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Online coupling electrochemical preconcentration and GFAAS technique as effective method for determination of ultratrace concentrations of antimony in groundwater and surface water samples

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Abstract: The present article describes a method of determination of low antimony concentrations using a graphite furnace AAS technique after electrochemical preconcentration. A 2-electrode flow-through cell was developed with a working electrode made of gold-coated porous carbon and an accessory Pt electrode. This cell worked in online coupling with the graphite furnace atomizer. Accumulation occurred from the 6 M hydrochloric acid solution and 2 M nitric acid was used to dissolve and transport antimony into the sampling loop. The sampling loop was placed on a 6-way valve. The preconcentrated solution was transported to the atomizer using an air jet. The detection limit (3σ) was 0.02 $\mu\text{g/L}$ and the overall linear range was 0.05–10 $\mu\text{g/L}$. The method could be used only to determine the concentration of total inorganic antimony. The method was validated through analysis of certified reference materials and various water samples. Good agreement with the reference values was observed in all cases.

Key words: Electrochemical preconcentration, antimony, flow-through system

1. Introduction

Antimony is a rather rare element in the earth's crust. Due to its many industrial uses, however, it is one of those elements that show anthropogenic mobilization into the environment. This leads to elevated Sb concentrations in soils and waters. 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.

HGAAS, HGAFS, and ICPMS techniques and electroanalytic methods are most frequently used to determine trace antimony concentrations.^{1–4}

The most frequently used instrumental techniques for determination of trace concentrations of metals and semimetals at the level of $\mu\text{g/L}$ in water solutions include graphite furnace AAS (GFAAS). This technique is notable especially for its speed and accuracy. However, when it is necessary to determine lower analyte concentrations in samples using this technique and to eliminate any interference, it is necessary to apply a suitable preconcentration method.

Extraction is one of the most used preconcentration techniques in AAS. It is a very versatile method that allows the obtaining of low detection limits. An overview of extraction techniques commonly used for

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determination of antimony by AAS is shown in Table 1. One of the most frequently discussed preconcentration techniques is electrochemical preconcentration. With electrochemical preconcentration the analyte is accumulated on an electrode from a larger volume of sample and subsequently upon dissolution it is transported to an electrothermal atomizer. Thus, it is possible to determine the trace concentrations of various analytes. Electrochemical accumulation is a highly effective process and a simple method of separation of interferents from the sample. Another advantage of electrochemical systems is their simple automation and integration in flow systems.

Table 1. Extraction techniques used for AAS determination of antimony.

| Extraction technique | Detection mode | Limit of detection | Precision (% RSD) | Additional information | Reference |
|----------------------|--------------------------------|------------------------------|--------------------|--|-----------|
| SPE | FAAS | 6 µg/L | <6% | Ammonium pyrrolidine dithiocarbamate (APDC) on a column of Chromosorb 102 resin | 5 |
| SPE | FI-HG-AAS | a) 1.47 ng/L b) 0.52 ng/L | a) 2.1% b) 2.4% | a) Nanoporous carbon (NPC) b) Multiwalled carbon nanotubes functionalised with L-proline (pro-MWCNTs) | 6 |
| Micro-SPE | a) SS-ETAAS b) Slurry-ETAAS | a) 0.02 µg/L b) 0.03 µg/L | a) 5.1% b) 4.5% | Ag nanoparticles functionalized with the Na salt of 2-mercaptoethanesulfonate (MESNa) | 7 |
| UA-CPE | HG-AAS | 3.6 ng/L | >1.8% | PONPE 7.5 in the presence of pyrogallol and NRH ⁺ at pH 6.0 | 8 |
| UA-CPE | FAAS | 0.03 µg/L | >2.3% | PONPE 7.5 in the presence of Morin + CTAB at pH 8.5 | 9 |
| CPE | FAAS | 0.25 µg/L | >0.24% | Victoria Pure Blue BO (VPB+) at pH 10 | 10 |
| LLE | ETAAS | 8 ng/L | 6.6% | N-benzoyl-N-phenylhydroxylamine (BPHA) as chelating agent | 11 |
| LLE | FAAS | 0.62 µg/L | 3.6% | Bromopyrogallol red as chelating agent | 12 |

SPE- Solid-phase extraction, CPE- cloud-point extraction, UA-CPE- ultrasonic-assisted extraction, LLE- liquid-liquid extraction.

