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Preconcentration and determination of inorganic arsenic using a multisyringe flow injection system and hydride generation-atomic fluorescence spectrometry

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Abstract

A new multisyringe flow injection system for inorganic arsenic determination at trace levels by hydride generation-atomic fluorescence spectrometry (HGAFS) is presented. Preconcentration on a solid-phase was carried out using a column packed with an anion-exchange resin (Amberlite IRA-410). The reagents are dispensed to the system using a multisyringe burette coupled with two multi-port selection valves.

Different parameters were changing in order to make the system as effective as possible. An analytical curve was obtained for arsenic determination between 50 and 2000 ng l^{-1}. This new approach improved five times the sensitivity over a MSFIA–HGAFS technique developed previously by the authors. Detection limit of the proposed technique was ($3\sigma_b/S$) of 30 ng l^{-1}. The relative standard deviation (R.S.D.) of As at 1 μg l^{-1} was 4.8% ($n = 7$). A sample throughput of 10 h^{-1} has been achieved. The proposed method has been applied to different reference solid and water materials with satisfactory results.

Keywords: Multisyringe flow injection analysis (MSFIA); Arsenic; Preconcentration; Hydride generation; Atomic fluorescence

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1. Introduction

Arsenic is a ubiquitous element found in the atmosphere, soils and rocks, natural waters and organisms. It is mobilized through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through a range of anthropogenic activities: mining activity, combustion of fossil fuels, wood preservation, the use of arsenical pesticides among others [1–3]. The concentration of arsenic in different environmental samples ranges from 0.5 to 5000 μg l^{-1} for natural waters [1] and from 0.1 to 4000 mg kg^{-1} for sediments [3]. Due to such wide concentration level of arsenic as well as its considerable toxicity, a great number of techniques for arsenic determination were applied [4–10]. A common technique also used is hydride generation (HG), which allows low detection limits and has found wide applications in the determination of trace levels of arsenic combined with atomic absorption spectrometry [11,12] or coupled with atomic fluorescence spectrometry (AFS) [13,14]. HGAFS technique is relatively inexpensive and offers a higher sensitivity [15–17].

The growing interest in the use of flow techniques was highlighted in several studies [11,12,14,16,18,19]. A recent flow injection technique, multisyringe flow injection analysis (MSFIA), described by Cerdà et al. [20], comprises the advantages of flow injection analysis (FIA) methodologies and the robustness and reagents saving of sequential injection system (SIA). The basic element is a multisyringe burette allowing the simultaneously movement of four syringes which are connected in block to the same step-by-step motor. By coupling of three-way solenoid valves to this technique leads to saving reagents since they are only injected to the system at the precise moment to perform the analytical determination. MSFIA has been applied to inorganic arsenic determination by the authors. The possibility to determine 0.25 μg l^{-1} of inorganic arsenic has been achieved [21]. The

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characterization and others applications of the multisyringe flow injection analysis method have been reviewed by Miró et al. [22].

The implementation of a solid-phase extraction using an anion-exchange resin in continuous flow systems has been described in several reports with the objective to improve the sensitivity of arsenic determinations [23–25]. Tesfalidet and Irgum [23] reported that arsine could be generated by passage of an acidified sample through a column packed with an anion-exchange resin (Amberlyst A-26) on which borohydride had been previously immobilized. The detection limit of 1.5 μg l^{-1} was obtained using a FIA-atomic absorption spectrometry system. Carrero and Tyson [24] have been described that the simultaneous retention of selenium(IV) and borohydride solutions followed by passage of acid to generate hydrogen selenide was the basis of a viable method for selenium determination. The retention of borohydride on an anion-exchange resin might result in a purer reagent and hence improved detection limits [23,24]. The extension of this technique to others hydride-forming elements such as arsenic has been also reported [24], achieving a detection limit of 0.6 μg l^{-1}.

Flow injection analysis (FIA) has been the commonest technique used to apply a solid-phase extraction. Nevertheless, FIA has some disadvantages such as high reagent and sample consumption due to the use of peristaltic pumps, which works uninterruptedly. Therefore, the application of the MSFIA to solid-phase preconcentration would be of great interest.

In the present work, MSFIA methodology for the determination of total inorganic arsenic based on the on-line solid-phase preconcentration of arsenic by hydride generation-atomic fluorescence spectrometry (HGAFS) has been described. The aim of this study is to improve the sensitivity of the technique at trace levels. For this purpose, the column was packed with an anion-exchange resin. Arsine was generated from the resin by passage of hydrochloric acid when both arsenic and borohydride were retained.

