Fresenius J Anal Chem (2000) 366 : 260–266

ORIGINAL PAPER

L'. Jurica · A. Manová · J. Dzurov · E. Beinrohr
J. A. C. Broekaert

Calibrationless flow-through stripping coulometric determination of arsenic(III) and total arsenic in contaminated water samples after microwave assisted reduction of arsenic(V)

Received: 14 July 1999 / Revised: 21 September 1999 / Accepted: 24 September 1999

Abstract A simple and rapid procedure for the calibrationless determination of trace concentrations of As(III) and total As in contaminated water samples is presented. Arsenic is preconcentrated as As(III) in a flow-through cell with a gold plated porous electrode and is then stripped anodically by a constant current. The stripping chronopotentiogram is registered and evaluated. The As concentration is calculated directly from the combined Faraday's laws. The total As content was determined after converting all As species to As(III) by microwave-assisted reduction with hydrazine hydrochloride in a closed vessel. The detection limit was found to be 0.15 μg/L and the linear response range was 0.5 to 10 000 μg/L. Tap water, surface water, and waste water samples were analyzed.

Introduction

There is a continuously growing demand for analytical methods which allow the determination of the arsenic species at trace levels in environmental and biological samples. Spectroscopic and electrochemical methods have mostly been used for the determination of total arsenic as well as for some selected species. The most toxic form of arsenic is As(III) which is virtually the only electrochemically active form. The more stable pentavalent As and the organic derivatives cannot be determined directly by electroanalytical methods [1].

Arsenic has been determined by several electroanalytical techniques, and stripping voltammetric techniques have mostly been used. Both anodic stripping voltammetry (ASV) mostly with gold or gold plated electrodes [2–9], as well as cathodic stripping voltammetry (CSV) with mercury or mercury film electrodes [10–15] have been used. Since As(III) is the species determined by voltammetric techniques, the other arsenic species can only be determined if they are converted As(III) prior to the analysis. Digestion procedures for the removal of the organic matrix can be used followed by a chemical reduction of As(V) to As(III) [16–26]. These procedures are tedious and there is a danger for losses of the more volatile As(III) species during the digestion/reduction steps. By digestion and reduction carried out in closed vessels these errors can be minimized and the procedure simplified significantly.

The aim of this paper is to show the utility and limitations of flow-through stripping coulometry for the determination of trace concentrations of arsenic in water samples. The utility of the method for the calibrationless determination of "typical" electrochemically active elements such as Zn, Cd, Pb, Cu, Hg and Mn has recently been documented [27–30]. The method is based on the preconcentration/stripping approach but, unlike the voltammetric techniques, the treated sample volume is electrolyzed as a whole, i.e. the analyte species in the sample solution undergo a complete electrodeposition followed by their stripping through the use of constant current. Hence, the combined Faraday's laws can be used for signal evaluation:

$$c = Q_{strip}/(R\ z\ F\ V_{sample}) \quad (1)$$

Here R denotes the electrochemical recovery, z the charge number corresponding to the stripping process, F is the Faraday constant and V_{sample} is the sample volume. The electrical charge Q_{strip} consumed for the stripping of the deposited species is obtained from the stripping current I_{strip} and the duration for the stripping τ for the corresponding element (chronopotentiometric transition time). For a complete electrochemical deposition and dissolution of the analyte species, R equals unity and Eq. (1) is reduced to the following simple equation:

$$c = I_{strip}\ \tau/(z\ F\ V_{sample}) \quad (2)$$

The main problems to be solved are the elucidation of the stoichiometry of the electrode reactions and the procedure for sample treatment facilitating the assessment both of the As(III) species and total arsenic.

L'. Jurica · A. Manová · J. Dzurov · E. Beinrohr ✉)
Department of Analytical Chemistry,
Slovak Technical University, SK-812 37 Bratislava, Slovakia

J. A. C. Broekaert
Institute of Analytical Chemsitry, University of Leipzig,
Linnéstr. 3, 04103 Leipzig, Germany

Experimental

Apparatus

An automatic flow-through coulometer/voltammeter EcaFlow Model 120 equipped with a flow-through cell EcaCell Type 353 was used in all experiments (all from ISTRAN Ltd, Bratislava, Slovakia). The cell contained a disposable porous working electrode E53 (ISTRAN Ltd.; Bratislava, Slovakia), a Pt wire auxiliary electrode and an Ag/AgCl reference electrode. The flow chart diagram of the instrument and its operational principle were described earlier [29]. Additionally, the system facilitated an automatic calibration by making use of the standard addition technique. The aspirated sample solution was automatically segmented and mixed with the carrier electrolyte. Flow rates of 2.5 to 3.0 ml/min were used throughout the experiment. The operational parameters of the instrument are listed in Table 1. The samples were digested in closed quartz vessels of 30 mL volume by making use of the microwave.assisted digestion system PMD (Anton Paar, Austria). Control measurements were performed with the aid of a laboratory-made continuous hydride generation/AAS system using a PE 5000 AAS spectrometer (Perkin Elmer Co.).

