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Determination of total inorganic arsenic in water using on-line pre-concentration and hydride-generation atomic absorption spectrometry

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Abstract

A rapid and sensitive method for the on-line separation and pre-concentration of inorganic arsenic in water samples is described. The analyte in the pentavalent oxidation state is reduced to its trivalent form with L-cysteine and the total inorganic arsenic is sorbed onto activated alumina in the acid form in a mini-column coupled to a FI-HG AAS system. Afterwards, it is eluted with $3\,\mathrm{mol\,l^{-1}}$ HCl. An enrichment factor of 7 was obtained, allowing an analytical flow rate of about 28 determinations per hour. The limits of detection (3σ) and of quantification (10σ) were calculated as $\mathrm{LOD} = 0.15\,\mu\mathrm{g\,l^{-1}}$ of As and $\mathrm{LOQ} = 0.5\,\mu\mathrm{g\,l^{-1}}$ of As, respectively. Relative standard deviations ($n = 10$) less than 8% were obtained for different arsenic concentrations and the accuracy was verified by analysing certified reference materials. Different kinds of samples, such as mineral water, drinking water, river water and natural spring water were analyzed and good agreement was obtained with the values from spiked experiments.

Keywords: Pre-concentration; Arsenic; Alumina; Atomic absorption spectrometry; Hydride generation; Water

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1. Introduction

Arsenic is a ubiquitous specie in the environment and it is a seriously toxic element for man, who is mainly exposed via drinking water and seafood. While organic species like dimethylarsenic acid (DMA) show a median lethal dose in animals of $\mathrm{LD_{50}}\ (\mathrm{DMA}) = 1200\,\mathrm{mg\,kg^{-1}}$, and are considered as non-toxic compounds, the inorganic forms arsenite and arsenate show $\mathrm{LD_{50}} = 4.5\,\mathrm{mg\,kg^{-1}}$ and $\mathrm{LD_{50}} = 14\,\mathrm{mg\,kg^{-1}}$, respectively, and should be considered to be rather toxic. Most of the international agencies established acceptable values for arsenic in drinking water in the range of $0.005–0.050\,\mathrm{mg\,l^{-1}}$ [1]. Consequently, there is an increasing interest in the development of methodologies characterised by simplicity, speed and economy of reagents and materials aiming at the determination of arsenic in water.

Atomic absorption spectrometry (AAS) is a well-established and well-known technique that has been used for the determination of many elements using flame or electrothermal atomization [2,3]. In 1969, Holak [4] used the concept of hydride generation to determine arsenic by AAS. When the acidified sample containing arsenic was put in contact with a reducing reagent, the volatile hydride $\mathrm{AsH_3}$ was generated, providing an excellent tool to detect and quantify this element.

Considering the benefits obtained with this technique, the development of a new analytical method employing FI-HG AAS is of significant interest. Sometimes, however, the concentration of the analyte is very low, considering other species present in the sample, so a pre-concentration step is necessary.

Pre-concentration techniques of trace metals, like sorption of the analyte on solid materials, modified or not with organic reagents have frequently been used. The metal or the metal-complex is eluted from the solid material by a suit-

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able solvent and afterwards the determination of the metal is performed.

The usual reactions for As pre-concentration make use of organic reagents which are able to separate As(III) from As(V), such as dithiocarbamate [5–7] and dithiophosphate [8–11] compounds sorbed on solid materials.

Some inorganic materials, such as ion-exchange resins [12], zeolites [1], and alumina [13,14] have also been used as sorbent materials for ions from aqueous solutions. Sperling et al. [13] in 1992 determined Cr(III) and Cr(VI) in water using FI-FAAS, after pre-concentration on activated alumina. In 1994, Ebdon et al. [14] used activated alumina in the acid form to pre-concentrate As, Cr, Se, and V before their determination by ICP-MS, with good pre-concentration factors. Recently, Lin and Wu [15] evaluated the use of activated alumina as a sorbent for arsenite and arsenate ions in a procedure for the decontamination of water.

In the present work, an on-line pre-concentration method employing activated alumina as sorbent for total inorganic arsenic, followed by its determination by HG AAS was developed. The method was applied to the determination of inorganic arsenic in rivers, mines and natural spring waters from Quadrilátero Ferrífero, a mining region in Minas Gerais, Brazil.

