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Determination of As(III) and total inorganic As in water samples using an on-line solid phase extraction and flow injection hydride generation atomic absorption spectrometry

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ABSTRACT

A simple and robust on-line sequential injection system based on solid phase extraction (SPE) coupled to a flow injection hydride generation atomic absorption spectrometer (FI-HGAAS) with a heated quartz tube atomizer (QTA) was developed and optimized for the determination of As(III) in groundwater without any kind of sample pretreatment. The method was based on the selective retention of inorganic As(V) that was carried out by passing the filtered original sample through a cartridge containing a chloride-form strong anion exchanger. Thus the most toxic form, inorganic As(III), was determined fast and directly by AsH_3 generation using 3.5 mol L^{-1} HCl as carrier solution and 0.35% (m/v) $NaBH_4$ in 0.025% NaOH as the reductant. Since the uptake of As(V) should be interfered by several anions of natural occurrence in waters, the effect of Cl^-, SO_4^{2-}, NO_3^-, HPO_4^{2-}, HCO_3^- on retention was evaluated and discussed. The total soluble inorganic arsenic concentration was determined on aliquots of filtered samples acidified with concentrated HCl and pre-reduced with 5% KI–5% $C_6H_8O_6$ solution. The concentration of As(V) was calculated by difference between the total soluble inorganic arsenic and As(III) concentrations. Detection limits (LODs) of 0.5 μg L^{-1} and 0.6 μg L^{-1} for As(III) and inorganic total As, respectively, were obtained for a 500 μL sample volume. The obtained limits of detection allowed testing the water quality according to the national and international regulations. The analytical recovery for water samples spiked with As(III) ranged between 98% and 106%. The sampling throughput for As(III) determination was 60 samples h^{-1}. The device for groundwater sampling was especially designed for the authors. Metallic components were avoided and the contact between the sample and the atmospheric oxygen was carried to a minimum. On-field arsenic species separation was performed through the employ of a serial connection of membrane filters and anion-exchange cartridges. Advantages derived from this approach were evaluated. HPLC–ICPMS was employed to study the consistency of the analytical results.

1. Introduction

Arsenic is widely distributed in soils, sediments, waters and living organisms in different oxidation states, mainly −3, 0, +3 and +5. It is mobilized through weathering processes, vulcanism, biological reactions and anthropogenic activities as mining, use of arsenical pesticides, wood preservation and combustion of fossil fuels [1,2]. The natural waters usually contain low concentrations of arsenic. Typical average concentrations in seawater range between 1 and 8 μg L^{-1} [3]. In freshwater, the concentrations range between 1 and 10 μg L^{-1} with values up to 5000 μg L^{-1} in mining areas [4]. The highest arsenic levels in aquatic environments have been reported in geothermal activity areas with concentrations over 6000 μg L^{-1} [2]. However, when the high arsenic concentrations are present in groundwater, the problem acquires a bigger magnitude, mainly if it is used for drinking. Although the levels are usually low [5], around 20 countries in the world suffer arsenical contamination in their aquifers affecting the quality of the water provision of more than 150 million people.

In the underground aquatic environment, arsenic arises mainly from weathering of the arsenic-containing minerals. Inorganic As(III) and As(V) forms are the most important species released from mineral dissolution. Their different properties and toxicity (arsenite > arsenate), in addition to the major removal efficiency for As(V) from water, have generated a great interest in the determination of the different species [6–8]. The increase of the toxicological and epidemiologic knowledge about arsenic and its species in addition to the advances of the analytical techniques have caused the

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reduction of the guideline value recommended by the World Health Organization (WHO, 1993) from 50 to 10 $\mu g\,L^{-1}$ [9]. The contaminant regulatory limit of 10 $\mu g\,L^{-1}$ was adopted by the United States Environmental Protection Agency (US-EPA) [10], the European Community (EC) [11] and recently by Argentina [12]. This limit, calculated from a linear dose–response curve estimated for risk of skin cancer in Taiwan population – chronically exposed to high arsenic concentrations [13,14] – has given rise to several controversies. In fact, some evidences on the non-linear relationship exposure/carcinogenesis [15], have revealed this value as overestimated. Even today, many countries in the world employ 50 $\mu g\,L^{-1}$ as regional or national standard, partially due to the lack of available analytical facilities for the determination of lower quantities in routine analytical laboratories.

Hydride generation atomic absorption spectrometry (HGAAS) with a heated quartz tube atomizer is a very widely used technique for the ultratrace determination of arsenic, selenium, bismuth and other elements able to generate volatile hydrides. This technique involves the reaction of arsenic in a reducing and acid media to produce arsine (AsH_3), allowing an increase of sensitivity and selectivity of the analytical determination [16]. The different reaction rates for the reduction of inorganic As(III) and As(V) to AsH_3 by sodium borohydride ($NaBH_4$), the most common reducing agent, have been often used for the speciation analysis. The use of diluted acid media [17–20] and/or low concentrations of $NaBH_4$ [21] permit the selective reduction of As(III) into AsH_3 with no significant interferences of As(V). However, these conditions usually lead to a minor efficiency of the hydride generation of As(III). Thus, in order to enhance sensitivity at the moment of As(III) determination, the removal of As(V) from the samples seems a good alternative. Flow techniques as flow injection (FI) or continuous flow (CF) are particularly advantageous to make easier the hydride generation and to carry out the on-line separation of species as well. Moreover, flow techniques diminish the volume of reagents and repetitive steps, avoid the off-line manipulations that increase the risk of contamination and/or looses of the analyte, improve precision and increase the sample throughput.