Reagents and solutions

Arsenic stock solution, containing 1.000 g/L As(III), was prepared by dissolving 1.320 g of analytical grade arsenic trioxide (Lachema Brno, Czech Republic) in a minimum amount of 20% (w/v) potassium hydroxide solution. The solution was acidified to pH 2.0 with 20% (v/v) hydrochloric acid and diluted to 1 L with deionized water. Working standard solutions were freshly prepared from the stock solution daily. As(V) standard stock solution containing 1.000 g/L As(V) was prepared by dissolving 4.146 g of $Na_2HAsO_4 \cdot 7H_2O$ in 1 L of deionized water. Standard stock solutions of Pb, Cu, Bi, Sb and Hg containing 1.000 g/L of the corresponding metals (SMU Bratislava, Slovakia) were used. All other reagents were A. R. grade. The carrier electrolyte for the coulometric measurements contained 0.1 mol/L and 0.001 mol/L sodium chloride and hydrochloric acid, respectively. The Au plating solution contained 0.0002 mol/L and 0.02 mol/L $HAuCl_4$ and HCl, respectively. The certified water reference sample MZ 1231 was obtained from CHEMMEA, Ltd. Bratislava, Slovakia. The soil sample P64A was analyzed by ICP OES and contained 0.12% of As. The soil extract was prepared by mixing 10 g of the soil sample with 100 mL of distilled water during 24 h.

Table 1 Instrumental parameters

Parameter	Value
Deposition current	–3.0 mA
Starting potential	–400 mV
End potential	800 mV
Stripping current	200 µA
Stripping mode	Stopped-flow
Sample volume	1.0 mL
Flow rate	2.8 mL/min

Procedure

Sampling and preservation of water samples. 250 mL polyethylene bottles were used for sample storage. Water samples were preserved by adding 0.25 g of hydrazinium chloride per 100 mL of water, at the collection site.

Plating of the electrode. 25 mL of the plating solution was pumped at a flow rate of 2.5 mL/min through the porous electrode cell which is set at a constant current of –2 mA. Then the current was enhanced to –3.5 mA and the plating process was repeated. The system was then rinsed with the electrolyte solution.

Determination of As(III). To 10 mL of water sample 0.1 mL of conc. hydrochloric acid was added and the solution was immediately analyzed at the experimental parameters listed in Table 1.

Determination of total As. 4 mL of the sample solution were transferred into the quartz digestion vessel of the microwave-assited digestion system and 0.5 mL of conc. HCl as well as 0.1 g of hydrazinium chloride were added. The solution was digested during 5 min at the power level No. 6. After cooling down the solution was transferred into a 10 mL volumetric flask and the volume was adjusted to 10 mL with deionized water. The solution was immediately analyzed at the experimental parameters given above.

Results and discussion

It was found that it was not possible to determine As by cathodic stripping coulometry from a mercury coated porous electrode. The reason was simple: The acidic sample and the carrier electrolyte gave rise to high currents in the cathodic range and no signal for the reduction of the