2. Experimental

2.1. Apparatus

The FI pre-concentration system coupled to HG AAS is shown in Fig. 1. In the FI-HG system, an eight-channel peristaltic pump (Ismatec®, ICP High Precision Multichannel Dispenser) introduced the sample and the reducing reagent into carrier flows using a merging-zones manifold. Samples and reagents were aspirated through Tygon tubes (Technicon) with appropriate flow rates for each solution. Sample loop, reaction coil and transmission lines were prepared using Teflon tubing (CPL, 0.8 mm i.d.). For the pre-concentration, the total inorganic arsenic present in the sample is reduced to As(III) with 0.1% (w/v) L-cysteine, which is then retained in a glass column ($\phi_i = 3$ mm; $L = 35$ mm) containing 70 mg of activated alumina (150 mesh) in the acid form by the passage of a solution flowing at 3.2 ml min^{-1}. After 2 min, the pre-concentrated species are eluted with 3 mol l^{-1} HCl (3.2 ml min^{-1}) loading a 150 μl loop, while a 1.0% (m/v) sodium tetrahydroborate solution loads the other loop (150 μl) of the system. The time of the elution step is 8 s and at the same time, the alumina is regenerated for the next pre-concentration cycle. The arsine generated is carried with N_2 (flow rate = 90 ml min^{-1}) to a quartz cell wound with Ni–Cr wire where the atomization process occurs. The temperature of the quartz cell needed for AsH_3 atomization was obtained and controlled with a Varivolt regulator, connected to the Ni–Cr coil of the cell. The As was measured with an atomic absorption spectrometer (Varian, Model Gemini AA 12/1475) equipped with a hollow cathode lamp for arsenic as well a deuterium lamp for background correction under the following conditions: wavelength, 193.7 nm; slit width, 0.5 nm; lamp current, 10 mA. For the adjustment of the solution pH, a Hanna Instruments pH meter equipped with a combined electrode was utilized.

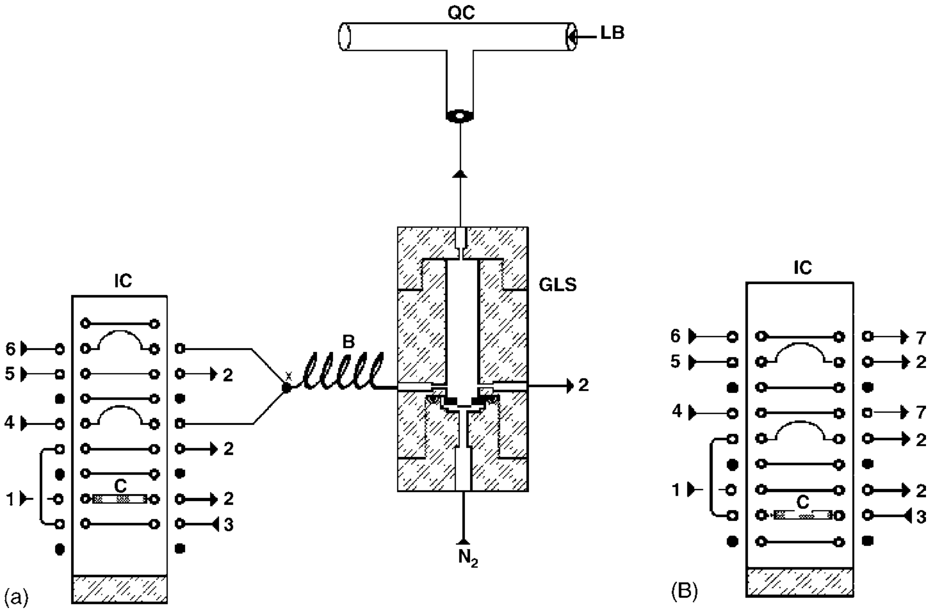

Fig. 1. (a) FI-HG AAS pre-concentration system in the sorption position for the determination of As: (1) sample (3.2 ml min^{-1}); (2) waste; (3) eluent (3.2 ml min^{-1}); (4) 1 mol l^{-1} HCl (2.8 ml min^{-1}); (5) 1% (w/v) $NaBH_4$ (2.8 ml min^{-1}); (6) H_2O (2.8 ml min^{-1}); (7) HG AAS system; (IC) injector; (B) reaction coil (30 cm); (X) confluence point; (GLS) gas–liquid separator; (QC) atomizer; (LB) optical path; (C) glass mini-column with sorbent material. (b) Injector–commutator in the elution position.

