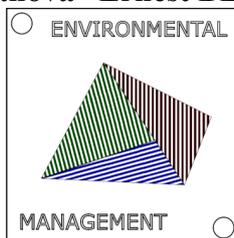


DETERMINATION OF ANTIMONY BY FLOW-THROUGH STRIPPING CHRONOPOTENTIOMETRY

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ABSTRACT

Flow-through stripping chronopotentiometry was used for the determination of antimony in soil samples. Antimony was deposited in potentiostatic mode on a glassy carbon porous electrode coated with Nafion® and mercury and then stripped with constant current. The accuracy of the results was confirmed by graphite furnace atomic absorption spectrometry. The LOD and LOQ were found to be 0.6 $\mu\text{g}\cdot\text{dm}^{-3}$ and 1.7 $\mu\text{g}\cdot\text{dm}^{-3}$, respectively. A linear response range was observed in the concentration range of 1 to 200 $\mu\text{g}\cdot\text{dm}^{-3}$ for sample volumes of 4 mL. The repeatability and reproducibility were found to be 2.9 % and 5.2 %, respectively.

KEY WORDS: antimony, soil samples, stripping chronopotentiometry, 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).

The galvanostatic stripping (galvanostatic stripping chronopotentiometry) exerts some special features, making this technique more suitable for routine use. The electronic control is simpler compared to voltammetric systems and the signal resolution is better due to smaller peak widths.

Flow-through stripping chronopotentiometry with porous working electrodes (Beinrohr et al. 1994, Beinrohr et al. 1996, Beinrohr et al. 1998, Beinrohr et al. 1999, Kozáková et al. 2000, Jurica et al. 2000) is a simple but powerful tool for trace analysis of various species. Owing to the flow system, the analysis can be completely controlled by a microprocessor or PC, making the method simple, fast and robust.

The goal of this paper was to apply this technique to the determination of Sb in soil samples.

Experimental

The flow-through chronopotentiometric measurements were carried out on an EcaFlow model GLP 150 electrochemical analyzer (Istran, Ltd., Bratislava, Slovakia) equipped with two solenoid inert valves, a peristaltic pump and a microprocessor controlled potentiostat/galvanostat.

A compact flow-through electrochemical cell of type 353c with Pt auxiliary, Ag/AgCl reference and E-53 compact porous working electrodes was used (Istran, Ltd., Bratislava, Slovakia). The operation parameters are listed in Table 1.

Table 1. Operation parameters of the electrochemical analyzer

Parameter	Value
Deposition potential, mV	-1000
Quiescence potential 1, mV	-800
Quiescence time 1, s	5
Quiescence potential 2, mV	-350
Quiescence time 2, s	10
Terminal potential, mV	-100
Stripping current, mA	0.1
Stand by potential, mV	-200

The accuracy of the results was checked by GF AAS on the atomic absorption spectrometer Perkin Elmer 5000 equipped with Zeeman background correction. The experimental parameters used were those recommended by the manufacturer.

The soil samples were digested in a high-pressure digestion DAB II (Berghof Maassen, Eningen, Germany) equipped with 50 mL PTFE vessels.

Coating of the Porous Electrode

The surface of the porous electrode E-53 (effective diameter 5 mm, length 3 mm, approximate void volume and surface 20 μ L and 25 cm², respectively) was moistened with 20 μ L of 0.1 % (V/V) solution of Nafion® in ethanol. On drying, the electrode was coated at -500 mV with 50 mL of Hg coating solution at a flow rate of 3 mL/min. After coating the electrode was rinsed with 10 mL of the carrier electrolyte solution at a potential of -200 mV. The electrode was used until fouling, then was replaced by a new one. To minimize electrode blocking with solid or colloidal particles, an in-line filter (0.45 μ m pore size, material nylon) was used downstream of the cell.