2. Experimental

2.1. Reagents

All chemicals used were of analytical reagent grade. All solutions were made with distilled water purified by Millipore equipment (18.2 MΩ cm). Stock solutions 1000 mg l^{-1} arsenic(III) and arsenic(V) were prepared by dissolving 1.320 g As_2O_3 (Merck) and 1.534 g As_2O_5 (Aldrich) in 1000 ml of 0.1 mol l^{-1} NaOH solution, respectively. These stock solutions were kept at 4 °C in darkness. Working solutions of arsenic (0.05–2.5 μg l^{-1}) were prepared daily by dilution of the stock solution with Millipore water. Hydrochloric acid 4 mol l^{-1} (37%, Riedel-deHaën) was used. The stock solution of 5.8% (w/v) $NaBH_4$ (Fluka, 97%) was prepared once a week by dissolving the appropriate amount of sodium tetrahydroborate in 0.2 mol l^{-1} NaOH (Merck) in water. The 0.05 and 0.1% $NaBH_4$ (w/v) working solutions were prepared daily by dilution of the $NaBH_4$ stock solution in Millipore water. The resin used was Amberlite IRA-410 (Aldrich, Milwaukee, WI, USA), which is a strongly basic gel-type anion-exchange resin (chloride form, styrene–divinylbenzene skeletal structure).

Glassware used for the determination of As was soaked in a 10% (v/v) nitric acid solution and rinsed with Millipore water.

2.2. Apparatus

The MSFIA–HGAFS system used for arsenic determination is shown in Fig. 1. The basic element of MSFIA is a multisyringe burette with programmable speed (MicroBU 2030, Crison, Alella, Barcelona). At the head of each syringe (5, 10, 5 and 5 ml) is a three-way solenoid commutation valve (E1, E2, E3, E4) (N-Research, Caldwell, NJ). The multisyringe burette also has two independent three-way solenoid commutation valves (E5 and E6) (N-Research, Caldwell, NJ). The manifold was built from 0.8 and 1.5 mm i.d. PTFE tubing. A cross-shaped (five-way) connector is coupled to the tubing manifold and to the column.

The column (70 mm long and 4 mm i.d.) for on-line preconcentration was made from poly(methyl)methacrylate. The column was packed by an anion-exchange resin with the aid of a Pasteur pipette. A small amount of glass-wool was placed at the ends of the column to prevent loss of resin. The column was used after washing alternately with sodium tetrahydroborate and hydrochloric acid solutions, followed by water.

A glass gas–liquid separator was employed to separate the gaseous hydrides from the liquid phase and a Permapure membrane (Perma Pure Inc., Toms River, NJ) was used to remove the moisture of the gaseous phase before their introduction into the detection unit. Argon and nitrogen were used as a carrier gas and a dryer gas, respectively. An external cylinder of hydrogen was required to support the flame.

Measurements were carried out with an atomic fluorescence spectrometer (10.044 Excalibur detector, PS Analytical), equipped with an arsenic boosted discharged hollow cathode lamp (primary current: 27.5 mA; secondary current: 35.0 mA; wavelength: 193.7 nm).

Instrumental control and data acquisition were performed using the software Autoanalysis[1] developed by our research group [26]. A 1200 Mega Milestone model mls microwave oven was used for sample digestion.

2.3. Procedure

To carry out the proposed MSFIA application, the four syringes (S1–S4) with their corresponding three-way

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[1] The program may be requested at: http://ww.sciware_sl@yahoo.es; http://www.sciware-sl.com.