2.2. Reagents

All reagents used in the experiments were of analytical grade. Deionized water (18.2 MΩ cm) obtained from a Milli-Q water system (Bedford, MA, USA) was used throughout.

The arsenic standard solution was prepared by dissolving 1.0000 g As_2O_3 (Carlo Erba) in 20% (w/v) NaOH with the addition of two drops of phenolphthalein. This solution was neutralised with 20% HCl (v/v), diluted to a final volume of 1000 ml with 1 mol l^{-1} HCl solution, and stored in a polyethylene bottle under refrigeration. Adequate dilutions were made, whenever necessary, with 1 mol l^{-1} HCl.

Solutions of sodium tetrahydroborate were prepared by dissolving $NaBH_4$ powder (Nuclear) in 0.05 mol l^{-1} KOH and stored in plastic bottles under refrigeration. This solution is stable for about 2 weeks with no loss of the observed absorption signal.

The L-cysteine used was from Synth and the alumina (acid form) was purchased from Aldrich.

Solutions of interfering ions were prepared by the dissolution of appropriate salts or metals in acid or deionized water.

The proposed methodology was applied to the determination of arsenic in certified reference materials (CRM-TMDW, Trace Metals in Drinking Water and NIST-SRM 1640, Trace Elements in Natural Water) as well as in other water samples (mineral water, mine water and river water).

2.3. Sample preparation

All kinds of water were collected at Quadrilátero Ferrífero, a region with mining activities located in Minas Gerais State, Brazil. After collection, the water was filtered through a 0.45 μm membrane, acidified with 1 mol l^{-1} HCl, and stored in a refrigerator in polyethylene bottles until use.

Mineral water was purchased in the local market, acidified with 1 mol l^{-1} HCl and stored in a refrigerator before use.

The certified reference water samples were appropriately diluted according to their arsenic concentration and the aliquots were treated with 0.1 g of L-cysteine for 30 min. Afterwards, the pH was adjusted to 5 with dilute NaOH, the solution was transferred to a 100.0 ml volumetric flask and the volume was completed with deionized water. The arsenic content was determined after a pre-concentration step.

For the water samples from river, mines, or natural spring water collected at the origin or from spring water piped to a roadside fountain, each replicate of adequate volume was treated with 0.1 g of L-cysteine for 30 min. Afterwards, the pH was adjusted to 5 with diluted NaOH, transferred to a 100.0 ml volumetric flask, and the arsenic content was determined after the pre-concentration step. Some samples were spiked to permit evaluating the analytical procedure.

3. Results and discussion

The flow system used in this study was previously described and optimised for the determination of arsenic without a pre-concentration step [12]. The replacement of the sample loop by the glass column filled with alumina in its acid form acting as sorbent material for arsenic required some changes in these optimised parameters, as well as in the optimization of others, as described below.

3.1. Effect of eluent

Considering that the eluent may significantly influence the determination of arsenic, this was the first parameter evaluated. According to the literature, [13,14] HNO_3, NH_3, and HCl can be used to elute arsenic from alumina. The effect of base and acid on the proposed pre-concentration system was verified and the experimental results obtained with HCl showed this to be the most adequate. Varying the concentration of the acid solution from 1.0 to 5.0 mol l^{-1}, good results were obtained with concentrations above 1.5 mol l^{-1}, as can be seen in Fig. 2. In order to guarantee the complete elution of the analyte, a concentration of 3 mol l^{-1} HCl was selected as eluent.

