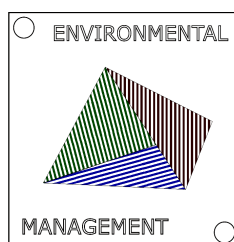


THE DETERMINATION OF ULTRA-TRACE AMOUNT OF ANTIMONY IN WATER SAMPLES


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ABSTRACT

The aim of this work was to develop an on-line coupling of electrochemical preconcentration to AAS method and the utilization of the developed system for the determination of ultra-trace amounts of Sb in water samples. A flow-through electrochemical analyzer EcaFlow (model GLP 150, Istran, Bratislava) was used as the preconcentration unit with a two-electrode cell. The working electrode was an RVC electrode coated with gold. An AAS spectrometer Spectraa-400 with graphite furnace atomizer (Varian) was used to measure the preconcentrated Sb species. The preconcentration parameters for the electrochemical process were optimized. Moreover, the determination of Sb by GFAAS was optimised enabling a direct measurement also from HCl media. The preconcentration step was optimised and characterised.

KEYWORDS: antimony, water samples, AAS, flow-through electrochemical analyzer, porous electrode

Introduction

Antimony is a rather rare element in the earth's crust 0.2 - 0.3 mg/kg (Flower and Goering 1991). Due to its many industrial uses, however, it is one of those elements that show anthropogenic mobilization into the environment. In the last decades the global fluxes of Sb have increased at least 10-fold. This leads to elevated Sb concentrations in soils and exposure to plants, animals and humans. Antimony enters the environment during the mining and processing of its ores and in the production of

antimony metal, alloys, antimony oxide, and combinations of antimony with other substances. Small amounts of antimony are also released into the environment by incinerators and coal-burning power plants.

There are various methods for antimony determination, the most frequently used being atomic absorption spectrometry both with electrothermal atomization and with the hydride generation technique. The former technique requires a careful choice of matrix modifier (Hagarova and Zemberyova 2004, Lima et al. 2004), the latter a chemical reduction of Sb(III) to the corresponding hydride (Moreno et al. 1998, De Gregori et al. 2001).

Electrochemical stripping techniques have proved to be sensitive methods for some electroactive elements such as lead, cadmium, mercury and others. In these techniques, the trace elements are deposited on a suitable electrode and then are stripped either potentiostatically, galvanostatically or chemically (Wang 1985).

For antimony determination differential pulse anodic stripping voltammetry (DPASV) is frequently used, which also facilitates a simple speciation of Sb(III) and Sb(V) (Bond 1997) through control of the HCl concentration: in 0.1 mol/L HCl Sb(III) is deposited only, in 5 mol/L both forms. The procedure is competitive to the more complex HPLC-ICPMS technique (Amereih et al. 2005). Adsorptive stripping can also be used for sensitive antimony determination (Wagner 1996), which enables a speciation analysis as well. Antimony and arsenic can be measured simultaneously on a gold rotating disk electrode (Tanaka and Sato 2001).

Determination of Sb in this paper was done by GFAAS, with preconcentration electrochemical unit. We inspected considerable decreasing limit of detection and influence of interferences could be removed too. On the surface of working electrode will be deposited quantitatively only Sb (III). The deposit is that stripped in on-line system directly to the graphite cuvette of the electrothermal atomizer. On-line take advance of coupling of two steps to one's. At first step, analyte is deposited on working electrode from flowing sample. At second step, the analyte is then quantitatively determined by suitable analytic method. The main topic of preconcentration step is maximize the concentration of the analyte with the simultaneously suppress the effect of interference (Tropp 2007).

Experimental

Material and methods

• GFAAS

An AAS spectrometer SP9 with graphite furnace atomizer (Pye Unicam) was used to measure the preconcentrated Sb species.

• FTC

A flow-through electrochemical analyzer EcaFlow (model GLP 150, Istran, Bratislava) was used as the preconcentration unit with a two-electrode cell. The working electrode was a RVC electrode coated with gold (Fig. 1).

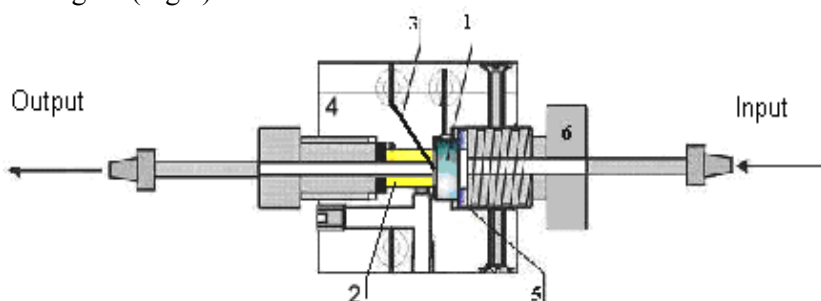


Fig. 1. Scheme of the flow-through cell with dual electrode connection
Legend: 1- working electrode E-53 Au, 2- inert inset, 3-auxilliary Pt electrode,
4-plexi glass body, 5-packing, 6-screw
 • Scheme of the on-line coupling FTC-GFAAS

The 6-way valve was connected by sampling loop with sampling volume 57.2 mL. Thereby on-line connection of electrochemical analyzer EcaFlow could be made by coupling with GFAAS over the 6-way valve (Fig.2).

