GOLD-PLATED CARBON PASTE ELECTRODES FOR ANODIC STRIPPING DETERMINATION OF ARSENIC

Petr CHADIM[a1], Ivan ŠVANCARA[a2], Boris PIHLAR[b] and Karel VYTŘAS[a3,*]

[a] *Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, nám. Čs. legií 565, CZ-532 10 Pardubice, Czech Republic; e-mail: [1] petrchad@usa.net, [2] ivan.svancara@upce.cz, [3] karel.vytras@upce.cz*

[b] *Department of Analytical Chemistry, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, SI-1000 Ljubljana, Slovenia; e-mail: boris.pihlar@uni-lj.si*

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The applications of gold-plated carbon paste electrodes in anodic stripping voltammetry have been studied in an effort to develop a simple and effective method for the determination of arsenic in water samples. The investigations performed included the choice of supporting electrolyte composition, the optimisation of important experimental parameters, search for appropriate procedure to reduce As(V) to As(III), and some tests of practical applicability of the method, including interference studies. Under optimised conditions, the signal of As was linear within 5–50 μg l^{-1} with a detection limit of about 1 μg l^{-1} As (deposition time 10 min). Common elements or ions did not interfere except for Cu(II). The analytical performance of the method has been tested in recovery measurements with model solutions.

Key words: Gold film electrode; Carbon paste support; Arsenic(III); Arsenic(V); Stripping voltammetry; Electroreductions; Electrochemistry

Compounds containing arsenic in all common oxidation states (–III, III and V) are very toxic. Arsenic is considered to be human carcinogen by organisations[1] EPA (1984b) and IARC (1980, 1987b). Currently, harmful effects of arsenic to human health can be documented on a serious situation in various parts of Bangladesh[2].

As quoted in a recent extensive review[3], arsenic in various types of samples can be determined using hydride generation technique in atomic absorption spectroscopy, graphite furnace atomic absorption spectroscopy, atomic emission spectroscopy with inductively coupled plasma, UV-VIS spectrophotometry or neutron-activation analysis. Methods based on these techniques require expensive instrumentation and rather complicated procedures, including special sample pretreatment.

Electrochemical methods are used relatively frequently. Besides favourable economical aspects, their main advantage is in selectivity which allows to diversify the oxidation states of arsenic featuring different level of toxicity. Almost all arsenic present in natural waters is pentavalent since the trivalent element is easily oxidised with dissolved oxygen. Pentavalent arsenic, however, is considered to be electrochemically inert under normal conditions[4–7] and for its electrochemical reduction, extremely negative potentials have to be applied[8]. This means that for the determination of total arsenic content, it is necessary to reduce As(V) to As(III). The reductants recommended were Na_2SO_3 (ref.[4]), N_2H_4 + HCl + HBr (ref.[9]), NaBr + N_2H_4 + H_2SO_4 (ref.[5]), gaseous SO_2 (ref.[5]), KI (refs[6,7,10]), HCl + NH_2OH (ref.[11]), and, most recently, L-cysteine[12,13].

Polarography as well as modern voltammetric methods were often employed to determine arsenic[14]. However, mercury was not found a suitable electrode material due to rather poor solubility of elementary arsenic in mercury and also because of interferences from some ions[4]. With respect to these limiting factors and due to more favourable electrochemical characteristics[4], gold appears to be a more suitable electrode material for the determination of arsenic. Nevertheless, there are also some drawbacks of solid gold electrodes. Apart from rather high costs, these types of gold electrodes require permanent control and care of the quality of their surface[14]. From time to time, special treatment procedures such as polishing, activating or regeneration of the electrode surface are necessary to avoid possible oxidation of the electrode surface and its memory effects[9]. Such troubles can be overcome by using the so-called gold-film electrodes. In this case, gold is deposited electrolytically in a form of thin metallic layer[15] on the surface of a suitable electrode support (graphite, platinum, or gold itself). More recently, it has been shown that carbon paste electrodes (CPEs) can also be used as convenient supports for gold film electrodes[15,16].