According to the method of transport and the type of used working electrode, electrochemical preconcentration techniques may be classified into several groups:

- In situ accumulation in the graphite tube atomizer, where the graphite tube is the working electrode. The sample solution is stuffed in the atomizer. The trace element is deposited on the wall of the tube through the electrochemical process, the solution is evacuated, and after that the measurement is performed.¹³

- Preconcentration on a probe (comb, rod, etc.). The analyte is accumulated on the probe in the external container. After deposition the probe is rinsed with water and placed in the atomizer, where the measurement is performed.¹⁴

- Use of a flow system. From the flowing solution the analyte is deposited on the working electrode, and after that it is dissolved and transported online or offline to the atomizer.¹⁵

Compared to other methods, flow systems are easy to automate and they are successfully applied in electrochemical preconcentration systems of various designs.

Electrochemical preconcentration achieves detection limits that are comparable with extraction techniques. Benefits of the connection of electrochemical preconcentration, electrothermal atomic absorption spectrometry, and a flow-through system are:

- Lower risk of losses of analyte or contamination of the sample.
- It is not necessary to add an organic compound.
- Easy connection of the online system and simple analysis.

In contrast to HGAAS, there is no need to use unstable solutions.

In the articles published to date, the authors almost always used flat metallic (Au, Pt, Pb, etc.) or carbon electrodes.^{16–18} These are noted for their good electrochemical properties but small surface and low efficiency of analyte accumulation. Electrochemical cells with a minimum internal volume and a working electrode with larger surface and minimum volume should be used to achieve high efficiency of preconcentration.

In this study, gold-coated crushed porous glassy carbon was used as the electrode material. This electrode has very good electrochemical properties and a large surface, and it is suitable for electrochemical deposition.¹⁹ A flow system was also used with an electrochemical microcell.^{20,21}

2. Results and discussion

2.1. Optimization

In the first step, the temperature program was optimized to determine antimony using the GFAAS technique without matrix modifier. An aqueous solution (2 M) of nitric acid was used for optimization with the concentration of antimony at 100 $\mu\text{g/L}$. The final temperature program can be seen in Table 2.

Table 2. The temperature program used for the determination of antimony in the preconcentrated solution.

| Step | Temperature, °C | Ramp, °C/s | Hold, s | Ar, mL/min |
|--------------------------|-----------------|----------------|---------|------------|
| Drying | 120 | 10 | 30 | 200 |
| Pyrolysis | 850 | 40 | 40 | 200 |
| Atomization | 2100 | 0 ^a | 3 | 0 |
| Cleaning | 2700 | 50 | 3 | 300 |
| ^a Full power. | | | | |

In the second step, working conditions of electrochemical preconcentration were optimized in an offline connection. During optimization the accumulation voltage changed from 0 mV to –3000 mV in 100-mV increments. Antimony was not found with the constant voltage accumulated. The search for accumulation current was performed in the same way. The value was modified from 0 mA to –14 mA in 0.5-mA increments. From –2 mA the antimony was reduced in the working electrode with growing efficiency. The highest efficiency was achieved at a current level of –8 mA. After accumulation, the dissolution of metallic antimony from the electrode surface was optimized as well. The lowest value of current at which repeated fast dissolution of the accumulated antimony was observed was accepted as the optimum dissolution current. The current gradually changed from 0 μA to 300 μA in increments of 20 μA . From 200 μA there was damage to the working electrode due to dissolution of electrochemically deposited gold. The optimum value of dissolution current was 120 μA .

In the last step, the concentration of the primary electrolyte (hydrochloric acid) was optimized as well as the secondary electrolyte (nitric acid). Optimization of the primary electrolyte resulted in the increase of