3.2. Effect of flow rate and time of pre-concentration

The pre-concentration time was evaluated and it was observed that a significant improvement in analytical signals was obtained when the pre-concentration time was increased from 1 to 2 min. However, there was no change for times longer than 3 min, for different sample flow rates as the column used became saturated with the passage of the sample for longer times. If the dimensions of the column and the amount of solid phase are different, it is possible to pre-concentrate the analyte for a longer time but analytical fre-

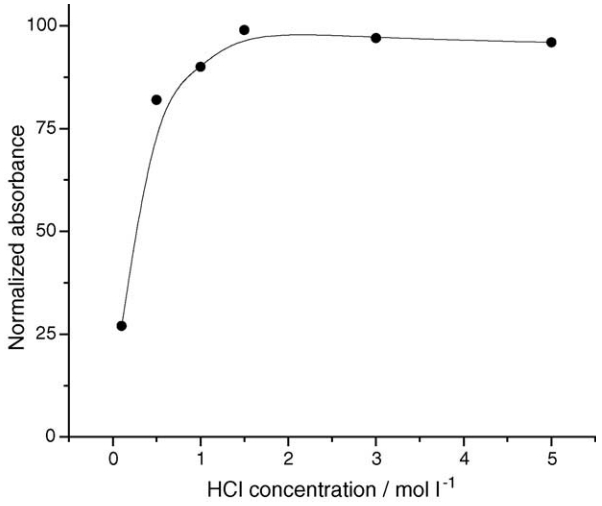

Fig. 2. Effect of eluent concentration for pre-concentration system using acid-activated alumina.

quency will be prejudiced. After changing the flow rate from 2.8 to 3.6 ml min^{-1}, a pre-concentration time of 2 min at 3.2 ml min^{-1} was chosen for continuing this study, which allowed good detectability and analytical frequency.

3.3. *Effect of flow rate and time of elution*

The elution step depends on the time necessary to fill the sampling loop (Fig. 1b) of the FI system, which is determined by the flow rate of the eluent, and this was also evaluated. The efficiency of elution may be evaluated considering either the nature and concentration of the eluent, or the elution flow rate. By changing this parameter from 2.8 to 3.6 ml min^{-1}, better analytical signals were obtained when the eluent (3 mol l^{-1} HCl) passed through the sample loop for 8 s at a flow rate of 3.2 ml min^{-1}. Under these conditions, an analytical frequency of 28 injections per hour was obtained.

3.4. *Effect of the amount of solid sorbent*

In order to evaluate the amount of solid sorbent, different sizes of the glass mini-column were evaluated using different mass of alumina. When a 20 mm × 3 mm column was used, retention of the analyte is low while with a column of 50 mm × 3 mm it was difficult to couple to the injector. A column of 35 mm × 3 mm (that contains 70 mg of alumina) was shown to be adequate for the proposed system, leading to good analytical signals and enrichment factors and it was selected for the pre-concentration of arsenic.

3.5. *Effect of pH on the adsorption*

The pH of the aqueous phase is an important factor in solute distribution with accentuated acid–base properties. As a result, the interaction between As and alumina may be affected, considering different surface modifications that take place according to the pH [15]. The effect of pH on liquid–solid extraction during the adsorption was investigated and Fig. 3 shows that the adsorption of arsenic was quantitative in the range of pH 3.0–10.0. Considering that all the samples are stored in acid solutions, it was convenient to work at pH 5.0 for the remaining studies.

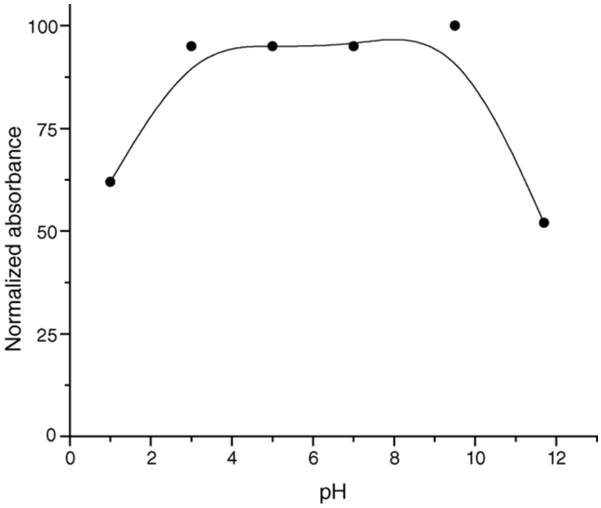

Fig. 3. Effect of pH on the sorption of As with acid-activated alumina.

3.6. *Study of pre-reduction of As(V)*

According to Tsalev and Zaprianov [16], arsenic levels in rivers and lakes are generally <10 μg l^{-1} and the trivalent species may represent up to 8% of the total arsenic. For environments with low aeration conditions, like groundwater, it may represent 50%. Thus, the presence of As(V) in a matrix, such as river water and mine water is obvious and it is important to guarantee the reduction of the inorganic arsenic using adequate reagents. Alumina is not selective to As(III) or As(V), even with different pH values and, in this case, the use of a pre-reducing reagent is very important in order to generate arsine from As(III).

