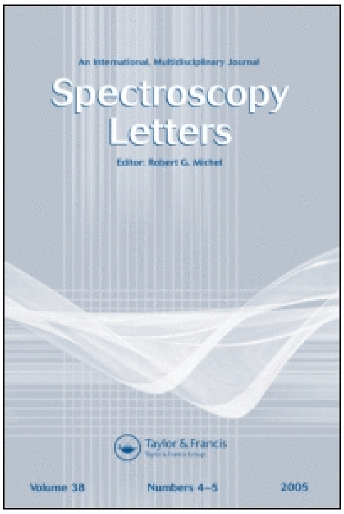

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ABSTRACT A flow injection system coupled to hydride generation atomic absorption spectrometry with heated quartz tube atomizer was employed for the selective determination of As(III) in real groundwater samples under nonacidic conditions. The use of low-acidity conditions was carefully evaluated in order to minimize the interconversion of redox arsenic species. The As(III) hydride was generated using $0.1\,\mathrm{mol\,L^{-1}}$ HCl as carrier solution and 0.2% (m/v) $NaBH_4$ in 0.025% NaOH as the reductant. A coil reaction larger than the used one for higher acidity conditions (480 mm instead of 115 mm) was selected. The generated hydride was transported to the atomizer by a nitrogen flow of $75\,\mathrm{ml\,min^{-1}}$. The main parameters that influenced the signal intensity and shape were studied. Under the best found experimental conditions, a detection limit (3σ) of $1.0\,\mu\mathrm{g\,L^{-1}}$ As(III) was obtained for a $500\,\mu\mathrm{l}$ sample volume. The analytical recovery ranged between 90% and 98%. In addition, the total inorganic arsenic concentration in the samples was determined on sample aliquots acidified with concentrated HCl and prereduced with 5% (m/v) KI–5% (m/v) $C_6H_8O_6$ solution. HCl $1.2\,\mathrm{mol\,L^{-1}}$ as carrier solution, $NaBH_4$ 0.2% (m/v) as reductant, and a nitrogen flow rate of $75\,\mathrm{ml\,min^{-1}}$ were used in this case. The concentration of As(V) was calculated by difference between the total inorganic arsenic and As(III) concentrations.

KEYWORDS arsenic speciation, atomic absorption spectrometry, flow injection, hydride generation, nonacidified water samples

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INTRODUCTION

Hydride generation atomic absorption spectrometry (HGAAS) with a externally heated quartz tube atomizer is a very widely used technique for the ultratrace determination of volatile hydride-forming elements such as arsenic.[1] Its relative simplicity and fast derivatization process using borane compounds, mainly sodium tetrahydroborate ($NaBH_4$), offers very attractive advantages for total trace element analysis and for speciation purposes. The differences between the pK_a values for the arsenic species have been often used for their speciation analysis by HGAAS. The use of diluted acid media allows the reduction of As(III) into arsine with no significant interferences of As(V).[2,3] In this way, most works reporting arsenic speciation by flow injection (FI) HGAAS use previously acidified water samples together with the acid condition of the carrier solution.[3] However, the changes on the arsenic species distribution observed when synthetic and natural water samples were acidified with 0.1–0.4% HCl or HNO_3[4] raises the necessity of studying the behavior of these systems under the conditions imposed by original samples.

The injection of a nonacidified sample volume to a diluted acid carrier flowing through a FI-HGAAS system adds some problems to the optimization process. For example, while transient signals with a single peak were obtained for As(III) when pH values ≤ 0 were used as carrier solution, double peaks of different heights were observed using diluted acid solutions.

The presence of double-peak signals has been associated in the literature with anomalies in the volatile hydride generation step or with the hydride atomization process. The volatile hydride formation from $NaBH_4$, attributed recently to the direct transfer of hydrogen from boron to analyte through the formation of intermediates,[5,6] is dependent on H^+ and BH_4^- concentrations. Its generation under alkaline conditions also has been reported, although a progressive decrease on the generation efficiency was observed as pH increased.[7] The losses of the completely protonated analyte (the reactive species) observed at high-pH values should be the cause for the decrease of the hydride generation efficiency. In this way, the nonhomogeneous pH distribution in the sample plug of the flow system could give rise to fluctuations on the arsine generation along the reaction zone.

