Atomic absorption spectrometry with electrothermal atomization to determine trace amounts of arsenic

A. Manová, E. Beinrohr, F. Čacho

*Slovak University of Technology, Faculty of Chemical and Food Technology,
Institute of Analytical Chemistry, Radlinského 9, 812 37 Bratislava, Slovakia*
alena.manova@stuba.sk

Abstract: The aim of this work was to develop an on-line coupling of electrochemical preconcentration to atomic absorption spectrometry method and to apply the developed system in the determination of ultra-trace amounts of As in water samples. A flow-through electrochemical analyzer EcaFlow (Istran Ltd, Bratislava, Slovakia) was used as the preconcentration unit with a two-electrode cell. The working electrode was a reticular vitreous carbon electrode coated with gold. An atomic absorption spectrometer SP9 with a graphite furnace atomizer (Pye Unicam) was used to determine the preconcentrated As species. Preconcentration parameters were optimized for the electrochemical process.

Introduction

Increasing of toxic element (As, Hg, Cd, etc.) concentration and their compounds in water, soil and air represents a serious problem for human society. Toxic properties of the elements can be transferred from the soil to the foodstuff and mammals by erosion cycles. Consequences of medical research indicate, that a number of compounds exhibits. Determination of toxic elements is a typical problem of ultra-trace analysis. In this work, we focused on the determination of As (III). Toxic level of arsenic starts at 30—50 mg, lowestan lethal dose is 60—80 mg for adult (Prousek, 2001; Pradosh & Anupama, 2002). The work is aimed on coupling of atomic absorption spectrometry with electrochemical preconcentration of the analyte — arsenic.

The sub-goal of this work was to develop at method suitable for the determination of arsenic by graphite furnace atomic absorption spectrometry (GF AAS) without matrix modification. Determination of arsenic without modification is still problematic (STN EN ISO 15586, 2003). Detection limits for the determination of arsenic range between 1 to 10 μL^{-1} (Burguera & Burguera, 1997; Torgov et al., 1995; Iglesias et al., 2003; Latva et al., 2000; Shemirani et al., 2005; Gonzalez et al., 2001; Hung et al., 2004; Alonso et al., 2001; Hsiang Man-Ching et al., 2004). Interferences also emerge as a big problem in the determination. A standard technique for arsenic determination is hydride generation atomic absorption spectrometry (HG AAS). Detection limits for this technique are around 0.1 $\mu g\ L^{-1}$ (Burguera et al., 1998; Kalahne et al., 1997; Nielsen et al., 1996).

The As determination was performed by GF AAS using a preconcentration electrochemical unit. The considerably decreasing limit of detection and the influence of interferences were also omitted. On the surface of the working electrode, only As (III) is deposited quantitatively. The deposit was then stripped in an on-line system directly to the graphite cuvette of the electrothermal atomizer. This system is the same as that used for electrochemical determination of As(III) and it works on the flow-through chronopotentiometry (FTC) principle, which is full validated for the determination of As(III) (Profumo et al., 2005; Švancara et al., 2002; He Yi et al., 2004).

The on-line approach takes advantage of coupling two steps into one. In the first step, the analyte is deposited on the working electrode from the flowing sample. In the second step, the analyte is quantitatively determined using a suitable analytic method.

The main aim of the preconcentration step is to maximize the analyte concentration with simultaneous suppression of the interferences effect. Many articles on As preconcentration have been published in the last decade. Basic principles utilized for on-line preconcentration and published detection limits are:

— on-line preconcentration on columns using different sorbents. Published detection limits differs from: LOD= 0.02 $\mu g\ L^{-1}$ at the sampling volume of 10 mL (Iglesias, 2003; Hung et al., 2004; Alonso et al., 2001; Dressler et al., 1998; Karthikeyan et al., 1999; Neto et al., 1999; Narcise et al., 2005; Jitmanee et al., 2005; Leal et al., 2004; Anthemidis & Martavaltzoglou, 2006)

— on-line "cloud-point" extraction with LOD = 0.01 μg L^{-1} at the sampling volume of 10 mL (Shemirani et al., 2005)
— "in situ" preconcentration in an atomizer (both GF-AAS and HG-AAS atomizers were applied). LOD = 0.05 μg L^{-1} at the sampling volume of 10 mL (Alonso et al., 2001; Kalahne et al., 1997; Niedzielski et al., 2002; Yang Li-Li et al., 2003)
— preconcentration with cryogenic trapping (only HG-AAS). LOD = 0.02 μg L^{-1} at the sampling volume of 10 mL (Burguera et al., 1998; Pinillos et al., 1995)
— preconcentration by liquid extraction: LOD = 0.05 μg L^{-1} at the sampling volume of 10 mL (Torgov et al., 1995).