According to the authors' knowledge, this article dealing with such gold-plated CPEs is actually the first attempt to use carbon paste electrodes for electrochemical stripping determination of arsenic.

EXPERIMENTAL

Apparatus

A polarographic analyser (model PAR-174A, EG&G Princeton Applied Research, U.S.A.) connected *via* ADDA interface to a PC (IBM compatible) or model V-174 (EG&G) connected to an X–Y recorder (model 704p, Hewlett–Packard, U.S.A.) were used in combination with an electrode stand adapted for measurements with CPE (ref.[17]). Home-made Pt plate as an auxiliary electrode and Ag/AgCl (1 M KCl) as a reference electrode completed the cell. Stirring was performed using a Teflon-coated magnetic bar rotating at 300 rpm.

Microscopic studies were performed with a scanning electron microscope using the already described procedure and equipment[18].

Chemicals and Reagents

All chemicals used were of analytical grade. Stock solutions of 10 M $HClO_4$ (Carlo Erba, Italy or Kemika Zagreb, Croatia), 10 M H_2SO_4 (Lachema, Czech Republic) and 2 M HCl (Lachema or Carlo Erba) were prepared.

A 0.01 M As(III) standard solution was prepared by dissolving an appropriate amount of solid As_2O_3 (Lachema) in 10 ml of 1 M NaOH and diluting to 100 ml. An As(V) standard solution of the same concentration was prepared by dissolving $Na_2HAsO_4{\cdot}7H_2O$ (Z.G. Chem Złoty Stok, Poland) in water. Fresh solutions of dilute standards ($1 \cdot 10^{-4}$ or $1 \cdot 10^{-5}$ mol l^{-1}) were prepared before use and stabilised by adding 1 ml of 0.3% solution of either $N_2H_4{\cdot}HCl$ (Lachema) or $N_2H_4{\cdot}H_2SO_4$ (Merck) per 100 ml of standard solution. For reducing As(V) to As(III), L-cysteine (Merck), $N_2H_4{\cdot}HCl$, $NaHSO_3$, Na_2SO_3 (Lachema) and KI (Merck) were tested.

A special plating solution[15] for the deposition of gold was prepared from a stock solution containing 0.02 g of Au(III) in 100 ml of 1 M HCl by mixing 10.15 ml of 0.01 M Au(III), 50 ml of 2 M HCl and with 39.85 ml of water. An 0.01 M Au(III) stock solution was prepared by dissolving $Na[AuCl_4]{\cdot}2H_2O$ (Fluka) in water. In some experiments, the gold film was generated *in situ* (ref.[16]) by adding an appropriate volume of 0.01 M Au(III). All solutions for analyses were purged with argon of 99.996% purity (MG Technogas, Czech Republic) and doubly distilled water was used throughout.

Working Electrodes

Four carbon pastes were made by intimate hand-mixing of carbon powder and the corresponding liquid binder; in all cases, as a mixture of 0.5 g of carbon powder with 0.2 ml of a liquid. The individual types of carbon pastes denoted below according to the previous literature[15–17] were always made from a spectroscopic graphite powder (RW-B, Ringsdorff-Werke, Germany) and contained Lukooil MV 15500 silicone oil (Lučební závody, Czech Republic) for C/SO electrode, paraffin oil (Uvasol, Merck) for C/Uv electrode and tricresyl phosphate (mixture of the isomers, Fluka) for C/TCP electrode. The prepared pastes were packed into piston-like electrode bodies[15,16].