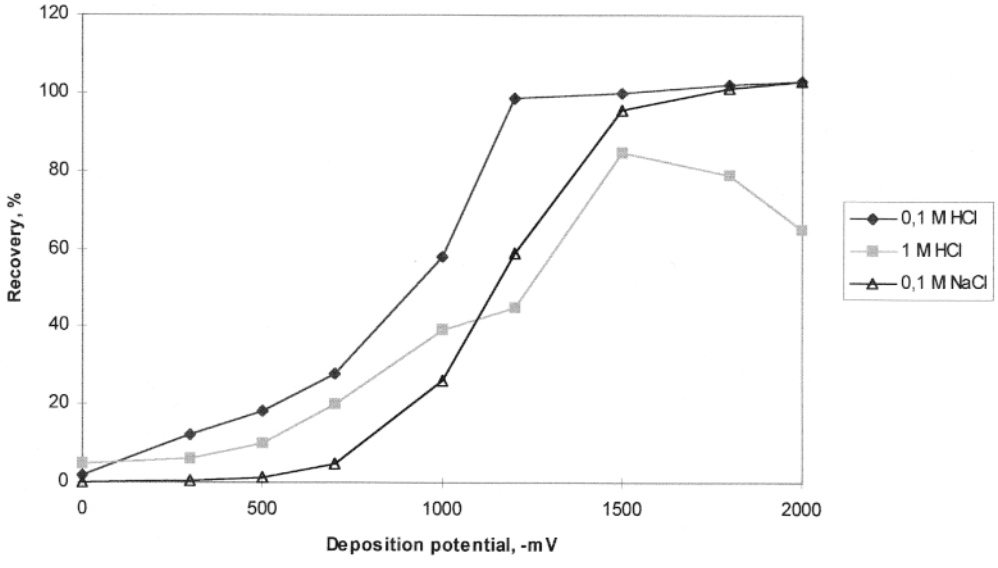


Fig. 1 Influence of the deposition potential on the recovery of 12.3 µg/l As(III) in 0.1 mol/L HCl, 1.0 mol/L HCl and 0.1 mol/l NaCl. Dissolution current: 200 µA, sample volume 1.0 mL. Potentiostatic deposition

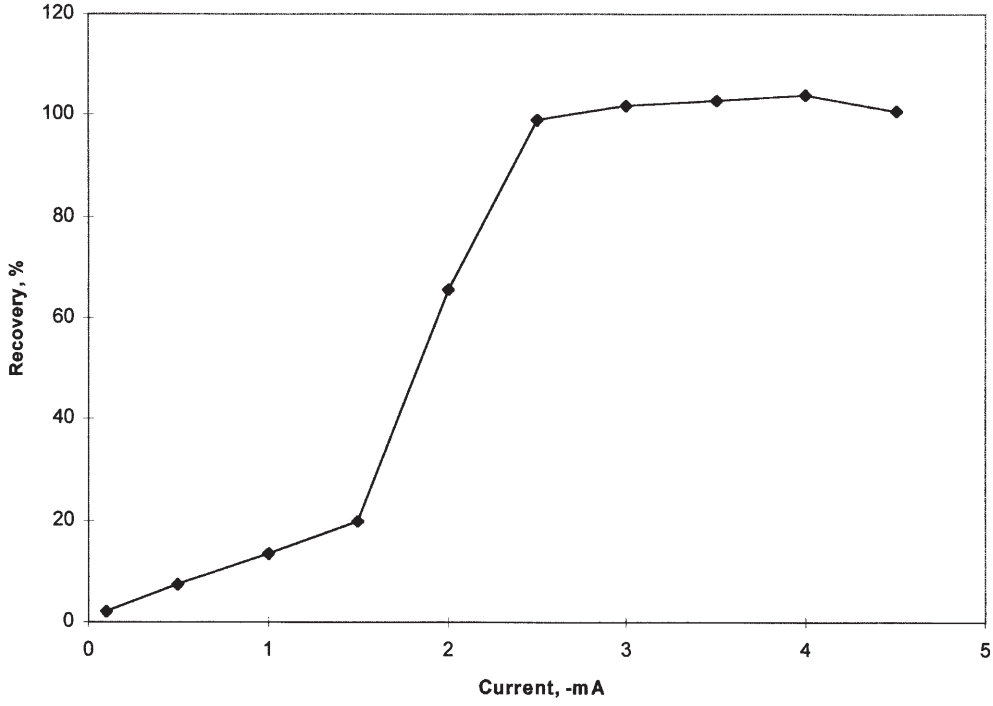


Fig. 2 Influcence of the deposition current on the recovery of 12.3 µg/L As(III) in 0.1 mol/L HCl. Dissolution current: 200µA, sample volume 1.0 mL. Galvanostatic deposition