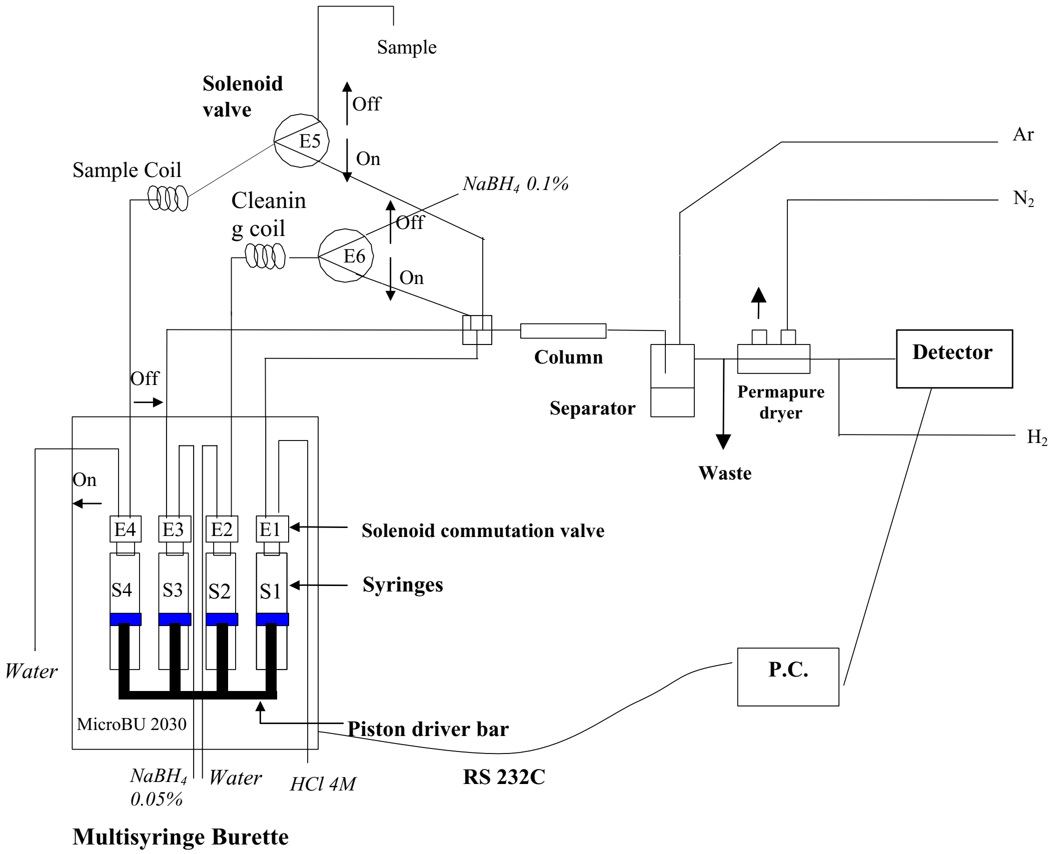

Fig. 1. MSFIA–HGAFS system used for preconcentration and determination of As.

commutation valves (E1–E4) were employed. The position "off" (solenoid disabled) of the valves connects syringes to the right channel and "on" (solenoid enabled) to the left one. Two additional three-way commutation valves (E5 and E6) were coupled to the multisyringe burette. The first syringe (S1, 5 ml), connected to valve E1, contains the hydrochloric acid solution. The syringe S2 (10 ml), which is connected to valves E2 and E6, is used for cleaning the column between samples with a 0.1% sodium tetrahydroborate solution (E6) and water through a cleaning coil (PTFE: 2.4 m long, 1.5 mm i.d.). The syringe S3 (5 ml), connected to valve E3, dispenses the 0.05% $NaBH_4$ solution. The fourth syringe (S4, 5 ml), connected to valves E4 and E5, is used for loading and dispensing the sample (PTFE sample coil, 3 m long, 1.5 mm i.d.). Each channel is connected to a five-way cross-shaped connector, which in turn is connected to the column, packed with Amberlite IRA-410. The 0.05% $NaBH_4$ solution was first loaded on to the anion-exchange column and, after washing with water, the sample was passed through the column and arsenic is retained on the resin. In the next step, the 4 mol l^{-1} hydrochloric acid solution is dispensed into the column, generating arsine and hydrogen. The procedure used for the arsenic determination is shown in Table 1. The indicated volumes are referred to syringe S1 (it corresponds two times more volumes for syringe S2).

The column was cleaned between samples by passing 1.5 ml of 0.1% sodium tetrahydroborate solution, followed by 1 ml of 4 mol l^{-1} hydrochloric acid and water. The cleaning step was not needed between replicate injections of the same sample.

2.4. Sample pre-treatment

Using the proposed system, two certified solid samples and hard drinking water have been analyzed. DORM-1 (fish muscle) and DOLT-1 (liver) are certified reference material purchased from National Research Council (NRCC, Ottawa, Ont., Canada). The 0.01 g of DORM-1 and 0.03 g of DOLT-1 were weighed and subjected to a microwave digestion. The procedure is described elsewhere [21]. After digestion procedure the samples were made up to 100 ml (for DORM-1) and 250 ml (for DOLT-1) with Millipore water.

The water certified material LGC-6010 (hard drinking water; LGC, UK) was diluted up to 100 ml with Millipore water.

3. Results and discussion

3.1. Construction of the system

In order to achieve the most efficient performance in terms of highest analytical sensitivity and lowest deviation of signals (measurement precision), some experimental parameters were investigated. After an initial assessment to select approximate values for each parameter, optimization of the variables was carried out by the univariate method. Although this method requires a great number of experiments, it allows to obtain detailed information about the behavior of the system. On the other hand, a multivariate approach demands a relatively small number of experiments, but it only provides knowledge of main effects [27]. Thus, a univariate method has been selected in order to observe graphically the influence of the variation of each parameter over the signal response.

