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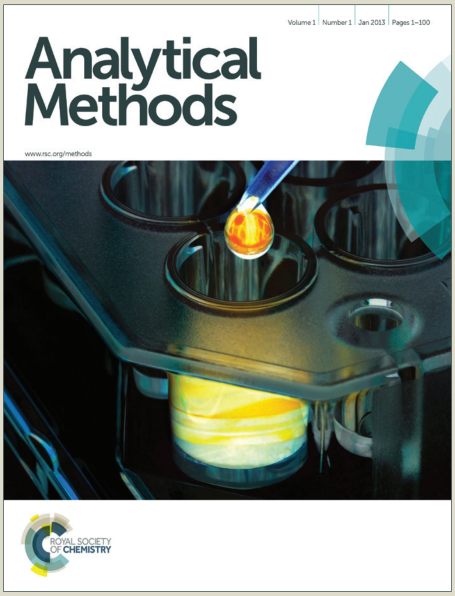

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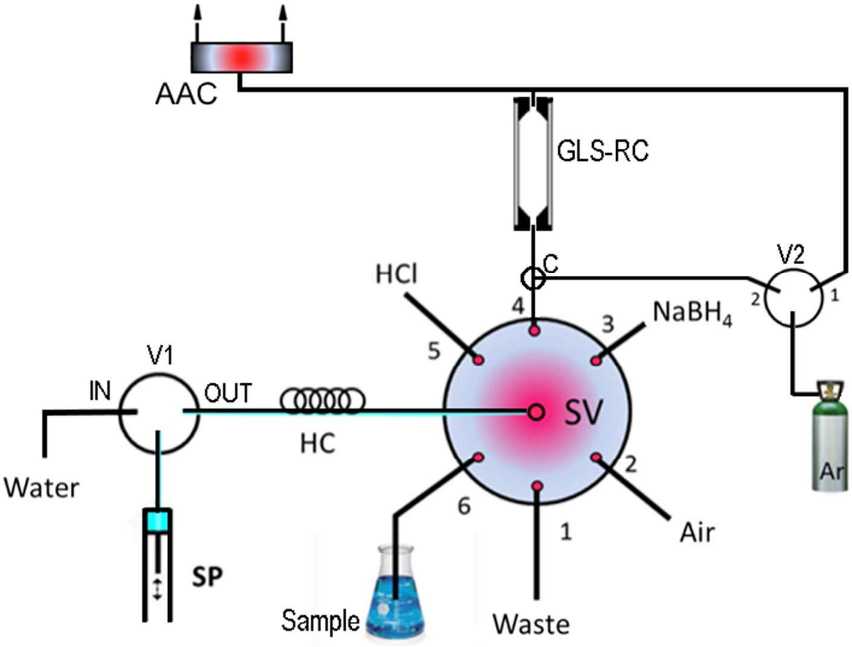

Text:

Sequential injection lab-at-valve (SI-LAV) platform for hydride generation atomic absorption spectrometry (HG-AAS)

Sequential injection lab-at-valve (SI-LAV) platform for hydride generation atomic absorption spectrometry (HG-AAS). On-line determination of inorganic arsenic

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Abstract

A novel automatic low-cost sequential injection lab-at-valve (SIA-LAV) system has been developed for inorganic arsenic determination coupled with hydride generation atomic absorption spectrometry (HG-AAS). The proposed manifold includes an integrated gas liquid separator / reaction chamber (GLS-RC) which was attached to one port of a conventional six-port multiposition selection valve. The arsine vapour is generated by reductant $NaBH_4$ into the GLS-RC, minimizing its dispersion and possible losses. All critical parameters affecting the efficiency of the system were studied and optimised. For 3.0 mL sample consumption the detection limit was 0.05 μg L^{-1} and the precision expressed as RSD was 3.2%. The proposed method was evaluated in comparison with a reference flow injection HG method and applied for arsenic determination in environmental water samples. The recovery was estimated by spiking the samples and ranged from 95.5% up to 102.5% for both As(III) and As(V).

Keywords: Sequential Injection, Lab-At-Valve, hydride generation, atomic absorption spectrometry, arsenic determination

Introduction

The chemical form of arsenic plays a crucial role in the biochemical, medicinal, and toxicological properties of the element. Inorganic arsenic is by far more toxic than the organic one, with arsenite (As(III)) and arsenate (As(V)) being of particular concern because of their high toxicity and water solubility. Human exposure to elevated levels of inorganic arsenic occurs mainly through the consumption of groundwater, food prepared with this water or food crops irrigated with high arsenic water sources [1]. Inorganic arsenic compounds are classified by the International Agency for Research on cancer [2] in Group 1 (carcinogenic to humans) on the basis of sufficient evidence for carcinogenicity in humans and limited evidence for carcinogenicity in animals. According to EPA and WHO, the recommended value for total arsenic in drinking water has decreased from 50 to 10 μg L^{-1} [3, 4].

