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Development of an on line miniaturized non-chromatographic arsenic speciation system☆

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ABSTRACT

An arsenic speciation method is proposed introducing selective hydride generation, UV photooxidation and hydride trapping on oxidized multiwall carbon nanotubes (CNTs) with electrothermal atomic absorption spectrometry (ETAAS) for detection. To this end a flow injection system was designed to focus on miniaturization with minimal reagent consumption. As a result reagent consumption was kept in μL level with no need of carrier gas for hydride transport. This study obtained an enhancement factor of 60 when 2 mL of sample were loaded in the gas–liquid separator, arsine adsorbed on CNTs, and eluted with 30 μL of 5% HNO_3 (v v^{-1}). A limit of detection (LoD) of 0.78 ng L^{-1} was obtained. The precision was evaluated by relative standard deviation (RSD%) corresponding to 8.3% (n = 10). The method determined organic and inorganic arsenic fractions; and As^{3+} and As^{5+} concentrations in well and cistern water samples from arsenic endemic regions of Argentina.

1. Introduction

Arsenic is recognized as a ubiquitous element in the environment, from both natural and anthropogenic sources. As occurs in various oxidation states (−3, 0, +3 and +5) and undergoes complex biotic and abiotic transformations to organic and inorganic compounds in the environment. In natural water, As is found mainly as inorganic oxyanions such as trivalent arsenite (As^{3+}) or pentavalent arsenate (As^{5+}), while organic arsenic compounds, as monomethylarsonate (MMA), can be found in low concentrations in surface water, product of the biological activity [1,2]. Arsenic toxicity varies depending mainly on the oxidation state, being inorganic species the most toxic [3,4]. According to this, research in the development of analytical methods for As speciation in environmental samples has a remarkable importance.

In literature, several researches have been reported on arsenic speciation [5]. Most of these researches involve the introduction of separation techniques like liquid chromatography (LC) coupled to atomic spectrometries like atomic fluorescence spectrometry (AFS) [6] or inductively coupled plasma mass spectrometry (ICP MS) [7]. Despite of their efficiency for analyte separation, LC is a relatively expensive technique that consumes ultrapure water and solvents. For these reasons, many of the best speciation procedures remain at the laboratory scale and cannot be used in routine analysis [8].

Non-chromatographic methods for arsenic speciation can involve two strategies: UV photooxidation and selective hydride generation [9,10]. UV irradiation treatment has been probed to efficiently transform methylated arsenic species (non-forming hydride species) to inorganic As species (hydride forming). In addition it has been previously shown that As^{3+} could be determined alone in a mixture of As^{3+} and As^{5+} by selective hydride generation through strict pH control [11].

Research involving UV photooxidation, selective hydride generation and hydride trapping with graphite furnace atomic absorption spectrometry (GFAAS) for detection has been already described in literature [12,13]. However research reporting As speciation by these strategies sometimes involves hydride trapping and selective release of trapped hydrides by means of temperature control [11]. These methodologies that employ different temperatures to trap and release hydrides, like cryogenic trapping, require complex instrumentation and sophisticated control mechanisms. Recently a novel methodology, exploits carbon nanotubes' (CNTs) properties of gas adsorption on their surface [14,15], to trap arsenic hydrides for analytical purposes [16].

A preference for online extraction systems involving solid phase extraction has been reported, due to advantages obtained in automation such as speed, sensitivity, reproducibility, simplicity and economy in the use of reagents. These systems consist in metal species retention or its derivatives on an appropriate solid sorbent contained in a column or micro column with subsequent recovery by elution with an adequate solvent [17–19]. Flow injection system design minimizes the amount and the toxicity of solvents and reagents employed in the measurement step, especially by automation and miniaturization, to be framed into Green Chemistry principles [20].

Despite the fact that there is an elevated number of researches involving As speciation in literature, most of it involves LC coupling to atomic spectrometries, mainly ICP MS, sophisticated instrumentation banned for many laboratories. The objective of this work is to

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encompass UV photooxidation and selective hydride generation with a simple hydride trapping strategy on CNTs to reach As speciation employing ETAAS for determination. To this end an FI design is proposed, focused on miniaturization and minimizing reagent consumption and waste generation. Different variables were optimized regard FI manifold and As speciation. The proposed methodology was applied to analysis of water samples from Arsenic endemic regions of Argentina.

2. Experimental

2.1. Reagents

Unless otherwise stated, the chemicals used were of analytical reagent grade and, therefore, no further purification was required. Standard As^{3+} solution (1000 μg mL^{-1}) was prepared by dissolving 0.3300 g of As_2O_3 (Sigma, St. Louis, USA) in 10 mL of 1 M NaOH and diluting to a final volume of 250 mL with 2 M HCl. Standard As^{5+} solution (1000 μg mL^{-1}) was prepared by dissolving 0.4526 g of $As_2O_5 \cdot 2H_20$ (Sigma, St. Louis, USA) in 10 mL of NaOH diluted to a final volume of 250 mL with 2 M HCl. Standard monomethylarsonate solution (1000 μg mL^{-1}) containing 543.21 μg mL^{-1} of As was prepared from analytical grade $CH_3AsO(ONa)_2 \cdot 6H_2O$ (Merck, Darmstadt, Germany) [21]. Thiourea and L-cysteine, used as reductants agents, were obtained from Sigma-Aldrich. Titanium dioxide, employed as photocatalyzer was obtained from (Sigma, St. Louis, USA) A 0.5% (w/v) sodium borohydride solution (Aldrich Chemical Co. 98%) was prepared in 0.5% (w/v) sodium hydroxide solution and was filtered through Whatman N° 42 filter paper to remove undissolved solids. This solution was prepared daily.