Procedures

Electrode preparation and treatment. Before the gold plating, a small portion of paste was extruded from the electrode body and the carbon paste surface was polished with a wet filtration paper. Then, the renewed surface was activated by applying a potential of +1.5 V *vs* Ag/AgCl for 60 s and –1.0 V for 15 s. This activation was carried out in a degassed solution of 0.001 M $HClO_4$. After washing the electrode, the gold film was deposited at a potential of –0.4 V from plating solution prepared as described above and deaerated by argon for 5 min. Electrolytical deposition of the film was performed in a stirred solution (approximately

300 rpm) for 7 min. After plating, the electrode was thoroughly rinsed with water and transferred to the analysed solution.

Determination of As(III). A sample (or model solution, 17.2 ml) was added to a mixture of 1.8 ml of 10 M $HClO_4$ and 1 ml of 2 M HCl. After purging this solution with argon, arsenic was deposited at a potential of –0.3 V for 10 min, left for equilibration in quiet solution (for 30 s) and stripped off by imposition of a scan from –0.3 to +0.6 V in the differential pulse mode. The scan rate used was 10 mV s^{-1} and the pulse amplitude was 50 mV.

Determination of total arsenic. Prior to determination of total arsenic, As(V) was reduced to As(III) by the following procedure: 2 ml of 0.3% $N_2H_4 \cdot HCl$ solution and 0.05 g of solid L-cysteine were added to 98 ml of the sample and the solution was heated on a water bath at 80 °C for 10 min. After cooling down to ambient temperature, the sample was prepared for analysis carried out in the same way as described for the determination of As(III).

Evaluation of measurements and of the results. The peaks were computed as peak areas by the software[17]. To quantify the concentration, standard addition of at least two aliquots was used. The results of analyses were evaluated as the recovery (in %).

RESULTS AND DISCUSSION

Choice and Characterisation of the Working Electrode

Based on previous results[16], the initial preliminary experiments were focused on the basic characterisation of three types of gold-plated carbon pastes, *i.e.*, Au(C/SO), Au(C/Uv) and Au(C/TCP). In accordance with the above-cited study, it was confirmed that silicone oil-based CPE provides the most satisfactory properties; namely, fairly shaped base-line and favourable signal-to-noise characteristics.

Gold-plating regime. Deposition of a gold film *in situ* was tested first. Reportedly[15], *in situ* generation from tetrachloroaurate is an easier approach sparing time and chemicals. However, As(III) at low concentrations may be readily oxidised with the $[AuCl_4]^-$ ions to electroinactive As(V) (ref.[4]), which makes *in situ* procedure very problematic for the determination of As at the trace level. Thus, the approach based on external plating of the gold film in a special solution was finally chosen as more convenient.

Other investigations were focused on setting an optimum stirring regime; a stirring rate about 300 rpm provided the most satisfactory results. Considerable attention was also paid to the choice of potential for the gold film deposition tested within an interval from –0.1 to –0.6 V. The best quality film (indicated by both the shape and magnitude of the arsenic peaks) was obtained for a potential of –0.4 V *vs* Ag/AgCl. Programmable changes of the potential, recommended in literature[15] to improve the quality of a gold film were carried out as well. Using predefined potential–time sequences[19], the following plating programme was tested: –0.6 V *vs* Ag/AgCl for 30 s,

–0.4 V for 90 s, –0.2 V for 30 s and 0.5 V for 30 s. Another program simulating a gradual change of the potential[15] was performed by applying a voltage ramp from –0.6 to –0.25 V at a constant scan rate of 2 mV s^{-1}. However, neither the plating by programmed potential–time sequences nor the deposition at the gradually changed potential led to any evident improvement of the film.

Activation of the electrode surface. The anodisation of the gold film surface by potential cycling, which is also quoted to improve properties of gold film electrodes[15,19], was studied next. Adapting the recommended procedure[19] to the type of electrode and instrumentation used, 50 cycles between 0.0 and +0.6 V at 50 mV s^{-1} were performed in 1.0 M H_2SO_4. Also, in this case, no significant improvement due to this rather time-consuming procedure[15,20] was observed.

