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Ultratrace arsenic determination through hydride trapping on oxidized multiwall carbon nanotubes coupled to electrothermal atomic absorption spectrometry

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Schematic diagram of the simple manifold employed for As hydride trapping on oxidized multiwall carbon nanotubes with analytical purposes.
Abstract

Arsenic determination in natural waters is an issue of current research. This article reports a novel hydride generation (HG) approach developed for As determination with electrothermal atomic absorption spectrometry (ETAAS) detection. The HG process was interfaced with ETAAS through hydride trapping onto a carbon nanotubes microcolumn. To this end a homemade gas-liquid separator was used, allowing arsine formation and its flow throughout the CNT microcolumn. The retention process involved thus a solid phase extraction from the gas phase to the solid support. Once arsine generation was completed, the elution was carried out with nitric acid directly onto the dosing hole of the graphite furnace. Outstanding sensitivity with detection limit of 1 ng L\(^{-1}\), quantification limit of 5 ng L\(^{-1}\) and the characteristic mass, 5.8 ± 0.4 pg could be achieved. A satisfactory correlation between concentration of As and absorbance (R = 0.9993) from the limit of quantification up to 500 ng L\(^{-1}\), with a relative standard deviation of 6.3% were obtained. A sensitive enhancement factor of 38 was reached when 2 mL of sample were processed and 50 µL of HNO\(_3\) were used as eluent. The system was successfully applied to the analysis of a standard reference material, QC LL2 metals in natural waters. In addition tap water analysis provided an As concentration of 0.29±0.03 µg L\(^{-1}\).

Keywords: Arsenic; Hydride trapping; Oxidized multiwall carbon nanotubes; Electrothermal Atomic Absorption Spectrometry
1. Introduction

Arsenic is widely distributed in the environment, both because of natural sources (e.g., volcanic activity) as through anthropogenic applications.\(^1\) As may exist in different oxidation states (As(III) and As(V)) or organic forms, however inorganic forms are the most toxic thanks to phosphate analogy, being readily taken up by organisms.\(^2\) Considered and classified as human carcinogen substances, inorganic forms of As are the predominant forms found in water.\(^3\)

A number of techniques, as for example, the inductively coupled plasma mass spectrometry (ICPMS)\(^4\), electrothermal atomic absorption spectroscopy (ETAAS)\(^5\), hydride generation atomic absorption spectroscopy (HG AAS)\(^6\) and hydride generation atomic fluorescence spectrometry (HGAFS)\(^7\) and even hydride generation inductively coupled plasma optical emission spectrometry (HG-ICPOES)\(^8\) have been employed for As determination. From these techniques the ones involving hydride generation are advantageous since the generation of gaseous analytes and their introduction into atomization cells eliminates the need for a nebulizer and enhances analyte transport efficiency. With this approach, detection limits can be significantly improved while achieving: (a) separation of the analyte from the matrix, which invariably leads to improved accuracy of determination; (b) ease of preconcentration; (c) chemical speciation which may be discerned in many cases and (d) procedures which are amenable to automation.\(^9,10\)

In ETAAS the adverse effect of the sample matrix on the results of analysis can be countered by the introduction of chemical modifiers. One group of modifiers includes nitrates of Ni\(^{11}\), Mg, Ca, rare-earth elements, and some other metals. The high efficiency of these chemical modifiers is determined by two processes. The first is the displacement of
the matrix chlorine from the atomizer at the pyrolysis stage as a result of exchange processes. Second, compounds of many elements are stabilized in the atomizer as a result of their interaction with oxides of the modifier.

When an enhancement of the method detection power is desired several liquid and solid adsorption media have been successfully applied for collection/preconcentration of hydrides (hydride trapping).\textsuperscript{10} In the case of ETAAS, the graphite furnace is used to decompose the volatile hydride and trap the analyte species on the tube surface, thereby effecting a clean, rapid separation from the matrix as well as concentration (collection). Cryogenic trapping is performed in a cold trap which is usually a U-tube immersed in liquid nitrogen. The U-tube contains the retention sorbent. The trap hydride is released by heating.\textsuperscript{10} Hsiung et al.\textsuperscript{12} retained As hydride with dimethyldichlorosilane 20 and 10\% OV-101 Chromosorb. Ellwood et al.\textsuperscript{4} employed the same sorbent but determinations were performed by ICP MS. Both graphite furnace and cryogenic trapping requires fine temperature control systems since hydride collection and release takes place at different temperatures.

