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Determination of As(III) and Total As in Water by Graphite Furnace Atomic Absorption Spectrometry after Electrochemical Preconcentration on a Gold-Plated Porous Glassy Carbon Electrode

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Arsenic(III) was preconcentrated in a flow-through electrochemical cell on a gold coated porous carbon electrode. On stripping, arsenic was eluted with diluted nitric acid and determined off-line by GF AAS. The deposition and stripping steps were optimized. The limit of detection and limit of quantification were found to be 1.9 μg L^{-1} and 6.4 μg L^{-1}, respectively. The repeatability and reproducibility were found to be 5.3 % and 9.3 %, respectively. Total arsenic was determined after a microwave assisted chemical reduction of As(V) to As(III) making the procedure suitable for speciation analysis. The method was applied in analysis of water samples.

Keywords: electrochemical preconcentration, speciation, arsenic, flow-through cell, GF AAS

INTRODUCTION

Food and water are the main sources of arsenic uptake by living organisms. The adverse effect of arsenic on humans is well documented [1] and it requires the development of more effective analytical methods for its reliable determination. Currently, the most frequently used methods of arsenic determination include atomic absorption spectrometry using a graphite furnace (GF AAS) or hydride generation techniques, atomic fluorescence spectrometry [2—5], and stripping voltammetry and chronopotentiometry.

Although electrochemical methods are simple and facilitate direct speciation analysis of arsenic, they are vulnerable to numerous interferences arising mainly from the sample matrix. The main interferences belong to species giving stripping peaks in the proximity of the arsenic signal, such as Bi, Sb, Cu, Pb, and Cd. There are no such interferences in atomic absorption spectrometry (AAS), hence, it would be reasonable to couple electrochemical preconcentration with AAS determination of the stripped sample.

Electrolysis as a separation principle of analyte enrichment has frequently been used in atomic spectroscopy [6, 7]. The graphite electrode in emission spectrography was used for trace metal enrichment and determination [8]. Though simple, the method suffered from low reproducibility. A more convenient solution involved the use of a graphite tube as the electrode [9]. The tube was put into a flow electrolyzer and on depositing the trace elements onto the inner surface of the tube it was placed into the graphite furnace (GF) of AAS and the amount of the deposited analyte was estimated. Here, more reproducible results were achieved for numerous metal species and the system was in principle amenable to automation. Another approach [10] made use of a graphite rod electrode for electrodeposition of Cd and Cu for a subsequent GF AAS determination.

Matousek et al. [11—13] have simplified the procedure by providing the electrodeposition directly in the graphite furnace. Here, the sampling tip of the autosampler made from a platinum capillary served as the anode, the graphite tube itself was the cathode. The sample was injected into the furnace and the analyte species were electrochemically deposited on the graphite tube, the solution was then sucked out by the sampler tip and the deposit was measured virtually without any interfering effects of the sample matrix. Off-line and on-line electrochemical preconcentration

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were used for the flame as well as for electrothermal atomization AAS [14—18].

Microporous electrodes promote the achievement of higher electrochemical yields or even complete recoveries. By application of such electrode materials it was possible to preconcentrate numerous metals such as Pb, Cd, Zn, Cu, Mn [19, 20] and Hg [21] for the flame AAS. The developed systems were tested analyzing real samples and with the use of flow systems directly coupled with the nebulizer of the AAS instrument.

For GF AAS, an original pneumatic system was developed [22], based on the electrochemical deposition of manganese in a small-volume flow cell and pneumatic transport of the dissolved deposit to the furnace.

Another simple design utilizing a reticulated glassy carbon electrode enabled the electrochemical preconcentration for GF AAS [23] and microwave induced plasma emission spectroscopy [24]. Flow cells with small surface electrodes and minute dead volumes were successfully used in the preconcentration of various trace metals in atomic spectroscopy [25—28]. The cells exhibited a fast response and negligible memory effects.

The goal of the paper is to demonstrate the utility of electrochemical preconcentration for the determination of As(III) and total arsenic by graphite furnace AAS in water samples. Emphasis is given to the optimization of the preconcentration conditions and the potential use of the procedure for speciation analysis.