However, several authors[8] have attributed the double-peak appearance to an inefficient atomization of the hydride when working under nonoptimized conditions. Welz and Guo[9] observed this effect using FI-HGAAS with a quartz tube externally heated at temperatures lower than optimal (<900°C). Those authors attributed the phenomenon and thus, the loss of sensitivity, to a hydrogen radical deficiency in the atomizer. The loss in sensitivity should be overcome by the addition of oxygen to the hydrogen produced by the reaction with $NaBH_4$.[10] At temperatures higher than 900°C, like those employed in this work, no effect on sensitivity was observed by the addition of extra oxygen since the dissolved oxygen in the solutions and/or the diffused oxygen inside the system was enough for the radical's generation.[11]

In this work, we studied the selective determination of As(III) in nonacidified aqueous samples by FI-HGAAS under low-acidity conditions. This alternative, scarcely reported in the literature, allows one to reduce the possibility of redox species interconversion. The influence on the analytical signal (intensity and shape) derived from changes on the acidity of carrier and sample solutions, concentration of $NaBH_4$, gas flow rate and composition, and size and shape of the reaction coil were systematically evaluated. The proposed method was applied to the determination of As(III) in groundwater samples. In order to know the inorganic species distribution in the analyzed samples, the total inorganic arsenic concentration was determined on samples acidified and prereduced under the acidic conditions usually employed in FI-HGAAS. The As(V) concentration was calculated by difference.

MATERIALS AND METHODS

Instrumentation

A Perkin-Elmer FIAS 100 MHS (Mercury and Hydrides System) (Connecticut, USA) flow injection hydride generation system with a heated quartz tube atomizer (10 mm i.d. × 160 mm length) was used. The rotation speed of the multichannel peristaltic pump and the process timing were programmed and automatically controlled by Perkin-Elmer AA WinLab, version 3.2, software. PTFE tubing was used for sample transfer. The sample solution flowed into a 500 μL sample loop. The reaction coil was formed by two different sections between which were located the nitrogen entrance. Arsenic absorbance was measured with a Perkin-Elmer Model 3110 (Connecticut, USA) flame atomic absorption spectrometer coupled

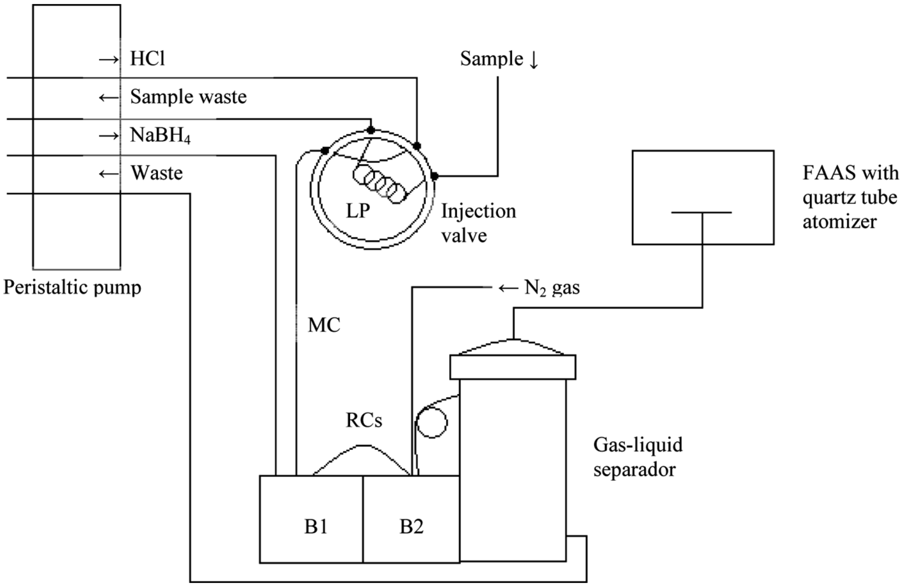

FIGURE 1 Manifold employed for the FI-HGAAS determination of arsenic in water samples. MC, mixing coil; RCs, reaction coils; LP, sample loop; B1 y B2, manifold devices used for the fluids and gas distribution.

to the FIAS and equipped with a Photron (Victoria, Australia) arsenic hollow cathode lamp as radiation source. Peak height was used for the measurements of the analytical signal. A scheme of the FI-HGAAS system that we used is shown in Fig. 1 The instrumental parameters are listed in Table 1.