Commercial multiwalled CNTs were obtained from Sunnano (Jiangxi, China). CNTs were treated with concentrated nitric acid to clean them and eliminate possible residues present in CNTs due to the generation process. This procedure also allowed the generation of —COOH and —OH groups on the CNTs' surface, improving their solubility. After this, CNTs were centrifuged, filtrated, and dried [22].

Chemical modifier solutions (100 mL of a concentration of 10,000 mg L^{-1}) were prepared by dissolution of the proper solid salt into deionized water as follows: for Ni chemical modifier, 4.9545 g of $Ni(NO_3)_2 6H_2O$ were weighed and diluted [23].

2.2. Sample preparation

Well and cistern water samples were collected in As endemic regions of Argentina, specifically from south of Córdoba province. Samples were collected directly from the tap of the pumping system. Then they were filtered through 0.45 mm pore size membrane. Samples were transported refrigerated at 5 °C to avoid any As species interconversion. Once in the lab they were analyzed immediately.

2.3. Apparatus

Determination of As concentration was carried out on a Shimadzu Model AA-7000 atomic absorption spectrometer (Tokyo, Japan) equipped with a background correction system employing a continuum source, a GFA-EX7 electrothermal atomizer, and an ASC-7000 auto sampler. L'vov graphite tubes (Shimadzu, Tokyo, Japan) were used in all experiments. An arsenic hollow-cathode lamp (Hamamatsu, Photonics K. K., Japan) was employed as radiation source operated at 10 mA, the analytical wavelength of 193.7 nm was employed for all measurements. Gilson Minipuls 3 peristaltic pumps (Villiers, Le-Bell, France) and Tygon-type pump tubes (Ismatec, Cole-Parmer Instrument Company, Niles, IL, USA) were employed to propel sample, eluent and reagents. The employed gas–liquid separator (GLS) was homemade (1 cm internal diameter, 8 cm high, 6 mL volume) and it can be observed in Fig. 1. Reagents were deposited directly in the bottom of the GLS to improve homogenization and hydride generation. All unions were sealed to avoid gas losses. A conical minicolumn (40 mm length, 4.5 mm internal upper diameter, and 1.5 mm internal lower diameter) was used as sorbent holder. It was prepared by placing 10 mg of oxidized CNTs into an empty conical tip by the dry packing method. To avoid CNTs losses when the simple solution passed through the conical minicolumn, small amounts of quartz wool were placed at both ends. The photoreaction system consists of a PTFE tube (I.D. 0.55 mm) from Cole Parmer (Vernon Hills, IL, USA) surrounding a high-pressure Hg vapor lamp Phillips (Hanau, Germany).

2.4. Preconcentration procedure and determination

To develop As speciation methodology, different variables like pH, UV exposure time, type of reducing reagent, addition of catalyst and flow rates were optimized. The system shown in Fig. 1 was used for this purpose.

Previous to all analysis, the gas–liquid separator (GSL) was filled with $NaBH_4$ solution (Pump P_1; valve V_1, $NaBH_4$) and valve V_4 was closed. For determination of hydride and non-hydride forming arsenic species sample was previously added with TiO_2 prior photooxidation. After this sample is loaded (pump P1; valve V_1, position S) and introduced into photoreactor (UV PR) to oxidize arsenic organic species or non-hydride forming species. Then it is merged with HCl_c (Pump P_2;

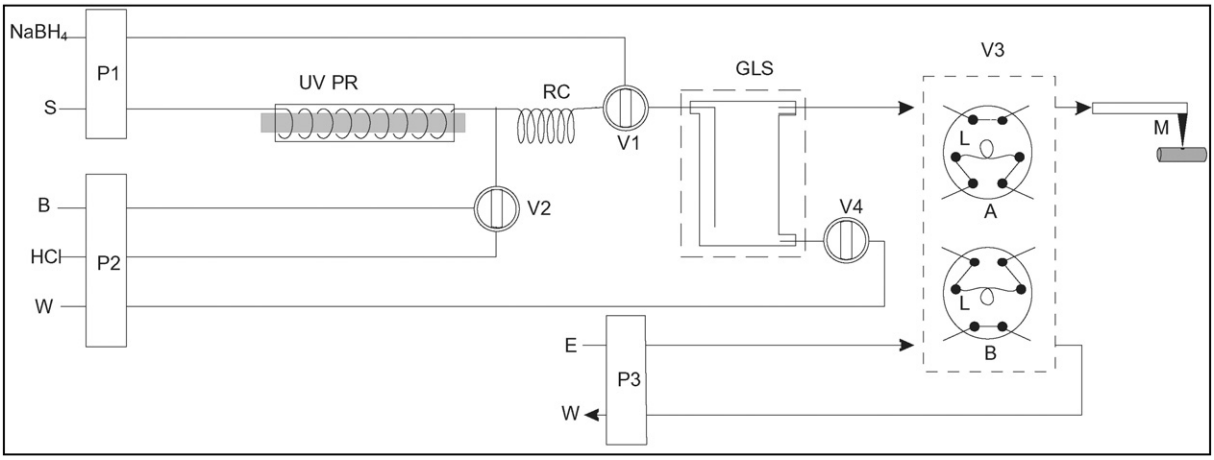

Fig. 1. Schematic diagram of the configuration of the instrumental. S, sample; B, buffer; E, eluent; V_1, V_2 and V_3, injection valves, valve positions: (A) sample loading; (B) injection; L, loop (30 μL volume); P_1, P_2 and P_3, peristaltic pumps; GLS, gas–liquid separator; RC, reaction coil; W, waste; M, mini-column filled with oxidized multi-walled carbon nanotubes mounted on the arm of ETAAS autosampler.

valve V_2, HCl) to reduce all arsenic species to As^{3+}, into the reaction coil RC. Finally the solution reaches GLS for hydride generation.