Reagents and Solutions

Analytical-grade reagents were used in all experiments. Nitric acid and hydrochloric acid were purified by subboiling and isopiestic distillation, respectively. Deionised and degassed water was used for the preparation of all solutions.

Carrier electrolyte: 1 mol.dm⁻³ HCl.

Hg coating solution: 1 mg.dm⁻³ Hg(II) in 0.1 mol.dm⁻³ KSCN.

The bulk standard solution of 10 mg.dm⁻³ Sb was prepared in the carrier electrolyte from a Certified Reference Material (1.000 g.dm⁻³ Sb, SMU Bratislava, Slovakia).

The Nafion® solution was prepared by diluting a Nafion® 117 solution (Fluka) in ethanol.

The calibration solutions were prepared by diluting the CRM solution in 4 mol/L HCl.

Sampling and Sample Digestion

The soil samples Cambisols and Orthic Luvisols were obtained from the monitoring localities in Slovakia: Raková (Cambisols), Nitrianske Hrnčiarovce (Orthic Luvisols). The samples were collected from a depth of 50-100 cm, dried and sieved through a 2 mm sieve. The other samples were obtained from the Geological Institute of UK Bratislava, Slovakia.

Decomposition of the Soil Samples

To 1 g of the sample in the PTFE decomposition vessel 2 mL of concentrated fluoric acid, and 4 mL of concentrated hydrochloric acid were added. On closing the device the sample was digested at 180 °C for 4 hours. On cooling the solution was evaporated to dryness in a PTFE vessel under an IR lamp. The residue was dissolved in an appropriate volume of 4 mol/L HCl, filtered if contained solids and the resulting solution was analyzed.

Results and Discussion

The deposition of Sb on mercury-coated porous carbon electrode proceeds in acidic solutions only, preferably in hydrochloric acid media. The efficiency of the deposition depends on the deposition potential, the highest recoveries were observed in the region of -900 to -1100 mV (Fig. 1). At more negative potentials the bubble formation due to hydrogen reduction in the electrode deteriorates the reproducibility. Hence a deposition potential of -1000 mV was used in further experiments.

The hydrochloric acid concentration affects the deposition efficiency, the higher the HCl concentration the higher the signal (Fig. 2). However, too high HCl concentrations are not welcome owing to its corrosive and irritating properties. Hence, the samples and standards were prepared in solutions with a final HCl concentration of 4 mol/L. Unlike the more diluted HCl solutions, both Sb(III) and Sb(V) were deposited here virtually with the same efficiency, as observed also in stripping voltammetry (Bond et al. 1997). Hence, total Sb is in fact determined.

The stripping step was done in the 4 mol/L HCl solution as well. Stripping into more diluted HCl solutions caused a shift of the stripping peak to more positive potential and a worse separation of Pb and especially Cu signals.

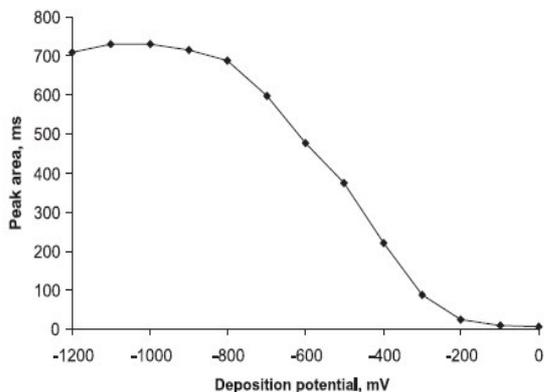


Fig. 1. Dependence of the signal on the deposition potential. Experimental parameters are in Table 1.