L-Cysteine has been widely used as a pre-reductor for the determination of arsenic by HG-AAS. Tsalev et al. [17] described some advantages for its use: rapid and efficient reduction compared to other pre-reductor systems, such as KI–mineral acid and KI–ascorbic acid; stability of the reducing solution, which may be stored for a long time; and higher tolerance to interfering species. Preliminary studies using L-cysteine in acidic medium showed that it required 30 min in order to guarantee the complete reduction of up to 5 μg l^{-1} of As(V), being impossible to carry this out on-line. Different concentrations of L-cysteine were evaluated, concluding that 0.1 g of reagent for 100.0 ml of solution is enough for complete reduction of low contents of As(V) if at least 30 min is allowed for complete reduction.

Ascorbic acid does not reduce As(V) effectively, considering its low reduction power. On the other hand, I_2 formed by KI increases the background signal and may interfere in the system due to its oxidant character. A mixture of potassium iodide:ascorbic acid (KI:AscA) leads to a good results since it reduces the I_2 formed by KI. Solutions with different proportions of KI:AscA (0.05:0.1%; 0.1:0.2%; 0.2:0.4%; and 0.5:1.0%) were also tested, again using 30 min for the completion of reaction [12].

However, considering the results obtained and the previously cited advantages of L-cysteine [19], the use of this reducing reagent was chosen.

3.7. *Interferences*

While Dedina [18] classified the interferences in the hydride generation technique into two groups, liquid-phase interferences and gaseous-phase interferences, Hershey and Keliher [19] described that arsenic is one of the hydride-forming elements less susceptible to interference. In order to identify species that could interfere in the determination of

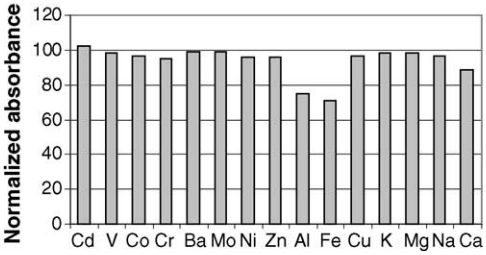

Fig. 4. Interference effect of cations on the determination of As, using acid-activated alumina.

arsenic using the proposed system concerning both the liquid and gaseous phases, a study was carried out considering the constituents and the ratios between arsenic and the foreign ions present in natural and mineral water.

The concentration of arsenic was fixed as 2 μg l^{-1} and possible interferences were evaluated, using the following concentrations: Cd (8 μg l^{-1}), V (16 μg l^{-1}), Co (14 μg l^{-1}), Cr (20 μg l^{-1}), Cu (20 μg l^{-1}), Ba (36 μg l^{-1}), Mo (16 μg l^{-1}), Ni (20 μg l^{-1}), Zn (26 μg l^{-1}), Al (160 μg l^{-1}), Fe (300 μg l^{-1}), K (2000 μg l^{-1}), Mg (4800 μg l^{-1}), Na (7000 μg l^{-1}), and Ca (18000 μg l^{-1}). The interference effect was evaluated considering the difference between the absorbance for arsenic in the presence and in the absence of the element studied. Fig. 4 shows that aluminium and iron interfered significantly in the arsenic determination, but this effect can be associated with the hydride-generation system, not with the pre-concentration step [12] and it may be efficiently overcome in the presence of L-cysteine.

Hydride-forming elements were also evaluated as interferences for the proposed system and the experiments were carried out considering two different concentrations, 1 and 2 μg l^{-1}, except for Pb (15 and 30 μg l^{-1}). The results obtained showed that Pb, Sb(V), Sb(III), Sn, Bi, and Se(VI) did not interfere at the concentrations evaluated and that the only serious interfering species was Se(IV). According to the literature [20,21], there is a competition for $NaBH_4$, although the interference may also occur during the atomization step resulting from the competition for hydrogen radicals. The interference of selenium may be minimized with the addition of small amounts of copper, avoiding the generation of H_2Se [20]. If copper is already present in the water, the interference of selenium will be masked naturally.