Columns of two different lengths (130 and 70 mm, 4 mm i.d.) were tested for four replicate measurements at three concentrations of arsenic (0.5, 1 and 2 μg l^{-1}). For this purpose, 3 ml of As(III) solution, 3 ml of 0.05% $NaBH_4$ solution and 2 ml of 4 mol l^{-1} HCl were dispensed into the system. The 70 mm length column provided a better reproducibility, more symmetric peaks and less noise of signals. The column of this length was chosen for further experiments.

The influence of different addition sequences of sample and reagents were studied using 3 ml of 1 μg l^{-1} As(III) standard solution, 3 ml of 0.05% $NaBH_4$ solution and 1.5 ml of 4 mol l^{-1} HCl. The following sequences were investigated. (1) To dispense $NaBH_4$ solution to the system, to wash with 1.5 ml of water followed by the loading sample and finally to elute with hydrochloric acid solution. (2) To use the system described above, but without the washing step. (3) To dispense $NaBH_4$ and As solutions simultaneously, followed by a washing step and elution with HCl solution. (4) To dispense $NaBH_4$ solution, followed by an acidified analyte solution. The first sequence provided both better reproducibility and the greatest ratio between As/blank signals, while using second sequence it verified that the washing step was necessary in order to have an uniform distribution of $NaBH_4$ solution throughout the surface of the resin and therefore a better reproducibility [23]. The third sequence, proposed by Carrero and Tyson [24] for selenium determination, decreased the height peak a half of the value obtained in the first sequence. Applying the last sequence, an asymmetric and noisy signal was obtained. The first sequence was selected as optimal for the MSFIA–HGAFS on-line preconcentration arsenic determination.

3.2. Influence of H_2, N_2 and Ar flow rates, gain influence

In order to study the influence of gas flow rates and the fine gain of the atomic fluorescence spectrometer, 3 ml of 1 μg l^{-1} As(III) standard solution, 3 ml of 0.05% $NaBH_4$ solution and 1.5 ml of 4 mol l^{-1} HCl were dispensed into the system. The effect of argon flow was evaluated in the range from 150 to 500 ml min^{-1}. The increase of the argon flow rate increases peak signal of As. Nevertheless, a flow rate between 400 and 500 caused a large flame fluctuation. Thus, a flow rate of 350 ml min^{-1} for Ar was chosen for further experiments. The use of an auxiliary external H_2 flow was necessary to support the flame, as there was not a continuous flow of the reducing agent. It was found that decreasing H_2 flow rate, signal of sample was more stable and the value of blank signal decreased. On the other hand, when the H_2 flow rate was less than 50 ml min^{-1} the flame is extinguished. A flow rate of 55 ml min^{-1} was selected as optimal for hydrogen. The flow rate of nitrogen used for drying purposes did not influence the value of the signal.

The influence of the fine gain was investigated in the range from 6 to 10 (gain was 100). An eight fine gain provided high sensitivity and good reproducibility. It was used in further experiments.

3.3. Effect of volumes and flow rates of sample and reagents

3.3.1. Effect of sample volume

Different sample volumes ranging from 1 to 11 ml were studied using an As(III) standard solution of 1 μg l^{-1}, 3 ml of 0.05% $NaBH_4$ solution and 1.5 ml of 4 mol l^{-1} HCl (Fig. 2a). It has been taken into account that up to 4 ml of sample an additional syringe loading is needed (4 ml of injection sample + 1.2 ml of sample to fill the tubing). In order to achieve a high sensitivity and a low relative standard deviation without reducing significantly the sample throughput, a volume of 3 ml was selected, being a reasonable compromise. No effect was observed up to 12 ml.

3.3.2. Effect of sample flow rate

Sample flow rates were also tested within the range 0.5 and 5 ml min^{-1} (Fig. 2b). One milliliter per minute retention flow rate was chosen as an optimal value. Higher flow rates could cause an increase of the pressure into the flow system, worsening the repeatability of the signal.