Hydride forming species, inorganic arsenic (As^{3+} and As^{5+}), were determined by not adding TiO_2 and turning off the UV photoreactor. In this way the only arsenic species able to form arsine are As^{3+} and As^{5+}, inorganic species. Organic arsenic concentration was calculated then by difference between total As concentration and inorganic As species.

As^{3+} was determined by changing valve V_2 to B position (pump P_2) being buffer introduced to the system. According to this, As^{5+} was not reduced to As^{3+} then only As^{3+} generates arsine. As^{5+} concentration was determined by difference with inorganic As concentration.

After arsine was generated it was adsorbed on CNTs loaded into minicolumn M, valve V_3, load position. At the same time eluent was loaded into the 30 μL loop L. Elution was achieved as follows: the arm of the autosampler, were the minicolumn M is mounted, was move to the graphite furnace injection position. After this valve V_3 was changed to elution position, eluent was pumped to the column and the retained arsine was eluted from the minicolumn M into the graphite furnace prior determination. Ni modifier was co-injected. After all analysis GLS was emptied by opening valve V_4, pump P_2, W, being ready for further analysis.

3. Results and discussion

3.1. Speciation conditions

FI system (Fig. 1) was designed based on speciation analysis and the novel arsenic hydride trapping on CNTs. To reach As speciation analysis, various sample treatments were introduced before GLS. Selective reduction of As^{3+} over As^{5+} discriminate between these hydride forming As species. In addition UV photooxidation with TiO_2 decomposed non-hydride forming As species like organic As (MMA). Despite the fact that selective hydride generation and UV photooxidation have been described in literature for As speciation, this novel hydride trapping strategy on CNTs requires an encompassing and optimization of these strategies into an FI system according to the hydride trapping strategy on CNTs.

3.1.1. Selective hydride generation

It has been extensively studied the selective generation of arsine from arsenic by variations in the medium acidity, to discriminate between As^{3+} and As^{5+} species. At high pH values, arsine formation by As^{3+} is quantitative. Hydride formation from As^{5+} decreases attributed to slower kinetics of hydride formation from these species since arsenate is ionized [24–26].

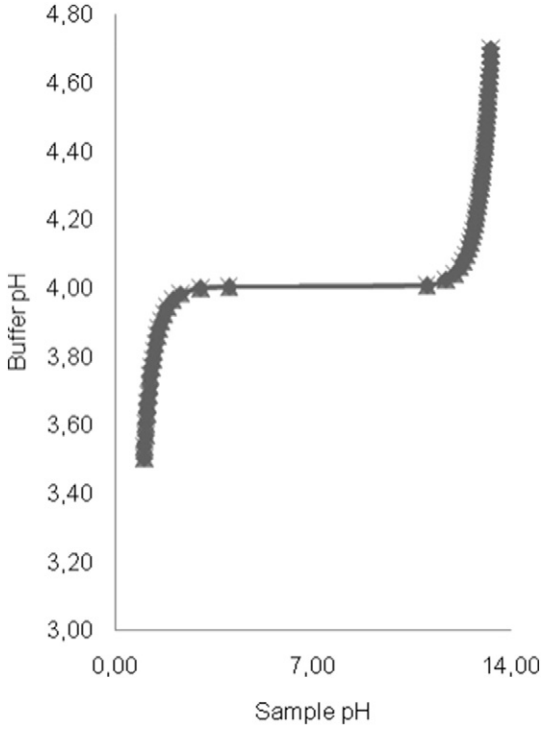

Fig. 3. On line pH variations of citrate buffer 0.1 mol L^{-1} according to different sample pH.

Fig. 2 shows As^{3+} and As^{5+} hydride generation efficiency according to hydrides trapping on CNTs followed by elution and determination by ETAAS. As observed, As^{3+} and As^{5+} hydride generation decreases as pH values increases. The decrease is more remarked for As^{5+} leading to a window at pH 4.0, where both species can be discriminated, since As^{5+} do not generate arsine, and arsine is quantitatively generated by As^{3+}. At pH 1.0 both species generate arsine. As^{5+} concentration can be calculated then from the difference between the signals obtained at pH 1.0 and 4.0. Results are correspondent to those obtained by Torralba et al. [21].

Since pH is the parameter discriminating between As^{3+} and As^{5+}, two types of buffers were evaluated to obtain an efficient control of pH at 4.0: tri-hydroxymethylaminomethane (TRIS)–HCl, 0.75 mol L^{-1}; and citric-citrate, 0.1 mol L^{-1} at a pH range between 4.0 and 7.0 [27,28]. Best arsine production was obtained with citric–citrate buffer.

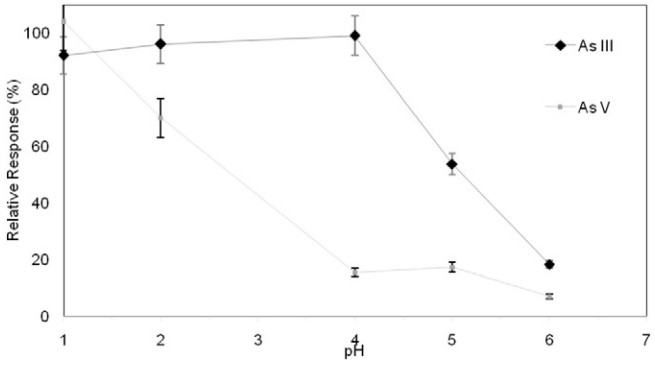

Fig. 2. Influence of pH on As (III) and As (V) retention during the loading step employing citrate buffer. Preconcentration of 2 mL of As (III) and As (V) solutions; Arsenic concentration, 100 ng L^{-1}; reducing agent, 0.5 mL $NaBH_4$ 1% (v v^{-1}); eluent, nitric acid 0.5% (v v^{-1}); loading flow rate, 0.5 mL min^{-1}; elution flow rate 0.5 mL min^{-1}; eluent volume 30 μL.

