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Influence of the Transport Conditions on Determination of Trace Arsenic by Cathodic Stripping Voltammetry*

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The cathodic stripping voltammetry has been used to study arsenic(III) and its determination in presence of copper. Dependence of stripping peak on convective transport during the deposition step for the system seems to be unique and its character indicates that stirring rate is an important factor and thus it should be carefully optimized. The optimal stirring rate depends on cell and stirring bar geometry, electrode size, copper concentration and deposition time. The existing in literature ambigouity on selenium influence on arsenic peak current is discussed and explained by taking into consideration the observed dependences. Detection limit for As(III) as low as 0.4 nM (0.03 ppb) at 50 s deposition time could be obtained when optimal stirring conditions were applied.

Key words: arsenic, cathodic stripping voltammetry, hydrodynamics conditions

Arsenic is an element which toxic and carcinogenic properties are widely known. Arsenic toxicity depends on its speciation *i.e.* compounds of As(III) are much more toxic than compounds of As(V). Inorganic arsenic is more toxic than organic. Very low concentration limits of arsenic permissible in environment, drinking water, food and other products cause that analytical method which enables speciation at ultratrace level is required. Methods such as inductively coupled plasma – mass spectrometry (ICP-MS), graphite furnace atomic absorption spectrometry (GFAAS) give favorable detection limits for elemental analysis, but fail in speciation. Cathodic stripping voltammetric method of arsenic(III) determination in presence of copper which has been introduced by Henze *et al.* [1] seems to be suitable for this task.

Other voltammetric methods for arsenic determination have been also used. Anodic stripping voltammetric methods (ASV) using gold, graphite, platinum and copper-coated glassy-carbon electrodes [2,3,4] or platinum rotating disk electrode [5] have been applied. Chiang *et al.* [6] presented the adsorptive stripping voltammetric determination of arsenic with 2,5-dimercapto-1,3,4-thiadiazole (DMTD). Another solution was described by Zima and van den Berg [7]. They described the arsenic de-

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[*] Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.
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termination by adsorption of a complex of arsenic(III) with pyrrolidine dithiocarbamate in weakly acidic conditions.

Cathodic stripping voltammetry (CSV) [1] the arsenic(III) determination even below 1 nM in presence of copper. Although the role of the copper ions was not completely explained one may assume that copper amalgam formed on the surface of the electrode may react with the arsenic ions (III). As a result the copper arsenide is formed. The latter is cathodically reduced to the arsenous hydride (AsH_3) [1,8]. Arsenic determination in those conditions depends on the number of factors such as: the copper concentration, time and the deposition potential, the concentration of supporting electrolyte and its pH. They were studied by Kowalska and Golimowski [9,10]. Electrochemistry of the system has been studied by Li and Smart [5]. They attempted to explain processes performed at the mercury electrode in 2M hydrochloric acid containing copper ions (II).

The use of voltammetry for arsenic determination seems to be very promising because of its ability to perform speciation analysis. Arsenic(V) is considered to be electrochemically inactive. In order to determine arsenic(V) the chemical reduction to As(III) must be performed. Several substances are used as an arsenic(V) reducing agents. Among them are ascorbic acid and potassium iodide [12], sodium thiosulfate [13], sodium sulfite [14,15], hydrazine [11], aqueous sulfur dioxide [16] and sodium bisulfite [17]. Other voltammetric method of arsenic(V) determination utilize D-mannitol [18,19].

Voltammetric stripping analysis is an analytical technique that utilizes a bulk electrolytic step to preconcentrate the analyte from the sample solution into or onto the working electrode. The preconcentration step is followed by an electrochemical measurement of the concentrated analyte. The combination of a preconcentration step with advanced measurement procedures generates the extremely favorable signal-to-background ratio characteristic for voltammetric stripping analysis. The efficiency of the deposition step in stripping analysis is increased by convective transport of the metal ions to the surface of the working electrode. The convective transport is achieved by stirring the solution, its flow or by using electrode rotation [20,21]. The sensitivity and precision of the determination strongly depend on the hydrodynamics which influence both the amount of the analyte delivered to the surface of the electrode during the deposition step and repeatability of the results.