Although in recent years the coupling between chromatography and highly sensitive detectors has dominated the scene for analytical speciation, it is also true that these instruments are still expensive and sophisticated. Moreover, they employ large times of running for complete separation. In this way, if the objective is the determination of the most toxic species and the total concentration of a given element, non-chromatographic procedures involving a selective extraction step, could be an excellent alternative. This speciation strategy provides advantages such as instrumentation simplicity, low cost, short time of analysis and even a better accuracy in comparison to the chromatographic techniques [22]. Moreover, the speed of the separation procedure is a very important issue at the moment of preventing the interconversion of chemical species during this operation. The redox equilibrium between species can be affected by the time involved in the extraction procedure yielding to inaccuracies in species determination. Thus, FI offers a good chance for increasing accuracy and reducing the time of operation.

In groundwater, As(III) and As(V) live dominantly in oxoanion forms with As(V) as $H_2AsO_4^-$ and $HAsO_4^{2-}$ and As(III) as the neutral form $HAsO_2$ [2,23]. The different first acid dissociation constants (pK_a) of H_3AsO_4 and $HAsO_2$ are 2.3 and 9.3, respectively, and allow the separation of As(III) and As(V) by means of ion-exchange mechanisms at the usual pH range of groundwater [24]. As(V) forms are retained on a anion exchange resin whereas the As(III) neutral form passes through.

This study aims to develop a flow injection hydride generation atomic absorption spectrometry system which involves the on-line separation of inorganic arsenic species using a strong anion exchange column for the selective removal of As(V) at the usual pH values of the groundwater samples and the direct determination of As(III) at trace levels. The method employs instrumentation usually available in routine laboratories and assures high sensitivity and sample throughput together with easiness of operation. Even though the separation at natural pH is not a minor issue since it is more prone to interferences from concomitants of natural occurrence in groundwater samples, no pH conditioning was chosen in order to keep the original arsenic speciation. Consequently, a conscientious study of anionic interferences and their influence on As(V) removal is presented here. Analytical results will be also shown and compared to HPLC–ICPMS.

2. Experimental

2.1. Instrumentation

A PerkinElmer Model 3110 flame atomic absorption spectrometer (Connecticut, USA) was used as detector. It was equipped with an arsenic hollow cathode lamp Photron (Victoria, Australia) set at 193.7 nm wavelength, 11 mA lamp current and 0.7 nm slit width. A PerkinElmer FIAS 100 flow injection hydride generation system (Connecticut, USA) with a heated quartz tube atomizer (10 mm i.d. × 160 mm length) was used for hydride generation and coupled to the AAS. An anion-exchange cartridge was placed before the injection valve to produce a SPE–FI-HGAAS system with on-line separation of the inorganic arsenic species. The flow rates were programmed and automatically controlled through the rotation speed of the multichannel peristaltic pump, the same for the time of the process. The software AA WinLab version 3.2 was provided by PerkinElmer. The sample solution flowed into a 500 μL sample loop. Polytetrafluoroethylene (PTFE®) tubing of 1.0 mm i.d. was employed for the movement of the fluids through the manifold. Flexible polyvinylchloride peristaltic pump tubing was used to transport the HCl carrier and the $NaBH_4$ reducing reagent. Peak height was used for the measurement of the analytical signal.

2.2. Reagents and chemicals

2.2.1. Standards and samples

All reagents were of high purity or at least of analytical reagent grade. Deionized–distilled water (DDW, resistivity 18 $M\Omega\,cm^{-1}$) was used to prepare all solutions. As(III) stock solution 1000 mg L^{-1} was prepared from 1.3204 g of As_2O_3 (Riedel-de Haën, Germany) dissolved in 20 mL of 1 mol L^{-1} NaOH, neutralized with 2 mol L^{-1} HCl and diluted to 1000 mL with 0.6 mol L^{-1} HCl. Working solutions were prepared daily by appropriate dilution of the stock solution in DDW. As(V) stock solution of 1000 mg L^{-1} was obtained from Merck (Darmstadt, Germany). For the determination of total inorganic arsenic, working solutions were prepared by pre-reduction of the As(V) standard stock solution with 5% potassium iodide (KI) Merck (Darmstadt, Germany)–5% ascorbic acid ($C_6H_8O_6$) Merck (Darmstadt, Germany) in HCl 1.2 mol L^{-1}. The same was employed for pre-reduction of As(V) to As(III) in the water samples.

The groundwater samples analyzed in this study were taken from aquifers from Santa Fe (Argentina), a central region of the country.

Reference material NIST 1643d (trace elements in water) was obtained from the International Atomic Energy Agency (Analytical Quality Control Services, Vienna, Austria).