The increasing concern for human exposure to arsenic species has led to the development of rapid analytical methods for their determination in trace levels. There are various examples of surveys concerning arsenic determination using hydride generation systems coupled with an element selective detector [5]. Hydride generation methods in batch or on-line mode involve the reaction of arsenic compounds, usually with sodium tetrahydroborate ($NaBH_4$) in acidic medium to produce arsine vapor (AsH_3) [6].

Undoubtedly, batch methods may lead to operating errors particularly in cases when a large number of samples have to be analyzed or a considerable number of reagents and repetitive steps are involved [7]. Automatic on-line flow techniques have proved to be rapid, simple, highly sensitive, precise and accurate for such type of analysis eliminating many disadvantages of batch-HG systems, like high sample and reagents consumption, laborious processes, great risk of contamination and analyte loss. In literature, many automated on-line hydride generation systems such as continuous flow (CF) [8, 9], flow injection (FI) [7, 10, 11], sequential injection (SI) [12, 13], lab-on-valve (LOV) [14, 15], multi-pumping (MPFS) [16] and multisyringe flow systems (MSFIA) [17, 18] have been developed in order to eliminate the above-mentioned drawbacks.

Following the new trends, according to the guidelines of Green Analytical Chemistry like simplification, miniaturization, automation of sample handling, shorter time of analysis, minimization of sample and reagents consumption as well as lower waste generation, various on-line systems into different concepts have been presented. The result is the development of analytical methods with demands that are put together in “SPARS” and “ZEC”, which mean methods with satisfying “sensitivity and selectivity”, “precision”, “accuracy”, “rapidity”, “simplicity” (SPARS), and quasi “zero emission” (ZEC) [19].

Sequential injection analysis (SIA) presented by Ruzicka et al. in 1990 offers several advantages in the automation and miniaturization of analytical methods [20]. Towards the direction of compactness, simplicity and low reagent consumption, a new platform, in which an integrated micro-conduit is placed on the top of the selection valve of a SIA system to incorporate and handle all the necessary unit operations required for a given essay acting as a small laboratory on the selection valve, namely lab-on-valve (LOV) has been proposed by Ruzicka in 2000 [21]. Coupling of SIA with the LOV platform has proven to be an excellent tool for downscaling fluidic manipulations of sample pretreatments for wet chemical or heterogeneous reactions [22].

Recently, Grudpan [23] introduced a "Lab-at-Valve" concept as an alternative simpler and low-cost micro total analysis system (μTAS) device than that of "LOV". Instead of replacing the stator plate of a multiposition selection valve by precisely fabricated monolithic structure as that of the "LOV", sample processing unit is attached or plugged onto a port of a conventional commercial multiposition selection valve. Such an integrated LAV device compiling analytical processes that take place in it, should be compact and economical compared to a normal SIA system. Various advantages similar to those of the LOV like compactness, robustness, low reagent consumption, should be gained with the use of LAV [24].

In the present work, a novel, simple and cost effective sequential injection lab-at-valve (SIA-LAV) system coupled with hydride generation atomic absorption spectrometry (HG-AAS) has been successfully developed for arsenic determination. The proposed system incorporates a newly designed and constructed gas liquid separator acting also as a reaction chamber (GLS-RC), which was attached at one port of the selection valve resulting in a more accessible and economical platform than the LOV systems. All critical chemical and flow parameters, affecting the performance of the proposed method were studied and optimized. The accuracy of the method was evaluated by comparing the analytical results with those obtained using the conventional on-line FI-HG-AAS method. The developed system was successfully applied in the analysis of environmental water samples for inorganic arsenic determination.

Experimental

Instrumentation

A Perkin-Elmer model 5100 PC atomic absorption spectrometer (Perkin-Elmer, Norwalk, CT, USA, http://las.perkinelmer.com) equipped with a deuterium background corrector was used as detector. A Perkin-Elmer arsenic hollow cathode lamp (HCL) was used as light source operated at 18 mA. The wavelength was set at 193.7 nm resonance line and the monochromator spectral bandpass (slit) at 0.7 nm. For hydride atomization a Perkin-Elmer FIAS 400 electrothermal quartz flow-through cell atomizer operated at 900 °C was used. The atomic absorption flow-through cell, AAC (16 cm length, 7.0 mm i.d., 14.5 mm e.d.) was sealed with removable quartz windows at either ends and consisted of one inlet, for the mixture of hydride and purge gas and two outlets.