Reagents and Standard Solutions

All reagents used were of high purity or at least of analytical reagent grade. Deionized-distilled water (DDW) was used in the work. As(III) stock solution of 1000 mg L^{-1} was prepared from 1.3204 g of As_2O_3 (Riedel-de Haën, Germany) dissolved in 20 ml of 1 mol L^{-1} NaOH neutralized with 2 mol L^{-1} HCl and diluted to 1000 ml with 0.6 mol L^{-1} HCl. Working solutions were prepared daily by appropriate dilution of the stock solution in DDW. Working solutions for total inorganic arsenic determinations were obtained from As(V) stock solution of 1000 mg L^{-1} (Merck, Germany), and successive dilutions were prepared in 10% HCl solution and prereduced with 5% (m/v) potassium iodure–5% (m/v) ascorbic acid solution.

TABLE 1 FI-HGAAS Operating Conditions

Variable	Value
Wavelength	193.7 nm
HCL current	11 mA
Slit width	0.7 nm
Integration time	15 s
Read time	20 s
Carrier solution flow rate	11.0 ml min^{-1}
Reductant solution flow rate	5.5 ml min^{-1}
Carrier gas flow rate (N_2)	75 ml min^{-1}
Sample loop volume	500 μl
Mixing coil length	310 mm (vol. 320 μl)
Reaction coil length I	115 mm (vol. 70 μl)
Reaction coil length II	310 mm (vol. 200 μl)
Prefill time	15 s
Fill time	10 s
Injection time	15 s

Solutions of 0.1, 0.3, 0.5, and 1.2 mol L^{-1} HCl (J. T. Baker, U.S.A.) were used to prepare carrier and sample solutions by appropriate dilution in DDW.

Sodium tetrahydroborate solutions of 0.05, 0.1, 0.15, and 0.2% (m/v) were prepared daily by dissolving $NaBH_4$ (Merck, Germany) in 0.025% (m/v) sodium hydroxide solution (Merck, Germany).

Nitrogen of 99.998% purity, hydrogen of 99.998% purity, and nitrogen with 1% oxygen were obtained from Linde, Argentina.

RESULTS AND DISCUSSION

Influence of Acidity

Typical peaks with a single maximum for As(III) in nonacidified sample solutions were obtained by FI-HGAAS, using 1.2 mol L^{-1} HCl as carrier solution and 0.2% (m/v) $NaBH_4$ stabilized with 0.025% (m/v)

NaOH as reductant solution, under the optimized conditions given in Table 1. More diluted carrier solutions yielded double peaks with two maxima of different heights together with a noticeable decrease of sensitivity. Fig. 2 shows the responses obtained for 45 μg L^{-1} As(III) solutions in water using carrier solution concentrations ranging between 0.1 and 1.2 mol L^{-1} HCl. However, in order to preserve the original arsenic species in the water samples, the study was carried out with nonacidified samples as in the discussion below.

Additional experiments were carried out to see the effect of the pH on the analytical signal of As(III). Fig. 3 shows the results obtained for nonacidified samples (pH = 6.8) and those acidified up to 0.1 mol L^{-1} HCl (the same concentration of the carrier). A similar performance was reported in the literature only for the latter.[12]

Due to the physical–chemical nonequilibrium status of FIA, special care needs to be taken in order to explain the behaviors above. The use of 0.1 mol L^{-1} HCl carrier solution in conjunction with a nonacidified sample implies a diminution of protons in the central zone of the sample plug, which should explain the double-peak appearance. However, another alternative for the double-peak formation should be related to the arsine incomplete atomization as a consequence of changes in the hydrogen yield when pH is changed.