Recent studies have shown that carbon nanotubes are favorable sorbents for light gases like CO and CO\textsubscript{2}\textsuperscript{13} and of Ar, N\textsubscript{2}, and CH\textsubscript{4}\textsuperscript{14}. Single-walled carbon nanotubes (SWNT) and multi-walled carbon nanotubes (MWNT) are formed by seamless roll up of single and multi layers of graphene sheets, respectively\textsuperscript{15}. Carbon nanotubes (CNT) have highly desirable mechanical, thermal, and electrical properties which make them attractive for a wide range of applications. CNT also have excellent sorbent characteristics which can be utilized in diverse applications. The main advantage of CNT is that they are non-porous, and the solute is held on the surface by van der Waals-type forces. The large specific capacity comes from the specific surface of the CNT and efficient removal during surface
desorption. The sorption sites on CNT are on the wall and in the interstitial spaces between tubes. These sites are easily accessed for both adsorption and rapid desorption.\textsuperscript{16} In addition, CNT have already been used for As extraction\textsuperscript{17} in SPE methods.

The present research describes an As hydride trapping method. Arsine was generated in batch mode through sodium borohydride reduction in acid media. The hydride (gas phase) was trapped on a minicolumn filled with oxidized multiwall CNTs. Desorption was reached by means of a nitric acid solution. This disposition allowed a simple hydride trapping method to enhance sensibility without sophisticated systems. Determinations were carried out by ETAAS. Parameters related to hydride generation, trapping and As atomization into the graphite furnace were optimized. This method was applied to a certified reference material (QC metals in natural waters) and tap water.

2. Experimental

2.1. Instrumentation

The determination of As concentrations was carried out on a Shimadzu Model AA-6800 atomic absorption spectrometer (Tokyo, Japan) equipped with a background correction system employing a continuum source, a GFA-EX7 electrothermal atomizer, and an ASC-6100 autosampler. L’vov graphite tubes (Shimadzu, Tokyo, Japan) were used in all experiments. A thallium hollow-cathode lamp (Hamamatsu, Photonics K. K., Japan) was employed as radiation source operated at 6mA, the analytical wavelength of 193.7 nm was employed for all measurements. The ETAAS instrumental and operating conditions are listed in Table 1.
A Gilson Minipuls 3 peristaltic pump (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 Figure 1. Reagents were deposited directly in the bottom of the GLS to improve homogenization and hydride generation. All unions were sealed to avoid gas looses. 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 CNT into an empty conical tip with the dry packing method. To avoid CNTs looses when the sample solution passed through the conical minicolumn, small amounts of quartz wool were placed at both ends.

2.2 Reagents

Unless otherwise stated, the chemicals used were of analytical reagent grade and, therefore, no further purification was required. A 1000 mg L$^{-1}$ As AAS standard solution was obtained from Sigma-Aldrich. A 0.6% (w/v) sodium borohydride solution (Aldrich Chemical Co. 98%) was prepared in 0.5% (w/v) sodium hydroxide solution and was filtered through Whatman No. 42 filter paper to remove undissolved solids. This solution was prepared daily. Commercial multiwalled CNTs were obtained from Sunnano (Jiangxi, China). Commercial multiwalled CNTs were treated with concentrated nitric acid to clean them and eliminate possible Fe residues present in CNTs due to the generation process. This procedure also allowed the generation of $-\text{COOH}$ and $-\text{OH}$ groups on the CNTs surface, improving their solubility$^{18}$. After this, CNTs were centrifuged, filtrated, and dried.
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 Mg chemical modifier, 10.5495 g of Mg(NO\(_3\))\(_2\)6H\(_2\)O (Merck, Darmstadt, Germany) were weighed and diluted; for Pd chemical modifier, 2.16 g of Pd nitrate (Merck, Darmstadt, Germany) were weighed and diluted; for Ni chemical modifier, 4.9545 g of Ni(NO\(_3\))\(_2\)6H\(_2\)O were weighed and diluted \(^{19}\).

