

On-line arsenic co-precipitation on ethyl vinyl acetate turning-packed mini-column followed by hydride generation-ICP OES determination

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Abstract

An alternative and new system for on-line preconcentration of arsenic by sorption on a mini-column associated to hydride generation – inductively coupled plasma – optical emission spectrometry determination was studied. It is based on the sorption of arsenic on a column packed with ethyl vinyl acetate (EVA) turnings and the use of La(III) as co-precipitant reagent. This polymeric material was employed here for the first time as filling material for column preconcentration. It could work both as adsorbent and as sieve material. Sample and co-precipitant agent (lanthanum nitrate) were off-line mixed and merged with ammonium buffer solution (pH 10.0), which promoted precipitation and quantitative collection on the small EVA turnings. The arsenic preconcentrated by co-precipitation with lanthanum hydroxide precipitate was subsequently eluted with hydrochloric acid, which was the medium used for hydride generation. Considering a flow rate of 5 ml/min, three enrichment factors were obtained, 28-, 38- and 45-fold at three different sampling times, 60, 120 and 180 s; respectively. The detection limits (3 s) obtained for each case were 0.013, 0.009 and 0.007 $\mu\text{g/l}$. Additionally, the calculated precisions expressed as relatively standard deviation (R.S.D.) were 0.9, 1.3 and 1.1%.

Satisfactory results were obtained for the determination of arsenic in standard reference material NIST 1643e Trace Elements in Water and drinking water samples.

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1. Introduction

The interest in the determination of arsenic, even at low concentrations, resides its ubiquitous nature and its toxicity. It is 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 a range of anthropogenic activities which include mining, combustion of fossil fuels, wood preservation, and the use of arsenical pesticides, herbicides and crop desiccants [1].

Average concentrations of As in freshwater are frequently less than 1 $\mu\text{g/l}$. Rarely, much higher concentrations are found, particularly in groundwater [1]. The biological effects of arsenic depend mainly on the chemical form in which the element is ingested, the route of entry, the dose and the duration of exposure. Inorganic As(III) and (V) are identified to be more toxic than its organic forms. The arsenic is built up through intake of food or potable water contaminated with arsenic [2].

Of the various sources of As in the environment, drinking water probably poses the greatest threat to human health [1,2]. Depending on local availability, drinking water is derived from a variety of sources such as surface waters (rivers, lakes, reservoirs and ponds), groundwater (aquifers) and rain water, which are variable in terms of As risk.

Due to such wide concentration level of arsenic as well as its considerable toxicity, a great number of techniques for arsenic determination have been applied [3–9]. In this

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sense a technique commonly used is hydride generation (HG). It allows low detection limits and has found wide applications in the determination of trace levels of arsenic combined with atomic absorption spectrometry [10–12], atomic fluorescence spectrometry (AFS) [13–15] or coupled with optical emission spectroscopy-inductively coupled plasma (ICP-OES) [16–21].

As the result of the lack of selectivity and the drawbacks of batch operation, such as time-consuming, labor-intensive, large sample consumption, great contamination risk and analyte loss, on-line preconcentration techniques are usually employed to obtain accurate, reliable and sensitive results [22].

Several on-line solid phase extraction (SPE) methodologies have been developed, and the majority of them employs ionic exchange resins [19,23,24], modified silica gel [25–27], coated polyurethane foam [19], ethyl vinyl acetate (EVA) knotted reactors [28–30], PTFE knotted reactors [31,32] and PTFE turning-packed mini-columns [20], among others adsorbent materials.

Because of the toxicological, biological and environmental importance of this element, further research is expected nowadays as it has been exposed by several research groups [15,17,18,21,31,33].

The aim of the present study was to carry out an on-line preconcentration of arsenic employing a new mini-column filling, which was capable to retain the $\text{La}(\text{OH})_3$ precipitate. This EVA filled mini-column, allowed the efficient separation of arsenic from the sample solution, due to its ability to retain $\text{La}(\text{OH})_3$ precipitate along with arsenic as co-precipitate; both by adsorption and by trapping the formed particles of $\text{La}(\text{OH})_3$.