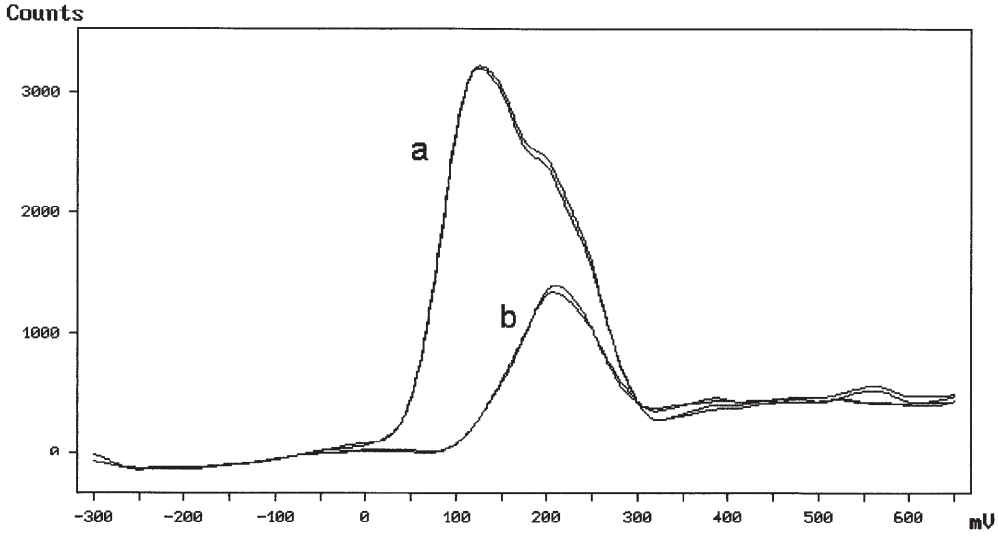


Fig. 3 Stripping signals of As at stopped-flow *(a)* and flow *(b)* stripping, respectively. As(III) concentration: 12.3 µg/L, sample volume: 1.0 mL, deposition current: –3.0 mA, dissolution current: 200 µA

deposited As could be observed. Therefore, it was attempted to perform anodic stripping from a gold plated porous electrode and this turned out to be useful.

Plating with Au

The electrochemical recovery and the electrode lifetime were found to significantly depend on the character of the gold plating on the porous electrode. The plating procedure should ensure a coating of the whole bulk of the porous electrode and the formation of a bright-yellow coating. Plating from Au solutions with concentrations above 0.001 mol/L in Au(III) produced red or brown coatings and were found to give high background currents. Only working with dilute Au(III) solutions in 0.01 to 0.05 mol/L HCl solutions was found to be suitable. The most uniform coating was obtained when the plating was carried out with a plating solution of 0.0002 mol/L and 0.02 mol/L in Au(III) and HCl, respectively. Both potentiostatic and galvanostatic platings were tested, the latter providing coatings with higher lifetimes. The optimum plating currents were found to be –2 to –4 mA at a flow rate of 2.5 mL/min.

Deposition

The deposition of As(III) species on the gold plated porous electrode can be performed potentiostatically or

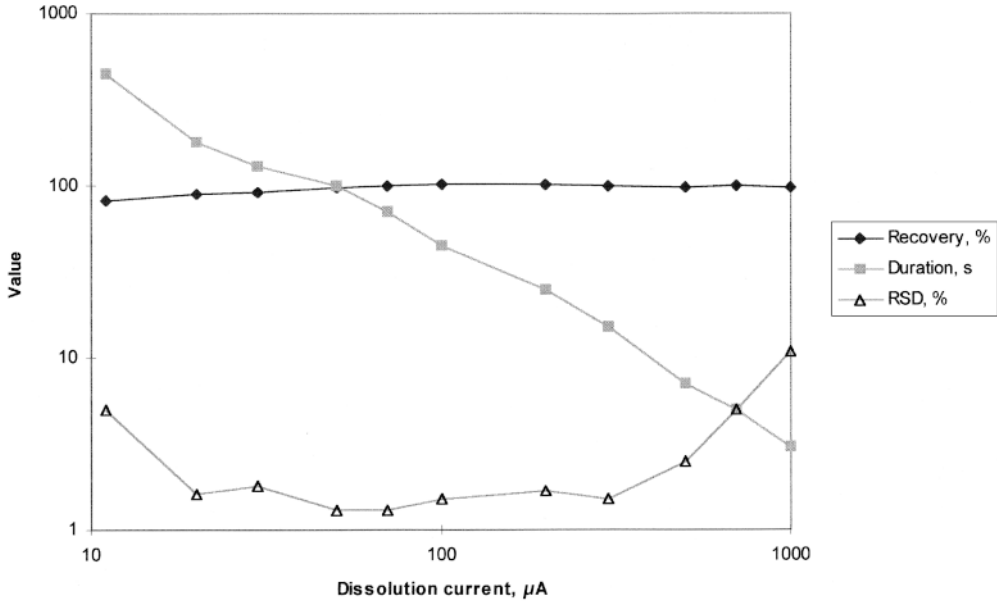
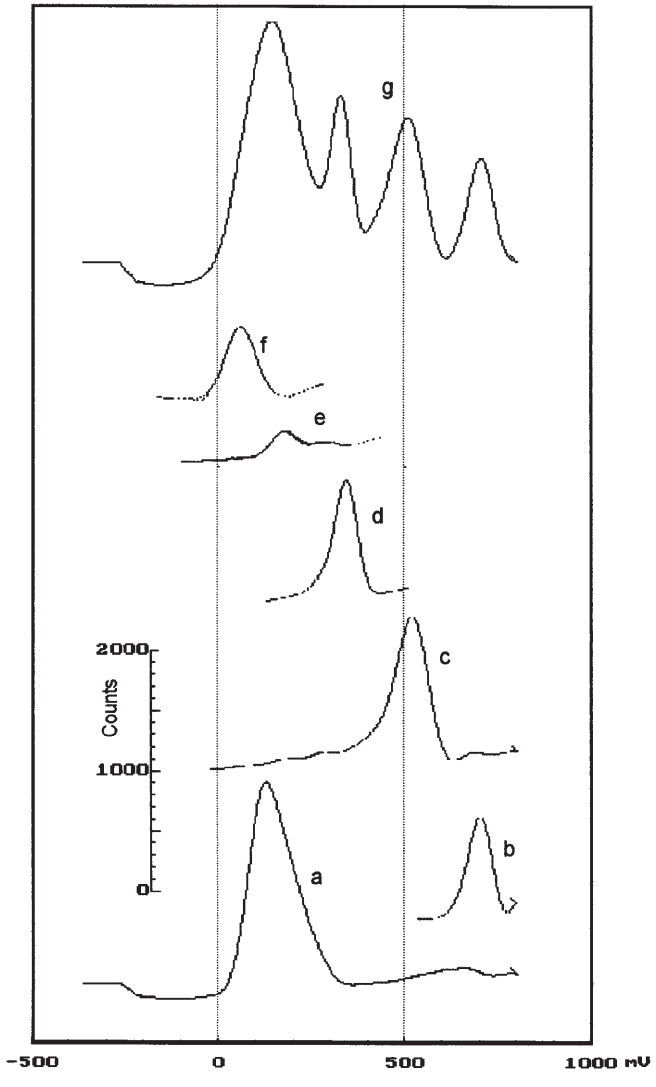