2.3 Sample preparation

Tap water samples were obtained directly from San Luis city water system. Tap was opened for five minutes before collecting the sample. Then it was filtered through 0.45 mm pore size membrane filters immediately after sampling. In addition the method accuracy was checked by applying it to As determination in the standard reference material (SRM), QC METAL LL2 (metals in natural water).

2.4 Procedure

As hydride adsorption on oxidized multiwall CNTs was studied by optimization of the reducing agent volume, reducing agent concentration, sample volume, sample flow rate and hydrochloric acid concentration. With regard to arsine elution, the eluent concentration and volume was also studied. To this end the manifold showed in Figure 2 was used. Sample loading was achieved by closing valve \(V_2\), and introducing the reducing reagent into the gas liquid separator (GLS) with pump \(P_1\), and valve \(V_1\) in position NaBH\(_4\). After that, the
sample was loaded with pump $P_1$, valve $V_1$ in position $S$, and valve $V_3$ in position $A$ (load). During the sample loading, As hydride was formed and adsorbed on the minicolumn ($M$) filled with oxidized multiwall CNTs mounted on the AAS autosampler robotic arm. After sample loading, the line before the GLS was filled with water until the reaction stops to avoid hydride loses.

Elution was achieved by filling the loop $L$ with the eluent $E$, valve $V_3$ position $A$. After that the minicolumn $M$ mounted on the AAS autosampler robotic arm was placed into the graphite furnace, valve $V_3$ was changed to position $B$ (elution), and valve $V_1$ to air position to push the eluent to the minicolumn and then to the graphite furnace. The graphite furnace modifier was co-injected with the eluent.

Finally valve $V_2$ was opened to empty and wash the GLS through pump $P_1$, completing the measurement cycle.

3. Results and discussion

3.1. Optimization of As pyrolysis in ETAAS

Generally, the analyzed samples by ETAAS prior As determination, introduced into the graphite tube are liquid$^5$. However, analyst have also introduced slurries$^{8,11,20}$ or solid samples$^{6,7,21}$ into the graphite furnace. The main advantage of these sample introduction modes is the avoidance of sample dilution, enhancing sensibility. There are several problems associated with As determination using ETAAS, including the low wavelength
of the most intense line of absorption, the formation of volatile compounds, possible interactions of As or its compounds with the graphite and spectral interferences.\textsuperscript{22}

In these context As pyrolysis was optimized for solutions containing 5\% HNO\textsubscript{3} (v v\textsuperscript{-1}) as eluent. Two modifiers were evaluated, Mg-Pd modifier since it is frequently used as a universal modifier stabilizing elements that hardly interact with Pd;\textsuperscript{23} and Ni since it has been suggested its suitability for As determination.\textsuperscript{11, 23} The evaluated temperatures ranged between 200 and 900 °C.

Figure 3 shows the pyrolysis curves obtained for the different modifiers. When Ni (5 µL) modifier was used, a 5-fold enhancement in As signals were obtained compared with no modification. Lower enhancement was observed when Pd-Mg modifier was assayed. In the search for best results, the amount of Ni modifier was doubled to 10 µL, as observed in Figure 3, however no improvements were observed in As signal but an increase in the background signal was observed. All further measurements were carried out using 5 µL of Ni nitrate with satisfactory reproducibility. Finally, a pyrolysis temperature of 300 °C was chose for further experiments corresponding to the maximum As signal reached by means of Ni (5 µL) modifier.

The atomization temperature was set at 2200° C according to many studies cited in bibliography\textsuperscript{24-26}. Higher temperatures were not evaluated since increase in the background intensity and As signal depression have been observed\textsuperscript{25}.

3.2. Evaluation of the reducing reagent concentration and volume.
Sodium borohydride has shown to be adequate to generate As hydride.\textsuperscript{12, 17, 27, 28} Since the developed method depends exclusively on the arsine generated prior to its adsorption on CNTs, the concentration of the As reducing reagent becomes relevant. The concentrations tested were 0.25, 0.5, 1.0, 1.5 and 3.0\% (m v\textsuperscript{-1}) and results can be observed in Figure 4. The amount of As adsorbed on the oxidized multiwall CNTs decreases with higher NaBH\textsubscript{4} concentration. The fact that H\textsubscript{2} has affinity through carbon-based surfaces may explain the observations, considering a possible competition towards CNT which is noticeably higher at higher NaBH\textsubscript{4} concentrations.\textsuperscript{29, 30} In addition high NaBH\textsubscript{4} concentrations can rapidly increase pressure into the gas-liquid separator and decrease the interaction time between CNTs and arsine. On the other hand, 0.25\% NaBH\textsubscript{4} (g mL\textsuperscript{-1}) seems to be not sufficient for effective arsine formation, for these reasons 0.5\% NaBH\textsubscript{4} (g mL\textsuperscript{-1}) concentration was chose for future studies.