2.2.2. Hydride generation

Hydrochloric acid solutions used as carriers were prepared from concentrated HCl J.T. Baker (USA) at different concentrations ranging between 1.0 and 4.7 mol L^{-1}. Sodium tetrahydroborate

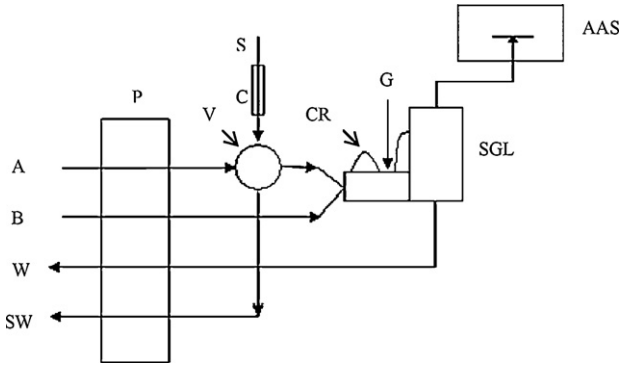

Fig. 1. SPE–FI-HGAAS configuration for selective As(III) determination. A, carrier acid solution; B, reductant solution; W, waste; SW, sample waste; P, peristaltic pump; S, sample; C, anion exchange column; V, injection valve; G, carrier gas; CR, reaction coils; SGL, gas–liquid separator; AAS, atomic absorption spectrometer with quartz tube atomizer.

solutions ($NaBH_4$) 0.10–0.47% (m/v) were prepared daily by dissolving $NaBH_4$ Merck (Darmstadt, Germany) in 0.025% (m/v) sodium hydroxide Merck (Darmstadt, Germany). Nitrogen 99.998% purity, obtained from Linde (Argentina) was used as carrier gas to transport the generated hydride to the atomizer.

2.2.3. SPE cartridges and filters

Silica-based chloride-form strong anion exchange (SAX) resin with trimethylaminopropyl functional groups (500 mg sorbent of 40 μm particle size and 60 Å pore size) packed in Bond Elut cartridges of 10 mL were obtained from Varian (Harbor City, USA). Cartridges were preconditioned with 1 mL methanol and DDW before use. The cellulose acetate membrane filters (0.45 μm pore size) were obtained from Microclar (Argentina).

2.3. SPE–FI-HGAAS system

The anion exchange cartridge was incorporated to the FI-HGAAS before the injection valve by means of a simple coupling with a flexible polyvinylchloride coil of 10 cm length and 2 mm i.d. Thus, the species separation process was carried out on the original sample, i.e. prior to its dilution in the carrier acid solution. The sample was loaded in the cartridge and then, it was propelled through the resin by means of the peristaltic pump whilst the injection valve remained in the load position. As(V) was retained onto the ion exchange resin and the eluent containing As(III) was inserted into the acid carrier stream when the injection valve was switched to the injection position. The eluent was transported to the chemifold where it was mixed with the reductant in the reaction coil to produce arsine. The liquid/vapor mixture flowed to a gas–liquid membrane separator and the gaseous hydride was transported by the nitrogen carrier stream to the quartz atomizer heated with an air-acetylene flame. The remaining liquid was removed from the separator by the peristaltic pump. A scheme of the SPE–FI-HGAAS system is shown in Fig. 1. Chemical and operational parameters such as reagent concentrations and flow rates were optimized using a multivariate approach.

2.4. Total inorganic arsenic

Total inorganic arsenic concentration was determined on 10 mL sample aliquots acidified with concentrated HCl (5 mL) and prereduced with 5% (m/v) KI–5% (m/v) $C_6H_8O_6$ solution (5 mL) in 50 mL volumetric flask. The instrumental and operating parameters routinely used for total inorganic As determination are shown in Table 1.

Table 1
FI-HGAAS instrumental and operating conditions for total inorganic As determination.

Wavelength	193.7 nm
HCL current	11 mA
Slit width	0.7 nm
Integration time	15 s
Read time	20 s
Carrier solution flow-rate	10.0 mL min^{-1}
Reductant solution flow-rate	5.0 mL min^{-1}
Carrier gas flow-rate (N_2)	75 mL min^{-1}
Sample loop volume	500 μL
Mixing coil length	310 mm (vol. 320 μL)
Reaction coil length I	115 mm (vol. 70 μL)
Reaction coil length II	310 mm (vol. 200 μL)
Prefill time	15 s
Fill time	10 s
Injection time	15 s

2.5. Sampling and sample preservation

Since the original distribution of the arsenic redox species should be modified when separated from their natural environment, procedures for preservation or stabilization are mandatory for analytical speciation. However, these procedures have not yet been standardized and in addition, the literature on the subject is controversial [7]. Consequently, the species separation in field is often recommended [25].

An immersion sampler of Delrin® and polypropylene was especially made for this work. The device allowed minimizing the exposure of the samples to atmospheric oxygen and metallic components. It was composed by a container of 450 mL capacity fitted with a shutoff valve formed by a spring and a Delrin® cone. The valve was located within a first rod screwed at the upper part of the container. A channel crossed inside a second rod located at the bottom of the container allowed the extraction and/or removal of the sample (see Fig. 2). The sampler was placed 1 m below the water level by using weights and floating. After the sampler was lifted to the surface, the water in the container was transferred to 100 mL high density polythene bottles.

