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Determination of Arsenic in Soil Extracts by Flow-Through Anodic Stripping Coulometry

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Abstract

Flow-through coulometry was used for the determination of arsenic in soil extracts in 2 mol.dm^{-3} HCl solution. Arsenic(III) species were deposited on gold plated porous working electrodes and then galvanostatically stripped. The procedure was optimized and possible interferences were identified. The total As content was determined after a reduction step in a microwave oven with hydrazine hydrochloride. The detection limit was found to be 0.15 µg·dm^{-3} in the analyzed solution. A linear response range was achieved up to As concentrations of several mg·dm^{-3}. The procedure was applied for the analysis of soil extract samples from three localities in Slovakia.

Keywords: arsenic, soil extract, flow-through coulometry

Introduction

This paper reports on the determination of arsenic in soils by flow-through anodic stripping coulometry. Though electrochemical methods have been seriously neglected in trace analysis during the last decades, there is a significant progress in their utilization in environmental studies. In recent years anodic and adsorptive stripping voltammetry have attracted considerable attention for the determination of trace and ultratrace metals, providing excellent sensitivity and good accuracy and precision [1, 2]. Arsenic can be determined as arsenite by anodic stripping voltammetry using a gold electrode [3-5] and by cathodic stripping voltammetry at the mercury drop electrode. The main drawback of the ASV method for arsenic determination is its poor reproducibility related to ready fouling of the gold electrode surface [6] and the time-consuming pre-reduction step.

Flow-through stripping coulometry with porous electrodes has become a routine method for the determination of trace and minor components of various environmental samples, especially waters and other aquatic samples. The method is based on the preconcentration approach, but unlike the voltammetric techniques, the treated sample volume is electrolyzed as a whole [9]. It brings an additional advantage, namely some absolute character of the analysis: In the case of complete electrochemical deposition and dissolution, the analyte amount can directly be calculated from the electrical charge consumed for the stripping process.

Arsenic(III) species can be collected virtually completely on gold-coated porous carbon electrodes [7] as elemental arsenic. In the next step the deposit can be completely dissolved to As(III) species by a suitable constant current, whereas the potential of the porous electrode is monitored and evaluated. The potential time dependence gives the duration of the dissolution (chronopotentiometric stripping time) which is proportional, according to Faraday´s laws of electrolysis, to the analyte amount treated.

The objective of this study was to develop a fast and accurate procedure based on this approach for the determination of arsenic in extracts of soil samples.

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Experimental

Instruments

The flow-through coulometric measurements were done on an EcaFlow 150 electrochemical analyzer (ISTRAN, Ltd., Bratislava, Slovakia) equipped with a potentiostat and galvanostat enabling measurements of chronopotentiometric transition times over 1 ms. The compact flow-through electrochemical cell of type 353b with Pt auxiliary, Ag/AgCl reference and E53-Au gold-coated porous working electrodes was used (ISTRAN, Ltd., Bratislava, Slovakia).

Operation parameters for the flow-through coulometer:

The deposition was made in the galvanostatic mode at –3 mA. The deposit was stripped galvanostatically as well.

Other parameters:

starting potential –400 mV,
end potential 600 mV,
stripping current 300 µA,
quiescence time 10 s,
sample volume 1 ml,
flow rate 3 ml/min.

The microwave oven PMD Paar (A. Paar, Graz, Austria) with 30 ml PTFE vessels was used for the reduction of As(V) to As (III) with a suitable reducing agent.

The accuracy of the results was checked by hydride generation AAS by means of the atomic absorption spectrometer VARIAN SpectrAA 300 equipped with the VGA 76 hydride generation module. The experimental parameters used were those recommended by the manufacturer.

Reagents and Solutions

Analytical grade reagents were used in all experiments.

Deionized and degassed water (conductivity 0.18 $\mu S \cdot m^{-1}$) was used for preparing all solutions.