On the contrary, occasionally advised electrochemical activation of the bare carbon paste surface before the film deposition[15] resulted in a marked improvement of the properties of the Au(C/SO). Hence, this procedure was included in the method as a simple electrode pretreatment.

Microscopic Studies of the Gold-Plated Carbon Paste Surface

A microscopic study on the carbon paste surface plated with a gold film was carried out in an effort to obtain additional information helpful for characterisation and interpretation of the behaviour of the Au(C/SO) under different gold-plating regimes. The whole study was arranged similarly to that performed recently, including the instrumentation and sampling of the pastes for microscopic scanning[18]. Figure 1 shows microscopic photographs of the surface structure of the original carbon paste (Fig. 1a) and of gold-plated surfaces (Figs 1b and 1c). As can be seen, gold deposited either *in situ* (Fig. 1b) or externally in a plating solution (Fig. 1c), forms a compact layer of unconsolidated structure which approximately copies the surface topography of the carbon paste itself. Figure 1 confirms that the overall structure of the gold layer strongly depends on the manner of its deposition[15,18]. Comparing Figs 1b and 1c, it is evident that the film plated externally is much thicker than that deposited *in situ*. As it is known that the thicker the metallic film the better is the resulting film electrode[18], these microscopic images have supported the decision on plating from an external solution.

Studies on Reduction As(V) → As(III)

In this work, special attention was paid to the reduction of pentavalent arsenic to its trivalent form. As already pointed out, this reaction belongs among the most important processes in the electrochemistry of arsenic. Generally, there are two key problems associated with the reduction. First, one has to ensure the quantitative pathway of the whole reduction process; the other task is to consider possible interference from some by-products or consequences of a possible excess of the reducing agent[4].

The first reducing agent tested – a mixture of hydrazine with hydrobromic and hydrochloric acids[9] – was found to be completely ineffective and no peak for the reduced form of As(III) was obtained. A similar situation was when Na_2SO_3 (or $NaHSO_3$) was used. There was a signal for As(III); nevertheless, its overlap with another response (coming probably from dissolved SO_2) practically eliminated the applicability of this agent.

Alkaline metal iodides frequently recommended as rather effective reductants for As(V) (refs[6,7,10]) were selected subsequently. However, neither KI nor NaI were found to be suitable for gold-plated carbon paste. The