The strategy adopted for the preservation of elemental species in waters relies, mainly, on the analytical technique and the need of

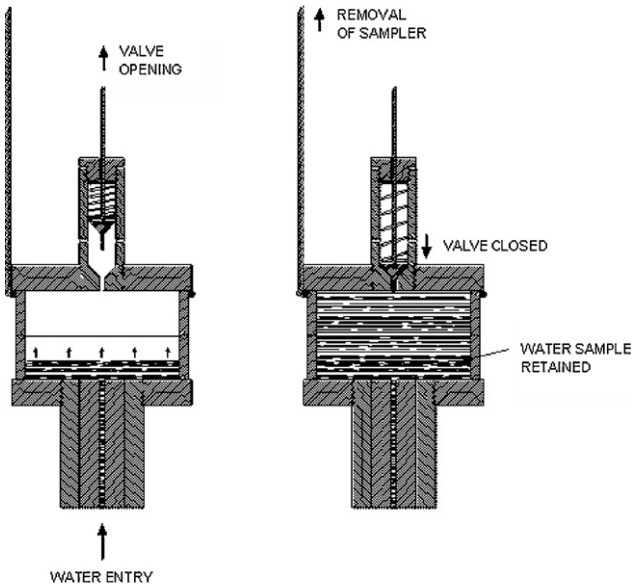

Fig. 2. Sampler device used for the groundwater extraction.

keeping constant the redox potential of the environment, preserving in this way any changes on the analytical speciation. Sample filtration and acidification have been the strategies typically used in the water sample collection for metal analysis. The use of membrane filters with pore size 0.45 μm allows standardizing the dissolved fraction of metals, acting as a barrier for microorganisms and particulate materials as well. The main purpose of the acidification is to prevent the precipitation of Fe, Mn and Al hydroxides which could adsorb arsenic species on the surface. In the presence of low concentrations of metals able to form hydroxides, the refrigeration at 4–5 °C was reported as an effective way to preserve the species distribution in filtered natural water samples for a period of up 30 days [26].

The water samples acidification with low concentrations of HCl is often recommended when arsenic is determined by HGAAS as, in this way, the sample media matches that of the carrier solutions. However, when anionic exchange is used to separate arsenic species, the presence of high concentrations of chloride ions seriously decreases the retention efficiency of the charged arsenic species by competition for the active sites on the resin. Moreover previous assays on the samples under study had showed very low levels of metal hydroxides and so, the following strategies were chosen to preserve the species distribution in the groundwater samples: (i) filtration and refrigeration at 4–5 °C for short-term speciation analysis; (ii) filtration and freezing at −18 °C for medium-term speciation analysis (for comparison of results with HPLC–ICPMS. See Section 3.6).

For comparison, the separation of inorganic As(III) and As(V) species was carried out on-site. Immediately after collection, 20 mL of each water sample was extracted from the sampler using disposable syringes. The sample was allowed to pass through a 0.45 μm filter and a silica-based strong anion exchange cartridge connected in series. The flow rate was 2–4 mL min^{-1}. Cartridges and solutions containing the separated arsenic species were cooled and brought to the laboratory for analysis.

3. Results and discussion

3.1. Evaluation of the selective retention of inorganic As(V) on the SAX resins

The difference between the dissociation constants of arsenious acid ($pK_a = 9.29$) and arsenic acid ($pK_{a1} = 2.25$, $pK_{a2} = 6.76$ and $pK_{a3} = 11.29$) allows to separate these species on the basis of ion exchange at a given pH. At neutral pH, arsenious acid is present in the neutral form $As(OH)_3$ and it is not retained by the anion exchange cartridge. In contrast, arsenic acid is dissociated to $H_2AsO_4^-$ and $HAsO_4^{2-}$ and the retention of these species should be expected [24].

Since methylated arsenic species such as monomethylarsinic (MMA) and dimethylarsinic (DMA) are not of usual occurrence in groundwater [2] (methylation is promoted by phytoplankton or microbial activity in lakes and rivers), the separation train developed here was suitable to carry out the complete separation of inorganic species followed by the determination via FI-HGAAS. However, the influence of DMA and MMA on arsine generation was tested. Results are displayed in Table 2. It can be observed that DMA and MMA seriously affect arsine generation and thus, the separation train employed here seems not suitable for natural waters with high contents of organic arsenic. In such cases others separation steps should be added to the train (i.e., a strong acid cation exchange column for DMA isolation).

Assuming that no organic forms of arsenic would be present in the groundwater samples (evidence was provided afterwards by HPLC–ICPMS, Section 3.6), synthetic samples containing inorganic As(III) and As(V) were prepared and the efficiency of separation by SAX cartridges was firstly evaluated through batch experiments.

Table 2
Influence of organic arsenic species on As(III) determination ($n = 3$).

MMA and DMA (μg As L^{-1})	Influence of MMA on the analytical signal of As(III) (%)	Influence of DMA on the analytical signal of As(III) (%)
15	22	60
30	23	62
45	26	63
60	32	67

A 15 mL solution spiked with 30 μg L^{-1} As(III) was passed through a SAX cartridge. As(III) was determined in the eluent and a quantitative recovery was obtained ($104 \pm 2\%$, $n = 10$).