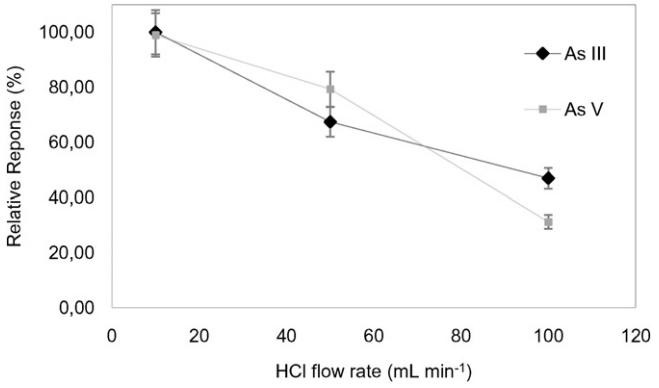

Fig. 4. Influence of HCl flow rate on As (III) and As (V) retention during the loading step. Preconcentration of 2 mL of As (III) and As (V) solutions; arsenic concentration, 100 ng L^{-1}; reducing agent, 0.5 mL $NaBH_4$ 1% (v v^{-1}); eluent, nitric acid 0.5% (v v^{-1}); loading flow rate, 0.5 mL min^{-1}; elution flow rate 0.5 mL min^{-1}; eluent volume 30 μL.

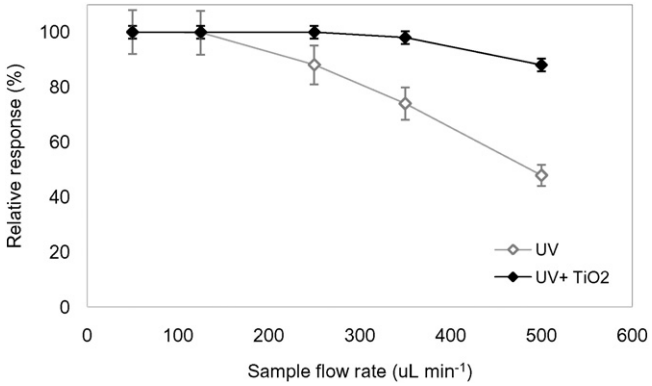

Fig. 5. Influence of sample flow rate on total As signal during the loading step in the UV-photoreactor. Preconcentration of 2 mL of As (III), As (V), MMA and DMA solutions; arsenic concentration, 100 ng L^{-1}; reducing agent, 0.5 mL NaBH4 1% (v v^{-1}); eluent, nitric acid 0.5% (v v^{-1}); loading flow rate, 0.5 mL min^{-1}; elution flow rate 0.5 mL min^{-1}; eluent volume 30 μL.

The buffer capacity of citrate at 0.1 mol L^{-1} concentrations was verified according to titrations and to Henderson–Hasselback equation [29]. Fig. 3 shows pH variations of citrate-buffered samples according to pH variations of the sample. As observed in acidic titration with HCl, when pH 1.0 solutions are introduced into the system, citrate buffered solutions pH decreased from pH 4.0 to 3.5. As observed in Fig. 2, at pH 3.5 arsine generation from As^{5+} can contribute to an overestimation of As^{3+} concentration. This point should be addressed when acidic solutions are introduced into the system. In alkaline titration pH of buffered samples with 0.1 mol L^{-1} citrate solution do not varies until pH 11.0.

In previously published work it was highlighted the importance of hydrochloric acid optimization prior reduction of As^{5+} to As^{3+} to generate arsine [16]. In addition since thiourea and L-cysteine are reducing agents mentioned in the literature [30,31] these were also evaluated. Thiourea and L-cysteine were introduced through HCl_c line, at concentrations ranging from 0.25 to 1.0% (m v^{-1}). The reduction efficiency was higher at 0.25% (m v^{-1}) for both reductants. Between reductants, the following order was obtained according to their reducing efficiency and the proposed experimental conditions: $HCl_c \gg$ L-cysteine > thiourea. For this reason HCl_c was introduced into FI system to reduce As^{5+} to As^{3+} to generate arsine.

3.1.2. UV photo-oxidation

Oxidation of As organic fraction (non-hydride forming species) prior arsine generation can be achieved by introduction of an UV photoreactor decomposing organic As species such as monomethylarsonate (MMA), dimethylarsinate (DMA), arsenobetaine and arsenocholine according to Rubio et al. observations [9]. In Fig. 1, it is observed the introduction of this reactor into FI system.

Numerous published studies have shown that organic compounds can be photooxidized more efficiently by incorporating TiO_2 as a photo-catalyst [10,32,33]. Titanium dioxide can be used either as a powder suspended in water solution, attached to a stationary glass or to polytetrafluoroethylene (PTFE) coiled around the UV-lamp [34]. The effect of titanium dioxide was evaluated adding a suspension in a concentrations range of 0.1 to 0.5% to samples, prior introduction to the UV photoreactor. Results showed that a concentration of 0.1% allowed an increment in hydride trapping by oxidized CNTs.

