

Electrodeposition and stripping voltammetry of arsenic(III) and arsenic(V) on a carbon black–polyethylene composite electrode in the presence of iron ions

Galina N. Noskova · Elza A. Zakharova ·
Nina A. Kolpakova · Alexander S. Kabakaev

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Abstract In this work, a new sensor is proposed for the stripping voltammetric determination (anodic stripping voltammetry—ASV) of total arsenic(V) or arsenic(III). The sensor is based on an Fe-modified carbon composite electrode containing 30 % carbon black–high-pressure polyethylene (CB/PE). The modification with iron is achieved by the addition of Fe(III) or Fe(II) ions to the sample solution and co-electrodeposition of iron and arsenic on the CB/PE electrode. In anodic stripping voltammetry, two peaks are observed: an Fe peak at -0.45 or -0.29 V and a peak at 0.12 ± 0.07 V which depends on the arsenic concentration and corresponds to the $\text{As}(0) \rightarrow \text{As}(\text{III})$ oxidation, as is the case with other solid electrodes. The optimum conditions proposed for ASV determination of As(V) and As(III) in solutions in the presence of dissolved oxygen are the following: the background electrolyte is 0.005 M HCl containing 0.5–1 mg/L Fe(III) for As(V) and containing 1.0–1.5 mg/L Fe(III) for As(III), respectively; $E_{\text{dep}} = -2.3$ V; rest period at -0.10 V for 3–5 s before the potential sweep from -0.2 to $+0.4$ V; scan rate is 120 mV/s. The detection limit (LOD, $t = 120$ s) for As(III) and As(V) is 0.16 and 0.8 $\mu\text{g/L}$, respectively. Various hypotheses on the effect of Fe ions and atoms on the electrodeposition and dissolution of arsenic are considered. The new method of determination of As(III) and As(V) differs from known analogues by its simplicity, low cost, and easy accessibility of the electrode material. It allows the voltammetric determination of total arsenic after

chemical reduction of all its forms to As(III) or after their oxidation to As(V).

Keywords Arsenic(III) · Arsenic(V) · Anodic stripping voltammetry · Solid electrodes · Carbon black composite electrode · Iron

Introduction

In stripping voltammetry of arsenic(III), various electrode materials, among which are platinum, gold, and a variety of carbon electrodes modified with metals (Pt, Au, Ag, Ir), are used. Anodic stripping voltammetry (ASV) of arsenic(III) on solid electrodes was pioneered in the 1970s [1–3]. Later, gold and gold-plated carbon electrodes found wide use in quantitative determination of As(III) due to a higher hydrogen overvoltage and higher reversibility of the electrode processes compared to platinum-based electrodes [4, 5].

In the last 10 years, more and more attention was focused on the determination of As(V) because the element is easier to obtain in this form by oxidation than to reduce its species to As(III), because the stability of As(V) solutions in air is higher. There are several papers on the stripping voltammetric determination of arsenic(V) [6–15]. The analytical procedures described in these papers all rely on the following points: (1) single or arrays of gold microelectrodes were used; (2) a preliminary accumulation of As(0) was performed at sufficiently negative potentials of the working electrode (less than -1.0 V); (3) vibration or rotation of the working electrode was used to enhance the mass transfer and eliminate bubbles of released hydrogen; and (4) high acid concentrations of background electrolyte. In contrast, Gibbon-Walsh et al. [15] used neutral or weak alkaline

G. N. Noskova · E. A. Zakharova · N. A. Kolpakova ·
A. S. Kabakaev (✉)
Department of Physical and Analytical Chemistry,
Tomsk Polytechnic University,
30 Lenina av.,
Tomsk 634050, Russia
e-mail: ask@tpu.ru

solutions (pH=7–8). As(V) was determined at a vibrating Au-microwire in the presence of Mn(II) in seawater. They also consider the electrode reaction as “unusual.” The possibility of As(V) reduction by Mn(0) deposited at the gold electrode was described by the following schemes:

1. $\text{Mn(II)} + 2\text{e}^- \rightarrow \text{Mn(0)}$ (electrochemical)
2. $\text{Mn(0)} + \text{As(V)} \rightarrow \text{As(III)} + \text{Mn(II)}$ (chemical)
3. $\text{As(III)} + 3\text{e}^- \rightarrow \text{As(0)}$ (electrochemical)