The effects of some anionic species (Cl^-, $NO_3{}^-$, $PO_4{}^{3-}$, $HCO_3{}^-$, and $SO_4{}^{2-}$) were studied at three different concentrations, representing an excess of 100, 1000, and 10000 times, the concentration of arsenic (2 μg l^{-1}) but no interference was observed.

3.8. *Figures of merit and the determination of As in water samples*

In order to calculate the enhancement factor for the system using alumina as sorbent material, analytical curves with and without the pre-concentration step were obtained and it was possible to note an increase in the sensitivity. An enhancement factor of 7 was calculated considering the increase of the analytical signal. The efficiency of the mini-column was not affected even after 200 pre-concentration runs.

Table 1
Results obtained in the analyses of certified reference materials

Sample	As concentration certified (μg l^{-1})	As concentration found (μg l^{-1})
CRM-TMDW	80.0 ± 0.4	83.0 ± 3.4
NIST-SRM 1640	26.7 ± 0.4	26.1 ± 2.4

The limit of detection (3σ) and the limit of quantification (10σ) were calculated as 0.15 μg l^{-1} of As and 0.5 μg l^{-1} of As, respectively, after pre-concentration. Relative standard deviations less than 8% were obtained for different concentrations of arsenic.

The accuracy of the method was evaluated by analyzing certified reference materials and the results are described in Table 1, showing that the values obtained with the proposed method were in agreement with the certified values considering a 95% confidence level. A matrix effect for the proposed method was evaluated from the slopes obtained with both analytical and analyte addition curves, and it was possible to conclude that it was not significant in the presence of L-cysteine, eliminating the requirement of a more complex sample preparation.

Samples of mineral water, mine water, river water, and natural spring water were analyzed. Using analyte addition and recovery experiments, 96–106% recoveries were observed, demonstrating the reliability of the proposed method. Table 2 shows the content of arsenic in the samples obtained with the proposed method. Considering these results, it is possible to conclude that, in a general way, the cited region sampled in this study may have problems related to arsenic contamination. Although the mining activities have ended, the effects of a long period of gold extraction still persists and may be a source of diseases contamination for the local population

Table 2
Results obtained in the analyses of different kinds of water samples after the arsenic pre-concentration using alumina as sorbent ($n = 3$)

Water	Arsenic found (μg l^{-1})
Piped spring 1	4.9 ± 0.4
Piped spring 2[a]	33.6 ± 2.3
Spring source	1.3 ± 0.6
Mineral	0.83 ± 0.03
Drinking	2.02 ± 0.05
River-point A[a]	24.2 ± 4.5
River-point B[a]	37.4 ± 6.4
Mine 1[a]	260 ± 5
Mine 2 A[a]	10.8 ± 0.6
Mine 2 B[a]	2262 ± 58

[a] Samples diluted before the analysis using the pre-concentration system.

due to the amount of arsenic that was liberated to the environment. Waters from natural springs piped to roadsides (A and B) and at their origin are generally used for consumption, although the value found for spring B (33.6 $\mu g\,l^{-1}$) is higher than that allowed by the appropriate Brazilian Agency (ANVISA), which is 10 $\mu g\,l^{-1}$. Depending on their origin, the waters showed different contents of arsenic. Waters from a river, collected at two different points, and from the interior of two mines showed high concentration levels and in these cases, the pre-concentration step is not necessary. In order to evaluate the performance of the method independently of arsenic concentration in the samples, dilution was required in some cases. On the other hand, the determination of arsenic content in uncontaminated waters was successfully carried out with the proposed method.

4. Conclusions

An efficient on-line system for arsenic pre-concentration using activated acid alumina as the sorbent material coupled to HG-AAS was developed and was shown to be fast (28 determinations h^{-1}) and of low cost (one column may be used for more than 200 cycles of pre-concentration, without loss of efficiency).

Although the enrichment factor is lower than some described in the literature, the proposed system was less susceptible to interference of many species usually present in waters, since the L-cysteine used to reduce the As(V) to As(III) may also act as a masking reagent.

The limit of detection of 0.15 $\mu g\,l^{-1}$ and the enrichment factor of 7 allowed the determination of arsenic in low concentrations, such as those found in mineral waters and in uncontaminated waters. This is important to control the levels of arsenic in waters from regions that may suffer contamination and that are used by the local population as drinking water.

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