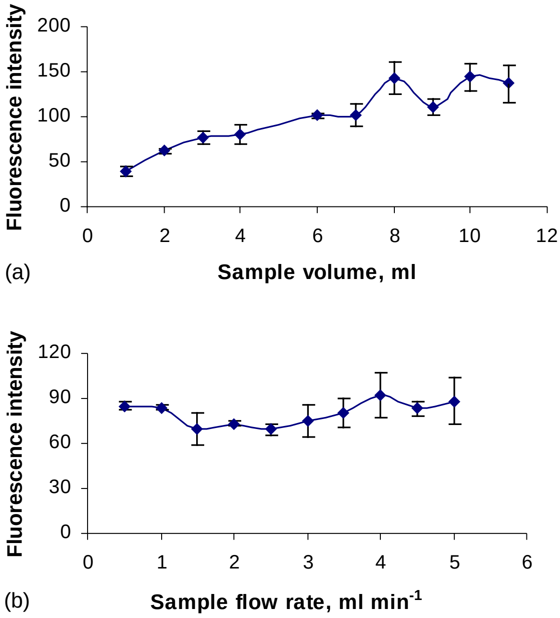

Fig. 2. (a) Effect of changing the volume of sample. Working conditions: 1 μg l^{-1} of As solution, 0.05% of $NaBH_4$, 4 mol l^{-1} HCl. (b) Effect of changing the flow rate of sample. Working conditions: 1 μg l^{-1} of As solution, 0.05% of $NaBH_4$, 4 mol l^{-1} HCl.

Table 1
Analytical procedure for preconcentration and elution of inorganic As

Step	Volume (ml)	Flow rate (ml min^{-1})	Operation	Position of solenoid valves						Commentary
				E1	E2	E3	E4	E5	E6	
1	4	3	Dispense	Off	Off	Off	Off	On	On	System, column and sample tube washing
2	1.158	5	Pick up	Off	On	Off	Off	Off	Off	Filling the sample tube with sample
3	3	7	Pick up	Off	On	Off	Off	Off	Off	Sample loading
4	0.137	4.5	Dispense	Off	On	On	On	Off	Off	Filling of the tube connecting S3 with the five channel cross fitting
5	3	3	Dispense	Off	On	On	On	Off	Off	Dispensing $NaBH_4$ solution to column
6	3.9	5	Pick up	Off	On	Off	On	Off	Off	Syringes loading
7	1.5	3	Dispense	Off	Off	Off	On	Off	On	Column washing
8	3	1	Dispense	Off	On	Off	Off	On	Off	Sample injection
9	4	6	Pick up	Off	On	Off	On	Off	Off	Syringes loading
10	0.177	4	Dispense	On	On	Off	On	Off	Off	Filling of the tube connecting S1 with the five channel cross fitting
11	2	1	Dispense	On	On	Off	On	Off	Off	Elution and measuring
12	1	5	Pick up	Off	On	Off	On	Off	Off	Syringes loading
13	2	3.5	Dispense	Off	Off	Off	Off	On	On	System washing
14			Repeat three times from Steps 3 to 13							

E1 and E3 on: dispense HCl and 0.05% sodium tetrahydroborate solutions to the manifold; E1 and E3 off: returns HCl and 0.05% sodium tetrahydroborate solutions to their bottles; E2 off/E6 on: dispense water or 1% sodium tetrahydroborate solution to the column; E4 off/E5 on: dispense sample to the system; E2 on/E6 off and E4 on/E5 off: dispense water to bottles.

3.3.3. *Effect of reagents volume*

For the purpose to investigate the effect of $NaBH_4$ and HCl volumes on the signal of As, ranges from 1 to 6 ml and 1 to 5 ml were tested, respectively. 1 μg l^{-1} As(III) solution was also used. In the case of 0.05% $NaBH_4$ solution, the height of peak increased with increasing $NaBH_4$ volume. Nevertheless, up to 4 ml the reproducibility of the signal gets worse and 6 ml provides an out of range signal, as can be seen in Fig. 3a. A $NaBH_4$ volume of 3 ml was adopted for further experiments. Volumes of 4 mol l^{-1} HCl up to 4 ml provides a lower signal and decrease sensitivity, whereas a volume of 3 ml shows a higher relative standard deviation. Two milliliters of HCl was selected as most convenient (Fig. 3a).

3.3.4. *Effect of reagents flow rate*

The influence of reagents flow rates was assessed over the 0.5–6 and 0.5–4 ml min^{-1} for $NaBH_4$ and HCl solutions, respectively (Fig. 3b). For this purpose, 1 μg l^{-1} As(III) solution, 0.05% $NaBH_4$ solution and 4 mol l^{-1} HCl were dispensed into the system. As can be seen in Fig. 3b, the signal increases significantly with increasing $NaBH_4$ flow rates from 0.5 to 2 ml min^{-1}, varying less at flow rates higher than 3 ml min^{-1}. It was observed that an HCl flow rate higher than 1 ml min^{-1} reduces the fluorescence signal of As. To simultaneously achieve a high peak signal and a good reproducibility, 3 ml min^{-1} for $NaBH_4$ and 1 ml min^{-1} for HCl were chosen as optimal values. As filling operations of the syringes do not influence arsenic determination, the rates for these steps were selected within the range of 5–7.5 ml min^{-1} in order to improve the sample throughput. Retention and elution flow rates higher than 3.5 are not recommended for the present application, since back-pressure is increased due to packing of the resin, with the subsequent worsening of the signal.