As mentioned in the experimental section, the employed gas-liquid separator was home made with an internal volume of 6 mL, and the reagents volumes needed to be studied. The low volume of the gas-liquid separator allowed a decrease of the reagents consumption and easiness of homogenization. The evaluated volumes were 0.25, 0.5, 1.0, 2.0, 3.0 and 4.0 mL. As it can be observed in Figure 4, Arsine adsorption increased as volumes decreased until 0.5 mL. This is in good agreement with previous statements since higher volumes generate higher pressures into the gas-liquid separator with the consequences discussed above. For further studies, 0.5 mL volume of NaBH\textsubscript{4} was chose.

3.3. Evaluation of acid concentration and volume.
Acid media, where the analyte is contained, is necessary in hydride generation prior reduction of As. Hydrochloric was the selected acid to this end and the evaluated concentrations were 1, 5, 10, and 20% (v v⁻¹). According to results observed in Figure 5, 1% was not sufficient to achieve quantitative As reduction whereas 20% (v v⁻¹) generates excessive reaction rates with NaBH₄. Compromise conditions between 5 and 10% (v v⁻¹) are then needed to reach the highest retention. Accordingly, 8% HCl concentration was chose for further experiments.

The volume of the acid solution containing As delivered to the gas-liquid separator is another important parameter to optimize. This acid solution correspond to standards or samples whether optimization or sample analysis are performed respectively. 0.5, 1.0, 1.5 and 2.0 mL were the proposed volumes and results can be observed in Figure 5. As hydride adsorption on CNTs increased with the sample volume. This indicates a high column retention capacity in response to increasing As quantities. Higher volumes were not tested considering the total volume of the gas liquid separator, 6 mL. For further studies 2 mL of either standards or sample were employed. The sum of NaBH₄ volume (0.5 mL) and the sample volume (2 mL) provides a total reagents volume of 2.5 mL, leaving 3.5 mL free in the gas-liquid separator for hydride production.

3.4 Evaluation of sample flow rate

The time of analysis depends almost exclusively of the sample flow rate. Additionally, this parameter will determine arsine production rate and the hydride pressure into the gas-liquid separator. It is worth mentioning that this system did not need a carrier gas and the hydride
is transported exclusively by the drop pressure between the gas-liquid separator and the exterior (atmospheric pressure). By observation of Figure 6 the previous statement can be confirmed. Effectively, at higher sample flow rates, As hydride retention on oxidized CNTs decreased. Despite a decrease between 0.01 and 0.5 mL min\(^{-1}\) was advised, there was still a relationship between the recorded signal and the concentration of As in the original solution. This fact enables choosing compromise conditions in order not to drastically enlarge the time of analysis. For further experiments a sample flow rate of 0.25 mL min\(^{-1}\) was set.

Additionally, since As\(^{5+}\) is reduced to As\(^{3+}\) at a lower rate than As\(^{3+}\), this sample flow rate (0.25 mL min\(^{-1}\)) allowed both species reduction, as it can be observed in further section from SRM analysis.

3.5 Elution

Many research have been dedicated to metal retention on oxidized CNTs.\(^3\)\(^1\) In most of them, authors agreed that metals stripping from solid substrates can be achieved with acids through an exchange process between the adsorbed metal ion and H\(^+\). This process occurs fast and instantaneously with high recoveries.\(^3\)\(^2\),\(^3\)\(^3\) Arsine is generally considered non-basic, but it can be protonated by strong acids to give [AsH\(_4\)]\(^+\) salts. Hydrochloric and nitric are the most common acids employed to carry out the elution. In this study nitric acid was used for elution. Different concentrations were studied for As elution from oxidized multiwall CNTs. A maximum absorbance was reached when 5% nitric acid concentration (v v\(^{-1}\)) was used in the elution step. Whilst 1% nitric acid concentration was not sufficient to reach
quantitative elution, concentration values higher than 5% are not recommended due to its effects on the graphite tube with the current temperature program. Issues related to As determination in acid media through ETAAS were discussed in section 3.1.