Because of the chemical resistance (to water and all reagents we used) of EVA, the column did not need any regeneration or refilling. It could work both as adsorbent and as sieve material. This polymeric material was employed here for the first time as filling material for column preconcentration.

On the other hand the flow injection (FI) manifold involved the coupling of hydride generation with ICP OES with time based preconcentration of arsenic by co-precipitation with lan-

thanum(III) at pH 10.0 and subsequent retention on EVA turnings.

In this procedure, an off-line mixing of the co-precipitant reagent with the sample was carried out. The dissolution process was performed by hydrochloric acid, which was the medium for the hydride generation procedure. This elution step was completed in 10 s.

2. Experimental

2.1. Equipment

The measurements were performed with a sequential ICP OES [BAIRD ICP 2070 (Bedford, MA, USA)]. The ICP operating conditions are listed in Table 1. The FI system used is shown in Fig. 1. A Minipuls 3 peristaltic pump [Gilson (Villiers-Le-Bell, France)] was used. Sample and eluent line were selected using a Reodyne (Cotai, CA, USA) Model 50, four-way rotary valve. The hydride unit used was a hydride generator (PS Analytical Ltd.) and the flow rate of the reagents was controlled by a Watson-Marlow 303X peristaltic pump. The mini-column (85 mm length, 2.5 i.d.) used as the EVA turnings holder was prepared using cross-linked ethyl vinyl acetate (EVA) Microline tubing. Tygon-type pump tubing (Ismatec, CleParmer, Vernon Hills, IL, USA) was employed to propel the sample, reagent and eluent. The As 193.696 nm spectral line was used.

Table 1
ICP OES instrumental parameters employed for arsenic determination

Forward power	1.0 kW
RF generator	40.68 MHz
Coolant gas flow rate	8.5 l/min
Auxiliary gas flow rate	1.0 l/min
Carrier gas flow rate	0.5 l/min
Observation height (above load coil)	15 mm
Window size	0.2 mm
Wavelength	188.972 nm

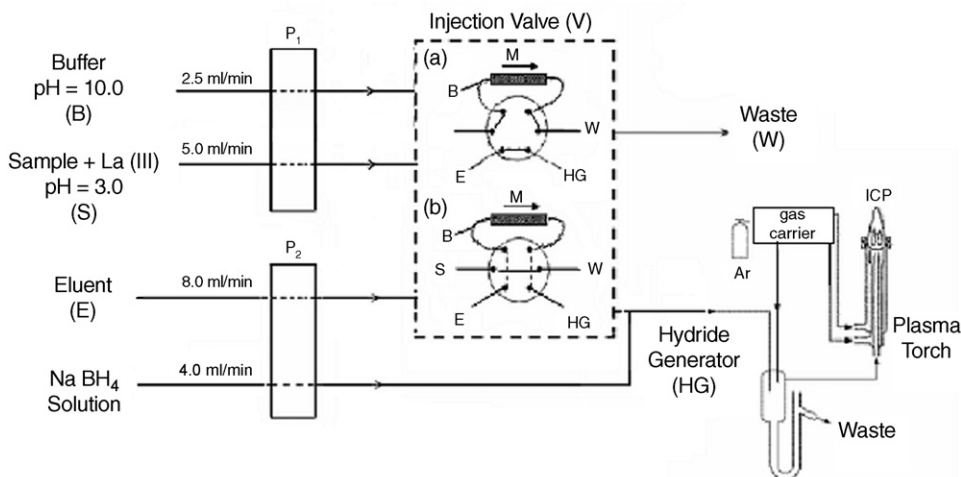


Fig. 1. Schematic diagram of the instrumental setup. P₁ and P₂, peristaltic pumps; M, mini-column; V, load injection valve [(a) load position; (b) injection position].