The carrier electrolyte for the determination was 0.002 $mol \cdot dm^{-3}$ HCl + 0.1 $mol \cdot dm^{-3}$ NaCl.

Bulk standard solution 0.25 $mg \cdot dm^{-3}$ of As(III) was prepared in carrier electrolyte.

Sample Pretreatment

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

Flow-Through Coulometry

10 g of the soil sample were mixed with 100 ml 2.0 $mol{\cdot}dm^{-3}$ HCl for 2 hours in a plastic vessel. After filtration 5 ml of extract was transferred into a PTFE vessel of the microwave digester and 0.1 g $N_2H_4{\cdot}2HCl$ was added. The vessel was closed and placed into PMD Paar microwave oven for 5 minutes at 100% power. After cooling, the sample was transferred into 50 ml calibrated flask, and the sample volume was adjusted to 50 ml with water.

HG AAS

10 g of the soil sample was mixed with 100 ml 2.0 $mol{\cdot}dm^{-3}$ HCl for 2 hours in a plastic vessel. After filtering, 5 ml was taken into a 50 ml flask, 10 ml of KI solution (5% w/V), 1 ml of 5% (w/V) ascorbic acid were added and the volume was adjusted to 50 ml with 3.8 $mol{\cdot}l^{-1}$ HCl. The resulting solution was analyzed after 1 h.

Results and Discussion

The electrochemical deposition of As(0) from flowing sample solutions containing As(III) species in the gold plated porous carbon electrode is based on the reaction:

$$AsO_3^{3-} + 6\,H^+ = As(0) + 3\,H_2O - 3\,e^-$$

The deposit is then galvanostatically stripped, whereas the change of the potential of the porous electrode is monitored. Hence, the method is called stripping chronopotentiometry.

Owing to the electrochemical irreversibility of As(V), only the As(III) species can be deposited. All other As species including As(V) have to be converted to As(III) prior to analysis. Various reducing agents have been used for this purpose [8-11]. Unfortunately, all these procedures are time consuming and there is an inherent danger of analyte loss due to the easy evaporation of As species in acidic media. Therefore, the microwave assisted reduction in closed vessel was chosen, which is fast and without losses [7].

The sensitivity in flow-through stripping coulometry is controlled by deposition efficiency, charge number corresponding to the stripping process and the sample volume taken for analysis. High deposition efficiencies can be achieved by suitable choice of the deposition potential or current. Moreover, it is also influenced by the composition of the electrolyte added to the sample. For samples with varying matrices the galvanostatic deposition has proved to be more advantageous. The influence of the deposition current is depicted in Fig. 1. Deposition currents of –3 mA and higher ensure virtually complete electrochemical deposition of As(III) species.

For the stripping step, the most reproducible results were achieved by applying stripping currents of 200 to 300 µA.

Since the flow system enables a simple adjustment of the sample volume taken to analysis, there is a possibility to match the parameters to samples with low and high As contents simply by choosing an adequate sample volume – small for high As contents and large for low concentrations. Hence, the linear response range embraces concentrations from below 1 $\mu g.dm^{-3}$ to almost 5 $mg{\cdot}dm^{-3}$ (Fig. 2). The detection limit was found to be about 0.15 $\mu g{\cdot}dm^{-3}$.

The linear range of measurements for the sample volumes of 1 ml, 0.5 ml, and 0.1 ml was tested. It is evident from Fig. 2 that the correlation between measured and given concentrations of As(III) is linear in the range of 0-5,000 µg·dm^{-3}. The linear range is limited by electrochemical conversion efficiency in deposition and stripping step. Repeatability of the measurements in the calibrationless mode was found better and more advantageous than that with calibration by means of standard addition.