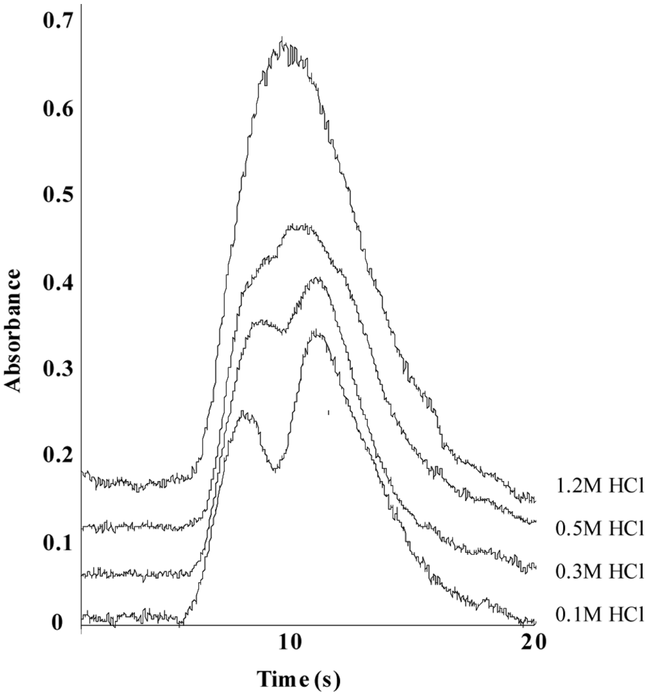

FIGURE 2 Absorbance signals for 45 μg L^{-1} As(III) in water sample solutions at low HCl concentrations as carrier solution using 0.2% (m/v) $NaBH_4$ in 0.025% (m/v) NaOH with carrier gas flow rate 75 ml min^{-1}. The signals were displaced at regular intervals for better visualization.

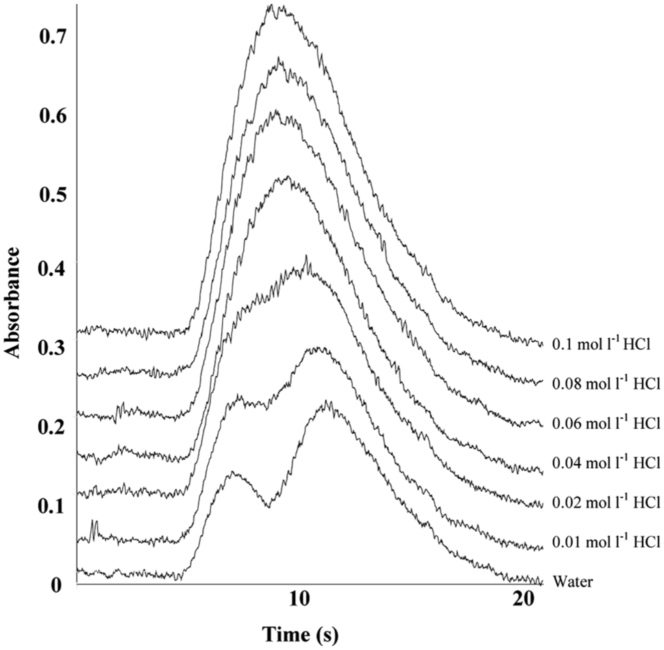

FIGURE 3 Absorbance signals for 30 μg L^{-1} As(III) at different HCl concentrations in the sample solution using 0.1 mol L^{-1} HCl carrier solution, 0.2% (m/v) $NaBH_4$ reductant solution, and carrier gas flow rate 75 ml min^{-1}. The signals were displaced at regular intervals for better visualization.

Influence of the Carrier Gas Flow Rate and Composition

The influence of the carrier gas flow rate and composition on the height and shape of the signal was investigated. A fall on the signal height and a deepening of the dip in the signal top were observed with the increase of the gas flow rate from 50 to 125 ml min^{-1}. Evidently, the lower values of gas flow rates allowed a longer reaction time for hydride generation, yielding an improvement of the signal (height and shape). At the same time, this increase in sensitivity is favored by an smaller dilution of the arsine in the gas stream and a larger time of residence in the quartz tube. Nevertheless, as long as the flow rates are decreased, the times of appearance are enlarged, and thus the analytical frequency is impoverished.

In order to evaluate the influence of the hydrogen amounts arriving to the quartz tube on the atomization process, an external addition of hydrogen varying from 15 ml min^{-1} to 45 ml min^{-1} was supplied to the nitrogen stream in order to keep a total gas flow of 100 ml min^{-1}. No significant changes were observed either on the shape or on the height of the transient signals. Similarly, no effect on the double-peaks production was observed when the carrier gas was spiked with 1% oxygen. Therefore, an inefficient arsine atomization should not be the cause of the double-peak formation.