3.2. Flow injection parameters

In order to reduce consumables, waste and energy involved in speciation analysis, miniaturization appears as an alternative to downsize pretreatments and measurements steps, moving from milliliters to microliters scales [35]. In addition automation and flow injection analysis deletes cleaning steps.

3.2.1. Sample flow rate

The system design of the proposed methodology does not require carrier gas, since hydride is transported exclusively by pressure generated in GLS. The production rate of arsine and hydride pressure into GLS is governed by the sample flow rate towards GLS. This parameter also determines the hydride trapping efficiency on CNTs and the time of analysis. For this reason the sample flow rate was optimized to maintain quantitative arsine generation and adsorption on CNTs, avoiding an excessive increase of the time of analysis during As^{3+} and As^{5+} selective reduction prior hydride generation.

As mentioned in previous studies [16] a sample flow rate of 100 μL min^{-1} reached a maximum arsine retention on CNTs from 2 mL of a 100 ng L^{-1} As solution, 8% (v v^{-1}) HCl. However since this low flow rates decreased the throughput sample, a compromise sample flow rate of 250 μL min^{-1} was chosen, decreasing approximately 10% arsine retention on CNTs on that previous study. Now, in this study, since arsenic speciation analysis is pursued, different reagents have to be introduced after sample injection with a subsequent increase of sample flow rate, a maximum sample flow rate of 500 μL min^{-1} was established, decreasing arsine retention on CNTs by 20% approximately, but increasing sample throughput.

3.2.2. HCl flow rate

The studied HCl flow rate ranged from 10 to 100 μL min^{-1}, results are shown in Fig. 4. As it is observed, the optimum flow rate was of 10 μL min^{-1} of HCl, obtaining a quantitative reduction of inorganic arsenic species. At higher flow rate an excessive arsine production is achieved, increasing pressure in the system and consequently reducing the interaction between CNTs and arsine. However, lower concentrations are not sufficient to achieve a quantitative reduction of these species.

3.2.3. Buffer flow rate

As mentioned previously buffer citric-citrate, 0.1 mol L^{-1}, pH 4.0 was chosen to discriminate between As^{3+} and As^{5+} according to their capacity to generate arsine under pH variations, as seen in Fig. 2. In order to keep a constant sample flow rate of 500 μL min^{-1}, a buffer flow rate of 50 μL min^{-1} and a buffer concentration of 1 mol L^{-1} were selected, along with a sample flow rate of 450 μL min^{-1}. Under this configuration, after buffer is delivered to the sample line in the FI system design, a buffer concentration of 0.1 mol L^{-1} is obtained.

Table 1
Experimental conditions for As speciation.

As species/fraction	Sample flow rate (μL min^{-1})	HCl flow rate (μL min^{-1})	Buffer flow rate (μL min^{-1})	UV lamp	Integrated sample flow rate (μL min^{-1})
As^{3+}	450	0	50	Off	500
As^{3+} and As^{5+}	490	10	0	Off	500
As^{3+}, As^{5+}, organic fractions	490	10	0	On	500
Volume consumed (mL)	6	0.085	0.220	—	—

Table 2
Comparison of methodologies introducing As speciation and hydride trapping.

Sample volume (mL)	Carrier gas	Trap	Hydride release	Speciation	Reference
10	Ar	Graphite furnace	Heating	Yes	[13]
10	Ar	Chromatographic trap in liquid nitrogen/quartz furnace	Heating	Yes	[11]
1	Ar	Graphite tube	Heating	No	[12]
6	None	CNTs	Acidic elution	Yes	This work

3.2.4. Sample flow rate through the UV photoreactor

This is a very important parameter to optimize, since determines the optimal exposure time of As organic compounds to UV radiation. MMA was used in this work to evaluate the photooxidation of arsenic organic fractions. Results are shown in Fig. 5. As it is seen, arsine retention on CNTs decreases close to 50% at the maximum established sample flow rate of 500 μL min^{-1}. This observation is explained considering a reduction of the exposure time to UV radiation of organic As compounds. To increase photooxidation efficiency 0.1% (m v^{-1}) TiO_2 was added to the samples as described previously. As observed in Fig. 4, an increase of photooxidation efficiency close to 50% was achieved by TiO_2 addition at sample flow rates of 500 μL min^{-1}.

Optimized flow rates to reach as speciation, as well as volumes employed, are listed in Table 1. As mentioned, integrated sample flow rate reaching GLS has been defined to totalized 500 μL min^{-1}. In the bottom line of Table 2, it is observed sample volumes as well as reagents employed for speciation. Buffer and HCl volumes were kept in the μL level. Sample volume corresponds to 6 mL. In Table 2 a comparison between some features of this technique and others employing FI, hydride trapping and ETAAS for As analysis are shown. Sample volume is comparable considering that this technique reaches speciation. Another remarkable feature is that this technique does not require Ar as carrier gas. This point contributes to reagents consumption minimization. Finally, hydride release is reached by acid elution. This is a simple releasing mechanism compared to thermal desorption that requires complex temperature control mechanisms.