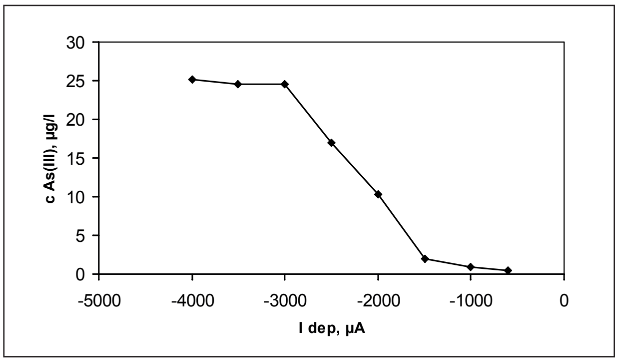

Fig. 1. Dependence of the found concentration of As(III) on the deposition current (added 25 µg·l^{-1} As(III); Electrolyte: 0.1 mol·l^{-1} NaCl, 0.002 mol·l^{-1} HCl; Volume of the sample: 1 ml; Stripping current: 0.2 mA). Measurements in the calibrationless mode.

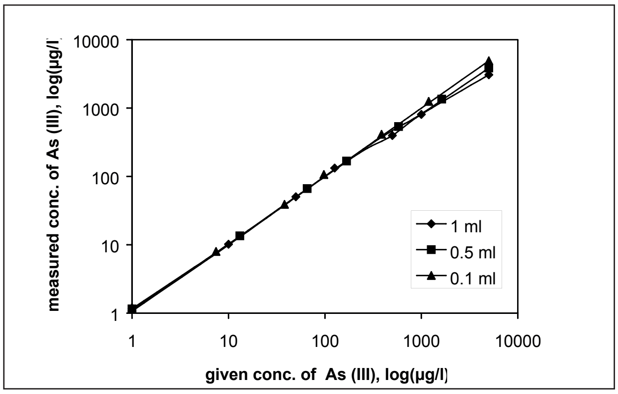

Fig. 2. Correlation between the measured and given concentration of As(III) in the range of 0 to 5000 µg·l^{-1} (volume of the sample: 0.1 ml, 0.5 ml a 1 ml; Electrolyte 0.1 mol·l^{-1} NaCl, 0.002 mol·l^{-1} HCl; Deposition current: -3 mA; Stripping current: 0.2 mA).

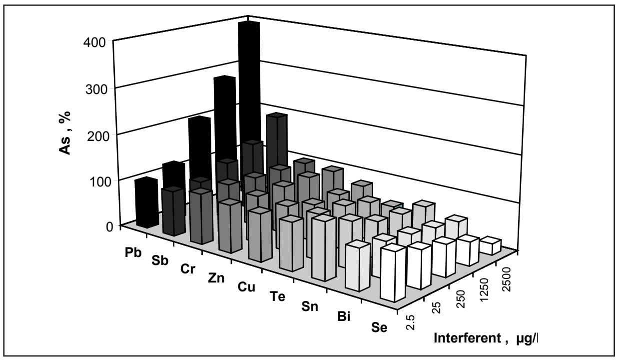

Fig. 3. Influence of some metal ions on the found values of As(III) (As(III) added: 25 µg·l^{-1} Electrolyte: 0.1 mol·l^{-1} NaCl, 0.002 mol·l^{-1} HCl, Volume of sample: 1 ml; Deposition current: -3 mA; Stripping current: 0.2 mA).

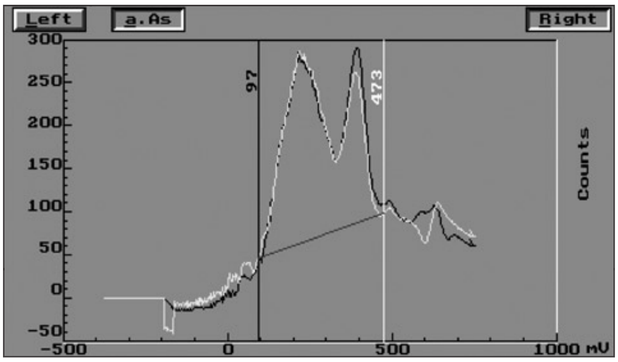

Fig. 4. Chronopotentiogram of 25 µg·l^{-1} As(III) in the presence of 500 times higher concentration of humic acid.

