions As(III) may be con-

Table 5
pH and composition of spiked water samples[a]

	River water	Ground water	Drinking water
pH	7.2	7.7	7.7
Na^+	7.0±0.2	36.2±0.3	19.0±0.2
K^+	0.9±0.1	7.1±0.2	5.5±0.2
Ca^{2+}	8.8±0.2	5.7±0.2	18.1±0.2
Mg^{2+}	2.4±0.1	5.2±0.2	5.1±0.2
Cl^-	3.3±0.2	16.8±0.3	33.3±0.3
NO_3^-	0.1±0.1	16.9±0.2	1.1±0.2
SO_4^{2-}	12.3±0.2	12.8±0.2	48.3±0.4

[a] Concentrations in μg ml^{-1}.

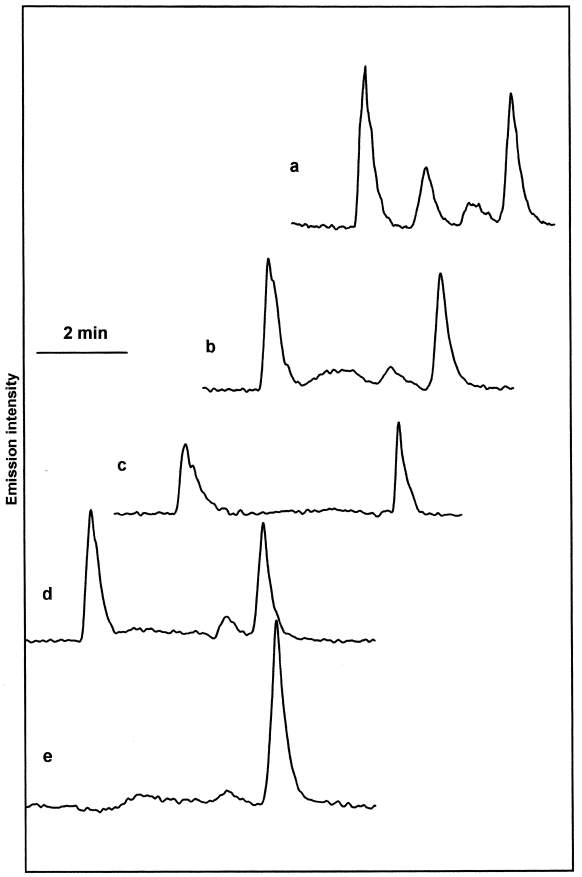

Fig. 5. Chromatograms of water samples spiked with 0.4 μg ml^{-1} (as arsenic) of each species. (a) Deionized water; (b) river water; (c) ground water; (d) drinking water after 20 days storage; (e) drinking water (spiked and analyzed immediately after sampling).

verted to the oxidized inorganic species. This is supported by the fact that the As(V) peak area is twice the area corresponding to As(V) in the standard, but is 91% of the of the sum of As(III)+As(V) area peaks in the same standard. Chromatogram (d) in Fig. 5 corresponds to the same sample as chromatogram (e), but the spiking was performed after 20 days. As chlorine possibly evaporated, As(III) seems not to be oxidized. Similar effects have been recently described in the literature [13,17,36,37].

The decomposition of MMA species due to the mentioned addition of chlorine as purifier is another possibility to be considered. Howard and Hunt [31] have applied photo-oxidation with alkaline persulfate, for example, and the same reagent was applied to decomposition of arsenicals, assisted by microwave heating, by Le et al. [30]. In our experiments with recently sampled drinking water only 42% of the MMA is recovered. The recovery of DMA is still relatively acceptable (90%), suggesting at most only a partial decomposition. However, the increase in the As(V) peak does not reflects the conversion of the corresponding amount of the organic As species to the oxidized inorganic form. The enhancement in the As(V) peak seems to be rather proportional to the sum of As(III) and As(V), as mentioned above. Moreover, after elimination of chlorine the spiked As(III), As(V) and DMA are almost completely recovered (Fig. 5d), but the MMA signal is still very low. Because the thermodynamics and kinetics aspects of the stability of organoarsenicals are too complex, as stressed by Cullen and Reimer [2], further experiments are required to unequivocally ascribe our results to decomposition effects. An alternative explanation could be based on variations in the efficiency of hydride generation due to unclear sample matrix effects, as in the case of ground water.

Table 6
Recovery of a standard mixture of the arsenic species (As 0.4 μg ml^{-1} each) added to water samples[a]

Sample	Recovery (%)			
	As(III)	MMA	DMA	As(V)
River water	97	73	91	93
Ground water	113	–	–	86
Drinking water	–	42[b]	90	208

[a] Average of four replicates.
[b] Calculated from peak heights.

4. Conclusions

The proposed method, based on ion chromatography–atomic spectrometry coupling, was demonstrated to be apt for the detection and quantification of four arsenic species in relatively contaminated natural waters. Although detection limits are poorer than those reported for ICP-MS detection, the simple chromatographic separation procedure described enables good resolution with elution times shorter than similar methods generally proposed for arsenic speciation. Because matrix effects are not totally absent in the case of samples with relatively high

saline content, the standard addition method should be employed for calibration, especially in the analysis of soils and sediment digestates.