In this work the determination of trace arsenic was carried out using (CSV) at the mercury electrode in presence of copper(II) ions. The experimental parameters, which influence convective transport conditions during deposition step, on the arsenic determination have been studied. The parameters such as stirring rate, type of stirring bar and the positioning of working electrode in voltammetric cell have been studied. On the contrary to other stripping determinations the transport conditions in case of arsenic may significantly decrease sensitivity and worsen detection limit and linearity.

EXPERIMENTAL

Apparatus. Multipurpose Electrochemical Analyzer EA9 (model M161) with the electrode stand (Controlled Growth Mercury Drop Electrode – CGMDE) [22] M164 (both MTM – Anko Poland) were used for all voltammetric measurements. A standard three-electrode cell consisted of CGMDE as working, Ag/AgCl in 3M KCl with additional electrolytic key filled with 3M KCl (Mineral Poland) as reference and platinum wire as an auxiliary electrodes. Several types of magnetic stirrers were used in experiments (Sigma-Aldrich) egg-shaped, polygon, spinplus, flea-micro, spinbar. The voltammetric cell and its geometry is shown in Fig. 1. The vertical position of the electrode has been changed but in most experiments Δh – a distance between the electrode tip and the magnetic stirrer bar was adjusted to 3 cm. Voltammograms were recorded, interpreted and stored by EAGRAPH (MTM-Anko, Poland) software.

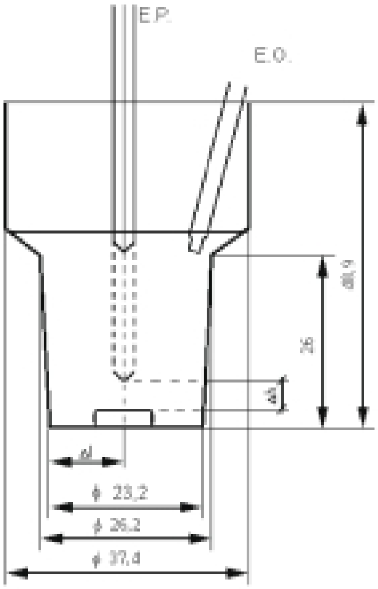

Figure 1. Schematic drawing of the voltammetric cell.

Reagents. Sodium arsenide (Merck) and sodium selenite (Sigma) both of analytical grade, $CuCl_2 \cdot 2H_2O$ of analytical grade (POCh, Poland) were used as delivered. Cadmium standard solution of 0.1 M was prepared by dissolution of 5N metal shot in nitric acid (Suprapur, Merck). HCl has been selected from several high purity products and production series to have extremely low arsenic and selenium contents (below 0.3 nM and 0.1 nM). The recently used HCl was produced by Cheman, Poland (serial number 18/06/03). All solutions were prepared with double-distilled water.

Procedure. The day before the measurements the electrodes and voltammetric cell were conditioned in double-distilled water and then, immediately before the measurements the electrodes and voltammetric cell were rinsed with distilled water. 10 mL of 2 M hydrochloric acid was poured into the voltammetric cell, than $CuCl_2$ was added to obtain final concentration 0.75 mM. The solution was stirred intensively for 30 min. The whole procedure was repeated twice. The same solution was introduced to voltammetric cell and afterwards purged with argon gas for at least 15 min. Finally $50\,\mu L$ of $1 \cdot 10^{-6}$ M As(III) was added (final concentration $5 \cdot 10^{-9}$ M) for optimization study.

All measurements were made using cathodic stripping voltammetry in differential pulse mode during the stripping step. The following parameters were adjusted: pulse amplitude –50 mV; step height 4 mV; probing and waiting time 20 ms; deposition potential –400 mV; resting time 5 s. The deposition time and stirring rate have been varied depending on experiment. The voltammograms were recorded in the potential range of –500 to –860 mV.