The proposed manifold, which is presented schematically in Fig. 1, comprised of a FIAlab-3000 sequential injection system with a 6-position selection valve (SV), a syringe pump (SP, Cavro, Sunnyvale, CA) of 5000 μL capacity with a valve (V1) on the top of it, a holding coil (HC, 120 cm length, 0.21 mm i.d., 4 mL capacity) as well as a 2-position valve (V2) for the manipulation of the purge gas.

The FIAlab-3000 SI system and the Perkin-Elmer 5100 AAS were controlled by a personal computer via the FIAlab v.5.9.245 and AA Lab Benchtop v.7.2. application softwares, respectively. A “T” type connector (C, VICI AG, Valco International) made of PEEK with a 0.5 mm i.d. bore size was used as shown in Fig. 1.

The design of the integrated gas liquid separator / reaction chamber (GLS-RC) unit was based on the total liquid phase (sample + acid + $NaBH_4$) loaded into it. The constructed unit should provide an appropriate space over the liquid mixture in order to be accomplished the liberation of hydride avoiding the aqueous droplets transportation to the flow-through cell. Experimental observations from previous studies [7, 25, 26] have shown that it takes at least twice the volume of the liquid phase. Thus, the GLS-RC unit was manufactured in our laboratory using a commercial polyethylene syringe tube (60 mm length, 14.0 mm i.d., 9 mL volume) and mounted directly on the connector C in vertical position via a push-fit union (Fig. 2). This connector C was adapted at port 4 of the selection valve by a very short (3 cm) and narrow tubing (0.3 mm i.d.) producing a LAV platform offers similar facilities with a more expensive LOV system.

At the top of the GLS-RC, there is another push-fit “T” type union with a conical cavity and a vertical channel for effective transfer of the evolved arsine vapor into AAC. The GLS-RC is connected to AAC with PVC tubing (30 cm length, 2.0 mm i.d.). A significant advantage arising from the above configuration is the fact that the purge gas flows either through the GLS-RC or by-pass it, resulting in minimization of vapor dispersion as pinpointed elsewhere [25].

Argon (Ar) was used as purge gas at a flow rate of 500 mL min^{-1} throughout the experiments.

Reagents and samples

All chemicals were of analytical reagent grade and ultra-pure quality water from a Milli-Q system (Millipore, Bedford, USA, www.millipore.com) was used throughout. Arsenic working standard solutions were prepared by appropriate stepwise dilution of 1000 mg L^{-1} As(III) stock standard solution to the required concentration levels just before use. The standard solution of 1000 mg L^{-1} As(III) was prepared by dissolving 1.3203 g of As_2O_3 in 25 mL of 20 % KOH, followed by neutralization with 20 % m/v sulfuric acid and diluting to 1000 mL with 1 % v/v sulfuric acid. Sodium tetrahydroborate solution in 0.1 % m/v NaOH were freshly prepared from $NaBH_4$ (Fluka, As < 0.000005 % m/m). Hydrochloric acid solutions were prepared by adequate dilution of concentrated HCl (Fluka, As < 0.0000005% m/m, 1.16 g mL^{-1}, 32 % m/m). All glassware were cleaned for at least 24 h in 10% (v/v) nitric acid solution and rinsed with ultra-pure water prior to use. The analyzed water samples were collected from the Northern Greece region (Axios river, water supply network of Thessaloniki). The wastewater sample was from a central ditch of the industrial area of Thessaloniki. All samples were filtered through 0.45 μm cellulose acetate membrane filter (Millipore), acidified to 0.01 mol L^{-1} HCl and stored at 4°C in polyethylene bottles.

On-line operating procedure

The SIA-LAV flow system coupled on-line to HGAAS for inorganic arsenic determination is presented schematically in Fig. 1 and the operational sequence of the proposed method is summarized in Table 1. Each analytical cycle started with flowing of the purge gas through the AAC flow-cell in order to stabilize the baseline. In order to avoid the dispersion of HCl and sample solutions into the holding coil (HC) during the loading procedure, a segment (30 μL) of air was interpolated between water and HCl solution into the HC (step 1). In step 7, a volume of 200 μL of $NaBH_4$ was injected rapidly into GLS-RC and the produced nascent hydrogen generated the arsine vapor. In the following step, valve V2 was actuated to 2-position and the Ar stream (purge gas) flowed through the GLS-RC to deliver arsine to the AAC for atomization and quantification. In the next steps (9, 10) the liquid mixture from the GLS-RC was aspirated into the HC and discarded to waste through port 1. Then, a volume of 4000 μL of water is aspirated into syringe barrel of SP and delivered into GLS-RC through the HC (steps 11, 12). By these operations both HC and GLS-RC were cleaned from possible residues of sample or reduction solution. Thereafter, the washings were aspirated into HC and discarded to waste. Considering the recovery and precision tests of arsenic determination, no sample or regent carryover problems were observed. Five replicate measurements were made in all instances.