Several elution volumes were assayed as follows: 30, 50 and 70 µL, and we could verify that an eluent volume of 50 µL was at least necessary to quantitatively elute the retained As. An elution flow rate of 0.5 mL min was chose to avoid sprinkling into the graphite tube. Table 2 summarized the conditions for As preconcentration and elution.

### 3.6 Validation studies

This study obtained an enhancement factor of 38 when 2 mL of sample were loaded on the column and eluted with 50 µL of 5% HNO₃ (v v⁻¹). The detection limit was of 1 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, n=3). The quantifying limit (LOQ) found in this study was 5 ng L⁻¹ calculated as 10 times the amount of As required to yield a net peak that was equal to three times the standard deviation of the background signal (3σ, n=3). The characteristic mass of analyte which produces an integrated absorbance signal whose net area is equal to 0.0044 was 5.8 pg. The precision was evaluated by relative standard deviation (RSD%) corresponding to 8.3% (n=3). The calibration graph using the preconcentration system for As was linear with a correlation coefficient of 0.9993 from the limit of quantification to the detection limit up to at least 500 ng L⁻¹. Column retention at these concentration levels was of 97.2%.
With regard to the time of analysis, the employment of a home made gas-liquid separator allowed the use of minimal reagents and sample. The time required for the preconcentration of 2 mL of sample (8 min, at a flow rate of 0.25 mL min⁻¹), elution (0.1 min, at a flow rate of 0.5 mL min⁻¹), washing and conditioning (0.4 min) and atomization (0.9 min) was about 10 min, reaching a throughput sample of 6 samples per hour.

3.7 Application

To validate the proposed methodology, the certified reference material (CRM) QC LL2 (metals in natural waters) was analyzed. Dilutions were made according to the effective concentration range of the method. Additionally five aliquots of tap water samples were collected and three of them were analyzed and the amount of As found was averaged as base value, while the other two aliquots were added with increasing amounts of As. The recovery was then calculated and results are shown in Table 3. Recoveries were between 97.6±9.5 and 102.8±9.2% regard the concentration value informed for As in the CRM. Tap water analysis provided an As concentration of 0.29±0.03 μg L⁻¹. This value is below the tolerance limit reported by the Environmental Protection Agency (EPA) of the United States of 10 μg L⁻¹.³⁴

It is worth mentioning that despite the fact that dilutions were necessary to accomplish with the working concentration range of the method, this system becomes more interesting when the samples to be analyzed need a previous digestion process and As concentration decreases due to dilution caused by digestion reagents.
4. Conclusion

The present research describes for the first time gas adsorption on oxidized multiwall CNTs with analytical purposes. An alternative to conventional hydride trapping method through arsine adsorption on oxidized multiwall CNTs was achieved. Adsorption was quantitative at the working concentration range, previous optimization of different FI parameters. The system was successfully coupled to ETAAS determination. The low elution volume required to strip As from CNTs complied with the volume needed to be introduced into the graphite furnace. The detection limits obtained with this hyphenation reach the nanogram range.

The homemade gas-liquid separator allowed volumes reduction, with minimal samples and reagents consumption. With a simple system design comparable performance was obtained regards those methodologies that employed different temperatures to trap and release hydrides requiring more sophisticated control mechanism.

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Table 1

Graphite furnace temperature program for the As determination

| Step          | Temperature (°C) | Ramp time (s) | Hold time (s) | Ar flow (mL min\(^{-1}\)) |
|---------------|------------------|---------------|---------------|---------------------------|
| Drying (I)    | 150              | 20            | -             | 250                       |
| Drying (II)   | 250              | 10            | -             | 250                       |
| Pyrolysis (I) | 300              | 10            | 10            | 250                       |
| Pyrolysis (II)| 300              | -             | 3             | 250                       |
| Atomization   | 2200             | -             | 3             | 0                         |
| Cleaning      | 2400             | -             | 3             | 250                       |
Table 2.