3.3. Analytical performance

Time of analysis of each As species is detailed. For As^{3+} determination, the time required for preconcentration of 2 mL of sample at a rate of 450 μL min^{-1}, adding a buffer solution of pH 4.0 at a flow rate of 50 μL min^{-1} was of 4.4 min. For determination of As^{3+} and As^{5+}, a flow rate of 490 μL min^{-1} was needed, adding HCl at a rate of 10 μL min^{-1}, which required a time of 4 min. A flow rate of 490 μL $min^{-1}$was used for the determination of As^{3+} and $As^{5+}$and organic fractions by employing the UV reactor. Then HCl was added at a rate of 10 μL min^{-1}, the time required was 4 min. For all mentioned fractions of arsenic, elution was performed with 30 μL of acid solution, which required 0.06 min at a flow rate of 0.5 mL min^{-1}. Washing and conditioning between each determination time required 0.4 min and 0.9 min ETAAS atomization. The concentration of the organic fraction of As^{3+} and As^{5}, is achieved by mathematical difference. The total time required for analysis of As organic and inorganic fractions, arsenite and arsenate per sample, was about 16.5 min.

Considering sample volume and eluent volume, this study obtained an enhancement factor of 60 when 2 mL of sample were loaded in the GLS, arsine adsorbed on CNTs and eluted with 30 μL of 5% HNO_3 (v v^{-1}). The detection limit was of 0.78 ng L^{-1} calculated as the amount of As required to yield a net peak that was equal to three times the standard deviation of the background signal (3σ). The calculated detection limit is comparable to our previous research [16] since despite the fact that an increase in the sample flow rate (from 100 to 500 μL min^{-1}) decreased methods´ sensibility, this is compensated by employing a lower eluent volume, 30 μL compared to 50 μL.

The precision was evaluated by relative standard deviation (RSD%) corresponding to 8.3% (n = 10). The calibration graph using the preconcentration system for As was linear with a correlation coefficient of 0.9994 from concentrations close to the detection limit up to at least 500 ng L^{-1}.

3.4. Method validation

In order to demonstrate the accuracy of the proposed arsenic speciation method, a tap water sample was analyzed by the standard addition method. Increasing concentrations of each As species were added to 1 mL aliquots according to Table 3 and diluted to 2 mL. Recovery values were between 97.12–101.99% for As^{3+}, 98.17–105.23% for As^{5+} and 95.74–103.77% for organic As (as MMA). Results were compared with the *t*-test and no significant differences were observed at 95% confidence level.

3.5. Application

The applicability of the methodology has been evaluated by analyzing well and cistern water samples from As endemics areas from Argentina. As species toxicity varies, being inorganic As more toxic (As^{3+} and As^{5+}) than organic As species. Between inorganic As species, As^{3+} is the most toxic arsenic species for human beings [36]. As a result it is clear that knowing total As concentration it is not sufficient to define precisely the risk that water consumption from As endemic regions represents for humans.

Previous analysis, water samples were diluted 1:100, because the origin of the sample corresponds to endemic As areas with elevated As concentration [37]. Results are shown in Table 4. The values obtained from 1:100 sample dilutions show higher As concentration than those allowed in drinking water established by WHO [38]. This fact is correspondent to samples origin from wells excavated in areas with arsenic-rich sediments. In addition As speciation analysis shows that most of As concentration (~85%) corresponds to As^{3+}, the most toxic

Table 3
Recovery study.

Aliquots	Base value (μg L^{-1})	Added As (μg L^{-1})	Found As (μg L^{-1})	Recovery (%)[a]
1[b]	–	0.00	1.37 ± 0.09	–
2[b]	1.37	1.00	2.38 ± 0.21	101.02
3[b]	1.37	1.50	2.85 ± 0.23	98.68
4[b]	1.37	2.00	3.34 ± 0.29	98.51
5[c]	–	0.00	1.41 ± 0.1	–
6[c]	1.41	1.00	2.42 ± 0.2	101.00
7[c]	1.41	1.50	2.92 ± 0.3	100.67
8[c]	1.41	2.00	3.39 ± 0.31	99.00
9[d]	–	0.00	1.6 ± 0.2	–
10[d]	1.6	1.00	2.59 ± 0.24	98.90
11[d]	1.6	1.50	3.12 ± 0.32	101.33
12[d]	1.6	2.00	3.61 ± 0.35	100.45

[a] 100 × [(found-base) / added].
[b] Recuperation study for As^{3+}.
[c] Recuperation study for inorganic As (As^{3+} + As^{5+}).
[d] Recuperation study for total As (As^{3+} + As^{5+} + MMA).

Table 4
Concentration of arsenic species in different cistern water samples (95% confidence intervals; n = 6).

Sample	As (III) concentration (μg L^{-1})	As (V) concentration (μg L^{-1})	Inorganic As concentration (μg L^{-1})	Organic As concentration (μg L^{-1})	Total As concentration (μg L^{-1})
A[a]	1.37 ± 0.09	0.04 ± 0.02	1.41 ± 0.07	0.19 ± 0.02	1.60 ± 0.11
B[a]	1.45 ± 0.09	0.04 ± 0.02	1.49 ± 0.09	0.71 ± 0.02	2.20 ± 0.11
C[a]	3.65 ± 0.08	0.08 ± 0.01	3.72 ± 0.09	0.68 ± 0.02	4.41 ± 0.10
D[a]	4.60 ± 0.09	0.03 ± 0.01	4.63 ± 0.09	0.87 ± 0.01	5.50 ± 0.11
E[b]	5.20 ± 0.08	1.30 ± 0.02	6.50 ± 0.08	0.50 ± 0.01	7.00 ± 0.11
F[b]	9.90 ± 0.09	1.30 ± 0.02	11.20 ± 0.09	0.30 ± 0.02	11.50 ± 0.09
G[b]	9.60 ± 0.07	2.30 ± 0.01	11.90 ± 0.07	0.80 ± 0.01	12.70 ± 0.10
H[b]	9.80 ± 0.09	2.80 ± 0.03	12.60 ± 0.08	0.70 ± 0.03	13.30 ± 0.11

[a] Cistern water samples.
[b] Well water samples.