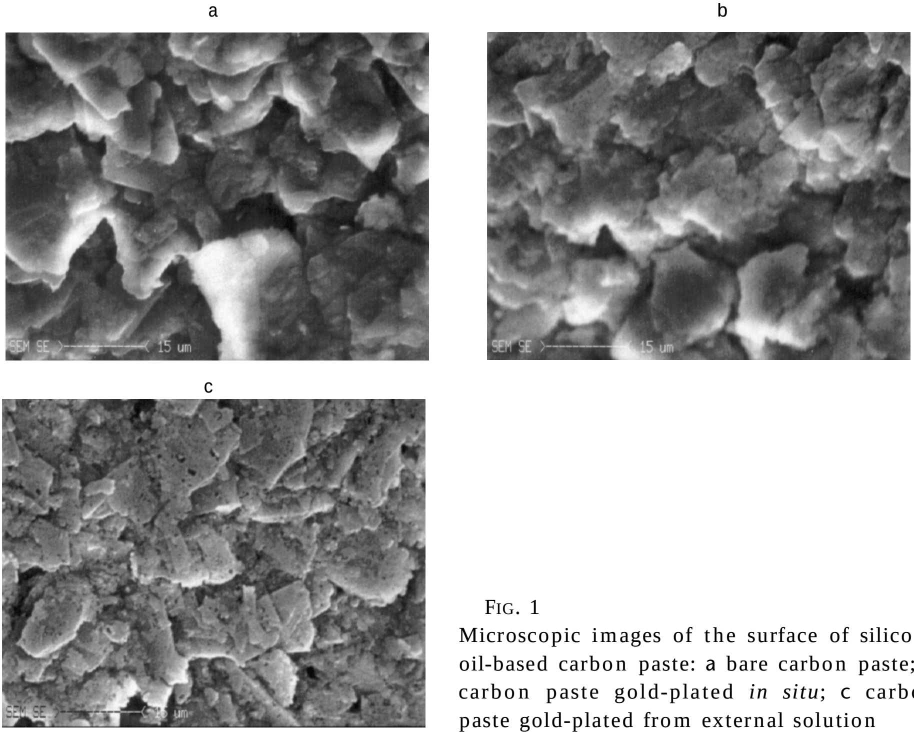

FIG. 1
Microscopic images of the surface of silicone oil-based carbon paste: a bare carbon paste; b carbon paste gold-plated *in situ*; c carbon paste gold-plated from external solution

reason is in oxidation of iodide by pentavalent arsenic to iodine which is extracted onto the carbon paste. Then, during voltammetric scanning, elemental iodine is reduced again to iodide, thus giving rise to large interfering signals[21].

Among all the reductants investigated, L-cysteine was found to be the most efficient agent. First described in ref.[12], the use of this compound has two main advantages: the experimental procedure is easy to perform (solid L-cysteine can be added directly to the sample) and the whole reduction process proceeds relatively rapidly (taking about 15 min) in comparison with the above-mentioned reductants. When using L-cysteine, only mild preheating of the sample is needed[12] to complete the reaction quantitatively (otherwise, the reduction in unheated solutions is terminated at approximately 50% conversion). It is also interesting to note that the presence of L-cysteine added to the solution resulted in a better defined response to As compared with trivalent As, *i.e.*, without the reduction step. This was likely due to the effect of the reductant itself hindering re-oxidation As(III) → As(V). Especially this process was assumed to cause some difficulties when analysing the solutions of As(III) which had to be stabilised by adding $N_2H_4 \cdot HCl$ (ref.[19]).

Optimisation of Experimental Conditions in Anodic Stripping Voltammetry of Arsenic

Choice of the supporting electrolyte composition. Based on previous results[4,16], two supporting electrolytes were selected, both based on H_2SO_4 and $HClO_4$. It was found that a solution containing $HClO_4$ was more convenient because the electrode base-lines recorded in this medium were smoother and without any background signals. By varying the $HClO_4$ concentration, it was ascertained that the highest peaks of arsenic were obtained in 0.9 M $HClO_4$. According to previous experience[4,20], the effect of Cl^- ions – in the form of HCl – was studied and it was confirmed that its concentration should not exceed 0.15 mol l^{-1}. The content of 0.1 M HCl in the electrolyte, resulting in a significant increase in the height of arsenic peak was chosen as an optimum; higher concentrations of the Cl^- ions already led to a decrease of this peak.

Optimisation of experimental parameters. Optimum potential for the deposition of As(III) was examined in the range from –0.6 to –0.1 V *vs* Ag/AgCl. It was observed that the accumulation of As(III) at more negative potentials gave already rise to a rapid decrease of the peak. Apparently, it might be caused by hydrogen evolution and its adsorption on the electrode surface[4].

The highest as well as the best-shaped response to As was obtained under conditions employing the accumulation at –0.3 V. This fully corresponded to the previously published results[4,20].

Optimisation experiments proved that the accumulation time from 15 s up to 10 min gave a proportional increase of the As peak, but the latter was shown to be a maximum value adjustable on the instrument. Longer periods did not result in any peak increase and when accumulation exceeded 10 min, peaks became even lower and markedly broader. With respect to this optimisation study, it should be noted that the presence of L-cysteine in the electrolyte solution allowed to prolong the deposition period considerably even above 10 min. The peak height *vs* accumulation time dependence remained linear up to 15 min. Undoubtedly, this phenomenon favourably contributed to achieving quite attractive detection limit (see below).