2.2. Column preparation

Ethyl vinyl acetate is a flexible (rubbery), transparent polymeric material with good low temperature flexibility, good chemical resistance (to acids, alkalis and alcohols among others) and high friction coefficient. It material was employed here to construct the preconcentration mini-column as the following.

The mini-column was prepared by replacing 100 mg of EVA turnings into an empty cylindrical EVA tubing, using the dry packing method. To avoid loss of EVA particles when the sample solution passed through the mini-column, a small amount of quartz wool was placed on both sides of mini-column. The column was then connected to a peristaltic pump with PTFE tubing to form the preconcentration system.

This study has comprised around 600 preconcentration cycles, and the retention capacity did not change under reproducible conditions.

2.3. Reagents

A 0.5% (m/v) sodium tetrahydroborate solution (Aldrich Chemical Co., >98%) was prepared in 0.5% (m/v) sodium hydroxide solution and then filtered through a Whatman No. 42 filter paper to remove undissolved solids. This solution was prepared daily.

Standard solution of 1000 mg/l arsenic(III) was prepared by dissolution of 1.320 g of As_2O_3 (Merck) in 50 ml of 1.0 mol/l hydrochloric acid solution, followed by dilution with ultra pure water. A 1.0% (m/v) L-cysteine (Fluka, Riedel-de-Haen) in 0.03 mol/l HCl solution was used for pre-reduction of As(V) prior to preconcentration step.

Ultra pure water (18 M Ω cm) was obtained from EASY pure RF (Barnstedt, IA, USA). All reagents were of analytical-reagent grade and the presence of arsenic was not detected in the working range (close to 0.1–25 $\mu\text{g/l}$).

2.4. Sample collection and pre-treatment

Water samples were collected in 1000 ml polyethylene flask and stored at 4 °C in darkness.

After analysis, water samples (100 ml) were filtered through a 45- μm pore size membrane filter. They contained L-cysteine (1.0% m/v) and HCl (0.03 mol/l) and were left for 50 min at 25 °C for complete reduction of As(V) to As(III). These conditions were those reported for Guo et al. [12] and Anthemidis and Martavaltzoglou [21]. An appropriate amount of $\text{La}(\text{NO}_3)_3$ solution was added (thus, each sample contained a 20 mg/l lanthanum final concentration). Finally, as solutions were in acid medium, the pH value was adjusted to 3.0 with an appropriate amount of $\text{NH}_4(\text{OH})$ diluted solution.

2.5. Preconcentration and determination procedure

The time-based FI-HG-ICP OES system with on-line addition of the $\text{NH}_3/\text{NH}_4\text{Cl}$ (0.2 mol/l, pH 10.0) buffer is shown in Fig. 1. In the precipitation procedure, the sample containing La(III) (20 mg/l) at pH 3.0 (S) and the buffer $\text{NH}_3/\text{NH}_4\text{Cl}$

(B) solutions were introduced by a peristaltic pump (P_1) at the entrance to the EVA turned-packed mini-column [line (a)]. The precipitate, which was formed instantaneously after the merging point of the mini-column, was collected on the retention material. During the precipitation sequence, both, a sodium tetrahydroborate (0.5% (m/v) in 0.5% (m/v) NaOH) and hydrochloric acid solution were pumped (P_2) directly into the gas–liquid separator of the hydride generator system. In this stage, the baseline for the final readout was established. At the end of the precipitation period, pump 1 was stopped, and the valve was actuated from the load mode [(a) position] to the inject mode [(b) position] for a period of 10 s. During this time the acid was introduced directly into the mini-column where the precipitate was dissolved. This concentrated plug zone was directed from the EVA mini-column to the hydride generating solution of sodium tetrahydroborate. After passing through a mixing cell, the gas–liquid mixture was guided into the gas–liquid separator in which the arsine and the evolved hydrogen were separated from the liquid phase and swept to the ICP OES torch by a steady argon carrier flow (0.5 l/min). The emission signal (peak height) which was proportional to As concentration in the sample was then recorded. The elution stage lasted 10 s and during this period, precipitate was completely dissolved.