3.4. *Optimization of reagents concentration*

The effect of $NaBH_4$ concentration on the arsenic determination was evaluated in the concentration range from 0.01

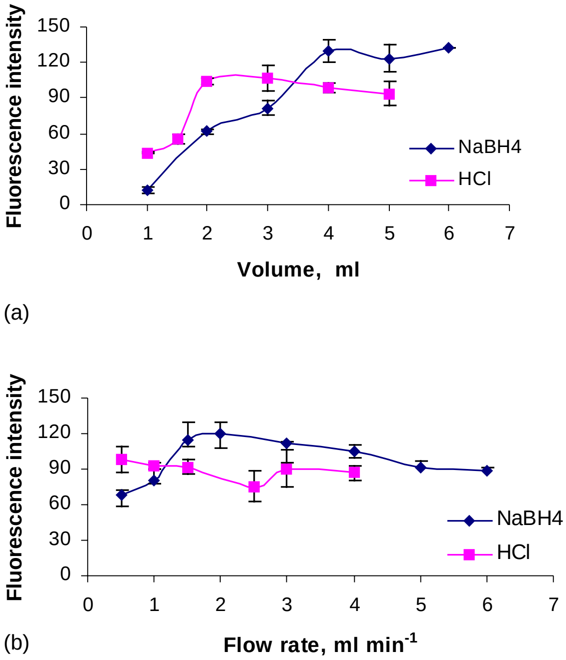

Fig. 3. (a) Effect of changing the volumes of $NaBH_4$ and HCl. Working conditions: 1 μg l^{-1} of As solution, 0.05% of $NaBH_4$, 4 mol l^{-1} HCl. (b) Effect of changing the flow rate of $NaBH_4$ and HCl. Working conditions: 1 μg l^{-1} of As solution, 0.05% of $NaBH_4$, 4 mol l^{-1} HCl.

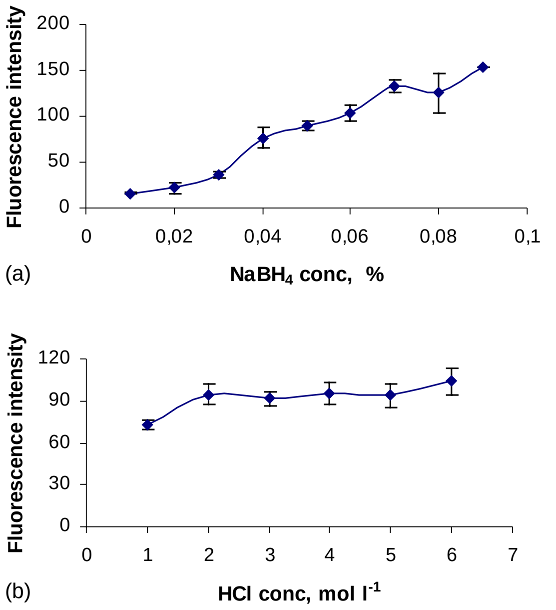

Fig. 4. (a) Effect of changing reducing agent concentration. Working conditions: 3 ml of 1 μg l^{-1} As solution, 1.5 ml of a 4 mol l^{-1} HCl. (b) Effect of changing HCl concentrations. Working conditions: 3 ml of 1 μg l^{-1} As solution, 3 ml of 0.05% of $NaBH_4$.

to 0.09% using 3 ml of 1 μg l^{-1} As(III) standard solution, 3 ml of different $NaBH_4$ solutions and 2 ml of 4 mol l^{-1} HCl. The flow rates were 1 ml min^{-1} for sample injection, 3 ml min^{-1} for $NaBH_4$ and 1 ml min^{-1} for HCl (Fig. 4a). It was observed that by increasing the concentration of $NaBH_4$ the height of the signal was in turn increased. However, the blank signal increased simultaneously. A 0.05% $NaBH_4$ concentration provided the greatest ratio between As/blank signals and has been selected for further studies.