RESULTS AND DISCUSSION

Influence of stirring rate during deposition step on As(III) DPCSV peak current. Analyte as a metal or its insoluble compound was gathered in/or on working electrode during deposition step in stripping techniques such as anodic, cathodic and adsorptive stripping voltammetry. Convective transport arising from the stirring was applied to intensify the process. Thus current during deposition may be expressed as [23,24]:

$$I_L = 4\pi r_0 nFD_{Ox}c^0_{Ox} + knr_0^2 D_{Ox}^{2/3} c^0_{Ox} f^{1/2} \tag{1}$$

Where k is a constant and f is the stirring rate. Thus the amount of deposited analyte and resulting stripping peak current should be proportional to square root of stirring rate. Such dependence is observed usually in stripping techniques. Even in case of Se(IV)–Cu(II) layout very similar to As(III)–Cu(II) dependence on stirring rate is different (curves a and b in Fig. 2, respectively). For low stirring rates current increases, but above certain value of stirring rate it drops nearly to zero. The peak height varies simultaneously with peak potential in both cases. In case of selenium peak potential

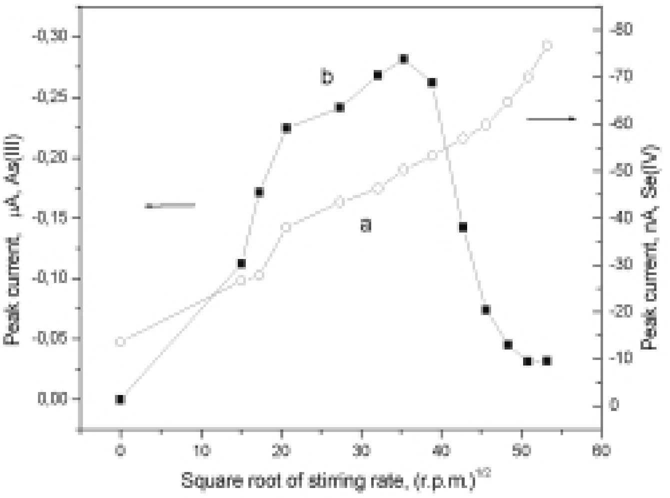

Figure 2. Dependence of stripping peak height on square root of stirring rate for a) selenium (100 nM Se(IV), 0.75 mM $CuCl_2$ in 1M HCl); b) arsenic (5 nM As(III), 0.75 mM $CuCl_2$ in 2M HCl). In both cases deposition time was 50 s.

changes monotonically from –554 mV at low stirring rate to –600 mV at high stirring rate. In case of arsenic the effect starts from –708 mV for low stirring rate, reaches extreme value of –724 mV at 1200 r.p.m. and goes back to –716 mV for high stirring rates.

Such dependence of arsenic peak current on stirring rate causes that other parameters a distance between stirring bar and electrode tip influencing hydrodynamic conditions at the working electrode may also influence sensitivity. This parameter is electrode tip positioning *versus* stirring bar (vertical distance – Δh). Also shape of magnetic stirrer bar influences the intensity of convection to electrode. Relative changes of arsenic peak current with axial position of the electrode tip for different types of stirring bars are shown in Fig. 3A. When the electrode tip is moved back from the stirring bar a significant decrease of peak current is observed in most cases. Cadmium stripping current, which exhibits close to theoretic dependence on stirring rate, is nearly proportional to axial position (Fig. 3B).

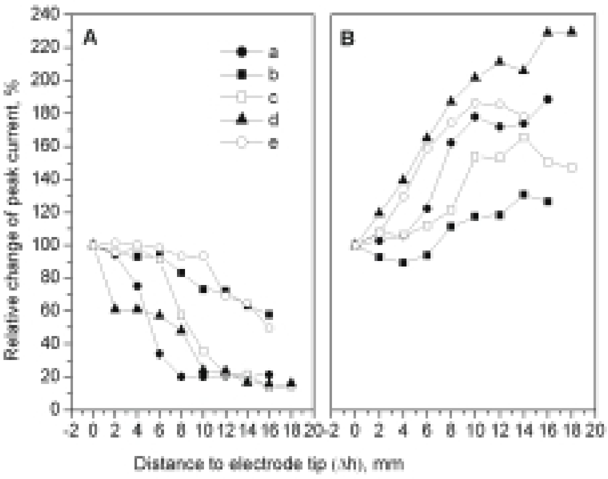

Figure 3. Relative changes of the stripping peak current *versus* axial position of the electrode tip. A – arsenic (5 nM As(III), 0.75 mM $CuCl_2$ in 2M HCl, deposition time 50 s); B – cadmium (0.2 μM Cd(II) in 0.5 M KCl, deposition time 30 s). In both cases stirring rate was optimal for each stirrer bar: a – spinplus, b – egg shaped, c – spinbar, d – flea micro, e – polygon.