The device used permitted to select the scan rate values from among 1, 5, 10, 20 and 50 mV s^{-1}. It was found that the peak height increased with a rising scan rate up to 20 mV s^{-1}; nevertheless, due to starting deformation of the peak, the value of 10 mV s^{-1} was finally chosen as an optimum. In the literature[4–6,20], it is recommended to set the pulse amplitude to 50 mV which provides the most satisfactory signal-to-noise characteristics together with a sufficient peak resolution. This fact was also confirmed in the present study.

Analytical parameters of the method. Three calibration plots were obtained: (i) As added as As(III), concentration range of 5–50 μg l^{-1}, deposition for 5 min, regression coefficient, $R = 0.996$; (ii) As as reduced As(V), 5–50 μg l^{-1}, 10 min, $R = 0.998$; (iii) As as reduced As(V), 2–10 μg l^{-1}, 10 min, $R = 0.997$. Typical voltammograms obtained by analysing the latter mentioned concentration level are shown in Fig. 2.

Experimental data presented in Fig. 1 were also utilised for evaluation of the detection limit. Its value calculated as 3σ-criterion was estimated to be approximately 1 μg l^{-1} for 10 min deposition. As can be seen from the figure, the estimation of detection limit was also affected by a broad plateau-like response of unknown nature that deformed the base-line near the potential of interest and which had to be taken into consideration (for details, see ref.[19]).

The reproducibility of the signal was checked in repetitive measurements with a model concentration of 10 μg l^{-1} of prereduced As(V). In ten replicates, the relative standard deviation of ±7% was obtained. Such a value is still acceptable if one considers the concentration range tested as well as the fact that measurements with heterogeneous carbon pastes are usually less reproducible compared to those at electrodes prepared from homogeneous materials[15].

Interference studies. Suppression of interferences from Hg(II), Ag(I), Se(IV) and Cu(II) is often a crucial point in developing a method for the determination of arsenic by electrochemical stripping analysis. These ions, in particular Cu(II), are regularly quoted in most literature sources[4,6,8–10,12,20] and their interfering effect is usually interpreted as a consequence of the formation of various intermetallic As–Cu compounds[13].

In this work, a special attention was paid to the influence of Cu(II) due to the fact that this ion commonly accompanies arsenic in real samples, including natural waters[3]. It was found that under optimum conditions for analysis of prereduced As, Cu(II) ions already affect the signal of As at comparable concentration levels. Some attempts to suppress this interference by masking Cu(II) with a suitable complexant (*e.g.*, EDTA) were unsuccessful, evidently, because of high acidity of the supporting electrolyte[22].

Neither Ag(I) nor Se(IV) interfered with the response to As even in a ten-fold excess in concentrations. In case of Hg(II), its ten-fold concentration excess already led to a decrease of the As signal to a half of its original magnitude. However, at comparable concentrations, the effect of Hg(II) on the peak of As was only negligible. Interference from Hg(II) ions at higher

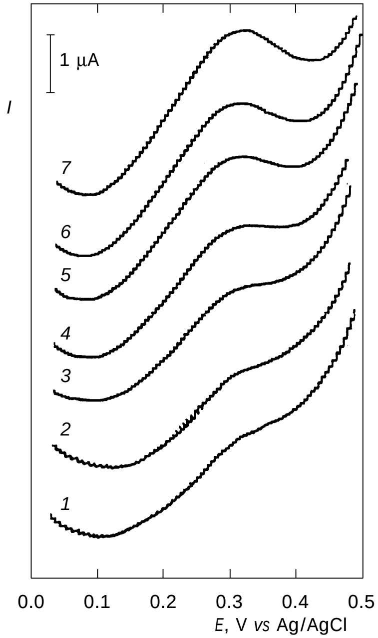

FIG. 2
Calibration voltammograms of As at the μg l^{-1} concentration level: *1*, *2* base-line (two replicates); *3*–*7* 2, 4, 6, 8 and 10 μg l^{-1} As (added as As(V)). Experimental conditions: anodic stripping voltammetry; C/SO carbon paste electrode gold-plated from external solution; supporting electrolyte, 0.9 M $HClO_4$ + 0.1 M HCl; deposition potential, –0.3 V *vs* Ag/AgCl; deposition time, 10 min; equilibration time, 30 s; initial potential, –0.3 V; final potential, +0.6 V; scan rate, 10 mV s^{-1}; pulse height, 50 mV