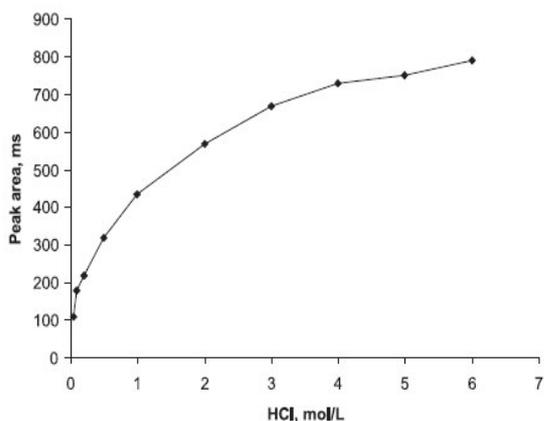


Fig. 2. Dependence of the signal on the hydrochloric acid concentration. Experimental parameters are in Table 1.

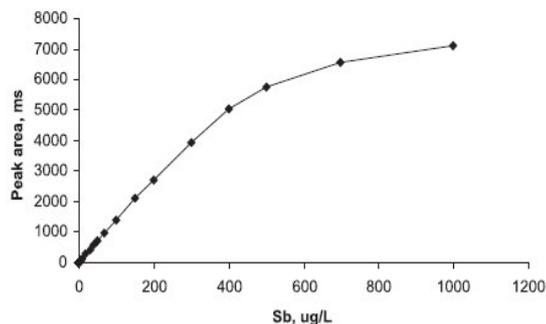


Fig. 3. Concentration dependence of the signal. Experimental parameters are in Table 1.

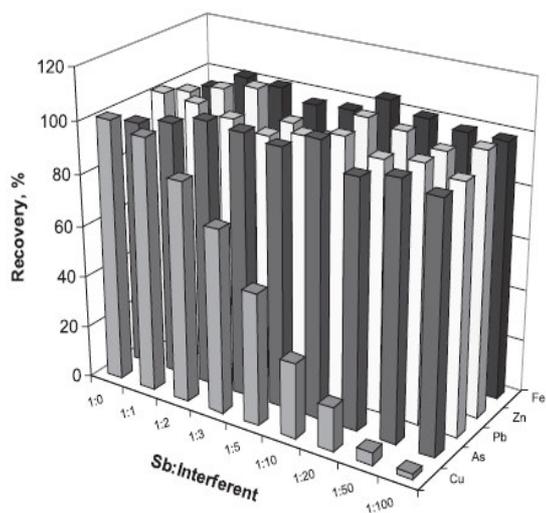


Fig. 4. Influence of some metal ions on the recovery of Sb. Antimony concentration 10 $\mu\text{g/L}$. Experimental parameters are in Table 1.

The stripping current influences the sensitivity but also the background signal, which predominantly comprises the double-layer charging. High signal sensitivity can be achieved with low stripping currents but the background signal will be high as well. On the other hand high stripping currents deliver low background signals but low and noisy net signals. For the applied electrode and electrolyte stripping currents of 100 to 200 μA delivered the best signal to noise ratios.

The signal response was found to be linear up to Sb concentrations of 200-300 $\mu\text{g/L}$ (Fig. 3). The limited dissolution of Sb in the mercury film may be responsible for the unlinearity at higher Sb concentrations. By making use of the lower concentration range, the values of the limit of detection and limit of determination were calculated according to an IUPAC-recommended procedure (Mocák et al. 1997). The corresponding values were found to be 0.6 $\mu\text{g/L}$ and 1.7 $\mu\text{g/L}$, respectively.

Soil samples may contain several metals with possible interfering effects on Sb determination with the elaborated procedure. The influence of some common metal ions on the recovery of Sb was tested (Fig. 4). The most significantly interfering species was copper, which provides a stripping peak in the vicinity of Sb and makes the integration of its peak difficult or even impossible. By setting the second quiescence potential to a more positive value for some seconds (Table 1), this interference can be partially depressed but not completely removed. At concentration ratios of Cu to Sb higher than 2, their stripping peaks tend to coalesce (Fig. 5). Accordingly, for higher copper contents its separation is inevitable, e.g. by separating Sb from Cu on a Chelex-100 column in ammonia solution - antimony passes the column whereas Cu is trapped almost completely (Bond et al. 1997).