Fig. 4 Dependence of the recovery, stripping time and relative standard deviation (RSD) on the stripping current. As(III) concentrations: 12.3 μg/L, sample volume: 1.0 mL, deposition current: –3.0 mA, dissolution current: 200 μA



galvanostatically. The former leads to the higher selectivity unless the sample matrix differs significantly from that of the carrier electrolyte. The latter offers robustness when analyzing samples with different sample matrices, pH values and conductivities.

The deposition of As starts at potentials of –200 mV and is virtually complete at potentials of –1200 mV (Fig. 1). The use of more negative potentials does not further improve the recovery but deteriorates the reproducibility as the result of an enhanced hydrogen evolution in the pores of the electrode. Similarly, the use of high acid concentration deteriorates the recovery due to a formation of hydrogen gas. For neutral sample solutions deposition potentials of at least –1500 mV should be used (Fig. 1).

The galvanostatic deposition ensures the realization of high recoveries at deposition currents which are more negative than –1.5 mA (Fig. 2) and the deposition is complete at currents more negative than –2.5 mA. Mostly a deposition current of –3 mA was used in the experiments.

Stripping

As(III) species are probably deposited on the gold plated electrode as elemental arsenic. The anodic stripping process could produce As(I) as well as As(III) species, i.e. the stoichiometry may be ambiguous. The effective charge number can be obtained from Eq.(1) by analyzing standard solutions of As(III). When stripping the deposit to a flowing carrier electrolyte, effective charge numbers of about 1.0 were observed. However, after stopping the flow

Fig. 5 Stripping chronopotentiograms for As *(a)*, Hg *(b)*, Cu *(c)*, Bi *(d)*, Sb *(e)*, Pb *(f)* and their mixture *(g)*. Concentration of all elements: 50 μg/L. Deposition current: –3 mA, dissolution current: 200 μA, sample volume: 1mL