Chemical reduction of As(V) with Fe in various forms on an electrode surface was also proposed in a few other papers [16, 17]. In abrasive voltammetry of arsenic(V), Cepriá et al. [16] used a solid-phase mixture of arsenic(V) compounds with hematite (Fe_2O_3) attached to the surface of an impregnated graphite electrode. Later, the same authors reported [17] the ASV determination of As(V) at an electrode made of a mixture of hematite powder and carbon paste. Cepriá et al. [16, 17] assumed that the effect of iron oxide paste was based on the electrochemical reduction $\text{Fe(III)} \rightarrow \text{(II)}$ on the electrode surface and the chemical reduction of As(V) to As(III). Next, after accumulation, the As(0) precipitate was dissolved and measured by anodic stripping voltammetry. Actually, arsenic(V) was supposed not to be reduced by Fe(II) in the solution, but directly from the solid phase with Fe(II) formed in the electrochemical reduction of hematite (Fe_2O_3). Later, Shin and Hong [18] reported on the electrochemical oxidation of arsenic(III) with a detection limit of 0.75 ppb using a glassy carbon electrode or a glassy carbon electrode modified with multiwalled carbon nanotubes in Nafion, both deposited with Pt–Fe(III) nanoparticles. The authors considered that the given composite has advantages over platinum because of a better electrocatalytic activity for As(III) oxidation and over gold (in ASV) in case there is no interference by copper and other transition metals.

Iron(III) compounds and elemental iron are widely used for water purification from arsenic because As(V) and As(III) are well adsorbed on Fe(III) hydroxides and oxides in the pH range of natural water in the presence of oxygen [19]. The removal of arsenic with the help of Fe(0) is based on the corrosion of iron in oxygenated waters and the subsequent adsorption of arsenic compounds at the surface of the corrosion products.

Previously, we have developed [20] a method of voltammetric and stripping voltammetric analysis with readily available composite electrodes based on 30 % carbon black and polyethylene (CB/PE) for the determination of traces of metals and nonmetals, including toxicants. A gold microelectrode array was used for the determination of arsenic(III). The working electrode was modified by metallic gold nanoparticles by electrolysis of aqueous gold chloride solutions on the CB/PE cathode. This way, low detection limits ($\text{LOD}=0.015 \mu\text{g/L}$, $t_{\text{dep}}=180 \text{ s}$) for arsenic(V) were attained [15]; however, the availability of cheap, accessible, and

reliable working electrodes and the feasibility of on-site measurements remained to be a problem.

The objective of the present work is to study the possibility of stripping voltammetric determinations of arsenic(III) and arsenic(V) after electrolysis from solutions on an Fe-modified CB/PE composite electrode (i.e., without gold modification). For this purpose, Fe(II) and Fe(III) compounds were added to the solution and were subjected to electrolysis under optimum conditions at high negative potentials with simultaneous deposition of As(0) on the electrode. In the following anodic potential sweep, a signal due to the transition $\text{As(0)} \rightarrow \text{As(III)}$ was detected. Experimental conditions were optimized in order to improve the ASV calibration plots of As(V) and As(III) signals in aqueous solutions in the presence of Fe(II) or Fe(III) ions and dissolved atmospheric oxygen.

Experimental

Materials and reagents

Russian State Standard purity grade solutions (reference solutions for attestation of laboratories, highest accuracy available locally, Center of Reference Materials and High-Purity Substances Co., Saint Petersburg, Russia) of 1 g/L Fe(III), Fe(II), Co(II), Ni(II), Cu(II), Bi(III), Sb(III), Sb(V), and As(III) were used. Appropriate solutions of lower concentration were obtained by diluting the initial standard solutions with double distilled deionized water. The As(V) standard was prepared from $\text{NaH}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$ (chemically pure) or by oxidation of the As(III) standard solution with O_3 and iodometric determination of concentration [21].