concentrations are logically explainable by the formation of elemental mercury and its ability to dissolve the gold film on the electrode surface[9].

Determination of Arsenic in Model Solutions

In order to evaluate the analytical performance of the method, two model samples were analysed using the recovery determination. Sample No. 1 contained 50 μg l^{-1} of prereduced As(V), sample No. 2 was made with As(III) compound, again, at the total concentration of 50 μg l^{-1} As. By two standard additions, the concentration of arsenic in sample No. 1 was found to be 47.2 μg l^{-1}, which can be expressed as 93% recovery. The voltammograms corresponding to this analysis are given in Fig. 3. Analysis of the other sample containing As(III) resulted in 84% recovery. This loss can perhaps be again assigned to oxidation of As(III) to As(V) with air[4]. By analysing model samples, it was also confirmed that As(V) did not interfere in the determination of As(III). Therefore, it seems that the method could be applied to speciation in solutions containing arsenic in both oxidation states. Such an approach would allow to determine first As(III) alone and the total arsenic subsequently, after reduction of As(V) (ref.[19]).

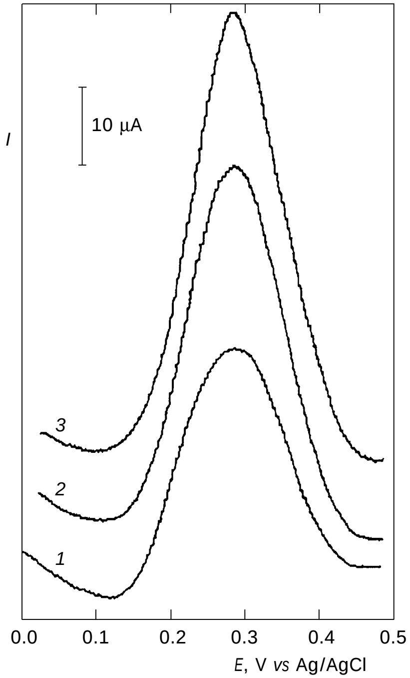

FIG. 3

Typical voltammograms obtained by analysing a model sample: *1* model sample (with 50 μg l^{-1} As(V)); *2* 25; *3* 50 μg l^{-1} As (added as As(III)). Experimental conditions: anodic stripping voltammetry; C/SO carbon paste electrode gold-plated from external solution; supporting electrolyte, 0.9 M $HClO_4$ + 0.1 M HCl; deposition potential, –0.3 V *vs* Ag/AgCl; deposition time, 10 min; equilibration time, 30 s; initial potential, –0.3 V; final potential, +0.6 V; scan rate, 10 mV s^{-1}; pulse height: 50 mV

CONCLUSIONS

The method developed for anodic stripping voltammetric determination of arsenic at a carbon paste electrode is rather simple and requires relatively short analysis time. The most advantageous seems that the method employs an inexpensive, easy-to-prepare and quickly regenerable working electrode. This minimises the problems connected with the use of solid gold electrodes (or solid electrode supports made of noble metals and of glassy carbon) where – sometimes inevitable – polishing, electrolytic surface activation or other ways of conditioning may considerably complicate practical analysis[14,23]. Other valuable characteristics of the method introduced here are the detection limit near to the ppb level and its perspectives for speciation of both As(V) and As(III) in real water samples[3,24]. The method thus needs further improvements, in particular, efficient suppression of serious interference from Cu(II).

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