efficiency of antimony accumulation with increasing concentration of HCl. Maximum efficiency of deposition was obtained using HCl with concentrations of 5.5 M and higher. At higher concentrations the measured signal did not change. A concentration of HCl of 6 M was selected as optimal. The concentration of nitric acid in this step was 2 M. Figure 1 shows the record of optimization of secondary electrolyte concentration. This is the relation between the concentration of antimony in the solution flowing from the preconcentration cell and volume. Each curve pertains to different concentrations of nitric acid (0.02 M, 0.1 M, 0.5 M, 1 M, and 2 M). With 0.1 M HNO₃ the antimony was flowing from the electrode at a slow speed. With increasing concentrations of HNO₃ the speed of antimony washing from the electrode increased, as well. This was reflected in the increased concentration of antimony in the initial fractions of eluate. The concentration of antimony in the original solution was always 10 µg/L and the volume of the preconcentrated solution was 1 mL. Each point was the average of five measurements. The concentration of hydrochloric acid in this step was 6 M. For 2 M HNO₃ the antimony washout profile was the narrowest and most of the accumulated antimony washed out within 0.2 to 0.4 mL of solution. From the beginning of this interval 60 µL was always added to the electrothermal atomizer.

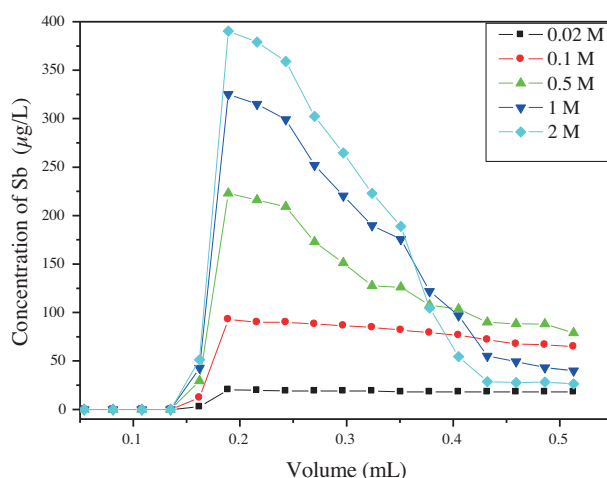


Figure 1. The relation between concentration of antimony in the solution flowing from the preconcentration cell and volume. Each curve pertains to different concentrations of nitric acid (0.02 M, 0.1 M, 0.5 M, 1 M, and 2 M).

2.2. Method validation

The detection limit is the basic characteristic of preconcentration system efficiency evaluation. Through the use of a flow system it was possible to change the sample volume and acquire various values of detection limits and linear ranges for different sample volumes. Maximum sample volume for validation of the determination method was 10 mL. Greater volume would excessively extend the duration of the analysis. The detection limit (3σ) was 0.02 µg/L for 10 mL of sample. The total linear range for sample volumes of 1–10 mL was 0.05–10 µg/L. The repeatability of determination for 10 mL of sample ($n = 11$) was $RSD = 2.8\%$. All analytical parameters are summarized in Table 3. For the purposes of validation, certified reference materials (CRMs) of ‘Trace Elements in Natural Water’ (CRM NIST 1640, US National Institute of Standards and Technology) and ‘Riverine Water’ (SLRS-2, National Research Council of Canada) were employed. Determination of Sb in CRMs was performed with calibration curve technique. Results were in good agreement with the certified values as follows: 13.80 ± 0.37 µg Sb/L (found) vs. 13.79 ± 0.64 µg Sb/L (certified) for CRM NIST 1640, and 0.26 ± 0.04 µg Sb/L (found) vs. 0.26 ± 0.05 µg Sb/L (certified) for CRM SLRS-2. The found values were not statistically different from the certified values based on a Student t-test at a 95% confidence level.

Table 3. The analytical parameters.

| Parameter | Sample volume | | |
|--|---------------|----------|----------|
| | 1 mL | 5 mL | 10 mL |
| Limit of detection, $\mu\text{g/L}$ | 0.16 | 0.03 | 0.02 |
| Limit of quantitation, $\mu\text{g/L}$ | 0.48 | 0.09 | 0.05 |
| Linear range, $\mu\text{g/L}$ | 0.48–10 | 0.09–2.0 | 0.05–0.7 |
| Repeatability, % | 2.1 | 2.8 | 4.0 |

2.3. Interferences

The influence of selected ions that may occur in water samples was tested. A 100-fold excess (m/m) of ions Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cr^{3+} , Cr^{6+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Al^{3+} , Sn^{2+} , Sn^{4+} , Pb^{2+} , As^{3+} , As^{5+} , Bi^{3+} , Se^{4+} , Se^{6+} , Br^- , I^- , F^- , SO_4^{2-} , PO_4^{3-} , SiO_4^{4-} , and NO_3^- was added to $0.2 \mu\text{g/L}$ Sb^{3+} . Only As^{3+} with 50–100-fold excess reduced the antimony signal by 5%–20%. Humic acids did not interfere at up to 20 mg/L concentrations.