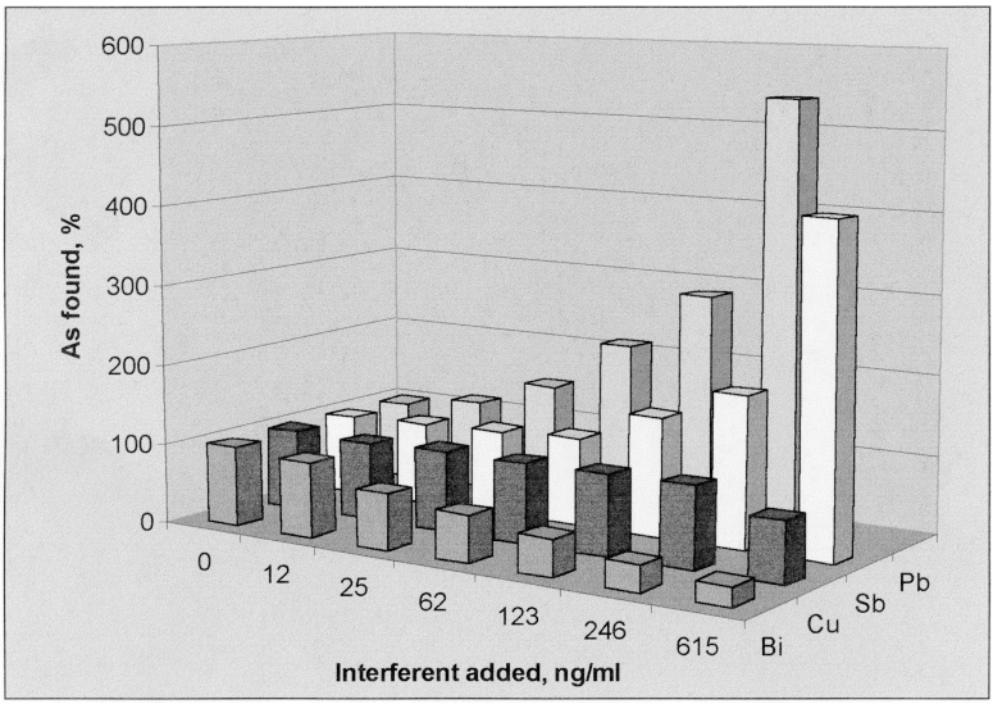


Fig. 6 Influence of the concentrations of Bi, Cu, Sb and Pb on the values found for As. Arsenic (III) given: 12.3 μg/L, deposition current: –3 mA, dissolution current: 200 μA, sample volume: 1 mL

during stripping, effective charge numbers of about 3.0 were observed. The stripping signal was non-symmetrical at the stopped-flow stripping indicating a complex oxidation mechanism (Fig. 3). Hence, the arsenic deposited at the electrode surface is probably oxidized by the stripping current first to As(I) species first and then to As(III). The flowing carrier electrolyte might wash out the As(I) species from the electrode bulk faster than a complete oxidation to As(III) could take place and accordingly, a lower charge number is virtually found. Owing to this observation the stripping process was performed after stopping the flow and an effective charge number of 3.0 was used in Eq. (1) for obtaining the arsenic concentrations.

As Eq. (2) implies, the stripping current significantly influences the sensitivity of the measurement. The smaller the dissolution current, the longer is the transition time and hence the higher is the sensitivity. However, the electrochemical yield and the repeatability of the measurements are influenced by the stripping current as well (Fig. 4). The optimum dissolution current was found to be in the range of 100 to 300 μA. Smaller dissolution currents ensure higher signal sensitivity, but the background signal both enhances and prolongs the stripping process significantly. The stripping process only takes a few seconds at stripping currents above 500 μA, but the signal-to-noise ratio enhances significantly and the precision of the measurements decreases. However, the recovery was found to be complete at stripping currents ranging from 30 to 1000 μA.

Influence of metals

There are a few metal ions which codeposit with As, giving stripping peaks under the above conditions. In Fig. 5 some stripping signals of different metals of the same concentration and deposited under optimum conditions for As are shown. It is evident, that mercury and copper will not interfere, but serious interferences can be expected from Sb and Pb. The signal for a sample containing all these elements confirmed this expectation (Fig. 5, curve g). The stripping peaks of As, Pb and Sb coalesced completely, the peak of Bi partly was separated and slightly interfered.

The influence of Bi, Cu, Pb and Sb on the signal of As is shown in Fig. 6. Copper interferes at concentrations above 500 μg/L, Bi already at 10 μg/L. The presence of both metals leads to the depression of the signal of As, which can be assigned to a partial coalescence of their stripping peaks. Antimony and lead enhance the signal of As. However, the occurrence of Sb and Bi species in water samples is less probable owing to an easy hydrolysis of these metal ions. The interference of Pb can be compensated for by measuring the Pb signal after oxidizing As(III) to electro-inactive As(V) species with hydrogen peroxide.

Figures of merit

An intrinsic feature of flow-through stripping coulometry is the broad linear concentration range. This results from the measurement principle, where the dissolution time is measured and this is virtually unlimited as well as from the simple adjustment of the sample volume. Indeed, small sample volumes can be used for high analyte concentrations and vice versa. The only limitation is the electrochemical conversion efficiency, both for the deposition and stripping steps.