Electrochemical processes were also used in the on-line flow-through systems with electrochemical cells applied for the preconcentration of the following elements Pd(II), Pb(II), Cd(II), Cr(III), Cr(VI). Godlewska (2002) and Bulska (1997) used electrochemical measured cell for on-line preconcentration of Pd(II), Pb(II) a Cd(II), which is, however, not suitable for As(III) preconcentration and determination. Also flame atomic absorption spectrometry (FAAS) was used in the on-line electrochemical preconcentration. In this work, sorption cell was employed for the separation and consequent determination of the Cr species by FAAS (Beinrohr et al., 1996).

## Experimental

Instrumentation
An atomic absorption spectrometer SP9 with a graphite furnace atomizer (Pye Unicam Ltd. Cambridge, England) was used to measure the preconcentrated As species. A flow-through electrochemical analyzer EcaFlow (model GLP 150, Istran Ltd., Bratislava, Slovakia) was used as the preconcentration unit with a two-electrode cell. The working electrode was a reticular vitreous carbon (RVC) plug electrode coated with gold (Fig. 1).

Scheme of on-line coupling FTC-GF AAS
A six-way valve was connected with the sampling loop with the sampling volume of 57.2 μL. Thus, on-line connection of an electrochemical analyzer EcaFlow with GF AAS via the six-way valve could be done (Fig. 2).

Reagents
Analytical-reagent grade chemicals were used in all experiments. Nitric acid and hydrochloric acid were purified by sub-boiling and isopiestic distillation, respectively. Deionised and degassed water was used for the preparation of all solutions.
Carrier electrolyte was comprised of 0.1 mol L^{-1} of HCl and 2 mol L^{-1} of HNO$_3$ for the deposition and stripping/AAS measurements, respectively.
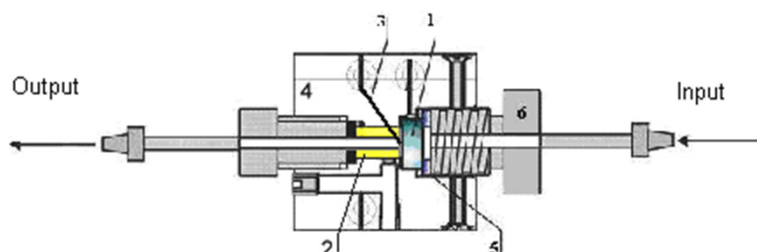
Fig. 1. Scheme of the flow-through cell with dual electrode connection. 1 – working electrode E-53 Au, 2 – inert inset, 3 – auxilliary Pt electrode, 4 – plexi glass body, 5 – packing, 6 – screw.
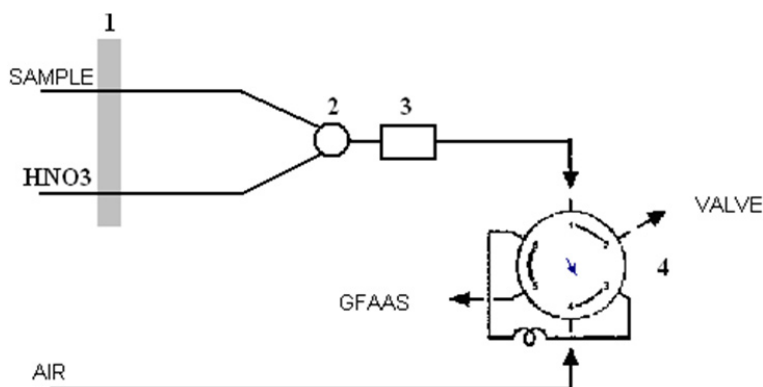
Fig. 2. Scheme of the flow-through system FTC-GFAAS. 1 – pump, 2 – valve, 3 – preconcentration cell, 4 – six-way valve with the sampling loop calibrated for the sampling volume of 57.2 μL.

The Au coating solution used contained 0.0002 mol L^{-1} of $HAuCl_4$, 0.002 mol L^{-1} of KSCN, 0.02 mol L^{-1} of HCl.

Standard solution of 1.000 g L^{-1} of As(III) and certified reference material CRM 12-3-10 (SMU, Bratislava, Slovakia) was used.

The calibration solutions were prepared freshly before the measurements by diluting the bulk standard solution in 0.1 mol L^{-1} of HCl.

Results and discussion

Three different feeding volumes of the sample were chosen for the validation of newly developed coupling FTC-GF AAS and a complete validation set was done for all feeding volumes. Linear range, limit of detection and limit of quantification were appointed. Finally, repeatability, reproducibility