Before a new loading stage, the column was conditioned during 10 s at the correct preconcentration pH with the buffer solution; with injection valve V in position (a) while sample flow was stopped.

The operating conditions were established and the determination was carried out.

3. Results and discussion

3.1. On-line preconcentration conditions

The chemical and FI variables of the proposed manifold, which affect the preconcentration were optimized using a 5.0 $\mu\text{g/l}$ As(III) standard solution in HCl stabilized medium (pH 3.0).

3.1.1. Co-precipitation step

In these dynamic conditions established in a flow injection system, several parameters were studied.

Buffer pH was tested and we could verify that there was an optimum range between 9.7 and 10.2 (Fig. 2).

Analytical response was monitored at different buffer concentrations (Fig. 3); in this study, the optimal buffer concentration was ranged between 0.15 and 0.25 mol/l. Accordingly, selected buffer concentration was 0.2 mol/l.

In addition, La(III) concentration was tested in the range of 15–30 mg/l. We could verify that a best retention was achieved with a $\text{La}(\text{NO}_3)_3$ concentration of 20 mg/l. These results were in good agreement with previous experiments [34].

Sample flow rate through the mini-column is an important parameter, since this is one of the steps that controls the time of analysis [22]. The effect of this variable was studied within the range of 3.0–8.0 ml/min at a buffer flow rate of 2.5 ml/min. The

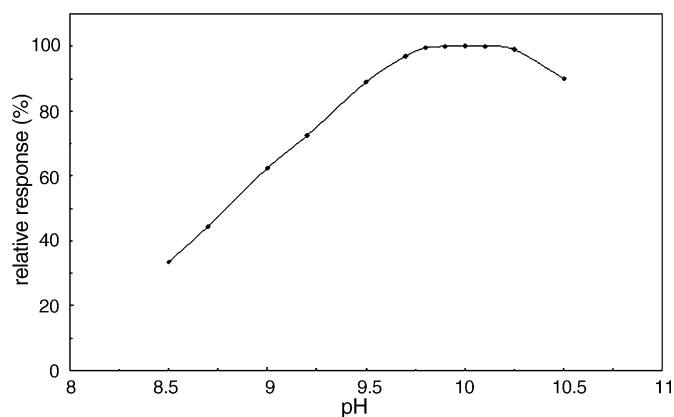


Fig. 2. Effect of pH on the retention of arsenic onto the EVA turnings. Sample flow rate = 5.0 ml/min at 5.0 $\mu\text{g/l}$ As(III) level. Buffer flow rate = 2.5 ml/min.

analytical response obtained was optimum at 5 ml/min sample loading flow rate.

These results could be explained as follows: in our dynamic conditions, the particles of $\text{La}(\text{OH})_3$ formed was retained efficiently onto our preconcentration device. When EVA knotted reactor was employed, small particles of $\text{La}(\text{OH})_3$ were well retained [30]. In this case, EVA turnings worked both as sorbent and as sieve material; because of this, particles of different size formed can be efficiently retained here.

This preconcentration system was able to retain As(V) slightly. Because of this, this system needed a pre-reduction of As(V) in order to determinate total inorganic As content in natural water samples.