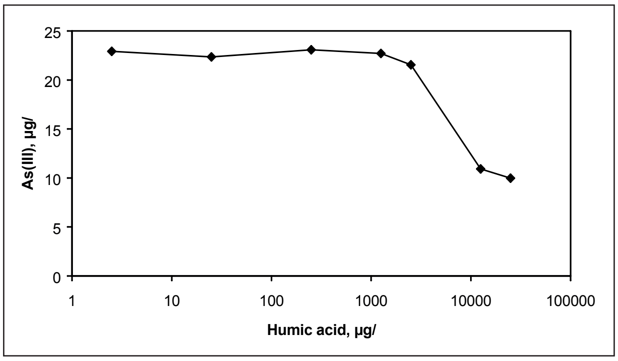

Fig. 5. Influence of humic acids on the found values of As(III) (As(III) added: 25 µg·l^{-1} Electrolyte: 0.1 mol·l^{-1} NaCl, 0.002 mol·l^{-1} HCl, Volume of sample: 1 ml; Deposition current: -3 mA; Stripping current: 0.2 mA).

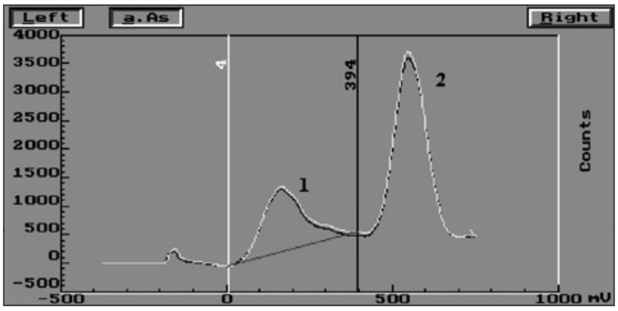

Fig. 6. Chronopotentiogram of the soil extract sample "Phaeozems": Peak No1 is the stripping peak of As and peak No 2 corresponds to Cu.

Real soil samples may contain heavy metals and/or organic matter which could interfere. Therefore, several inorganic species were tested as possible interferents. As Fig. 3 implies, Pb and Sb increase the signal of As(III) owing to their similar stripping peak potentials. Cu, Zn, Cr virtually do not interfere. The presence of Te, Sn, Bi

Table 1. Analyses of the soil extracts by flow coulometry and HG AAS.

Method	Flow coulometry		HG AAS	
Sample	As(III) $\mu g.l^{-1}$	Stand. deviation	As(III) $\mu g.l^{-1}$	Stand. deviation
Orthic Luvisol	32.37	0.22	30.79	1.50
Phaeozems	39.03	0.96	40.14	1.80
Cambisol	51.88	0.55	53.04	2.60

and Se leads to the depression of the signal of arsenic, which can be assigned to a partial coalescence of their stripping peaks (Sn, Bi) and formation of intermetallic compounds (Se, Te). If the concentration of these species in soil were 100 times higher than the concentration of As, the results became unreliable.

Humic substances in soils may also deteriorate the determination of arsenic. The arsenic peak splits at high contents of humic acids in the sample (Fig. 4) and a sensitivity drop occurs. However, such an interference was observed at humic acid contents higher than 2,500 $\mu g \cdot dm^{-3}$ (Fig. 5). The above interference might be attributed to some blockage of the electrode surface by humic substances.

The method described was applied to the determination of arsenic in soils in which we did not expect the occurrence of Sb, Se, Bi, Te at the above high levels. Copper at the experienced concentration level does not interfere as its stripping peak is sufficiently separated from that of arsenic (Fig. 6). The results of the measurements are listed in Tab.1 together with the control analyses by means of hydride generation AAS. The values found by the coulometric method match satisfactorily the reference data obtained by the standard AAS method.

Acknowledgements

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