and accuracy were assessed by analyzing the standard reference material.
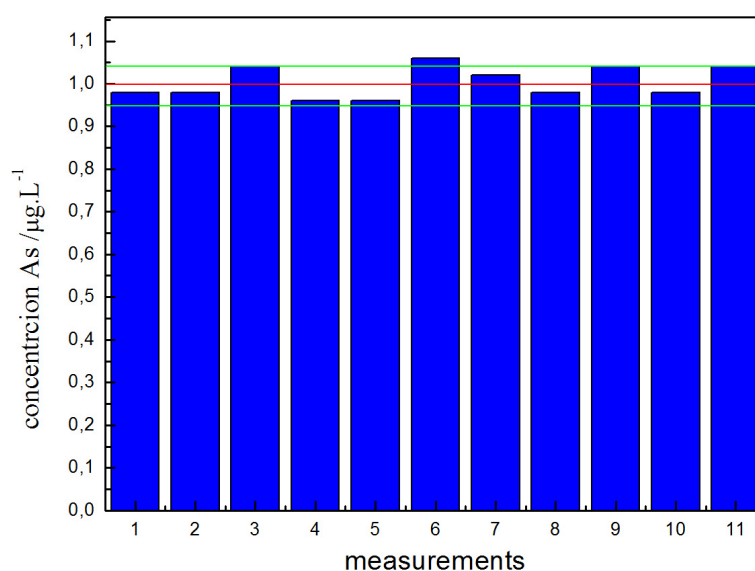
Linear ranges
Linear ranges of As(III) are summarized in Table 1. Listed results show broad ranges, parameters of calibration curves, coefficients of determination and regression coefficients for different feeding volumes.

Limit of detection (LOD) and limit of quantification (LOQ)
Values of the limit of detection and the limit of quantification for the determination of As(III) are listed in Table 2.

Repeatability
Fig. 3 represents the dependence of measured concentration of As(III) against the measurement

Fig. 3. Repeatability of As (III) determination (ρ = 1.00 µg L^{-1}, feeding volume of 1 mL).

Tab. 1. Linear ranges of As(III), equations of linear regressions and their coefficients for different feeding volumes of As(III).

Feeding volume [mL]	Linear range [µg L^{-1}]	Equation of regression	R^2
1	0.20−5.0	A = 0.00154 + 0.13932ρ	0.99986
5	0.06−2.0	A = −0.01273 + 0.36449ρ	0.99968
10	0.01−0.5	A = 3.01584E−5 + 1.08665ρ	0.99854

Tab. 2. Summarized values of slopes and increments for the assessment of LOD, LOQ in the ULA-2 approach (Mocák, 1997).

Volume [mL]	Increments	Slopes	LOD [µg L^{-1}]	LOQ [µg L^{-1}]
1	0.0027568	0.3829	0.06	0.2
5	0.0022268	0.38214	0.02	0.07
10	0.0015779	1.0625	0.004	0.01

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Tab. 4. Summarization of preconcentration factors (PF) and analysis rate.

Feeding volume [mL]	ρ As(III) before the preconcentration step [µg L⁻¹]	ρ As after the preconcentration step [µg L⁻¹]	PF	Analysis rate [number/hour]
1	1	8	8	27
5	1	42	42	23
10	1	84	84	11

order (significance level α = 0.05, selected concentration of 1.00 µg L⁻¹). Repeatability characterized by RSD was 3.5 % (n = 11).

Trueness
Trueness was determined in standard reference material CRM 12-3-10 by on-line FTC-GF AAS of the total As. The FTC-GF AAS technique developed at these conditions has also some limitations. It is suitable only for the determination of As(III) species and the total As must be converted to As(III). Many publications on the selective reduction of total As to As (III) can be found. An appropriate procedure for the selective reduction step, using L-cysteine can be considered (Chen, 1992).
Table 3 provides the results of total As determination in certified reference material after selective reduction by L-cysteine. The analysis was done using 1 mL of the sample volume.

Tab. 3. Results of the total As content in CRM 12-3-10.

FTC-GF AAS	ρ As [µg.L⁻¹] found	ρ As [µg.L⁻¹] certified
	21.0 ± 0.1	21 ± 5

Preconcentration factor and analysis rate
Preconcentration factor (PF) was calculated by:

$$PF = \frac{concentration\ As\ after\ preconcentration\ step}{concentration\ As\ before\ preconcentration\ step} \quad (1)$$

It is a value determining how many times has the analyte concentration increase due to the preconcentration step.
The analysis rate expresses the number of analyse finished per hour.
Table 4 summarized the determined preconcentration factors and the predicted analysis rate respectively, at different feeding volumes.

Conclusions

The aim of this work was to develop on-line coupling of electrochemical preconcentration with the AAS method and to apply the developed system for the determination of ultra-trace amounts of As in water samples. Preconcentration parameters for the electrochemical process were optimized. The deposition runs at the constant current of –2500 µA and the optimum stripping current was found to be 100 µA.
The deposition was made from a hydrochloric acid solution, which was then replaced on-line by diluted nitric acid facilitating the AAS measurement of As. An advantage of the used preconcentration system was in an automatic and reliable matrix exchange facility. Optimum electrolyte concentrations were found to be 0.1 mol L⁻¹ of HCl and 2 mol L⁻¹ of HNO₃ for the deposition and stripping/AAS measurements, respectively. The trueness was determined by means of CRM 12-3-10 with the As content of 21.0 ± 5.0 µg L⁻¹. The analysis was performed after a fast and simple selective reduction of As(V) to As(III) using L-cysteine.

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