Influence of the Reductant Concentration

Figure 4 shows the influence of $NaBH_4$ concentration on the height and shape of the analytical signal. A disappearance of the double peak was observed with the decrease of the reductant concentration. According to previous works,[9] this circumstance should be attributed to a decrease in the amount of arsine released to the atomizer when the concentration of $NaBH_4$ is lowered. In this way, if the shape of the double peak depends on the arsine concentration in the atomizer, those signals obtained for arsenic concentrations lower than 45 µg L^{-1} As(III) should present a smoother depression as long as As(III) concentration is decreased. However, 15 µg L^{-1} and 30 µg L^{-1} As(III) solutions presented the same shape as that of 45 µg L^{-1} As(III), making support of the interpretation above difficult. Perhaps a more-adjusted explanation should be provided by the effect of pH: a lower concentration of $NaBH_4$ involves a less-drastic increment of pH in the reaction coil as a consequence of dilution.

Effect of the Mixing and Reaction Coil Sizes

The smoothing of the double peak was also observed when a longer mixing coil was used. However, the effect of a greater dilution of the sample volume in the acid carrier solution deteriorated the frequency of analysis. The replacement of the first section of the reaction coil, that is the segment previous to the carrier gas entrance (115 mm; i.d. = 0.89 mm) by a longer straight conduit (480 mm; i.d. = 0.89 mm) gave rise to single-peak signals of typical Gaussian shape derived from an increment of the time of contact between reactants with no need for slowing down the gas carrier flow rate. In this case, an increase of the peak height was obtained as a consequence of the greater amount of generated hydride (see Fig. 5). No significant differences on the analytical signal were observed with knotted reactors.

Proposed Method for As(III) and Total as Determination

The experimental results of this work were useful to develop a simple methodology, suitable to the

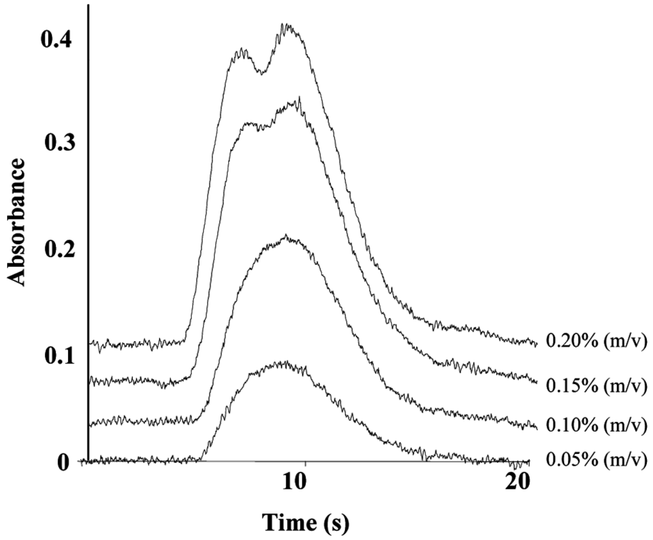

FIGURE 4 Absorbance signals for 45 µg L^{-1} As (III) at different $NaBH_4$ concentrations using 0.1 mol L^{-1} HCl carrier solution and nitrogen carrier gas flow rate 75 ml min^{-1}. The signals were displaced at regular intervals for a better visualization.

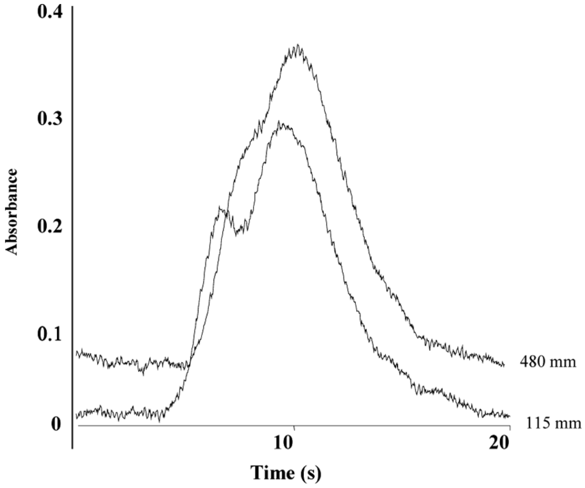

FIGURE 5 Absorbance signals for 45 µg L^{-1} As(III) using two different reaction coil (first section) lengths; 0.1 mol L^{-1} HCl carrier solution; 0.2% (m/v) $NaBH_4$ reductant solution in 0.025% (m/v) NaOH; and carrier gas flow rate 75 ml min^{-1}. The signals were displaced for better visualization.