Equipment and electrodes

SEM images were obtained with the help of a Philips SEM 515. Voltammograms were recorded with a computer-controlled TA-4 potentiostat (Tomanalyt Company, Tomsk, Russia). Three sets of three-electrode systems allowed simultaneous measurements in three independent quartz cells with a built-in vibration device for the working electrodes and gas purging with nitrogen for oxygen removal, when needed.

The electrode system was a three-electrode arrangement, with reference and auxiliary electrodes each being a silver/silver chloride electrode in 1.0 MKCl. All reported potentials refer to the Ag/AgCl, 1 MKCl reference electrode. The electrically conducting material of the working electrode was a carbon–polyethylene composite; fabrication of the electrode is described in detail in [20]. Briefly, the composite is a commercially available mixture containing 30 % of carbon black with a particle size of 24–33 nm and 70 % of

heat-stabilized high-density polyethylene. The composite, when molten, is injected into a low-density polyethylene tube to form the final electrode body. Figure 1 shows SEM images of the composite that reflect the carbon particle distribution in the material. It can be seen from Fig. 1c that the electrode body and the conducting composite are welded. Therefore, there is no gap between the insulating body of the electrode and the conducting material. The electrode surface is a disk of diameter $d=3.9$ mm. The surface was renewed by cutting off a thin layer of ~ 0.3 mm by a special knife with a stainless razor blade with no further activation or grounding.

The surface of the CB/PE electrode electrodeposited with gold is shown in Fig. 2 giving evidence that electroactive sites form a random microelectrode array. Voltammetric measurements in the three-electrode cell with a vibrating working electrode were performed using the computer-controlled sequence: (1) conditioning of the electrode at 0.3 V for 10 s to clean the electrode from all substances precipitated in electrolysis; (2) accumulation of arsenic and iron at -2.3 V for 10–300 s with vibration of the CB/PE working electrode; (3) giving the electrode and solution a rest period of 1–10 s to dissolve electronegative or interfering substances at a potential E_{rest} between -0.8 and -0.1 V, which was chosen to be at least 0.2 V more negative than the arsenic peak potential; and (4) linear potential sweep from -0.3 to $+0.4$ V with a scan rate of 120 mV/s. Polarization of the CB/PE electrode at potentials higher than 0.4 V is undesirable, due to a irreversible increase of the residual current.

The typical procedure of arsenic measurements was as follows: A background solution was transferred to a 20-mL quartz cell; next, the required volume of Fe(II) or Fe(III) standard solution was added. The resultant solution was analyzed by stripping voltammetry (with four repeated curves, of which the first one was usually discarded and the other three were averaged). Next, a test sample of arsenic solution was added and the determination was performed under the same conditions as those used to analyze

the background solution with added Fe ions. The anodic peak of arsenic was obtained at $0.12 (\pm 0.05)$ V. The arsenic concentration was determined by applying the standard addition method.

Results and discussion

The general recommendation of the majority of the reviewed publications is that arsenic(V) is best reduced in solutions with pH not greater than 2 at negative potentials of -1.0 V and lower, under conditions which prevent, to a certain extent, the formation of arsenic hydrides and accumulation of hydrogen bubbles on the electrode surface. These requirements are met by both vibration of working electrode and the choice of such electrode materials which possess a low (or medium) hydrogen overvoltage (Pt, Au, Cu). To the best of our knowledge, the stripping voltammetric response of arsenic(V) and arsenic(III) on (unmodified) carbon or CB/PE electrodes has not been reported before.

It was found that the presence of Fe(III) or Fe(II) ions in oxygen-containing solutions with $\text{pH} < 3$ allows for elemental arsenic being deposited from As(V) and As(III) solutions on the CB/PE electrode at potentials more negative than -2.1 and -1.8 V, respectively. Depending on the concentration of Fe and As ions, two or three peaks may appear in the anodic stripping voltammogram. The first anodic peak is at -0.45 V, which is connected with the oxidation of Fe(0). The peak of As(0) oxidation (here referred to as *As peak*) is the most positive among the others, and it appears at 0.12 V. The peak of iron-arsenic intermetallic compound (IMC) appears at -0.29 V only after a certain ratio of Fe/As is reached. Simultaneous multiple peaks can only be registered in the scan between -0.8 and 0.4 V.