This effect may be attributed to more intensive convection in upper layers egg-shaped, spinbar, spinplus, polygon and flea-micro which gives the highest intensity. Similar dependence may be observed for radial position of the electrode tip. Shifting electrode from the symmetry axis of the cell towards the wall causes increase of the convection and decrease of the arsenic stripping peak.

Influence of the drop size on DPCSV As(III) peak current. For constant transport geometry the peak current is proportional to the electrode surface area. The dependence is theoretically known from Ilkovic, Cottrel, Bauer or Randles-Sevcik equations. For DPCSV determination of arsenic such dependence is not linear. Fig. 4

shows dependence of arsenic peak current on electrode surface area. For low stirring rates during deposition step even maximum is observed. What refers to the optimal surface area for particular stirring rate. For example (Fig. 4a) for stirring rate 300 r.p.m. with flea-micro stirring bar the maximum current refers to the drop area of 0.0079 cm^2. At larger and smaller drops lower current is observed.

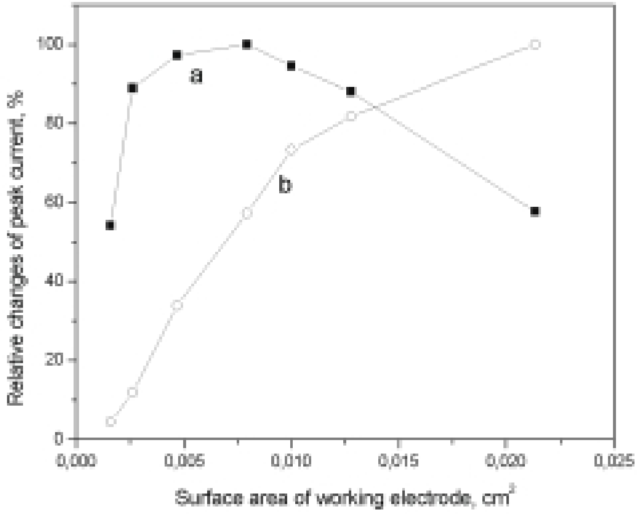

Figure 4. Dependences of arsenic stripping peak current on the electrode surface area for $5 \cdot 10^{-9}$ M As(III) and 0.75 mM $CuCl_2$ in 2M HCl at 300 r.p.m. (curve a) and 640 r.p.m. (curve b), flea micro stirring bar.

If higher stirring rates were applied (Fig. 4b) peak current increases monotonously with electrode surface. However the observed dependence is not linear for the range being investigated.

Considering dependence of arsenic peak current on stirring rate (Fig. 2) it is possible to determine the stirring rate for which the peak current reaches maximum. At each drop size the value of optimal stirring rate depends on electrode surface area. For very small drops of 0.0016 cm^2 optimal stirring rate is 130 r.p.m. For larger drops of 0.0026; 0.0079 and 0.0213 cm^2 optimal stirring rates are 300; 640; 810 r.p.m. respectively. Higher stirring rates are necessary for larger drop area what explains why maximum of dependence peak current *vs*. drop area is observed at low stirring rates.

Influence of copper concentration on optimal conditions of arsenic(III) determination. Concentration of copper in solution in which DPCSV determination of arsenic(III) is performed is a very important factor [11]. The concentration of copper should be relevant to determined concentration range of arsenic. For a given copper concentration optimal stirring rate should be found. Dependence of arsenic(III) peak current on stirring rate during deposition step for different copper concentration is shown in Fig. 5. Optimal stirring rate depends linearly on copper concentration according to regression line as follows:

$$\textit{optimal stirring rate [r.p.m.]} = -3.2 \pm 0.3 \cdot 10^3 C_{Cu}[mM] + 4.2 \pm 0.2 \cdot 10^3 \qquad (2)$$

(correlation coefficient r = –0.9843).

The optimal stirring rate (3000 r.p.m.) for 0.4 mM copper concentration could not have been reached under conditions of this experimental work. Thus, better detection limit and higher sensitivity are possible to obtain if copper concentration is kept as low as possible. Copper concentration influences arsenic(III) peak potential. If optimal stirring rate is used at each copper concentration and 50 s deposition time, the peak potential shifts from –680 mV at 0.15 mM Cu(II) to –724 mV at 1.25 mM Cu(II).