Results and discussion

Study of purge gas flow rate

In hydride generation systems the purge gas flow rate affects the shape of the transient recorded signal considering its height and width. On the other hand, high values of the purge gas flow rate can transport droplets of aqueous phase into the flow-through cell resulting in deterioration of signal reproducibility. The Ar flow rate was studied within the range of 100 - 300 mL min^{-1}. The recorded signal became narrower with flow rates up to 250 mL min^{-1} while for higher flow rates it leveled off. Thus for higher sensitivity the argon flow rate was fixed to 250 mL min^{-1} for further experiments.

Volume of the liquid mixture

The liquid mixture into the GLS-RC consisted of sample, hydrochloric acid and sodium tetrahydroborate solutions in various volumes. The large sample volume results in high sensitivity of the method as it has been reported elsewhere [25]. On the other hand, the increase of the volume of the liquid mixture affects positively the solubility of the arsine resulting in the restriction of its release [7]. In order to facilitate the use of high sample volume, the limited volume of HCl and $NaBH_4$

solutions were adopted and fixed at 400 μL and 200 μL, respectively, throughout the experiments. The effect of sample volume on the absorbance was studied in the range of 1.0 - 3.0 mL using 0.2 μg L^{-1} As(III) standard solution. The results showed an increase in absorbance by increasing the sample volume, as illustrated in Fig. 3. At higher volumes the absorbance was increasing with a lower rate due to arsine dilution in the aqueous phase. The method can be used for sample volume up to 3.0 mL with proportional sensitivity. Thus, for higher sensitivity, 3.0 mL of sample volume was adopted as optimum.

Study of acidity and reductant solution

The majority of hydride generation methods for inorganic arsenic determination that are reported in literature make use of a pre-reduction step of arsenate, As(V) to arsenite, As(III) before the arsine generation procedure. Arsine can be also generated from As(V) using harsh chemical conditions with a slower reaction rate, than that of As(III) [7, 27]. For selective As(III) determination, the concentration of hydrochloric acid and $NaBH_4$ solutions were studied using the manifold presented schematically in Fig. 1. The volumes of HCl and $NaBH_4$ solutions were 400 and 200 μL, respectively.

The effect of HCl solution on the absorbance was examined in the range 0.5-8 mol L^{-1} using 1.0 % m/v $NaBH_4$ as reductant. The obtained results are presented in Fig. 4. The absorbance increased rapidly up to 4.0 mol L^{-1} while for higher concentrations it remained unchanged. Thus, a concentration of 4.0 mol L^{-1} HCl was selected for As(III) determination taking into account that As(V) reduction to arsine was statistically insignificant at the above HCl concentration.

The formation of arsine is completed due to the presence of nascent hydrogen, which is generated from the decomposition of $NaBH_4$ at acidic environment ($pH \leq 1$). Decomposition of $NaBH_4$ lasts just few μs [6]. Since $NaBH_4$ solution was prepared in alkaline with NaOH solution, the neutralization of the alkalinity should be taken into account. The effect of the concentration of $NaBH_4$ solution on the absorbance was studied from 0.2 % m/v up to 3.0 % m/v $NaBH_4$ using HCl solution at 4.0 mol L^{-1} concentration level. As shown in Fig. 5, the signal increased by increasing the concentration of $NaBH_4$ up to 1.0 % m/v and leveled off for concentrations up to 1.0 % m/v. Slight decrease was observed for higher concentrations, likely due to the dilution of the gas phase by great hydrogen generation. Hence, a concentration of 1.0 % m/v $NaBH_4$ was selected for the proposed method considering the insignificant contribution of As(V) on the absorbance.