Let us take a closer look at the As peak above 0.12 V, which can be used for determination of both As(III) and As(V). It is convenient to perform the potential scan between -0.2 and 0.4 V, when other peaks are out of scope (Figs. 3 and 4). The

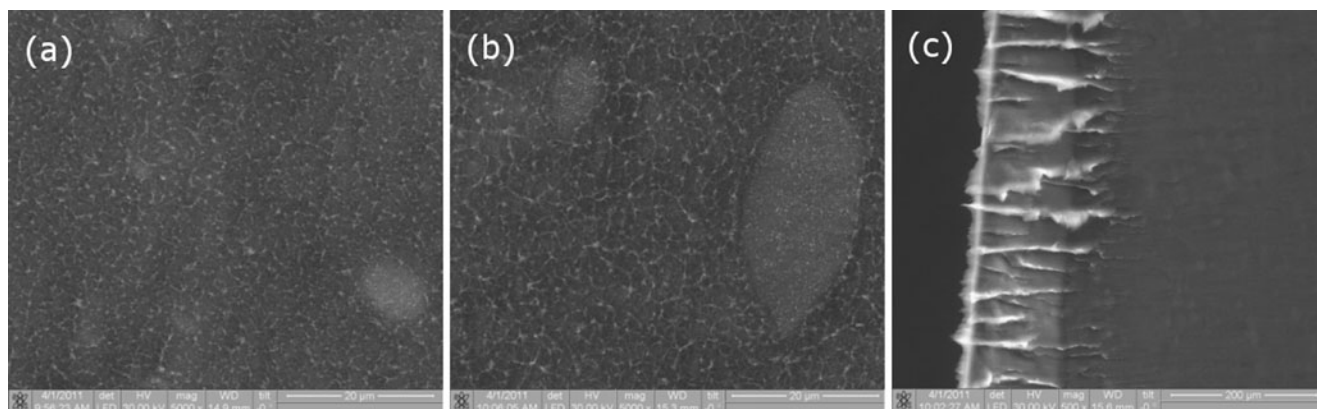


Fig. 1 SEM images of the composite: **a** electrode cross-section; **b** longitudinal section; **c** melt between the electrode body (lighter) and the composite

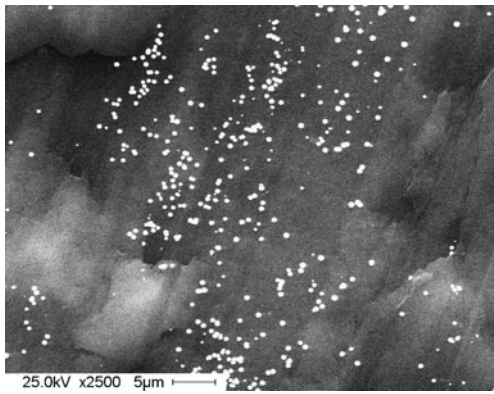


Fig. 2 Surface of the CB/PE electrode electrodeposited with gold from 0.005 M AuCl_3 at -0.1 V for 10 s

oxidation peaks of arsenic electrodeposited from both As(III) and As(V) solutions are of the same form and are recorded at a potential of (0.12 ± 0.05) V. This means that the oxidation reaction is the same: $\text{As}(0) \rightarrow \text{As}(\text{III}) + 3e^-$. The stripping voltammetric peak of As(III) is 2 to 2.5 times higher than that

for As(V) of the same arsenic concentration (Fig. 3). Another difference is that the As(V) peak grows linearly only in the background solution containing more than 0.1 mg/L of Fe ions, whereas the As(III) peak is already linear at $[\text{Fe}] > 0.02$ mg/L. The residual current in the anodic potential region increases within the first 0.5–1.0 h of operation of the freshly cut CB/PE electrode in the presence of Fe(II, III) ions in the solution, whereupon it is stabilized being further dependent only on the Fe and As ion concentrations in the solution.