As species, representing consumption of these waters a higher risk to human health.

4. Conclusion

The present research encompasses for the first time an As speciation strategy to a simple hydride trapping on CNTs employing ETAAS for As determination focused on reagent consumption, reduction and miniaturization. As speciation strategy involved two well-known methodologies: selective hydride generation and UV photooxidation, introduced into an FI system. However, this novel and simple hydride trapping strategy on CNTs required an adaptation of these speciation methodologies that involved a thoughtfully study of different variables.

Prior selective hydride generation, different pH conditions allowed determination of As^{3+} and As^{5+}, hydride forming species by citrate buffer and HCl introduction to the FI system. In addition a study was performed to determine whether the pH of different samples will affect the determination conditions. Results showed that only extreme acidic samples can modify the buffer pH. UV photooxidation required the introduction of TiO_2 catalyst to increase hydride generation production from non-hydride forming As species like organics, at higher sample flow rates. This point allowed a decrease of the time of analysis and a higher throughput sample.

The developed technique was successfully applied to well and cistern water samples from As endemic regions from Argentina. Speciation strategy established that human consumption of this water represents a risk not only for their elevated As concentration, but also because As is present mainly in inorganic As^{3+} species, the most toxic.

Reagent consumption was reduced to μL for speciation, including no need of carrier gas, contributing to miniaturization of quantitative methods, encompassing with principles of Green Chemistry. The proposed methodology extends the application of conventional arsine hydride trapping based on adsorption on multiwall CNTs to speciation analysis. Future studies of this technique will be extended to other hydride forming elements and applications.

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References

[1] P. Smedley, H. Nicolli, D. Macdonald, A. Barros, J. Tullio, Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina, Appl. Geochem. 17 (2002) 259–284.
[2] L. Thunus, R. Lejeune, in: H.G. Seller, A. Sigel, H. Sigel (Eds.),Handbook on Metals in Clinical and Analytical Chemistry, 1994.
[3] S.J. Marlborough, V.L. Wilson, Arsenic speciation driving risk based corrective action, Sci. Total Environ. 520 (2015) 253–259.
[4] H. Wu, X. Wang, B. Liu, Y. Liu, S. Li, J. Lu, J. Tian, W. Zhao, Z. Yang, Simultaneous speciation of inorganic arsenic and antimony in water samples by hydride generation-double channel atomic fluorescence spectrometry with on-line solid-phase extraction using single-walled carbon nanotubes micro-column, Spectrochim. Acta B At. Spectrosc. 66 (2011) 74–80.
[5] M.L. Chen, L.Y. Ma, X.W. Chen, New procedures for arsenic speciation: a review, Talanta 125 (2014) 78–86.
[6] M. Sun, G. Liu, Q. Wu, W. Liu, Speciation analysis of inorganic arsenic in coal samples by microwave-assisted extraction and high performance liquid chromatography coupled to hydride generation atomic fluorescence spectrometry, Talanta 106 (2013) 8–13.
[7] G. Samanta, U.K. Chowdhury, B.K. Mandal, D. Chakraborti, N.C. Sekaran, H. Tokunaga, M. Ando, High performance liquid chromatography inductively coupled plasma mass spectrometry for speciation of arsenic compounds in urine, Microchem. J. 65 (2000) 113–127.
[8] A. Gonzalvez, S. Armenta, M.L. Cervera, M. de la Guardia, Non-chromatographic speciation, TrAC Trends Anal. Chem. 29 (2010) 260–268.
[9] R. Rubio, A. Padró, J. Alberti, G. Rauret, Determination of arsenic speciation by liquid chromatography—hydride generation inductively coupled plasma atomic emission spectrometry with on-line UV photooxidation, Anal. Chim. Acta 283 (1993) 160–166.
[10] M. Vilanó, A. Padró, R. Rubio, Coupled techniques based on liquid chromatography and atomic fluorescence detection for arsenic speciation, Anal. Chim. Acta 411 (2000) 71–79.
[11] J.Y. Cabon, N. Cabon, Speciation of major arsenic species in seawater by flow injection hydride generation atomic absorption spectrometry, Fresenius J. Anal. Chem. 368 (2000) 484–489.
[12] S.N. Willie, First order speciation of As using flow injection hydride generation atomic absorption spectrometry with in-situ trapping of the arsine in a graphite furnace, Spectrochimica Acta - Part B Atomic Spectroscopy 51 (1996) 1781–1790.
[13] J.Y. Cabon, N. Cabon, Determination of arsenic species in seawater by flow injection hydride generation in situ collection followed by graphite furnace atomic absorption spectrometry stability of As(III), Anal. Chim. Acta 418 (2000) 19–31.
[14] T.Y. Ng, Y.X. Ren, K.M. Liew, Adsorption of hydrogen atoms onto the exterior wall of carbon nanotubes and their thermodynamics properties, Int. J. Hydrog. Energy 35 (2010) 4543–4553.
[15] Q. Zhang, Y.-Z. Zuo, M.-H. Han, J.-F. Wang, Y. Jin, F. Wei, Long carbon nanotubes intercrossed Cu/Zn/Al/Zr catalyst for CO/CO_2 hydrogenation to methanol/dimethyl ether, Catal. Today 150 (2010) 55–60.
[16] A. Maratta, M. Acosta, L.D. Martinez, P.H. Pacheco, R.A. Gil, Ultratrace arsenic determination through hydride trapping on oxidized multiwall carbon nanotubes coupled to electrothermal atomic absorption spectrometry, J. Anal. At. Spectrom. 28 (2013) 916–922.
[17] J. Koh, Y. Kwon, Y.-N. Pak, Separation and sensitive determination of arsenic species (As3+/As5+) using the yeast-immobilized column and hydride generation in ICP–AES, Microchem. J. 80 (2005) 195–199.
[18] O. Yıldız, D. Citak, M. Tuzen, M. Soylak, Determination of copper, lead and iron in water and food samples after column solid phase extraction using 1-phenylthiosemicarbazide on Dowex Optipore L-493 resin, Food Chem. Toxicol. 49 (2011) 458–463.
[19] J. Zhang, G. Zhang, C. Zhao, X. Quan, Q. Jia, On-line preconcentration/separation of inorganic arsenic and antimony by poly (aryl ether ketone) containing pendant carboxyl groups prior to microwave plasma atomic spectrometry determinations, Microchem. J. 100 (2012) 95–99.
[20] S. Armenta, S. Garrigues, M. de la Guardia, Green analytical chemistry, TrAC Trends Anal. Chem. 27 (2008) 497–511.
[21] R. Torralba, M. Bonilla, L. Perez-Arribas, A. Palacios, C. Camara, Speciation and simultaneous determination of arsenic (III), arsenic (V), monomethylarsonate and dimethylarsinate by atomic absorption using inverse least squares multivariate calibration, Spectrochim. Acta B At. Spectrosc. 49 (1994) 893–899.
[22] P. Liang, E. Zhao, Q. Ding, D. Du, Multiwalled carbon nanotubes microcolumn preconcentration and determination of gold in geological and water samples by flame atomic absorption spectrometry, Spectrochim. Acta B At. Spectrosc. 63 (2008) 714–717.