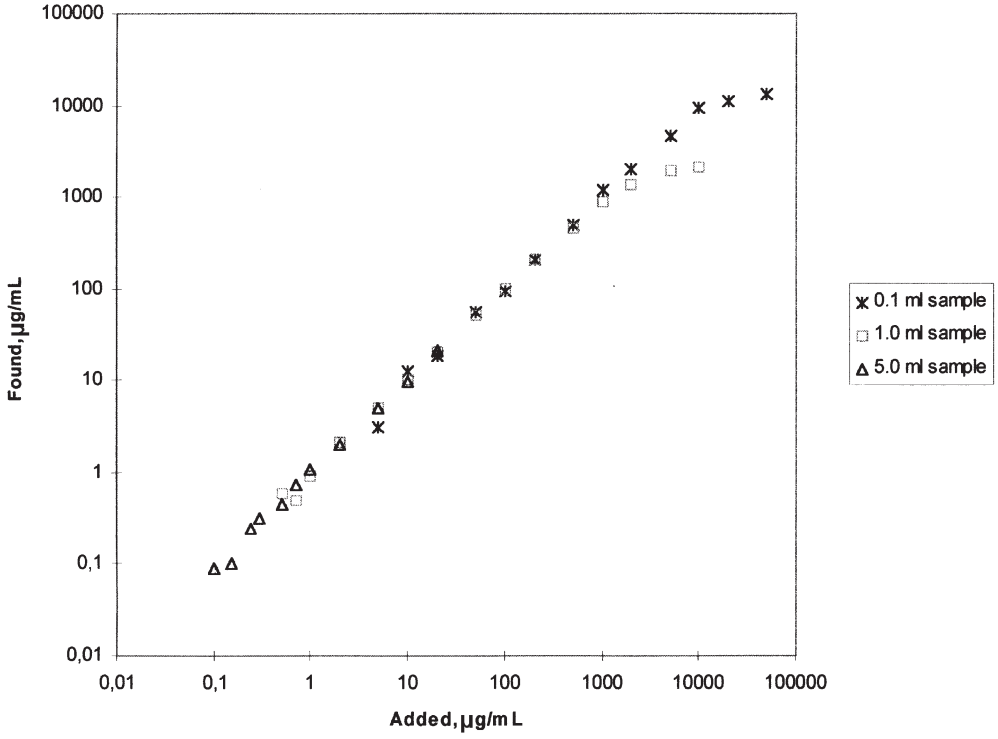


Fig. 7 Recovery test for As. Deposition current: –3 mA, dissolution current: 200 µA, sample volume: 0.1, 1.0 and 5.0 mL

In Fig. 7 the response range for the measurement of various As concentrations in 5.0 mL, 1.0 mL and 0.1 mL sample volumes is shown. The relative standard deviation (RSD) increases to about 40% at an As(III) concentration of 0.1 µg/L. These data imply that As can be determined in a concentration range of about 0.2 µg/L to 20 mg/L, i.e. over 5 orders of magnitude. The figures of merit are collected in Table 2.

As the above data imply, the method enables the determination of As at concentrations up to 10 mg/L without a dilution of the sample solution. However, after analyzing a sample with high As concentration, some memory effect could occur. Indeed, after analyzing a solution with 10 mg/L of As, only the first two measurements indicate some carry-over and the 3rd one already gives a result near to the detection limit (about 0.2 µg/L). Hence, owing to the built-in self-cleaning property of the flow-through analyzer, no significant memory effects are to be expected.

Table 2 Analytical figures of merit

Parameter	Value
Blank (0.1 mol/L HCl)[a]	0.03 µg/L
Limit of detection (3 s)[a]	0.15 µg/L
Limit of determination (10 s)[a]	0.5 µg/L
Linear response range (5.0 mL sample volume)	(0.5–100) µg/L
Linear response range (1.0 mL sample volume)	(1.0–1 000) µg/L
Linear response range (0.1 mL sample volume)	(9.0–10 000) µg/L
RSD (20.0 µg/L 1.0 mL sample volume, 10 analyses)	3.5 %
Analysis time (1.0 mL sample volume)	3 min

[a] Valid vor 5.0 mL sample volume

Determination of total As

Only the As(III) species, which are in the form of H_3AsO_3, or its salts can be deposited under the conditions given above. All other As species, especially those present as As(V) have to be converted to As(III) prior to the measurement step. Various procedures have been used to reduce As(V), such as a reduction with potassium iodide, ascorbic acid, sodium sulfite, L-cystein, etc. [16–26]. All these procedures are time consuming and need reaction times of up to one hour even at elevated temperatures. Moreover, at an increase of the reaction temperature some losses of As(III) species may occur as a result of the evaporation as volatile chlorides.

A reasonable solution for the acceleration of the reduction rate without enhancing the risks for losses of volatile As species lies in performing a reduction step in the closed vessel of the microwave-assisted digestion system. In the choice of the reducing agent we were limited to L-cystein, hydroxylamine and hydrazine. Potassium iodide and ascorbic acid interfered during the anodic stripping measurements as they significantly enhance the background signal. The best results were achieved with hydrazine hydrochloride. The digestion time required to completely convert As(V) to As(III) was 4 min. The cool-down time was another 5 min, and accordingly, the reduction can be performed within 10 min. The resulting solution can be analyzed directly for the total As content in the sample.