Optimal conditions for the deposition step. For a given solution and cell geometry the amount of arsenic deposited on electrode depends on deposition time and stirring rate. Fig. 6 shows dependencies of arsenic(III) DPCSV peak current on stirring rate for several deposition times. For each deposition time optimal stirring rate may be observed.

The longer deposition time the lower stirring rate is required. The dependence is linear. The regression line for seven different deposition times in range 20–80 s may be presented as:

$$\textit{optimal stirring rate [r.p.m.]} = -16 \pm 2 t_{dep}[s] + 1530 \pm 100 \qquad (3)$$

The correlation coefficient for this relation was r = 0.9684.

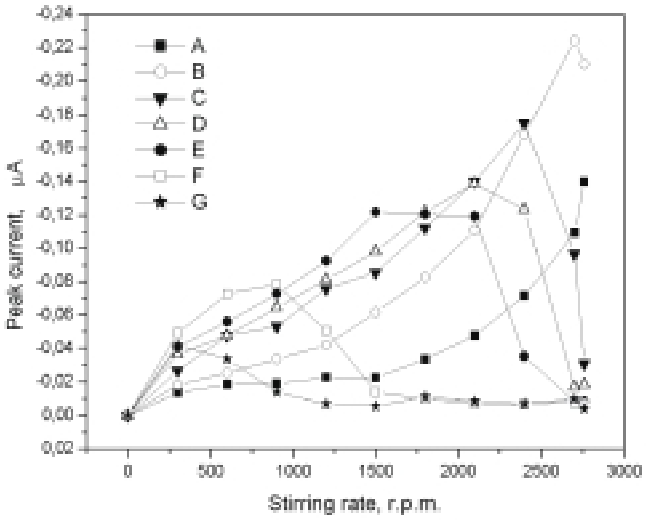

Figure 5. Dependence of arsenic(III) peak current on stirring rate for $5 \cdot 10^{-9}$ M As(III) in 2M HCl at different $CuCl_2$ concentrations: A – 0.4; B – 0.5; C – 0.6; D – 0.65; E – 0.75; F – 1; G – 1.25 deposition time 50 s, spinbar stirring bar.

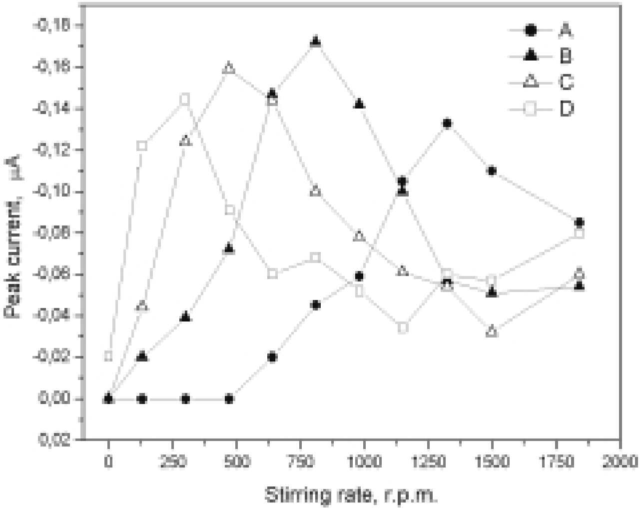

Figure 6. Dependence of DPCSV arsenic(III) peak current on stirring rate for $5 \cdot 10^{-9}$ M As(III) and 0.75 mM $CuCl_2$ in 2M HCl at deposition times: A – 20; B – 40; C – 60; D – 80 s. Flea-micro stirring bar.

If the deposition step is performed with optimal stirring rate for each deposition time, the resulting arsenic peak current is nearly only slightly dependent on deposition time (Fig. 7).