Interference studies

On-line vapor generation methods have an inherent advantage related to the improved tolerance against interferences compared to batch methods [28]. Besides, by varying HCl and $NaBH_4$ concentrations, an improvement in the range of interference-free determination of some typical transition metals can be accomplished during the arsenic determination [29]. The effect of potential interferences occurring in environmental water matrices for As(III) determination was investigated by analyzing a standard solution of 3.0 μg L^{-1} As(III) containing given metal species. A recovery deviation more than ± 5 % was considered as significant interference. The experimental results showed that the method could tolerate concentrations of Al(III), Cu(II), Cr(III), Fe(II), Fe(III), Mn(II) and Pb(II) at least up to 5.0 mg L^{-1} , Co(II), Ni(II), Zn(II) and Sn(II) up to 1.0 mg L^{-1}, while Se(IV) can be tolerated up to 1.0 mg L^{-1}. Other common matrix elements such as Ca, Mg, Ba were tolerated at least up to 500 mg L^{-1}.

Analytical performance and applications

The analytical performance data of the developed SIA-LAV-HG-AAS method for arsenic determination under the optimized conditions are summarized in Table 2. For 3.0 mL sample consumption the sample frequency was 9 cycles per hour. The detection limit (c_L) based on the 3s criterion (according to IUPAC regulations [30] was calculated as 3 times the standard deviation of the blank solution measurements (n = 11) divided by the slope of the corresponding calibration curve was 0.05 μg L^{-1}, and the precision of the method, expressed as relative standard deviation (RSD), was 3.2% at 2.0 μg L^{-1} As(III) concentration level. The working linear range varied between 0.15 to 6.0 μg L^{-1} with a good correlation coefficient (r) of 0.9994. The analytical performance of the proposed SIA-LAV-HG-AAS method has been improved in terms of sensitivity comparing to SIA and multisyringe flow injection (MS-FI) systems [7, 12, 17] and relatively comparable to other systems using atomic fluorescence spectrometry [14-16], or ICP-MS [8] as detector. Regarding the precision, it is better than other MS-FI procedures reported in the literature [14, 17, 18].

The accuracy of the proposed method was evaluated by comparing the analytical results (Table 3) for total arsenic determination in the environmental samples with those obtained with the conventional on-line FI-HG-AAS using a FIAS-400 flow injection system in hydride generation mode coupled with atomic absorption spectrometry, which was considered to be reference method. Total inorganic arsenic was determined after off-line prereduction of As(V) to As(III), in 0.5 % (m/v) KI, 0.5 % (m/v) ascorbic acid, 1.0 mol L^{-1} HCl media for 45 min at room. Paired *t*-test was employed to examine statistically significant differences between the obtained values of a series of samples using both the proposed and the reference method as described above. No statistically significant differences were found at 95 % probability level, since $t_{exp.} = 1.9432$ was lower than the $t_{crit,\,95\%} = 2.4469$. In addition the batch standard method 3114 B (Manual Hydride Generation/Atomic Absorption Method) [31] was employed for comparison purposes. Since the obtained results for total arsenic determination in the waste water sample were 12.50 ± 0.5 (*n*=3) and 13.20 ± 0.9 (*n*=3) for the SIA-LAV-HG-AAS and 3114 B standard method respectively, the relative error was 5.3%. In addition, the above mean values were tested by *t*-test at 95% probability level and was proved that $t_{exp.} < t_{crit.}$ showing that there is no statistically significant difference between the two methods.

The method was applied to the analysis of local natural water samples (river, tap and mineral water) as well as waste-water samples. The recovery was estimated by spiking the samples with known amounts of As(III) and As(V). The obtained results are presented in Table 3. The recoveries were varied in the range 95.5 - 102.5% showing the good performance of the proposed method for the analysis of environmental water samples.

Conclusions

A novel automatic sequential injection Lab-At-Valve hydride generation atomic absorption spectrometry system incorporating a newly designed gas liquid separator coupled with atomic absorption spectrometry has been developed and optimized for arsenic determination. The GLS-RC was easily constructed with low-cost materials and placed to one port of the conventional selection valve of a SIA system, resulting in a more compact and miniaturized manifold. The usefulness and efficiency of the proposed system was demonstrated for arsenic determination in environmental water samples revealing good analytical performance characteristics. The developed method is readily applied to other hydride forming elements without significant changes.