In order to evaluate the optimal concentration of HCl, 3 ml of 1 μg l^{-1} As(III) standard solution, 3 ml of 0.05% $NaBH_4$ solution and 2 ml of different HCl solutions were dispensed into the system. The range of HCl concentrations was from 1 to 6 mol l^{-1}. Results of these experiments are shown in Fig. 4b. The concentration of 4 mol l^{-1} was chosen as optimal value. It has been taken into account that higher HCl concentrations will can lead to a decreasing the interference from transition metals [23].

The optimal operation conditions are summarized in Table 2.

3.5. Recovery of As(III) to As(V)

Under the selected conditions described above, recoveries of separately prepared As(III) and As(V) solutions were investigated. One microgram per liter of As standard solutions from As_2O_3 and As_2O_5 were prepared. The recovery of As(III) was 99.9 ± 6.1%, whereas a value of 93.8 ± 8% was obtained for As(V). This confirms the ability of the technique to determine inorganic arsenic.

Table 2
Optimal operation conditions

Parameter	Value
Flow rate of H_2 (ml min^{-1})	55
Flow rate of Ar (ml min^{-1})	350
Flow rate of N_2 (ml min^{-1})	1500
Sample volume (ml)	3
Flow rate of sample (ml min^{-1})	1
$NaBH_4$ volume (ml)	3
Flow rate of $NaBH_4$ (ml min^{-1})	3
$NaBH_4$ concentration (w/v) (%)	0.05
HCl volume (ml)	2
Flow rate of HCl (ml min^{-1})	1
HCl concentration (mol l^{-1})	4
Fine gain	8

The process of formation of arsine from As(V) suggests that there are two steps in the reaction: the reduction of As(V) to As(III) and the subsequent formation of AsH_3. The value obtained for As(V) can be explained as a result of the rather slow reduction reaction to As(III) carried out by $NaBH_4$ [28]. Some authors [15,18,23,29] reported that the signal achieved from As(V) using $NaBH_4$ as a reductor is about 30–70% lower than that of As(III). Burguera and Burguera [28] mentioned that the response obtained from As(V) can be 10% lower than that of As(III).

3.6. Analytical parameters

The analytical curve was obtained with As(III) standards. It was linear from 50 to 2000 ng l^{-1} with a correlation coefficient of 0.997 ($n = 36$). Peaks corresponding to As standards were obtained by carrying out cycles of three injections for each standard solution. Fig. 5 shows an example of an analytical curve. The relative standard deviation (R.S.D.), evaluated from seven successive injections of 1 μg l^{-1} As standard solution, was 4.8%. The detection limit achieved is 30 ng l^{-1}. It has been calculated from $3\sigma_b/S$, where σ_b is the blank standard deviation and S the sensitivity of the method calculated as the calibration slope. A sample throughput of 10 h^{-1} was obtained.

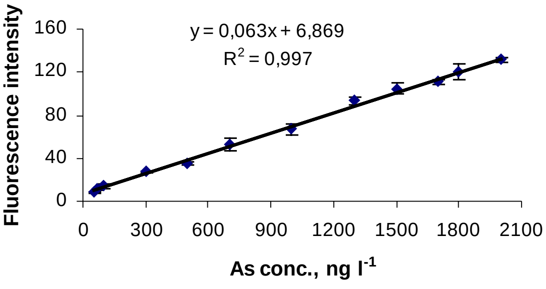

Fig. 5. Analytical curve obtained by dispensing of 3 ml of As solution, 3 ml of 0.05% of $NaBH_4$, 2 ml of 4 mol l^{-1} HCl.

Table 3
Results of the analysis of reference materials using the proposed method[a]

Sample	Certified value	Obtained value
Solid reference material		
DORM-1 (mg As kg^{-1})	17.7 ± 2.1	19.5 ± 4.9 ($n = 8, 3$)[b]
DOLT-1 (mg As kg^{-1})	10.1 ± 1.4	8.8 ± 1.5 ($n = 9, 3$)
Water reference material		
LGC-6010 (μg As l^{-1})	55 ± 5	57 ± 7 ($n = 6, 3$)

[a] Mean + S.D.

[b] $n = 8$, three means eight independent samples, three injections each.

3.7. Interferences

Interferences due to coexisting ions on the determination of $1\,\mu g\,l^{-1}$ As standard solution were studied. An element was considered not to interfere if the highest peak variation is three times less than the standard deviation. The following metal ions: Fe, Zn, Mg, K, Ca, Cr and Ba do not interfere when their % (w/w) concentration is up to 1000 times higher ($1000\,\mu g\,l^{-1}$) than that of As. In some cases (for Hg, Ni, Cd, Co, Cu, Al, Se), the interference decreased the signal. The tolerated concentrations of these elements were 200, 25, 15, 50, 450, 100, $10\,\mu g\,l^{-1}$, respectively. On the other hand, the signal was increased when concentrations of Pb $\geq 200\,\mu g\,l^{-1}$ and Mn $\geq 400\,\mu g\,l^{-1}$ were added to $1\,\mu g\,l^{-1}$ As standard solution.