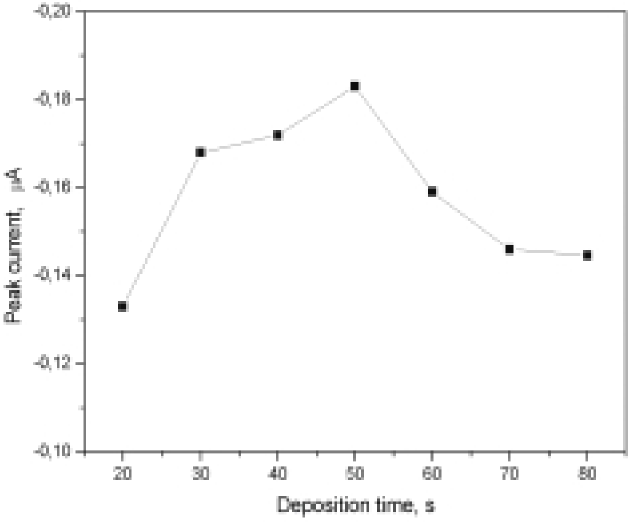

Figure 7. Dependence of arsenic peak current on deposition time for optimal stirring rate (different for each deposition time).

However since the highest peak current is obtained for 50 s deposition time and stirring rate 640 r.p.m. such conditions were applied in most measurements.

Influence of stirring rate on selenium(IV) interferences. Selenium(IV) is considered as major interferent for arsenic(III) determination by DPCSV method. Selenium(IV) may be determined in similar conditions using DPCSV method in presence of copper. Similar mechanism of deposition was suggested by Holak [25]. Influence of selenium on arsenic determinations is ambiguous. Several authors [11,13] have observed decrease of the signal from arsenic in presence of selenium. Others [10,19] on the contrary have observed increase of sensitivity for arsenic determination if selenium is present in supporting electrolyte. This ambiguity may be explained when dependence on stirring rate is considered. The dependence of arsenic(III) DPCSV peak current on Se(IV) concentration is shown in Fig. 8 for to the chosen two stirring rates.

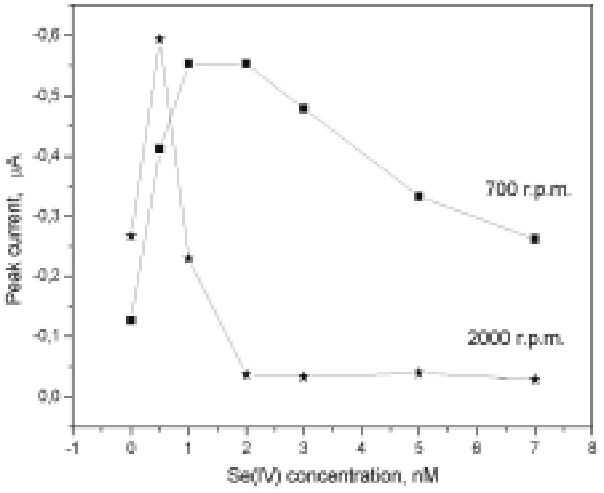

Figure 8. Influence of Se(IV) on As(III) DPCSV peak at low (700 r.p.m.) and high (2000 r.p.m.) stirring rates for 5 nM As(III) and 0.75 mM of $CuCl_2$ in 2M HCl. Spinbar stirring bar, deposition time 50 s.

For low stirring rate of 700 r.p.m. selenium(IV) causes considerable increase of arsenic peak. More than three times increase of peak current was observed for Se(IV) concentration of 1–2 nM. On the contrary for high stirring rate 2100 r.p.m. only very low selenium(IV) concentration 0.5 nM gives current enhancement. Higher selenium concentrations cause suppression of arsenic peak. Such behavior explains very well the influence of selenium on the peak current, which have been observed and reported by several authors.

Analytical performance. Reproducibility of arsenic(III) DPCSV peak depends on the slope of the stirring bar for optimal determination conditions. Relative standard deviations of arsenic(III) peak and compared to ASV peak current of cadmium are shown in Table 1.

Table 1. Relative standard deviations for DPCSV 5 nM As(III) peak current (deposition time 50 s) and ASV 200 nM Cd(II) peak current (deposition time 30 s). For different types of stirrings bars numbers of repetitions for each measurement n = 11.

Stirring bar	egg-shape	flea-micro	polygon	spinbar	spinplus
rsd As(III) [%]	8.61	3.45	4.81	4.22	5.44
rsd Cd(II) [%]	4.48	0.99	1.01	1.31	1.11

Best reproducibility is obtained with flea micro stirring bar. This type of stirring bar gives quiet and effective stirring. The worse egg-shape bar was unstable during stirring. Parameters of calibration curves strongly depends on the stirring rate. Even small deviation from optimal stirring rate gives significant decrease of sensitivity and worse detection limit and correlation. Calibration curves parameters for optimal and non-optimal stirring rates are shown in Table 2.