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Figures

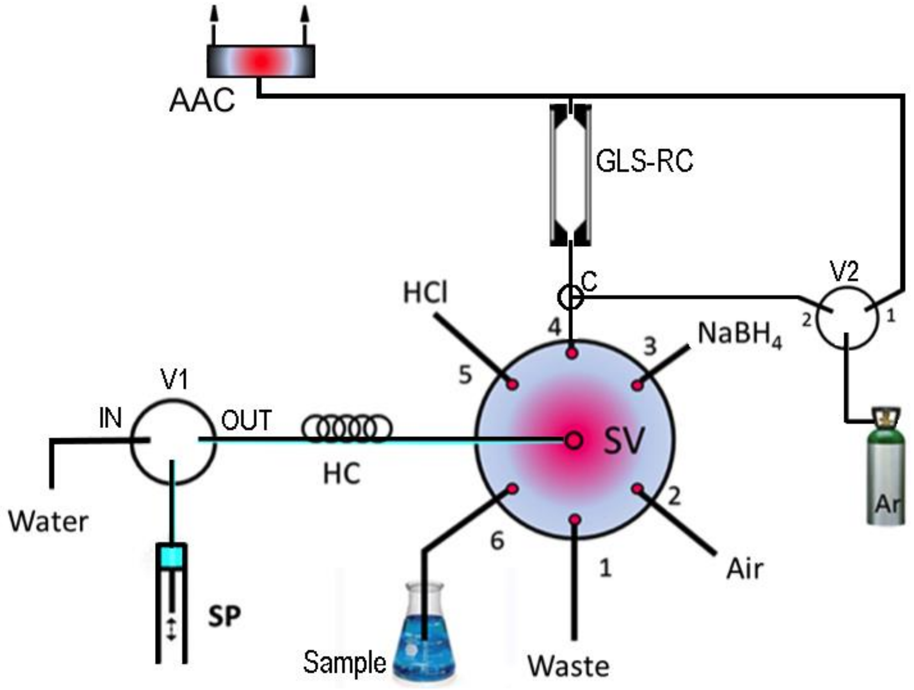

Fig. 1. Schematic diagram of the SIA-LAV-HG-AAS system for arsenic determination. SV, 6-port selection valve; SP, syringe pump; V1, V2, valves; HC, holding coil; C, “T” type connector; GLS-RC, gas liquid separator / reaction chamber; AAC, electrothermal quartz flow-throw cell atomizer.

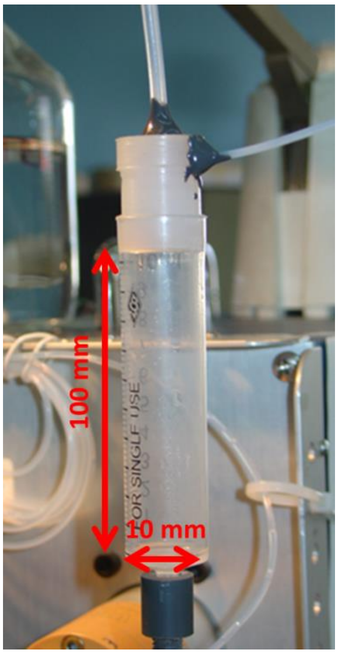

Fig. 2. Image of GLS-RC attached to port 4 of the SV.