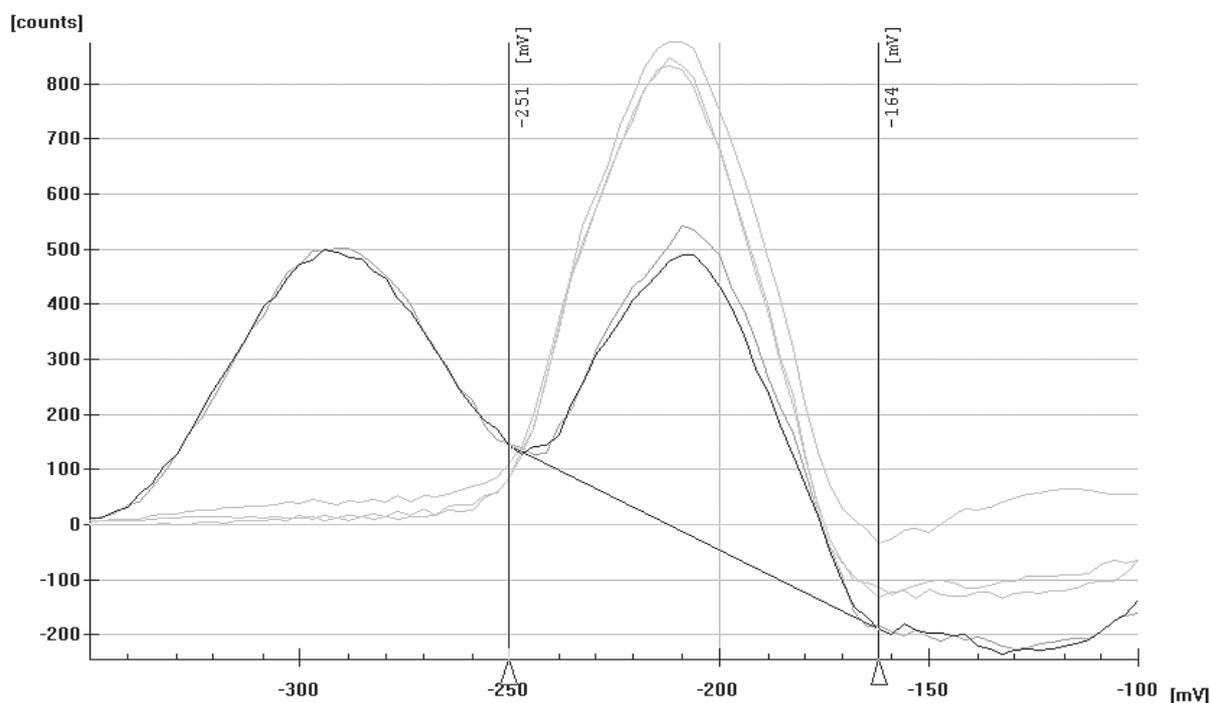


Fig. 5. Stripping chronopotentiograms of 10 µg/L Sb in the absence of Cu (gray signals) and in the presence of 20 µg/L Cu (black lines, the left peak belongs to Cu). Y-scale (counts): s/mV. Experimental parameters are in Table 1.

The Nafion coating of the electrode ensured a better discrimination against organics and a significantly longer lifetime of the mercury film. There was no need to remove the mercury film after measurement, the same film could be used for several days. Due to the low cost of the porous electrodes, it was simpler to take a new one after fouling.

The analytical figures of merit of the method are collected in Table 2.