EXPERIMENTAL

The measurements were done on a Pye Unicam SP9 (Pye Unicam, USA) and Perkin—Elmer 5000 atomic absorption spectrometers with graphite furnace atomizers. The former was equipped with a deuterium lamp the latter with a Zeeman background correction. Experimental parameters recommended by the manufacturer of the instruments were used.

Flow-through electrochemical analyzer EcaFlow 150 (Istran, Ltd., Bratislava, Slovakia) was used for electrochemical preconcentration. The instrument was equipped with solenoid valves and a peristaltic pump. The software enabled the adjustment of all parameters including the automatic exchange of the electrolytes between the deposition and stripping steps.

The flow-through preconcentration cell (Fig. 1) of the type 353b (Istran, Ltd., Bratislava, Slovakia) comprised a platinum auxiliary, silver/silver chloride reference electrode and a porous glassy carbon working electrode (type E-53C) coated with a thin layer of gold.

The samples were digested in closed quartz vessels of 30 mL volume using a microwave-assisted digester PMD (Anton Paar, Austria).

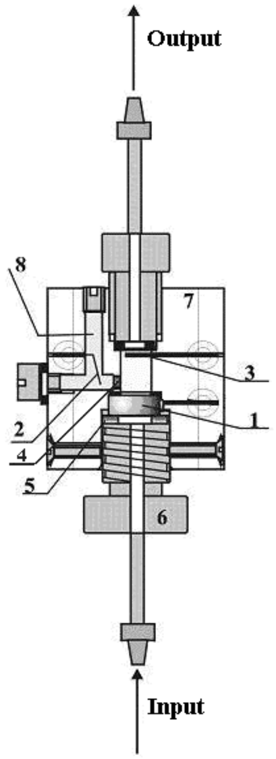

Fig. 1. Flow-through preconcentration cell: 1 – working electrode, 2 – reference electrode, 3 – auxiliary electrode, 4 – membrane, 5 – packing, 6 – screw, 7 – cell body, 8 – space for reference electrolyte (saturated KCl).

Deionized and freshly distilled water was used in all experiments. All reagents used were of analytical grade purity. Hydrochloric acid was purified by isopiestic distillation. The electrolyte solution for sample adjustment and arsenic deposition was 0.1 mol L^{-1} HCl (Slavus s.r.o., Bratislava, Slovakia). The electrolyte solution for stripping and GF AAS measurement was 0.02 mol L^{-1} HNO_3 (Slavus s.r.o., Bratislava, Slovakia). The As(III) solutions for testing and calibration were prepared from an arsenic stock solution prepared by dissolving analytical grade As_2O_3 (Lachema, Brno, Czech Republic) in 0.1 mol L^{-1} NaOH. The diluted As(III) solutions were stabilized by the addition of 0.1 g of hydroxyl ammonium hydrochloride to a 100 mL solution.

The gold plating solution contained 0.0002 mol L^{-1} H_4AuCl_4 (AGNO s.r.o., Nové Zámky, Slovakia) in 0.02 mol L^{-1} HCl. The solution was stored in a refrigerator.

Plating of the porous carbon electrode was carried out in 100 mL of gold plating solution at –2000 mV and a solution flow rate of 3 mL min^{-1}. On plating, the electrode was rinsed with 10 mL of 0.1 mol L^{-1} nitric acid solution.

For the analysis, the sample solution was acidified with hydrochloric acid so that the final concentration of HCl in the sample ranged between 0.1 mol L^{-1} and 0.5 mol L^{-1}. As(III) was then deposited by applying 10 mL of the sample onto the porous carbon electrode

Table 1. Operation Parameters for Electrochemical Preconcentration/Stripping Procedure

Parameter	Value
Deposition potential/mV	−2000
Deposition current/mA	−3
Stripping current/mA	0.2
Quiescence potential/mV	−200
Terminal potential/mV	900
Flow rate/(mL min^{-1})	3.0

using the instrument parameters listed in Table 1. The flow of 0.02 mol L^{-1} HNO$_3$ electrolyte was switched on. The deposit was stripped into 10 mL of this flowing electrolyte and the resulting solution was collected and analyzed by GF AAS.