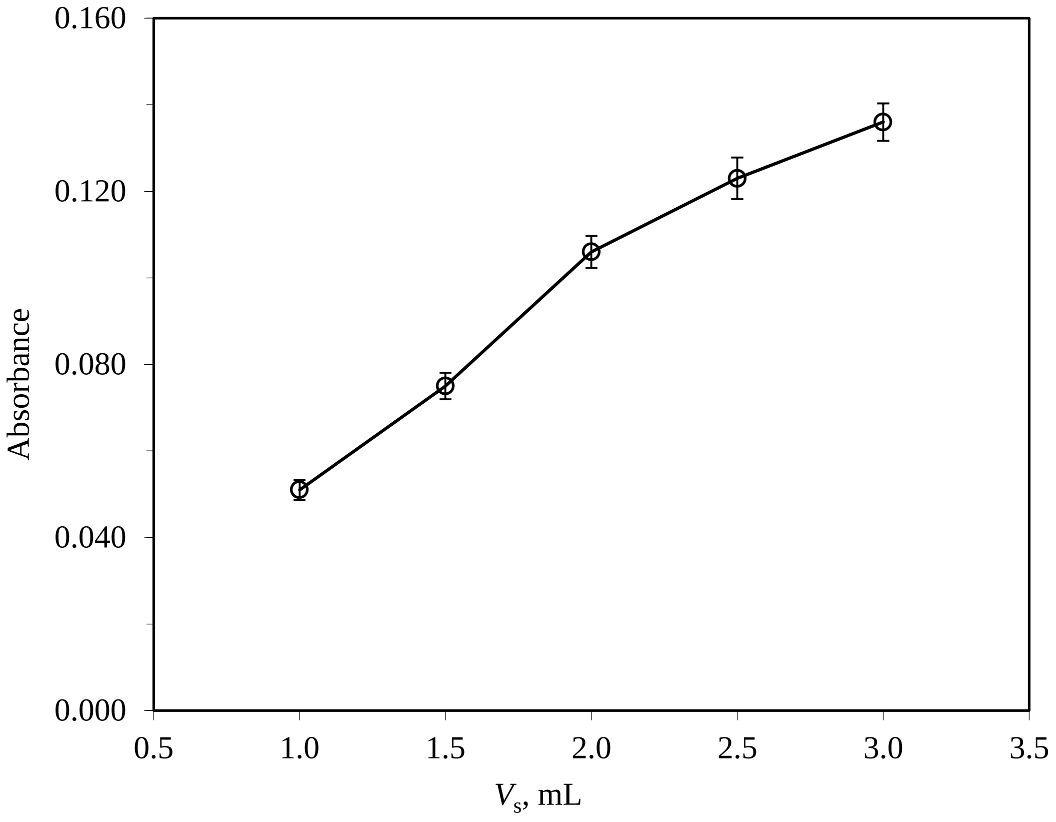

Fig. 3. Effect of sample volume on the absorbance (mean value ± standard deviation) at 2.0 μg L^{-1} As(III) concentration level. All other parameters as in Table 1.

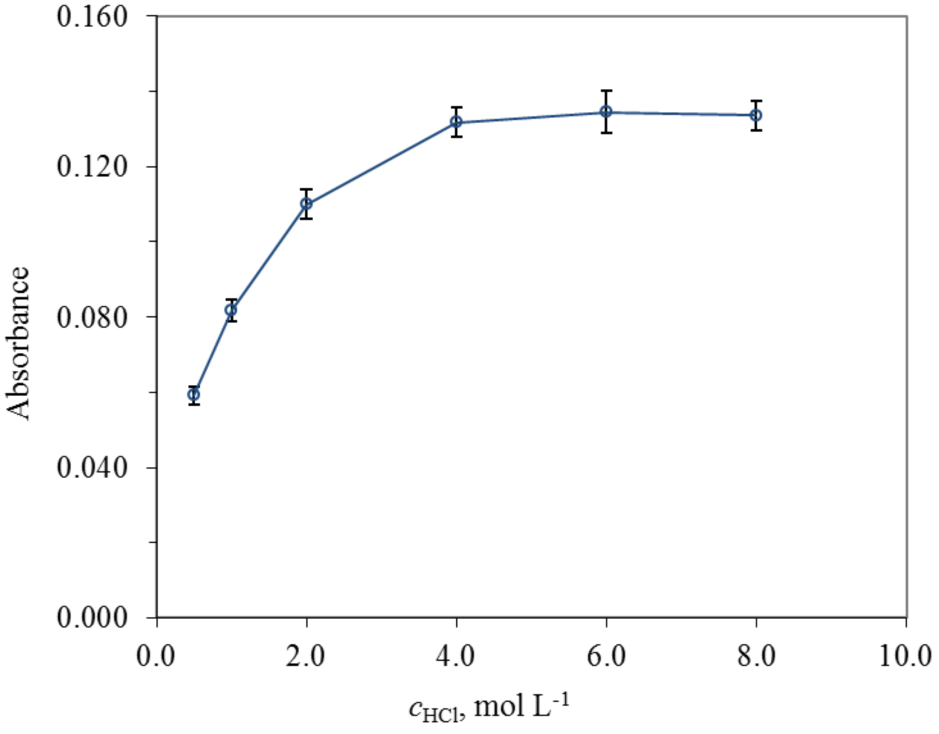

Fig. 4. Effect of HCl on the absorbance (mean value ± standard deviation) at 2.0 μg L^{-1} As(III) concentration level. All other parameters as in Table 1.