TABLE 2 Inorganic Arsenic Speciation Analysis in Groundwater and Aqueous Synthetic Samples by FI-HGAAS

	As(III) (μg L^{-1})[a]			Total inorganic As (μg L^{-1})[a]	
Sample identification	Concentration spiked	Concentration found	Recovery (%)	Concentration spiked as As(V)	Concentration found
Groundwater 1	—	nd[b]		—	216.0 ± 4.2
Groundwater 2	—	nd[b]		—	58.5 ± 1.0
Groundwater 2 spiked	15.0	14.7 ± 0.7	98	—	74.3 ± 1.8
Synthetic sample 1	15.0	13.5 ± 1.8	90	85.0	97.6 ± 1.0
Synthetic sample 2	30.0	27.7 ± 2.4	92	70.0	98.5 ± 1.1

[a] Mean and standard deviation ($n = 3$).

[b] nd (not detected): $<1.0\,\mu$g L^{-1}As(III).

direct determination of inorganic As(III) in water samples without previous acidification, while the As(V) concentration can be calculated by direct subtraction of the former from the total inorganic arsenic content. Since the low-acid conditions assayed for arsine evolution resulted in double-peak signals, compromise choices were performed in order to obtain Gaussian-shape single-peak signals without a significant loss of sensitivity.

The proposed method for the determination of As(III) in nonacidified water samples involved the use of 0.1 mol L^{-1} HCl as carrier solution, 0.2% (m/v) $NaBH_4$ as reductant solution, nitrogen at a flow rate of 75 ml min^{-1} as gas carrier, and a larger reaction coil, which composed the unique modification for the conditions given in Table 1. Total inorganic arsenic concentration was determined on 10 ml sample aliquots acidified with concentrated HCl (5 ml) and prereduced with 5% (m/v) KI–5% (m/v) $C_6H_8O_6$ solution (5 ml) in 50 ml volumetric flask. In this case, 1.2 mol L^{-1} HCl carrier solution, 0.2% (m/v) $NaBH_4$ reductant solution, and nitrogen gas flow rate of 75 ml min^{-1} were used. Besides ground waters, the proposed method can be applied to river waters with low content of organic matter and to sea water, but not thus to chlorinated drinking water because the chlorine presence could produce changes in the behavior of the used system that were not evaluated.

Analytical Figures of Merit

A calibration curve in the range of 3.4–45 μg L^{-1} was obtained for inorganic As(III) with a linear correlation coefficient of 0.9986 and a slope of 6.8×10^{-3} L μg^{-1}. The analytical recovery of different amounts of As(III) spiked to synthetic and groundwater samples ranged between 90% and 98%. The limits of detection and quantification calculated from three and ten times the standard deviation of the blank signals were 1.0 and 3.4 μg L^{-1} respectively, whereas a detection level of 0.11 μg L^{-1} was reported in previous studies using acidified water samples with 0.04 mol L^{-1} HCl and 0.03 mol L^{-1} HCl carrier solution.[13] A calibration curve in the range of 2–50 μg L^{-1} As(V) was used for the quantification of total inorganic arsenic.

Sample Analysis

The method was applied to the determination of inorganic arsenic species in groundwater samples from Santa Fe, Argentina, in the central region of the country, whose oxidant aquifers characterized by high values of Eh and pH, elevated salinity, and presence of dissolved oxygen suffer from a natural arsenic contamination. The groundwater samples were filtered and collected in high-density polythene bottles and maintained at 4°C for 48 hr before analysis. The results obtained are shown in Table 2.

CONCLUSIONS

The in-field acidification of water samples in order to preserve the original contents of arsenic species is inconvenient since low pH values favor the interconversion of arsenic redox species at low levels and impede reliable analytical speciation. The employment of FI-HGAAS for the selective determination of inorganic As(III) in nonacidified water samples involves the use of diluted acid carrier solutions for arsine generation, requiring at the same time a very careful optimization of the operational parameters.

Double-peak formation observed under nonoptimized conditions was attributed to a decrease in the hydride generation efficiency caused by the rise of the pH in the central zone of the sample plug. The use of a longer reaction coil became the best choice to obtain optimized signals.

All the experiences were useful for explaining the behavior of the FI-HGFAAS system under low-acid conditions and contributed to optimizing a methodology that was satisfactorily applied to the inorganic arsenic speciation analysis in natural waters.

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