In order to test the complete isolation of As(V) onto the SAX resin, the following experiments were performed:

(i) A 15 mL solution containing 30 μg L^{-1} As(V) was passed through the SAX cartridge. No arsenic was found in the eluent showing the complete retention of As(V) onto the resin.
(ii) A 20 mL solution of DDW was passed through the same cartridge and again, As was not detectable in the eluent.
(iii) Last, 1 mL of HCl 1.0 mol L^{-1} was employed to elute As(V) from the resin and a quantitative recovery (102 ± 2, $n = 10$) was obtained.

When a 15 mL solution containing both As(III) and As(V) (30 μg L^{-1} each) was passed through the SAX cartridge, a quantitative recovery ($100 \pm 1\%$, $n = 10$) of As(III) was obtained in the remaining solution. Then, As(V) retained onto the cartridge was completely released by means of 1 mL volume of 1.0 mol L^{-1} HCl as eluent.

The experiments described above, allowed us to conclude the efficiency of the SAX resin for the quantitative retention of As(V) together with the complete release of As(III).

3.2. Optimization of the SPE–FI-HGAAS system

The injection of a given volume of non-acidified sample into a diluted acid carrier flowing through a FI-HGAAS system, adds some problems to the optimization process mainly related to the decrease of sensitivity and splitting of the analytical signal (double peaks) [27]. Thus, chemical and operating parameters must be carefully evaluated in order to get the best combination. A Plackett–Burman fractional factorial design [28] at two levels was used for screening purposes in order to identify the most significant variables that influence the system performance. Five factors: HCl concentration, $NaBH_4$ concentration, carrier gas flow rate, peristaltic pump rotation rate (controlling in turn HCl, $NaBH_4$ and sample flow rates) and flame air/acetylene ratio were selected to optimize the As(III) absorbance signal using only 12 experiments. Six dummy factors were included in the design to estimate the experimental error. The significance of the factor effects was determined according to a test-*t*. A factor was considered as significant when its *t*-value was higher than the tabulated two-sided critical *t*-value at a 95.0% confidence level and n_{dummy} degrees of freedom. Just HCl concentration, $NaBH_4$ concentration and solution flow rates revealed themselves as statistically significant variables and this finding was applied to the multivariate design described below.

A multivariate design (central composite circumscribed, CCC) [28] involving 23 experiments was used to estimate the optimum values for each statistically significant variables: HCl concentration, $NaBH_4$ concentration and solution flow rates (established through

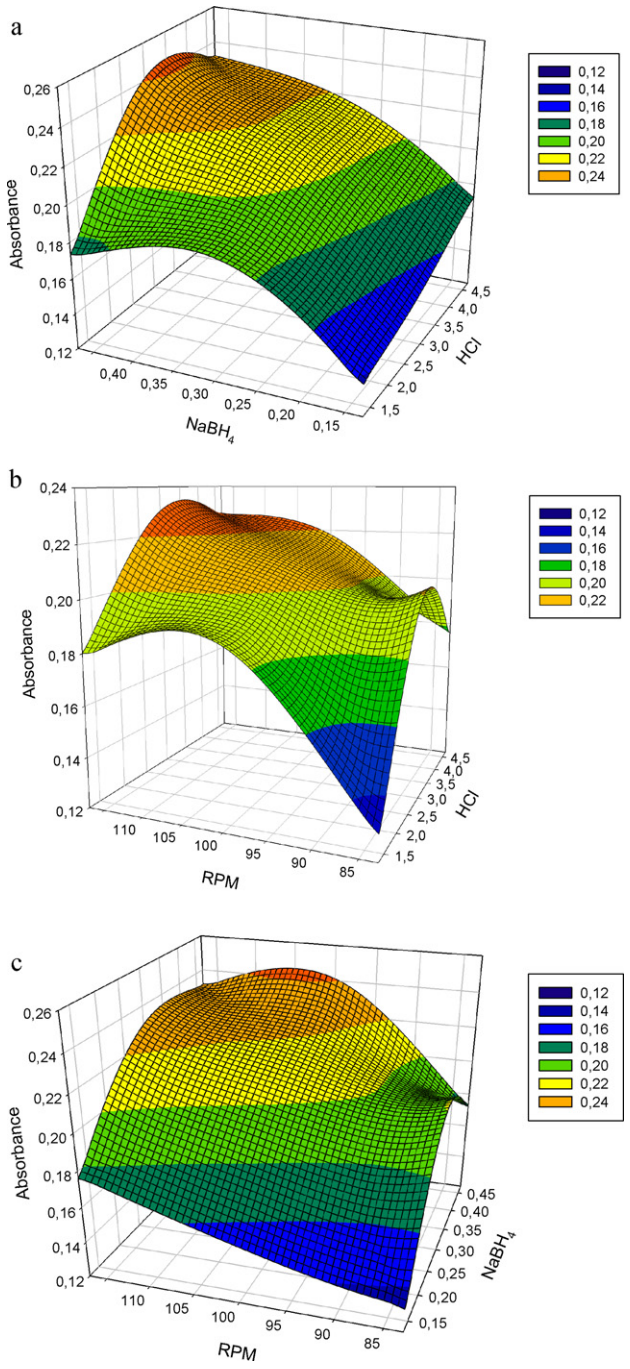

Fig. 3. Multivariate study for the optimization of the statistically significant variables: (a) absorbance vs HCl and $NaBH_4$ concentrations; (b) absorbance vs. HCl concentration and solution flow rates (expressed as rpm of the pump); (c) absorbance vs $NaBH_4$ concentration and solution flow rates.