Optimized preconcentration and elution parameters

| Parameter            | Value          |
|----------------------|----------------|
| NaBH₄ concentration  | 0.1% (m v⁻¹)   |
| NaBH₄ volume         | 0.5 mL         |
| HCl concentration    | 8% (v v⁻¹)     |
| Sample volume        | 2 mL           |
| Sample flow rate     | 0.25 mL min⁻¹  |
| Eluent concentration | 5% (v v⁻¹)     |
| Eluent volume        | 50 µL          |
| Eluent flow rate     | 0.5 mL min⁻¹   |
Table 3

Analysis of SRM and recovery study.

| Sample                  | Aliquot | Base Value (µg L⁻¹) | Added Value (µg L⁻¹) | Found Value (µg L⁻¹) | Recovery (%) |
|-------------------------|---------|---------------------|----------------------|----------------------|--------------|
| QC LL1                  | 1       | 26.1±1.3            | ---                  | 26.05±1.5            | 99.8ᵃ         |
| Tap water               | 1       | 0.29±0.03           | ---                  | ---                  | ---          |
|                         | 2       | 0.29±0.03           | 0.50                 | 0.80                 | 102ᵇ         |
|                         | 3       | 0.29±0.03           | 1.00                 | 1.30                 | 101ᵇ         |
|                         | 4       | 0.29±0.03           | 5.00                 | 5.29                 | 100ᵇ         |
|                         | 5       | 0.29±0.03           | 10.00                | 10.26                | 99.7ᵇ        |

ᵃ as 100*(found/base);ᵇ as 100*(found-base)/(added)

Confidence intervals: \( t_{(0.05, df)} S/\sqrt{n} \)

Informed values as average amount of three replicate determination (n = 3)
Figure 2
Figure 3

![Graph showing the relationship between As signal and pirolysis temperature for Pd-Mg, Ni, and Ni+](image-url)
Figure 4

- Graph showing the relationship between As normalized concentration and NaBH₄ volume (ml).
- Graph showing the relationship between As normalized concentration and NaBH₄ concentration % (g mL⁻¹).
Figure 5

Graph showing the effect of HCl concentration and sample volume on normalized concentration.
Figure 6

![Graph showing the relationship between sample flow rate (mL min⁻¹) and As normalized concentration. The graph includes error bars and a downward trend.]
**Figure captions**

**Figure 1.** Detailed diagram of the home-made gas-liquid separator. W, waste; M, minicolumn; S, sample.

**Figure 2.** Schematic diagram of the instrumental set up. S, sample; E, eluent; L: loop 50 µL volume; W, waste; P, peristaltic pump; M, minicolumn packed with oxidized multiwall carbon nanotubes mounted on the arm of ETAAS autosampler; V₁, V₂ and V₃, valves; GLS, gas-liquid separator. Injection valve positions: (a) sample loading; (b) injection.

**Figure 3.** Optimization of pyrolysis temperature. Volume injected: 50 µL, As solution 5 µg L⁻¹ 10% v/v HNO₃, modifiers concentration 10.000 mg L⁻¹, modifiers injected volume: Pd-Mg, 5 µL; Ni 5 µL; Ni 10 µL.

**Figure 4.** Influence of NaBH₄ concentration and volume on As signal during loading step.

Preconcentration of 2 mL of As (III) solutions; As concentration was 100 ng L⁻¹, HCl 30 % (v v⁻¹), eluent: HNO₃ 10% (v v⁻¹), loading flow rate 0.25 mL min⁻¹, elution flow rate 0.5 mL min⁻¹, eluent volume 50 µL.

**Figure 5.** Influence of HCl concentration and sample volume on As signal during loading step. As concentration was 100 ng L⁻¹, reducing agent: 0.5 mL NaBH₄ 1% (v v⁻¹), eluent: HNO₃ 10% (v v⁻¹), loading flow rate 0.25 mL min⁻¹, elution flow rate 0.5 mL min⁻¹, eluent volume 50 µL.

**Figure 6.** Influence of sample flow rate on As signal during loading step. Preconcentration of 2 mL of As (III) solutions; As concentration was 100 ng L⁻¹, HCl 8 % (v v⁻¹), reducing agent: 0.5 mL NaBH₄ 1% (v v⁻¹), eluent: HNO₃ 10% (v v⁻¹), elution flow rate 0.5 mL min⁻¹, eluent volume 50 µL.