Acknowledgements

The authors thank J.P. Garavaglia for technical assistance. This work was performed as part of Comisión Nacional de Energía Atómica (CAC, UAQ) Project 95-Q-02-01. Financial support was provided by Agencia Nacional de Promoción Científica y Tecnológica Project PICT 06-00000-00354.

References

[1] J.E. Ferguson, in: The Heavy Elements – Chemistry, Environmental Impact and Health Effects, Pergamon Press, Oxford, 1990, p. 552.
[2] W.R. Cullen, K.J. Reimer, Chem. Rev. 89 (1989) 713.
[3] R. Braman, C.C. Foreback, Science 182 (1973) 1247.
[4] R.S. Braman, D.L. Johnson, C.C. Foreback, J.M. Ammons, J.L. Bricker, Anal. Chem. 49 (1977) 621.
[5] F.E. Brinckman, W.R. Blair, K.L. Jewet, W.P. Iverson, J. Chromatogr. Sci. 15 (1977) 493.
[6] R.A. Stockton, K.J. Irgolic, J. Environ. Anal. Chem. 6 (1979) 313.
[7] F.E. Brinckman, K.L. Jewet, W.P. Iverson, K.J. Irgolic, K.C. Ehrhardt, R.A. Stockton, J. Chromatogr. 191 (1980) 31.
[8] D.S. Bushee, I.S. Krull, P.R. Demko, S.B. Smith, J. Liq. Chromatogr. 7 (1984) 861.
[9] C.T. Tye, S.J. Haswell, P. O'Neill, K.C.C. Bancroft, Anal. Chim. Acta 169 (1985) 195.
[10] A. Woller, Z. Mester, P. Fodor, J. Anal. Atom. Spectrom. 10 (1995) 609.
[11] S.H. Hansen, E.H. Larsen, G. Pritzl, C. Cornett, J. Anal. Atom. Spectrom. 7 (1992) 629.
[12] E. González Soto, E. Alonso Rodríguez, P. López Mahía, S. Muniategui Lorenzo, D. Prada Rodríguez, Anal. Lett. 28 (1995) 2699.
[13] J. Stummeyer, B. Harazim, T. Wippermann, Fresenius J. Anal. Chem. 354 (1996) 344.
[14] D. Heitkemper, J. Creed, J. Caruso, F.L. Fricke, J. Anal. Atom. Spectrom. 4 (1989) 279.
[15] B.S. Sheppard, J.A. Caruso, D.T. Heitkemper, K.A. Wolnik, Analyst 117 (1992) 971.
[16] S. Saverwyns, X. Zhang, F. Vanhaecke, R. Cornelis, L. Moens, R. Dams, J. Anal. Atom. Spectrom. 12 (1997) 1047.
[17] T. Taniguchi, H. Tao, M. Tominaga, A. Miyazaki, J. Anal. Atom. Spectrom. 14 (1999) 541.
[18] X. Chris Le, M. Ma, Anal. Chem. 70 (1998) 1926.
[19] L. Ebdon, S. Hill, A.P. Walton, R.W. Ward, Analyst 113 (1988) 113.
[20] B. Aizpurn Fernandez, C. Valdes-Hevia y Temprano, M.R. Fernandez de la Campa, A. Sanz Medel, P. Neil, Talanta 39 (1992) 1517.
[21] R. Rubio, A. Padró, J. Albertí, G. Rauret, Mikrochim. Acta 109 (1992) 39.
[22] N. Furuta, T. Shinofuji, Fresenius J. Anal. Chem. 355 (1996) 457.
[23] D.A. Batistoni, R.N. Garavaglia, R.E. Rodríguez, Fresenius J. Anal. Chem., in press.
[24] S. Matsushita, J. Chromatogr. 312 (1984) 327.
[25] G. Schwedt, B. Kondratjonok, Fresenius J. Anal. Chem. 362 (1998) 313.
[26] W.F. Lien, B.K. Boerner, J.G. Tarter, J. Liq. Chromatogr. 10 (1987) 3213.
[27] E.A. Gautier, R.T. Gettar, R.E. Servant, Anal. Chim. Acta 283 (1993) 350.
[28] P.R. Haddad, P.E. Jackson, Ion Chromatography – Principles and Applications, Elsevier, Amsterdam, 1990.
[29] E.H. Larsen, Spectrochim. Acta 53B (1998) 253.
[30] X.C. Lee, M. Ma, N.A. Wong, Anal. Chem. 68 (1996) 4501.
[31] A.G. Howard, L.E. Hunt, Anal. Chem. 65 (1993) 2995.
[32] L.M. Bertini, I.M. Cohen, S.M. Resnizky, C.D. Gomez, J. Radioanal. Nucl. Chem. 170 (1993) 225.
[33] N. Furuta, T. Shinofuji, Fresenius J. Anal. Chem. 355 (1996) 457.
[34] J. Feldmann, Anal. Commun. 33 (1996) 11.
[35] J. Dedina, D.L. Tsalev, Hydride Generation Atomic Absorption Spectrometry, Wiley, Chichester, 1995.
[36] M.L. Magnuson, J.T. Creed, C.A. Brockhoff, J. Anal. Atom. Spectrom. 12 (1997) 689.
[37] G.E.M. Hall, J.C. Pelchat, G. Gauthier, J. Anal. Atom. Spectrom. 14 (1999) 205.