Addition of $0.4 \mu\text{g/L}$ Sb^{5+} to the standard resulted in the same increase of antimony signal as the addition of $0.4 \mu\text{g/L}$ of Sb^{3+} . Only the total content of inorganic antimony could be determined using the discussed method. It was impossible to determine the individual oxidation forms.

2.4. Real samples

Two types of real water samples (underground and surface water samples) were analyzed by the elaborated method. Samples were collected in the vicinity of antimony mines near Pezinok in Slovakia ($48^\circ 20' 57.9''\text{N}$, $17^\circ 13' 09.8''\text{E}$). Water samples were collected into polypropylene flasks and transported to the laboratory. The water samples were also analysed by hydride generation AFS by making use of standardized procedures. The results are listed in Table 4. Good agreement with the reference values was observed in all cases.

Table 4. Analyses of real water samples.

| Sample | Found, $\mu\text{g/L}$ | HGAFS, $\mu\text{g/L}$ | Student t-test ^a |
|---------|------------------------|------------------------|-----------------------------|
| Water 1 | 1.01 ± 0.04 | 1.02 ± 0.05 | 0.75 |
| Water 2 | 0.62 ± 0.03 | 0.61 ± 0.04 | 0.99 |
| Water 3 | 0.40 ± 0.03 | 0.41 ± 0.03 | 0.99 |
| Water 4 | 1.38 ± 0.03 | 1.37 ± 0.05 | 0.99 |
| Water 5 | 1.53 ± 0.04 | 1.54 ± 0.08 | 0.75 |
| Water 6 | 3.34 ± 0.09 | 3.38 ± 0.13 | 1.33 |
| Water 7 | 6.51 ± 0.14 | 6.42 ± 0.32 | 1.93 |

1–4, Groundwater, 5–7, surface water.

^aThe one-paired critical t value is 2.26 for nine degrees of freedom at a probability level of 0.05.

2.5. Conclusions

The resulting flow preconcentration system enables the determination of ultratrace concentrations of total inorganic antimony in water samples using GFAAS. The main advantage lies in the elimination of possible interferences and the significant reduction of the detection limit. The system may be used to determine additional elements (As, Se, Hg, etc.) and successfully compete with the hydride generation AAS method

and cold vapor techniques. The preconcentration system may be combined with other atomic spectrometry techniques such as FAAS, ICP-OES, MIP-OES, and others.

3. Experimental

3.1. Reagents and solutions

All solutions were prepared in highly purified water (18.5 M Ω /cm) in polypropylene flasks. HCl (6 M) was used as the primary electrolyte and HNO₃ (2 M) as the secondary electrolyte. Standard solutions of Sb³⁺ and Sb⁵⁺ were prepared by dissolving Sb₂O₃ or Sb₂O₅ (Sigma-Aldrich) in 2 M NaOH (Slavus, Bratislava, Slovakia). Gold-coated electrodes were prepared using a solution containing 0.2 mM HAuCl₄, 2 mM KSCN, and 0.02 M HCl.

3.2. Instruments

The AAS measurements were done on a Shimadzu AA-6300 atomic absorption spectrometer with deuterium background correction and a GFA-EX7i electrothermal atomizer. Pyrolytically coated graphite tubes were used. An HCL lamp for antimony (current: 10 mA, wavelength: 217.3 nm, slit: 0.2 nm) and deuterium lamp were used as the source of radiation. Peak height was the measured signal.

An EcaFlow computer-controlled flow electrochemical system (Istran s.r.o., Bratislava, Slovakia) with integrated peristaltic pumps and switching valves was used for electrochemical preconcentration of antimony. The flow was always constant (3 mL/min).

A three-electrode flow cell (Istran s.r.o.) was modified into a two-electrode preconcentration cell with minimum internal volume (Figure 2). The preconcentrated solution was removed from the proximity of the electrode through a Teflon tube. The conical space above the surface of the electrode was about 0.5 mm high with a volume of about 3 μ L.