Selenium produced the highest suppression on the signal. As Se is a hydride-forming element, it can compete with arsenic for the reductant during the hydride generation step. Therefore, selenium can suppress the signal by affecting both the retention of the analyte and the generation of arsine [24,30]. The use of a higher concentration of reductant was avoided since it increases the blank signal, affecting the sensitivity of the technique.

Low tolerance levels of transition-metal Ni, Cd and Co can be due to their reduction and precipitation by the borohydride during the preconcentration step. Since the rate at which metal ions are reduced is slow in comparison with the rate of arsine generation, a technique such as traditional flow injection, which shortens the sample–reagent interaction period, would suppress the magnitude of the interferences, whereas a preconcentration system increases the sample–reagent interaction period and the interference [23,31]. In addition, it has been reported that polystyrene-matrix resins have a high affinity for metal chloro complex ions and, therefore, as the resin is in the chloride form, metals may be retained on the resin [24,30,32].

3.8. Validation of the proposed technique

Table 3 shows the results obtained for the determination of arsenic in two solid reference materials, fish muscle (DORM-1) and liver (DOLT-1) and one water reference material, hard drinking water (LGC-6010), as well as the certified values for each sample. Three replicates of each sample were analyzed. As can be seen from the table, satisfactory recoveries of As were obtained applying the proposed technique to solid and water samples.

3.9. Comparison between different flow techniques: MSFIA, MSFIA with preconcentration, FIA and SIA using HGAFS

Comparison of results obtained by the authors using the commercial FIA system (PS Analytical), SIA and MSFIA–HGAFS systems (with preconcentration step and without it) has been done. Results presented in Table 4 showed that applying the preconcentration step, the detection limit decreased in two times and the lowest detected concentration decreased in five times in comparison with the conventional MSFIA technique. The MSFIA system with preconcentration step gives approximately the same detection limit as the commercial FIA system and provides a minimal detected concentration two times lower. Nevertheless, MSFIA-preconcentration system allows to decrease

Table 4
Comparison results obtained by multisyringe flow injection analysis (MSFIA)[a], MSFIA with preconcentration, commercial flow injection analysis (FIA)[b] and sequential injection analysis (SIA)[a] systems

Parameters	FIA	SIA	MSFIA	MSFIA preconc.
Detection limit ($\mu g\,l^{-1}$)	0.05	0.67	0.07	0.03
Linear range ($\mu g\,l^{-1}$)	0.1–8	2.5–70	0.25–12	0.05–2
% R.S.D.	–	1.9	4.9	4.8
Sample throughput (h^{-1})	–	6	36	10
Injection throughput (h^{-1})	45	33	113	30
$NaHB_4$ concentration (%)	1.2	0.12	0.24	0.05
$NaHB_4$ consumption (ml per injection)	4.7	0.5	0.3	3
$NaHB_4$ consumption (mg per injection)	56.4	0.6	0.7	1.5
HCl consumption (ml per injection)	11.3	0.5	0.6	2
Sample volume needed (ml per injection)	11.5	0.5	0.6	3

[a] Results obtained by the authors.

[b] Results obtained by the authors using commercial system made by PS Analytical Ltd.

considerably the reagents and sample consumption in comparison with the FIA technique, from 5.6 to 37.6 times less consumption of reagents and 3.8 times less sample volume. In comparison with SIA system the MSFIA-preconcentration system provides a number of advantages: increasing almost in two times the sample throughput, decreasing in 22 times the detection limit, decreasing in 50 times the lowest detected concentration.

4. Conclusions

The MSFIA–HGAFS with solid-phase preconcentration system proposed has proved to constitute an effective approach for the determination of inorganic arsenic at $\mathrm{ng\,l^{-1}}$ levels. The methodology includes a sequential retention of borohydride and arsenic on an anion-exchange resin followed by an elution with hydrochloric acid. The preconcentration of the analyte on the column improved five times the sensitivity over a MSFIA–HGAFS technique previously developed by the authors, diminishing simultaneously the sample throughput in three times. The overall MSFIA approach developed, however, in comparison with FIA techniques, provides a significant reduction in reagent consumption, which leads to a lower waste generation. The MSFIA–HGAFS with on-line solid-phase preconcentration system has been applied to the determination of arsenic in reference solid and water materials.

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