3.1.2. Elution step

A satisfactory eluent should effectively dissolve the precipitate with a discrete volume in order to obtain the best enrichment factor (EF) under the optimized experimental conditions [34]. In this sense, HCl solutions were employed as eluent because these solutions facilitated both the hydride generation and elution procedure. As shown in Fig. 4 the effect of the eluent concentration was examined in the range 10–50% (v/v). We could verify that with concentrations higher than 30% (v/v), there is no effect on the analytical response; at lower concentrations, the response

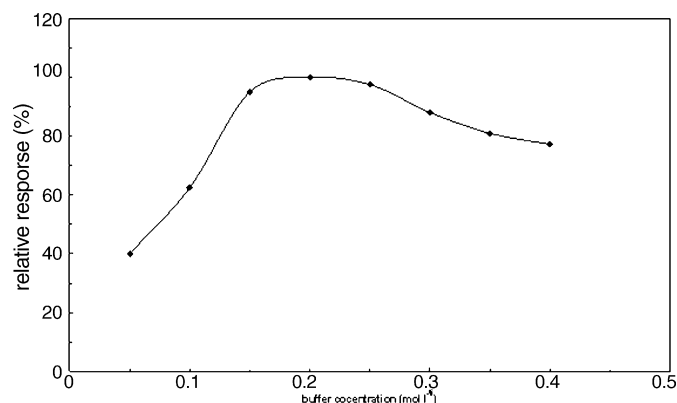


Fig. 3. Effect of the Buffer concentration on the retention of arsenic onto the EVA turnings. Sample flow rate = 5.0 ml/min at 5.0 $\mu\text{g/l}$ As(III) level (pH 10.0).

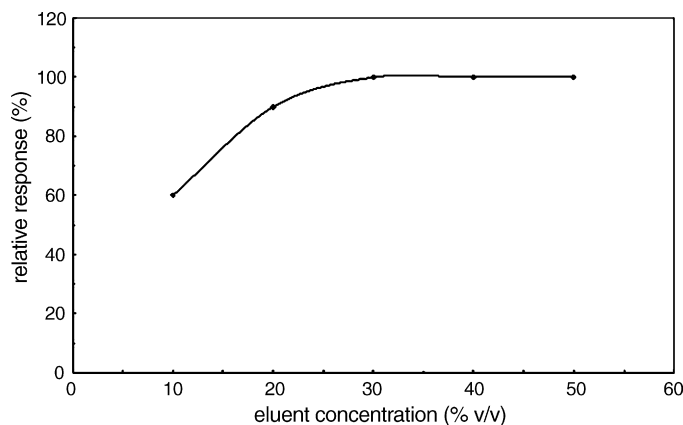


Fig. 4. Effect of the eluent (HCl) concentration (% v/v) on the retention of arsenic onto the EVA turnings. Eluent flow rate = 8.0 ml/min. NaBH_4 flow rate = 8.0 ml/min. Preconcentration of 5.0 $\mu\text{g/l}$ As(III) at pH 10.0.

decreases, due to resulting acidic concentration in the HG system was not enough for efficient arsine generation.

Table 2 shows a comparison between the analytical performance of the proposed system at three different preconcentration times, 60, 120 and 180 s, respectively.

3.2. Interference studies

The proposed coprecipitation system can tolerate the presence of ions at the concentration levels that may be found in natural water samples. Thus, Cu^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Cr^{3+} , Mn^{2+} and Al^{3+} could be tolerated up to at least 2500 $\mu\text{g/l}$. Fe^{2+} and Fe^{3+} could be tolerated up to at least 5000 $\mu\text{g/l}$. Commonly encountered matrix components, such as alkaline and alkaline hearth elements, are not retained on the mini-column.

3.3. Analytical performance

The sample volume required for 60 s preconcentration time (at a 5 ml/min flow rate) was 5 ml. The time required for elution and registration steps was about 10 s. Additionally, conditioning time was 10 s. Overall, it allowed a throughput sample of 45 h^{-1} .

A 28-fold total enrichment factor (EF) for these sample volume was obtained with respect to the arsenic determination by HG-ICP OES without preconcentration.