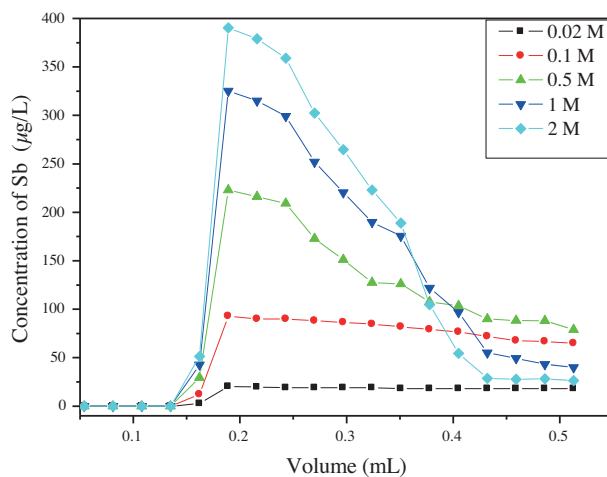


Figure 2. Scheme of the preconcentration cell. 1- Cell body, 2- working electrode, 3- platinum contact to the working electrode, 4- platinum auxiliary electrode (0.5 mm diameter), 5- screw holding the working electrode, 6- silicone O-rings, and 7- PTFE tube (internal diameter: 1 mm). The flow direction is indicated by arrows.

The working flow electrode was made of a charcoal cylinder, 4 mm high and 5 mm in diameter. The cylinder was filled with crushed porous carbon and enclosed with porous frits. Crushed porous charcoal was gold-coated. The effective volume of the electrode was 20 μ L and its active surface was 25 cm².

The preconcentration unit was connected with the atomizer through a manually controlled 6-way valve (LATEK, Eppelheim, Germany) and PTFE tubes. A loop with volume of 60 μL was connected to the valve (internal diameter of the tube 1 mm, length 76 mm, same connection as used in HPLC injection valves), a supply of preconcentrated solution from the cell, a supply of compressed air, and a sampling tube leading to the atomizer. The flow-through scheme of online coupling can be seen in Figure 3.

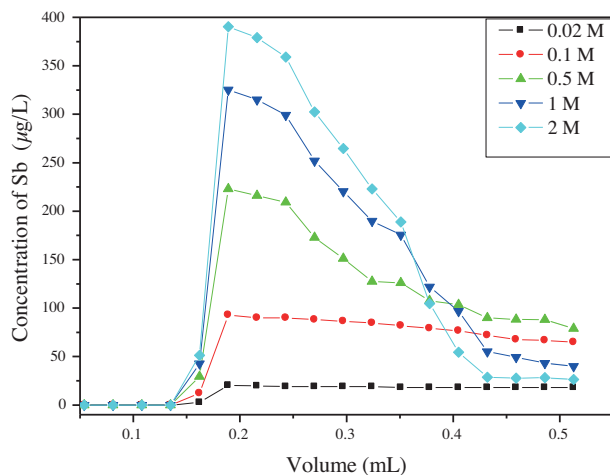


Figure 3. The flow-through scheme of online coupling. 1- Two-way solenoid inert valve, 2- peristaltic pump, 3- preconcentration cell, 4- 6-way valve with sampling loop (PTFE tubing of 1 mm inner diameter, volume 60 μL). Lengths indicated in the figure were used.

3.3. Coating of the electrodes

The porous working electrodes were coated at -2 mA with the coating solution at a flow rate of 3 mL/min for 10 min from each side. Then the current was enhanced to -3.5 mA and the coating process was repeated.¹¹

3.4. Sequence of analysis

Constant current of -8 mA (result of optimization) was used to precipitate antimony as elementary Sb on the working electrode from the flowing solution of antimony in 6 M hydrochloric acid. The electrode was rinsed with 2 M nitric acid to remove chlorides. The accumulated antimony was dissolved with a constant current of 0.15 mA (result of optimization) and rinsed using 2 M nitric acid in the sampling loop. After switching the valve, the preconcentrated solution was transported from the sampling loop using a jet of air through the PTFE tube into the atomizer. Analysis on atomic absorption spectrometers was started.

3.5. Treatment of samples

After filtration the samples of ground and surface water were treated by adding hydrochloric acid to a final concentration of 6 M HCl. Reference results were acquired using the HGAFS method.

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