the peristaltic pump rate). Obtained results are shown in Fig. 3 and selected values are displayed in Table 3. Even though Fig. 3(a) gives a maximum of absorbance for HCl 3.5 mol L^{-1} and $NaBH_4$ concentrations above 0.35% (m/v), $NaBH_4$ concentration was set in 0.35% since higher values promoted an intense bubbling together with an increment in the standard deviation values. As a matter of fact the liquid phase passes through the separation membrane and condensates inside the tube that carries the gaseous phase towards the quartz cell. Consequently, a compromise between sensitivity and precision was considered.

Fig. 3(b) and (c) shows maximum absorbance values for flow rates higher than those selected in Table 3. Again, an increase in standard deviation values because of bubbling was observed and sensitivity was surrendered to improve precision.

Table 3
Optimized variables of the SPE–FI-HGAAS system for selective As(III) determination.

Factor	
HCl concentration (mol L^{-1})	3.5
$NaBH_4$ concentration (% m/v)	0.35
Peristaltic pump rate (rpm)	110
- HCl flow rate (mL min^{-1})	(10.9)
- $NaBH_4$ flow rate (mL min^{-1})	(5.6)
- Sample flow rate (mL min^{-1})	(5.1)

3.3. Study of anionic interferences on As(V) retentions

According to the manufacturer, the chloride-form SAX resin has an exchange capacity of 29 μg $HAsO_4^{2-}$/mg resin. However, the high exchange capacity can be affected by the competitive uptake of other anions present in the samples since it is not a selective resin. In order to study the influence of different anions on As(V) retention by SAX at neutral pH, several model solutions containing 20 μg L^{-1} As(V) and different amounts of Cl^-, SO_4^{2-}, NO_3^-, $H_2PO_4^-$ and HCO_3^- were prepared and the retention of As(V) was assessed. Table 4 shows the percentage of retention of As(V) for different concentrations of concomitants. Except for the case of sulfate, all the interfering anions can coexist with As(V) at their usual concentrations in natural waters. Sulfate concentrations above 800 mg L^{-1} seriously interfere As(V) retention. However, a sample dilution of 3:5 was enough to become despicable the anionic interference. Even though the LOD was decreased accordingly, it remained useful and in agreement with regulations (Fig. 4).

Table 4
Studies of anionic interferences in the inorganic As(V) retention.

Interfering anion	Concentration (mg L^{-1})	Retention efficiency (%)
SO_4^{2-}	200	98
	600	97
	800	97
	1000	55
	1200	32
	2000	19
Cl^-	1000	99
	2000	93
NO_3^-	500	99
$H_2PO_4^-$	400	100
HCO_3^-	400	100

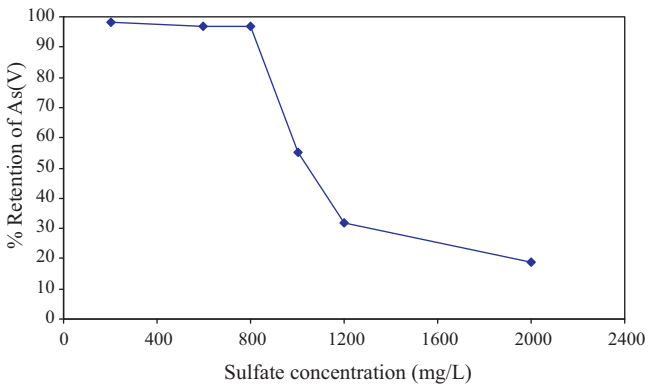

Fig. 4. Influence of sulfate concentration on retention efficiency of As(V).

Table 5
Inorganic arsenic speciation in synthetic samples.

As(III) added (μg L^{-1})	As total [As(III) + As(V)] added (μg L^{-1})	As(III) found (μg L^{-1})	Recovery As(III) (%)
1	10	<LOQ (1.7)	–
5	50	5.0 ± 0.1	100 ± 2
10	100	10.2 ± 0.3	102 ± 3
20	200	19.8 ± 0.2	99 ± 1

Errors are expressed according to Miller and Miller [29] (95% confidence level; $n = 10$).

3.4. Analytical performance of the proposed method

The analytical performance for As(III) determination was obtained using the optimum conditions described above. The limits of detection (LODs) and quantification (LOQ) (calculated from three and ten times the standard deviation of the blank signal, respectively) were 0.5 and 1.7 μg L^{-1} of As(III) [29]. The detection limit was found to be comparable with other values reported elsewhere using hydride generation coupled to atomic detectors: off-line SPE and HGAFS, 0.05 μg L^{-1} [25]; FI-HGAAS with variable $NaBH_4$ concentrations, 0.3 μg L^{-1} [19]; FI-SPE–HGAAS 0.2 μg L^{-1} [24]. The calibration curve for As(III) was linear over the concentration range 1.7–25 μg L^{-1} (regression equation: y (Absorbance in arbitrary units) = 0.0159 + 0.0179 [As(III)], $R^2 = 0.9908$). The sampling throughput was 60 samples h^{-1}.