The relative standard deviation (RSD) for 6 replicates containing 5.0 $\mu\text{g/l}$ of As was 0.9%. The calibration curve was linear, with a correlation coefficient of 0.9992. The detection limit (DL) calculated as the amount of the arsenic required to yield a net peak equal to three times the standard deviation of the background signal (3 s), was 0.02 $\mu\text{g/l}$.

Additionally, Table 2 shows the analytical performance of this preconcentration/determination FI-system at other preconcentration times, there can be observed that with a lowest preconcentration time, the best concentration efficiency (CE) was reached. It means that there was a compromising situation between DL and CE.

Table 2
Analytical performance of the preconcentration system under different sample load flow rates

Preconcentration time (s)	60	120	180
Buffer pH/concentration (mol/l)	10/0.2	10/0.2	10/0.2
La(NO ₃) ₃ concentration (mg/l)	20.0	20.0	20.0
Calibration range (μg/l)	0.01–10	0.01–10	0.01–10
Sample consumption (ml) (sample flow rate = 5 ml/min)	5	10	15
throughput sample, <i>f</i> (h ⁻¹)	36.0	22.5	16.4
Relative standard deviation [<i>n</i> = 6, at 5.0 μg/l As(III) level] (%)	0.9	1.3	1.1
Detection limit (μg/l)	0.013	0.009	0.007
Enrichment factor, EF	28	38	45
Concentration efficiency, CE = EF/ <i>f</i> 60	16.8	14.3	12.3

Table 3
Concentration of arsenic in water samples and certified reference material (95% confidence interval; *n* = 6)

Sample	As concentration			Recovery ^a (%)
	Base (μg/l)	Added (μg/l)	Found (μg/l)	
A (drinking water, 1st week) ^b	1.23 ± 0.08	0.00	1.23 ± 0.08	–
A	1.23	0.3	1.53 ± 0.08	100.0
A	1.23	0.6	1.82 ± 0.09	98.3
A	1.23	0.9	2.12 ± 0.07	98.8
A	1.23	1.2	2.42 ± 0.09	99.1
B (drinking water, 2nd week) ^b	0.97 ± 0.11	0.00	0.97 ± 0.11	–
C (drinking water, 3rd week) ^b	0.88 ± 0.09	0.00	0.88 ± 0.09	–
D (drinking water, 4th week) ^b	1.11 ± 0.10	0.00	1.11 ± 0.10	–
E (NIST CRM 1643e) ^c	59.59 ± 0.25	0.00	59.59 ± 0.25	–

^a Recovery (%) = [(found – base)/added] × 100.

^b Drinking water samples collected in our laboratory.

^c Certified value = 60.45 ± 0.72 μg/l.

3.4. Recovery study and application to real samples and reference materials

In order to evaluate the arsenic recovery of this method, 100 ml of drinking water sample was collected in our laboratory and divided in ten portions of 10 ml each. The proposed method was applied to six portions and the average quantity of the arsenic obtained was taken as base value. Then, increasing quantities of arsenic were added to the other aliquots of sample and arsenic was by the same method. The recoveries were in the range of 98.6–100.1%.

Additionally, the accuracy of the proposed method was evaluated by total arsenic determination in certified reference material NIST CRM 1643e, with an As content to 60.45 ± 0.72 μg/l and a Density equal to 1.016 g/ml at 22 °C.

These results are showed in Table 3.

4. Conclusions

The application of a new preconcentration column packed with EVA turnings was demonstrated and evaluated to be promising for on-line As preconcentration and determination by hydride generation combined with ICP OES.

The methodology proposed has shown adequate accuracy and selectivity. In addition, the proposed procedure is simple and economical due to the fact that only EVA turnings are used to preconcentrate arsenic and the use of organic complexing reagent was unnecessary.

The unlimited lifetime and preconcentration usage of the retention material, easy operation and high sensitivity of the proposed method make it attractive for routine determination of arsenic in water samples.

This on-line solid-phase preconcentration system was successfully applied to the determination of total arsenic in natural water samples and in water certified reference material.

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