Sample preparation for determination of the total As content [29] consisted of transferring 4 mL of the sample solution to the quartz digestion vessel of the microwave digester, to which 0.5 mL of concentrated HCl and 0.1 g of hydrazinium chloride were added. The solution was digested for 5 min at the highest power. After cooling down, the solution was quantitatively transferred to a 10 mL volumetric flask and the volume was adjusted to 10 mL with deionized water. The solution was immediately analyzed applying the experimental parameters given above.

RESULTS AND DISCUSSION

As(III) can be deposited at a constant potential or galvanostatically, applying a suitable deposition current. As Figs. 2 and 3 imply, both techniques ensure high recoveries. Optimum deposition potential and deposition current were found to be about –2000 mV and –3 mA, respectively.

Stripping of the deposit can be performed by scanning the potential, applying a potential step, or forcing a constant current, depending on the signal we are interested in (electrochemical or AAS).

The applied preconcentration technique presents an inherent advantage over other ones, namely the stripping step itself can provide a useful analytical signal, which in fact is the electrochemical stripping signal, and after stripping the analyte concentration can be measured by AAS in the solution flowing from the electrode. However, a rightful question is; what makes the procedure more complex when measuring the As content spectroscopically? The answer could be related to interferences occurring during the electrochemical stripping analysis which is inherently absent in atomic spectroscopy. From investigation of the influence of some metal ions on the electrochemical stripping signal of As (Fig. 4) it is evident that the species with stripping peaks in the vicinity of the arsenic peak would interfere. Bismuth, for example depresses the arsenic signal, lead increases it. The Bi peak appears at more positive potentials compared to that of As signal and, due to the partial coalescence

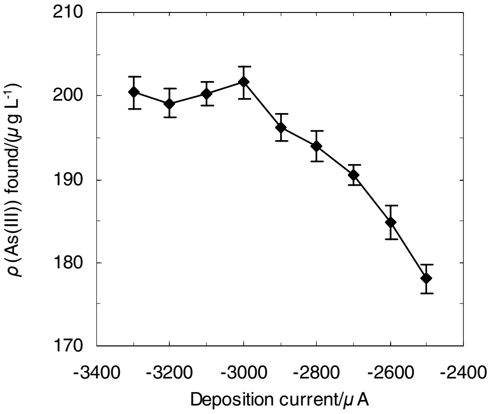

Fig. 2. Influence of deposition potential on signal. As(III) given 200 μg L^{-1}.

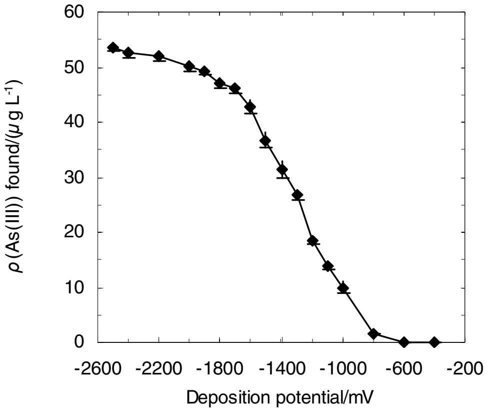

Fig. 3. Influence of deposition potential on signal. As(III) given 50 μg L^{-1}.

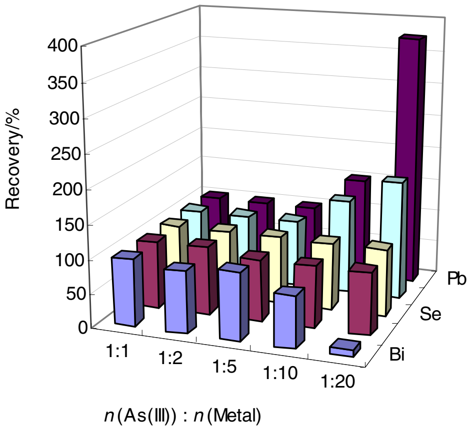

Fig. 4. Influence of some metals on recovery of As(III). As(III) given 50 μg L^{-1}.

of these peaks, the As peak intensity decreases. Lead is virtually stripped at the same potential as As, so its presence enhances the As signal and the virtual As concentration. To eliminate such interferences, the interfering species have to be removed prior to the enrichment step. These interferences could successfully be eliminated by means of a column packed with a cation exchanger (Dowex 50W, column dimensions: 5 mm and 30 mm in diameter and length, respectively) linked to the sampling tube of the electrochemical analyzer. No such sample pretreatment is required when the stripped solution is measured by GF AAS, where, as expected, no such interferences were observed.