In order to test the reliability of the results for total As determination, a working curve with As(V) standard solutions pre-reduced as told under Section 2.2.1 was prepared. The curve was linear up to 25 μg L^{-1}. The linear regression equation was: y (Absorbance in arbitrary units) = 0.0167 + 0.0208 [red As], $R^2 = 0.9878$). Both experimental curves are in agreement within 10% experimental error.

In order to evaluate the strength of the proposed method, As(III) was determined in synthetic samples prepared with a ratio 1:10 As(III) to total inorganic As. Relative standard deviation (RSD%) was less than 2% (RSD, $n = 3$) at the 5 μg L^{-1} level in synthetic samples. Recovery values of 98–100% were found for the analyzed samples. Results are shown in Table 5. Total arsenic quantification was performed by pre-reduction of the samples according to Section 2.2.1 and interpolation of the analytical signal in the working curve for As(V) standards.

Table 6
Chemical characterization of the groundwater samples.

Parameter	Units	Minimum	Maximum	Media
pH		7.80	8.53	8.00
Dissolved oxygen	mg L^{-1}	2.8	5.6	4.16
Conductivity	μS cm^{-1}	980	3600	1472
Chlorides	mg L^{-1}	75	610	271
Alkalinity	mg L^{-1}	193	320	264
Bicarbonate	mg L^{-1}	61	183	124
Hardness	mg L^{-1}	23	416	245
Sulfates	mg L^{-1}	92	974	440
Nitrates	mg L^{-1}	3.7	11.3	6.5
Phosphates	mg L^{-1}	<1.0	<1.0	<1.0
Ammonium	mg L^{-1}	<0.05	<0.05	<0.05
Sodium	mg L^{-1}	124	787	380
Potassium	mg L^{-1}	10	46	31
Calcium	mg L^{-1}	6.1	50	32
Magnesium	mg L^{-1}	2.6	56	27
Zinc	mg L^{-1}	<0.01	<0.01	<0.01
Manganese	mg L^{-1}	<1.0	<1.0	<1.0
Iron	mg L^{-1}	<0.1	<0.1	<0.1

3.5. Speciation analysis in groundwater samples

The inorganic arsenic species were determined in the groundwater samples described under Section 2. These samples are characterized by high pH values and salinity and by the presence of considerable amounts of dissolved oxygen (See Table 6).

In order to test both, the complete removal of As(V) together with an accurate measurement of As(III) concentration, filtered real samples were spiked in the field with known amounts of As(III) and then, passed through the SAX cartridge As(III) was determined by SPE–FI-HGAAS by simple interpolation of the analytical signal in the calibration curve. Recoveries between 98–106% were found, assuring the goodness of the separation process.

The samples containing the highest concentrations of SO_4^{2-} were analyzed again by simple dilution 3:5. Total soluble inorganic arsenic was measured in the filtered water sample according to Section 2.4. Results obtained from the analysis of the certified reference material NIST 1643d for total arsenic was 55.6 ± 1.5 μg L^{-1} (95% confidence level; $n = 3$) which was in good agreement with the certified value of 56.02 ± 0.73 μg L^{-1}. Since As(III) was not detectable

Table 7
Determination of inorganic arsenic species in groundwater samples.

No. sample	[As(III) + As(V)] (μg L^{-1})	As (III) added (μg L^{-1})	As(III) found (μg L^{-1})	Recovery As(III) (%)
	FI-HGAAS		SPE–FI-HGAAS	
1	177.8 ± 0.1	0	<0.5	
2	216.0 ± 4.2	0	<0.8	
3	119.9 ± 5.0	0	<0.8	
4	86.1 ± 1.9	0	<0.5	
5	58.5 ± 1.0	0	<0.5	
6	90.0 ± 1.9	0	<0.5	
7	40.4 ± 2.0	0	<LOQ (1.7)	
		10	10.4 ± 0.4	104 ± 4
8	127.6 ± 2.4	0	<LOQ (1.7)	
		10	10.6 ± 0.4	106 ± 4
9	111.7 ± 2.9	0	<LOQ (1.7)	
		10	10.4 ± 0.6	104 ± 6
10	79.4 ± 1.2	0	<LOQ (1.7)	
		10	10.1 ± 0.6	101 ± 6
11	40.0 ± 0.4	0	<LOQ (1.7)	
		10	9.9 ± 0.4	99 ± 4
12	128.5 ± 3.3	0	<LOQ (1.7)	
		10	10.6 ± 0.5	106 ± 5
13	32.4 ± 0.2	0	<LOQ (1.7)	
		10	9.8 ± 0.2	98 ± 2
14	91.6 ± 2.9	0	<LOQ (1.7)	
		10	10.5 ± 0.4	105 ± 4

Errors are expressed according to Miller and Miller [29] (95% confidence level; $n = 3$) LOD for original samples: 0.5 μg L^{-1}; LOD for samples diluted with a 3:5 ratio: 0.8 μg L^{-1}.