Table 3 Analyses of water samples

Sample	Reference value µg/L	As(III) found µg/L	As(total) found µg/L	Standard addition µg/L	Found µg/L
Reference water MZ 1231	21.0 ± 2.0[a]	0.55 ± 0.10	21.9 ± 1.1	–	–
Tap water	< 5.0[b]	< 0.15	< 0.3	8.0	8.35 ± 0.14
Mineral water (Salvator)	< 5.0[b]	< 0.15	< 0.3	10.0	10.10 ± 0.12
Surface water (Kuchajda sea)	< 5.0[b]	< 0.15	< 0.3	10.0	10.47 ± 0.72
Sea water (Adriatic sea)	< 5.0[b]	< 0.15	< 0.3	10.0	10.27 ± 0.53
Waster water I (Chlor-alkali plant)	< 5.0[b]	< 0.15	< 0.3	10.0	9.72 ± 0.51
Waste water II (Chlor-alkali-plant)	25.2 ± 6.2[b]	< 0.15	24.6 ± 4.8	–	–
Soil extract, P64A	124 ± 10.2[b]	< 0.15	114 ± 9.4	–	–

[a] Reference value
[b] Hydride generation ASS

Real samples

Several water samples were analyzed by the elaborated procedure including a reference material (Table 3). In all samples, if any, mainly As(V) species were found. However, when spiking the samples with As(III), complete recoveries were found, indicating the potential use of the method for the direct determination of As(III) species.

Conclusion

The method elaborated enables a reliable and rapid determination of As(III) and total arsenic in water samples at concentrations above 0.5 µg/L. The extremely broad dynamic range facilitates the analysis of contaminated water samples with high As concentrations as well. The microwave-assisted reduction was found to significantly accelerate the analytical procedure. The procedure can easily be adapted to analyses of other types of samples such as geological, biological and industrial materials.

Acknowledgement The work was supported by The Slovak Grant Agency, Slovakia, Grant No 1/6103/99 and The Volkswagen Foundation, Germany, through the I/F1 023 Collaboration Research Grant.

References

1. Wang J (1985) Stripping Analysis, VCH Publishers Inc, Durfield Beach, Florida
2. Forberg G, Olaughlin JW, Megargle RG (1979) Anal Chem 47: 1986
3. Hamilton TW, Ellis J, Florence TM (1980) Anal Chim Acta 119:225
4. Leung PC, Subramanian KS, Meranger JC (1982) Talanta, 29: 515
5. Wang J, Greene B (1983) J Electroanal Chem Interfacial Electrochem 154:261
6. Lexa J, Štulik K (1983) Talanta 30:845
7. Pretty JR, Blubaugh EA, Caruso JA (1993) Anal Chem 65: 3396
8. Viltchinskaia EA, Zeigman LL, Garcia DM, Santos PF (1997) Electroanalysis 9:633
9. Sun YC, Mierzwa J, Yang MH (1997) Talanta 44:1379
10. Henze G, Joshi AP, Neeb R (1980) Fresenius Z Anal Chem 300: 267
11. Sadana RS (1983) Anal Chem 55:304
12. Greulach U, Henze G (1995) Anal Chim Acta 306:217
13. Equiarte I, Alonso RM, Jimenez RM (1996) Analyst 121:1835
14. Li H, Smart RB (1996) Anal Chim Acta 325:25
15. Henze G, Wagner W, Sander S (1997) Fresenius J Anal Chem 358:741
16. Forberg G, Olaughlin JW, Megargle RG (1979) Anal Chem 47: 1986
17. Hamilton TW, Ellis J, Florence TM (1980) Anal Chim Acta 119:225
18. Bodewig FG, Valenta P, Nürnberg HW (1982) Fresenius Z Anal Chem 311:198
19. Sadana RS (1983) Anal Chem 55:304
20. Kotoucek M, Vasicova J, Ruzicka J (1993) Mikrochim Acta 111:55
21. Mrzliak RI, Bond AM, Cardwell TJ (1994) Analyst 119:1051
22. Zima J, Van den Berg CMG (1994) Anal Chim Acta 289:291
23. Equiarte I, Alonso RM, Jimenez RM (1996) Analyst 121:1835
24. Schickling C, Yang J, Broeakaert JAC (1996) J Anal Atom Spectrom 11:739
25. Sun YC, Mierzwa J, Yang MH (1997) Talanta 44:1379
26. Bubnik J (1997) Chem Listy 91:200
27. Beinrohr E, Chémi P, Rojas FJ, Hofbauerová H (1994) Analyst 119:1355
28. Beinrohr E, Cakrt M, Dzurov J, Kottas P, Kozakava E (1996) Fresenius J Anal Chem 356:253
29. Beinrohr E, Dzurov J, Annus J, Broekaert JAC (1998) Fresenius J Anal Chem 362:201
30. Beinrohr E, Jurica L, Cakrt M, Dzurov J, Broekaert JAC, Electroanalysis (in press)