Table 2. Parameters of calibration curves for As(III) in concentration range 0.5–20 nM for several stirring rates 0.75 mM $CuCl_2$ in 2M HCl n = 16. Stirring bar flea micro.

Stirring rate [r.p.m.]	Slope [μA/nM]	Intercept [μA]	Correlation coefficient	Detection limit [nM]
300	0.042 ± 0.001	0.021 ± 0.006	0.9981	0.47
470	0.070 ± 0.001	0.004 ± 0.008	0.9986	0.40
640	0.034 ± 0.001	–0.017 ± 0.012	0.9901	1.1

Even change of stirring rate of about 30% r.p.m. causes significant worsening of calibration curve parameters. Especially harmful is when applied is higher stirring rate than optimal. When higher than optimal stirring rate is applied the parameters worsen. Very low detection limit 0.4 nM (0.03 ppb) allows to determine arsenic in natural samples. The results of arsenic determination in chosen environmental samples are collected in Table 3.

Table 3. Determination of arsenic in several environmental samples.

Sample	As(III)	As(V)	As_{tot}	Remarks
River sediment CRM 320	< 0.03 ppb	77.5 ± 2.2 ppm	77.5 ± 2.2 ppm	Certified value 76.7 ± 3.4 ppm
Water from Rudawa river	< 0.03 ppb	0.5 ± 0.01 ppb	0.5 ± 0.01 ppb	AAS determination below detection
Water from aquarium	28.2 ± 1.4 ppb	–	41.6 ± 1.6 ppb	AAS determination 42 ppb ± 2.1 ppb
Algea *Elodea canadensis*	< 0.03 ppb	25.6 ± 0.4 ppm	25.6 ± 0.4 ppm	AAS determination 26.9 ± 2 ppm
Water from Dobczyce reservoir depth 28 m	3.22 ± 0.21 ppb < 0.03	– 7.36 ± 0.4 ppb	5.79 ± 0.1 ppb_1 7.36 ± 0.4 ppb_2	Difference $As(tot)_2$– $As(tot)_1$ 1.6 ± 0.4 ppb of As(organic)

Arsenic (V) was determined after reduction to As(III) using sodium thiosulfate [13]. Analysis of Certified Reference Material river sediment – CRM 320 (Commission of the European Communities – Community Bureau of References) shows that method results are in very good agreement with certified values. However concentration of arsenic is quite high – over four orders of magnitude above detection limit. Very low detection limit makes possible the arsenic determination in natural water and even drinking water. Example with water from Rudawa river shows that DPCSV method allows the arsenic determination whereas AAS fails. In case of algea *Elodea canadensis* a good agreement of voltammetric and AAS determinations was observed. The last two examples show possibility of arsenic speciation. In case of water from aquarium – both forms of arsenic *i.e.* As(III) and As(V) are present. Amount of total arsenic is in good agreement with AAS results. In case of water from Dobczyce reservoir two analysis have been performed. First without mineralization allows to determine inorganic As(III) and As(V). Second after UV mineralization gives the total concentration of arsenic. From difference of total arsenic without mineralization and with UV mineralization the concentration of organic arsenic may be obtained.

CONCLUSIONS

In DPCSV determination of arsenic convective transport conditions during deposition step significantly influence analytical performance of the method. Such influence origins from unusual dependence of As(III) stripping peak current on stirring rate during deposition step. Optimal stirring rate should be established taking into account geometry of the cell, type and size of the stirring bar, mercury drop size, copper concentration and applied deposition time. In conditions used in present work, the best results were obtained when flea-micro stirring bar, drop of area 0.47 mm^2, copper concentration 0.75 mM and 50 s deposition time were applied. In such conditions usually the stirring rate of 470 r.p.m. was optimal. Application of stirring rate which differs even 10% of optimal may cause severe deterioration of analytical parametres such as sensitivity and detection limit. Under optimal conditions detection limit was as low as 0.4 nM (0.03 ppb) As(III) and reproducibility expressed by relative standard deviation was 3.45%.

Acknowledgments

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