Table 8
Operational parameters for HPLC–ICPMS.

RF power	1400 W
Plasma gas flow	15 L min^{-1}
Auxiliary gas flow	1.08 L min^{-1}
Nebulizer gas flow	1.15 L min^{-1}
Sampler and skimmer cones	Pt
Ion lents	7.2 V
Data collection mode	Single monitoring ^{75}As
Dwell time	250 ms

in the analyzed samples, the measurement of total arsenic concentrations was ascribed to As(V). Results are summarized in Table 7.

The separation of soluble inorganic As(III) and As(V) carried out on-site by using filters and cartridges showed poor performance for the samples containing the highest concentrations of SO_4^{2-}, so the on-site separation by SPE resulted of low interest for the arsenical speciation purpose in these cases (Table 8).

3.6. Comparison of the results with HPLC–ICPMS

Validation of the SPE–FI-HGAAS method proposed here by means of the use of water samples certified for As(III) is not possible as there is a lack of offer for certified reference materials for species. So, five groundwater samples were analyzed for arsenic speciation by high performance liquid chromatography (HPLC) for separation and inductively coupled plasma mass spectrometry (ICPMS) for detection, employing a methodology described previously in the literature [30]. A volume of the filtered sample solution was injected in a LC system assembled with a quaternary pump (Model Series 200, PerkinElmer), a 200 μL sample loop and a separation column (Dionex, IonPac AS14,250 × 4 mm i.d.) and then, analyzed by ICPMS (PerkinElmer Sciex spectrometer, Model Elain DRC II, Thornhill, Canada). Single ion monitoring at *m/z* 75 was used to collect the data by integrating peak area, using the Chromera software (PerkinElmer, version 1.2, 2006).

Arsenic species in the groundwater samples were identified by comparison of the retention times with those of references. As(III) and As(V) separation was carried out using a mobile phase containing 20 mM ammonium carbonate at pH 8.7 (isocratic elution mode) which took only 8 minutes. Calibration curve ranged between 0.1 and 1.0 μg L^{-1} for As(III) and 10 and 100 μg L^{-1} for As(V). The LODs were 0.02 μg L^{-1} and 0.1 μg L^{-1} for As(III) and As(V), respectively. The samples were diluted 1:5 with distilled water in order to minimize chloride the interference giving rise to $^{40}Ar^{35}Cl^+$ polyatomic ion formation (*m/z* 75).

Moreover, preliminary tests of the samples using mobile phases containing 1.5 mM, 12 mM and 20 mM ammonium carbonate at pH 8.7 (gradient elution mode) had shown the absence of methylated arsenic species, allowing us to assure that only inorganic arsenic is present in the analyzed waters from Santa Fe.

Table 9
Result comparison between SPE–FI-HGAAS and HPLC–ICPMS.

N° sample	As(III) (μg L^{-1}) SPE–FI-HGAAS	As(III) (μg L^{-1}) HPLC–ICPMS	As(V) (μg L^{-1}) HPLC–ICPMS
1	<0.5	0.38 ± 0.02	175.1 ± 2.9
2	<0.8	0.44 ± 0.02	207.1 ± 5.8
3	<0.8	0.30 ± 0.03	123.2 ± 1.2
4	<0.5	0.40 ± 0.02	82.1 ± 2.3
5	<0.5	0.44 ± 0.02	62.0 ± 2.7

Errors are expressed according to Miller and Miller [29] (95% confidence level; $n = 3$)
LOD for original samples: 0.5 μg L^{-1}; LOD for samples diluted with a 3:5 ratio: 0.8 μg L^{-1}.

Table 9 shows the results obtained for As(III) by both methodologies and As(V) by HPLC–ICPMS. A good agreement (95% confidence level) was found for As(V) by comparison with FI-HGAAS shown in Table 7. As(III) was not detected by the method presented here but the results (below LODs), are fully consistent with the HPLC–ICPMS quantification.

4. Conclusions

The incorporation of anion-exchange SPE to a FI-HGAAS system allowed to develop a simple, sensitive, rapid (throughput of 60 sample h^{-1}) and low cost methodology for direct and selective determination of the As(III) in water samples without pre-treatment in acidic media. The whole operation reduces the possibility of interconversion of species at the moment of acidification. The loss of sensitivity typically arising from the use of non-acidified samples was prevented by working with concentrations of HCl and $NaBH_4$ higher than those usually recommended. The optimized method is robust and easily applicable in routine laboratories for inorganic arsenic speciation at trace level. It shows a high efficiency for the retention of As(V) under relatively low salinity conditions together with a good recovery of As(III). The limit of detection, less than μg L^{-1}, leaves the presented methodology in a competitive place with regard to the current regulations imposed by national and international standards. The levels of trivalent arsenic found in groundwaters from Santa Fe revealed to be below the limit of detection of the method presented whilst the pentavalent inorganic arsenic species was shown to be widely prevalent. The employment of a more sophisticated technique such as HPLC–ICPMS allowed us to test the consistency of our results at the time that revealed the absence of methylated arsenic species in a set of groundwater samples from Santa Fe, Argentina.

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