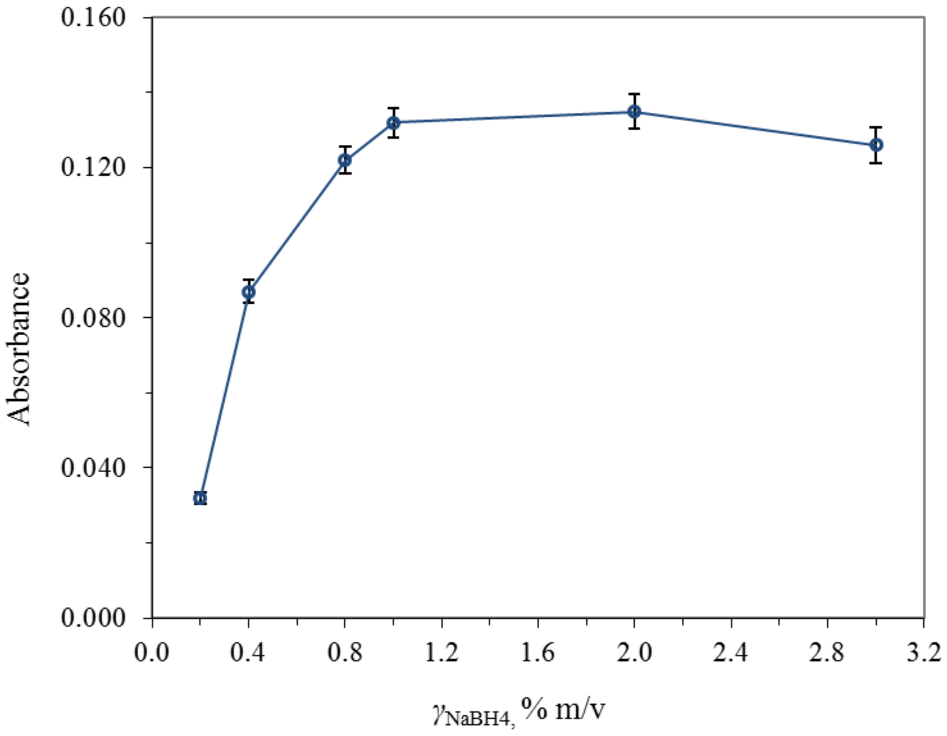

Fig. 5. Effect of $NaBH_4$ on the absorbance (mean value ± standard deviation) at 2.0 µg L^{-1} As(III) concentration level. All other parameters as in Table 1.

Tables

Table 1. Operational sequences of SIA-LAV-HG-AAS method for arsenic determination

Step	position			operation	flow rate (μL s^{-1})	Volume (μL)	Commentary
	V1	V2	SV		SP		
1	OUT	1	2	Aspirate	5	30	Segment of air into HC
2	OUT	1	6	Aspirate	100	400	HCl into HC
3	OUT	1	5	Aspirate	400	3000	Sample into HC
4	OUT	1	4	Dispense	400	3430	Loading of HCl & sample into GLS-RC
5	OUT	1	2	Aspirate	10	30	Segment of air into HC
6	OUT	1	3	Aspirate	50	200	$NaBH_4$ into HC
7	OUT	1	4	Dispense	100	230	Loading of $NaBH_4$ into GLS-RC
8	OUT	2	4	-	-	-	Ar flows through the GLS-RC / release of AsH_3 / its transportation to AAC for atomization and quantification
9	OUT	1	4	Aspirate	400	4000	Evacuation and cleaning of GLS-RC
10	OUT	1	1	Dispense	400	4000	
11	IN	1	4	Aspirate	400	4000	
12	OUT	1	4	Dispense	400	4000	
13	OUT	1	4	Aspirate	400	4000	
14	OUT	1	1	Dispense	400	4000	

Table 2. Analytical performance characteristics of the SIA-LAV-HG-AAS method for arsenic determination

sample consumption (mL)	3.0
sampling frequency (h^{-1})	11
regression eq.	(0.0590 ± 0.0024) [As(III)] + (0.0030 ± 0.0070)
correlation coefficient (*r*)	0.9994
linear range (µg L^{-1})	0.15 - 6.0
detection limit, c_L (µg L^{-1})	0.05
quantification limit, c_Q (µg L^{-1})	0.15
precision, s_r, % (n = 10)	3.2 % (at 2.0 µg L^{-1})

Table 3. Analytical results for arsenic determination in natural and waste water samples

		SIA-LAV-HG-AAS				FI-HG-AAS
sample	added$^{\alpha}$ As(III) : As(V)	found$^{\alpha}$ As(III)	found$^{\alpha}$ As(T)	*R* (%) As(III)	*R* (%) As(T)	found$^{\alpha}$ As(T)
river water	-	1.40 ± 0.07	4.20 ± 0.22	-	-	4.15 ± 0.15
	2.0 : 2.0	3.32 ± 0.15	8.10 ± 0.28	96.0	97.5	8.25 ± 0.18
tap water	-	-	1.80 ± 0.08	-	-	1.90 ± 0.06
	2.0 : 2.0	1.94 ± 0.15	5.62 ± 0.22	97.0	95.5	5.70 ± 0.24
mineral water	-	-	2.20 ± 0.08	-	-	2.30 ± 0.05
	2.0 : 2.0	1.96 ± 0.10	6.30 ± 0.22	98.0	102.5	6.20 ± 0.30
waste water	-	-	12.50 ±0.50	-	-	12.40 ± 0.40

$^{\alpha}$Concentrations in µg L^{-1}; mean value ± standard deviation (n = 3); *R*, recovery.