Interferences during the deposition step cannot be eliminated by the spectroscopic measurement step. The influence of surfactants as possible interferents was, therefore, investigated. Neutral (Triton X-100) and anionic (sodium dodecylsufate) surfactants did not affect the deposition step. Some deteriorating effects of cationic Hyamine at concentrations above 10 mg L^{-1} were observed causing a 30 % decrease in the deposition efficiency. This interference can probably be attributed to adsorption of the cationic species on the surface of the negative electrode. Humic acids did not interfere up to concentrations of 100 mg L^{-1}, their higher contents resulted in blocking of the electrode pores by humic substances.

For the applied preconcentration mode – 10 mL sample preconcentrated to 10 mL final solution, a linear As(III) concentration range of about 1.0—300 μg L^{-1} was found. The values of the limit of detection (LOD) and the limit of quantification (LOQ) were calculated from the lower concentration response range (up 10 μg L^{-1}) by means of a procedure recommended by IUPAC [30] and were found to be 1.9 μg L^{-1} and 6.4 μg L^{-1}, respectively. The repeatability of the whole procedure was calculated on the basis of 10 values obtained within a short period of measurement of a sample containing 5 μg L^{-1} As(III), and was found to be 5.3 %. The reproducibility was evaluated by means of data obtained for the same sample but with different measurement cells and electrodes and with a day pause between the measurements. The reproducibility value was found to be 9.3 %. The LOD and LOQ values could be significantly improved by decreasing the electrolyte volume to which the deposit is stripped.

Arsenic(V) is generally considered to behave electrochemically irreversibly and can hardly be deposited as elemental As. Its deposition is possible after its preliminary chemical reduction to As(III) by a suitable reducing agent such as sulfite, ascorbic acid, iodide, *etc.* [31]. However, all these procedures are time consuming and are handicapped by possible losses of arsenic during the reduction. Reduction performed in a closed vessel within a microwave oven eliminates the above mentioned disadvantages [29] and makes the reduction fast and secure. Hence, this procedure was used for the determination of the total arsenic content. On the other hand, the irreversibility of electrochemical reactions of As(V) species makes it possible to deposit As(III) selectively in the presence of the former one facilitating a simple speciation analysis.

Table 2. Results of the Water Sample Analyses

Sample	This method		GF AAS
	$\rho/(\mu g\ L^{-1})$		$\rho/(\mu g\ L^{-1})$
	As(III)	Total As	Total As
Waste water	32.1 ± 0.2	32.6 ± 0.8	31.6 ± 2.3
Ground water 1	< LOD	2.4*	< 4
Ground water 2	3.9*	15.6 ± 1.2	11.2 ± 2.8
Ground water 3	30.1 ± 0.4	52.3 ± 2.9	55.2 ± 2.6
Ground water 4	2.2*	33.9 ± 2.5	31.5 ± 1.8
Ground water 5	457 ± 25	478 ± 28	456 ± 25
Ground water 6	772 ± 26	953 ± 19	1010 ± 53

Mean value from 5 measurements ± standard deviation. * Values below LOQ (approximate values).

The presented procedure was applied in the determination of As(III) and of total arsenic in various water samples. One sample originated in the waste water treatment facility of a microelectronic factory, others were taken from a former antimony mine near the town of Pezinok, Slovakia. The results were validated by GF AAS which, obviously, delivered data about the total arsenic content only (Table 2). The concentration of As(III) in the ground water samples No. 1, 2, and 4 were found to be below or near the limit of quantification. Regarding the total arsenic contents, the results from the preconcentration technique fit well with those from the GF AAS measurements.

CONCLUSION

Electrochemical preconcentration of As(III) on a gold coated porous carbon electrode can successfully be used for GF AAS. Total arsenic can be deposited after the preliminary reduction of As(V) to As(III), preferably by a fast microwave-assisted reduction with hydrazine [29]. The method enables a simple speciation of inorganic As(III) and As(V). The detection limit could further be improved by decreasing the preconcentration cell volume.

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