Table 2. Analytical figures of merit

Parameter	Value
Limit of detection	0.6 µg/L
Limit of determination	1.7 µg/L
Linear range	2 - 300 µg/L
Repeatability	2.9 %
Reproducibility	5.2 %
Duration of a measurement	4 - 5 min
Electrode lifetime	30 - 50 measurements

The repeatability was calculated from 10 repeated measurements of the same solution (10 µg/L Sb) within a short period of time. The reproducibility was calculated from values obtained from analyses in different days. The procedure enables performing 3 repeated measurements for 4 samples in one hour average. The response of the electrode is virtually constant up to 30 - 50 measurements, then a slow decrease in sensitivity is observed. A repeated coating of the electrode renews the signal sensitivity. Owing to the microporous structure the electrode is vulnerable to solid and colloidal particles in the solutions and therefore an in-line filter should be used to prevent blocking of the electrode.

The method was applied to analyses of soils samples, two of them coming from Slovakia, the others serve as internal standards in a geological laboratory. The samples were also analysed by GF AAS. The results listed in Tab. 3 imply an acceptable agreement between the two independent methods.

Table 3. Analyses of soils samples

Sample	Found/ mg/kg	Reference value* / mg/kg
P 58B	0.46 ± 0.05	0.50 ± 0.06
P 60B	0.52 ± 0.05	0.50 ± 0.05
P 62A	0.34 ± 0.04	0.38 ± 0.06
P 63AO	0.35 ± 0.04	0.38 ± 0.05
P 64AO	1050 ± 85	1070 ± 105
P 65B	16.6 ± 1.2	17.4 ± 2.1
Cambisols	3.83 ± 0.08	3.78 ± 0.09
Orthic Luvisols	2.09 ± 0.06	2.12 ± 0.07

* GF AAS

Conclusion

The determination of antimony in soil samples by flow-through chronopotentiometry proved to be a simple, sensitive, and accurate method. There is no need to remove dissolved oxygen from the solutions. The measurement of the digested soil samples is fast, an average measurement cycle does not exceed 3 - 6 min, the most time-consuming step being digestion.

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References

- Amereih S, Meisel T, Kahr E, Wegscheider W (2005) *Anal. Bioanal. Chem.* 383: 1052;
 Beinrohr E, Csemi P, Rojas JF, Hofbauerova H (1994) *Analyst* 119: 1355;
 Beinrohr E, Cakrt M, Dzurov J, Kottáš P, Kozáková E (1996) *Fresenius J. Anal. Chem.* 356: 253;
 Beinrohr E, Dzurov J, Annus J, Broekaert JAC (1998) *Fresenius J. Anal. Chem.* 201: 362;
 Beinrohr E, Cakrt M, Dzurov J, Jurica L, Broekaert JAC (1999) *Electroanalysis* 11: 1137;
 Bond AM, Kratsis S, Newman OMG (1997) *Electroanalysis* 9: 681;
 De Gregori I, Pinochet H, Fuentes E, Potin Gautier M (2001) *J. Anal. At. Spectrom.* 16: 172;
 Flower BA, Goering PL (1991) Antimony. In: *Metals and their Compounds in the Environment* (Merian E., ed.), VCH Weinheim;
 Hagarova I, Zemberyova M (2004) *Chem. Listy* 98: 926;
 Jurica J, Manova A, Dzurov J, Beinrohr E, Broekaert JAC (2000) *Fresenius J. Anal. Chem.* 366: 260;
 Kozáková E, Bodor R, Jursa J, Beinrohr E (2000) *Chem. Papers* 54: 144;
 Lima EC, Brasil JL, Dos Santos AHDP (2004) *MicrochimActa* 146:1436;
 Mocák J, Bond AM, Mitchell S, Scollary G (1997) *Pure Appl. Chem.* 69: 297;
 Moreno ME, Perez-Conde C, Camara C (1998) *J. Anal. At. Spectrom.* 13: 1181;
 Tanaka T, Sato T (2001) *J. Trace Microprobe Tech.* 19: 521;
 Wagner W, Sander S, Hence A. (1996) *Fresenius J. Anal. Chem.* 354: 11;
 Wang J (1985) *Stripping Analysis*. VCH Publishers Inc, Durfield Beach, Florida.

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