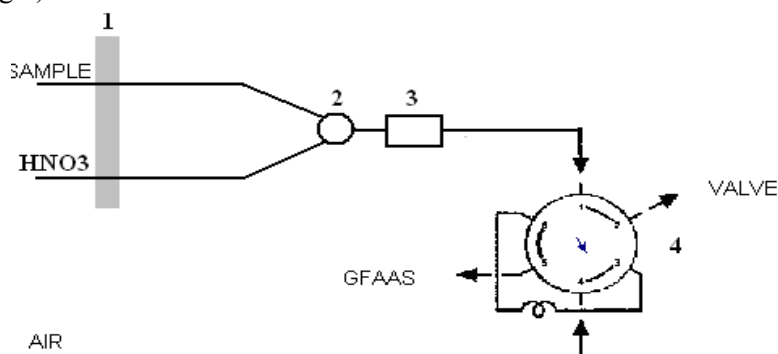


Fig.2. Scheme of the flow-through system FTC-GFAAS

Legend: 1- pump, 2- valve, 3- preconcentration cell, 4- six way valve

Results and Discussion

For validation process of the new developed coupling FTC-GFAAS were chosen three different feeding volumes of the sample and complete validation set were surveyed for all feeding volumes. The linear range, limit of detection and limit of quantification were appointed, respectively. Finally were assessed repeatability, reproducibility and accuracy by analyzing the standard reference material.

• Linear ranges

Table 1. Linear ranges, equations of the linear regressions and their coefficients for different feeding volumes Sb (III)

Feeding volume [mL]	Liner range [$\mu\text{g/L}$]	Equation of regression	R2
1	0.5 – 30	$\tau = 1.861 + 0.079 \cdot c$	0.9973
5	0.1 – 10	$\tau = 1.601 + 0.224 \cdot c$	0.9976
10	0.05 – 0.7	$\tau = 1.226 + 0.432 \cdot c$	0.9938

• Limit of detection (LOD) and limit of quantification (LOQ)

Table 2. Summarized values of LOD and LOQ over ULA-2 approach

Volume [mL]	LOD [$\mu\text{g/L}$]	LOQ [$\mu\text{g/L}$]
1	0.16	0.48
5	0.03	0.09
10	0.017	0.051

• Repeatability

Repeatability of the determination of Sb (III) represent the dependence of measured concentration of the Sb(III) against measurement order (significance level 0,05, selected concentration was $20 \mu\text{g} \cdot \text{dm}^{-3}$). Repeatability characterized by RSD was 1.8 % (n = 20).

• Trueness

The FTC-GFAAS technique developed at these conditions have some limitations. It is suitable only for determination of Sb (III) species and total Sb must be converted to the Sb(III) form. Many

publications were pointed to the selective reduction of total Sb to Sb (III) form. As appropriate procedure for selective reduction step seems to be utilizing L-cysteine.

Table 3. Results of the total Sb in soil samples

FTC-GFAAS*	Found /mg/kg	Reference value /mg/kg
Cambisols	3.83 ± 0.08	3.78 ± 0.09
Orthic Luvisols	2.09 ± 0.06	2.12 ± 0.07

*sample volume 1 mL

• Preconcentration factor and speed of the analysis

It is a value which determines how many times have been increased the concentration of the analyte by preconcentration step.

The speed of the analysis expresses how many of the analysis could be finished per hour.

Table 4. Summarized preconcentration factors and speed of the analysis

Feeding volume [ml]	ρ Sb(III) [mg.dm ⁻³] before preconcentration step	ρ Sb(III) [mg.dm ⁻³] after preconcentration step	PF	Speed of the analysis [number/hour]
1	1	8	8	27
5	1	42	42	23
10	1	84	84	11

Conclusions

The preconcentration parameters for the electrochemical process were optimized. The deposition runs at a constant current of -8 mA and the optimum stripping current was found to be 150 μ A.

The deposition was made from a hydrochloric acid solution, which was then on-line replaced by a diluted nitric acid facilitating the AAS measurement of Sb. The 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.dm⁻³ HCl and 2 mol.dm⁻³ HNO₃ for the deposition and stripping/AAS measurement, respectively.

Acknowledgement

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