[23] D.J. Butcher, J. Sneddon, A Practical Guide to Graphite Furnace Atomic Absorption Spectrometry, John Wiley & Sons, 1998.
[24] H.M. Anawar, Arsenic speciation in environmental samples by hydride generation and electrothermal atomic absorption spectrometry, Talanta 88 (2012) 30–42.
[25] A. D'Ulivo, J. Dědina, Z. Mester, R.E. Sturgeon, Q. Wang, B. Welz, Mechanisms of chemical generation of volatile hydrides for trace element determination (IUPAC technical report), Pure Appl. Chem. 83 (2011) 1283–1340.
[26] S. Musil, A.H. Pétursdóttir, A. Raab, H. Gunnlaugsdóttir, E. Krupp, J. Feldmann, Speciation without chromatography using selective hydride generation: inorganic arsenic in rice and samples of marine origin, Anal. Chem. 86 (2014) 993–999.
[27] A. Hernández-Zavala, T. Matoussek, Z. Drobná, D.S. Paul, F. Walton, B.M. Adair, J. Dědina, D.J. Thomas, M. Stýblo, Speciation analysis of arsenic in biological matrices by automated hydride generation-cryotrapping-atomic absorption spectrometry with multiple microflame quartz tube atomizer (multiatomizer), J. Anal. At. Spectrom. 23 (2008) 342–351.
[28] D. Sanchez-Rodas, W. Corns, B. Chen, P. Stockwell, Atomic fluorescence spectrometry: a suitable detection technique in speciation studies for arsenic, selenium, antimony and mercury, J. Anal. At. Spectrom. 25 (2010) 933–946.
[29] D.C. Harris, Quantitative Chemical Analysis, Macmillan, 2010.
[30] H.C. Rezende, N.M.M. Coelho, Determination of total arsenic and arsenic (III) in phosphate fertilizers by hydride generation atomic absorption spectrometry after ultrasound-assisted extraction based on a control acid media, J. AOAC Int. 97 (2014) 736–741.
[31] T. Matoušek, A. Hernández-Zavala, M. Svoboda, L. Langrová, B.M. Adair, Z. Drobná, D.J. Thomas, M. Stýblo, J. Dědina, Oxidation state specific generation of arsines from methylated arsenicals based on L-cysteine treatment in buffered media for speciation analysis by hydride generation-automated cryotrapping-gas chromatography-atomic absorption spectrometry with the multiatomizer, Spectrochim. Acta B At. Spectrosc. 63 (2008) 396–406.
[32] S. Gelover, P. Mondragón, A. Jiménez, Titanium dioxide sol–gel deposited over glass and its application as a photocatalyst for water decontamination, J. Photochem. Photobiol. A Chem. 165 (2004) 241–246.
[33] K.A. Mace, R.A. Duce, On the use of UV photo-oxidation for the determination of total nitrogen in rainwater and water-extracted atmospheric aerosol, Atmos. Environ. 36 (2002) 5937–5946.
[34] J. Golimowski, K. Golimowska, UV-photooxidation as pretreatment step in inorganic analysis of environmental samples, Anal. Chim. Acta 325 (1996) 111–133.
[35] M. de la Guardia, S. Garrigues, The Concept of Green Analytical Chemistry, Handbook of Green Analytical Chemistry, John Wiley & Sons, Ltd, 2012 1–16.
[36] B. Sadee, M.E. Foulkes, S.J. Hill, Coupled techniques for arsenic speciation in food and drinking water: a review, J. Anal. At. Spectrom. 30 (2015) 102–118.
[37] R.O. Benitez, J.A. Álvarez, M.O. Dahbar, S.I. Rivero, Alternativas tecnológicas a tener en cuenta para la toma de decisiones frente a la problemática del arsénico en el agua de bebida, Programa Nacional de Minimización de Riesgos por Exposición a Arsénico en Agua de Consumo, Res. Ministerial 253 (2008).
[38] W.H. Organization, Guidelines for Drinking-Water Quality: Recommendations, World Health Organization, 2004.