Effect of chlorides and pH

The presence of chlorides in the solution increases the anodic peak current of arsenic and shifts the peak potential toward positive values (Fig. 4): the addition of 0.01 M KCl changes the peak potential by more than 0.02 V. The result was surprising: when As was deposited on gold electrodes, the addition of Cl^- shifts the As stripping peak to the negative side. So the positive shift at Fig. 4 may be connected with the effect of Fe changing the surface of

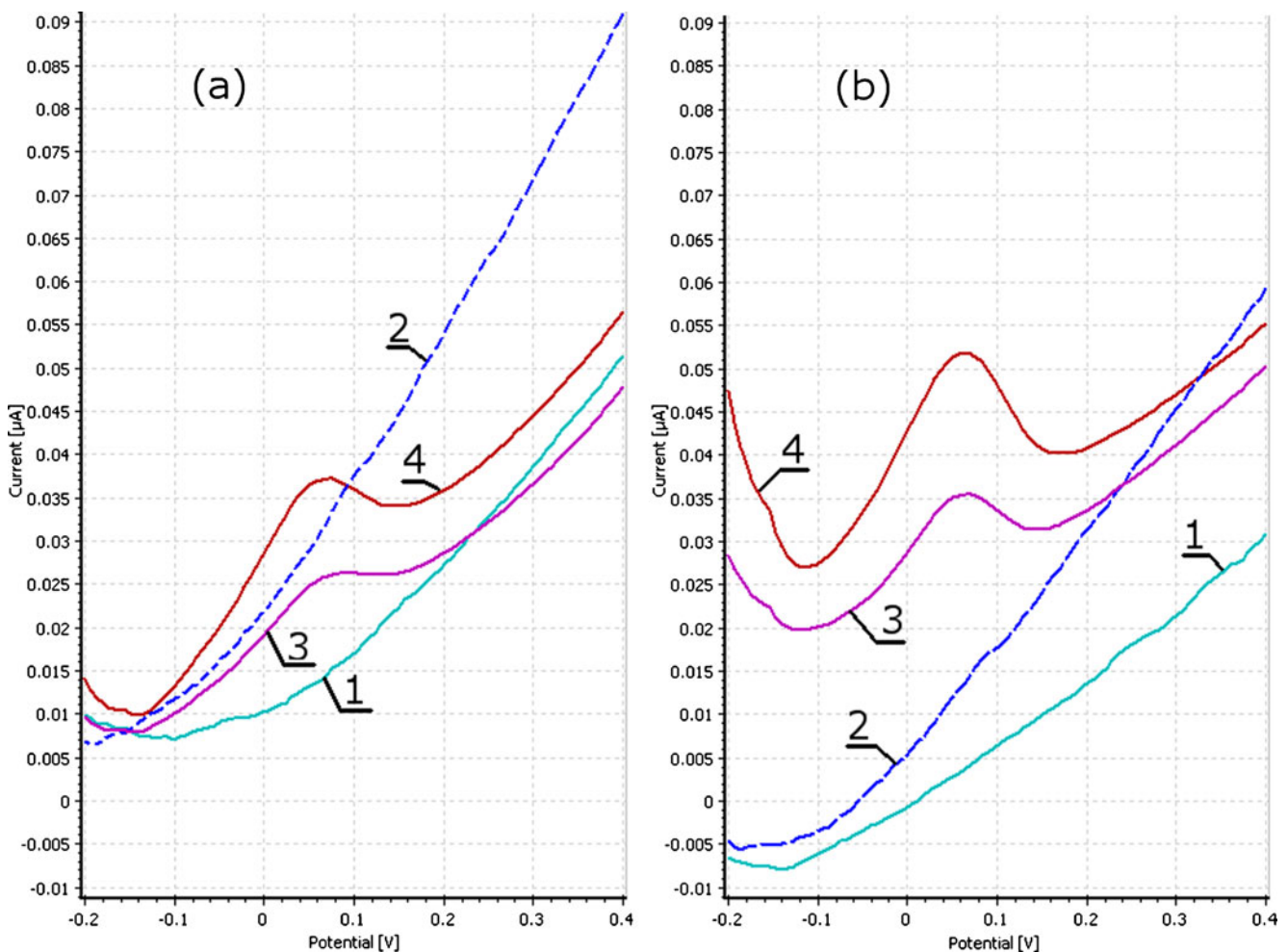


Fig. 3 Voltammograms of **a** As(V) and **b** As(III) on the CB/PE in 0.005 M HCl (curve 1); 0.005 M HCl+0.005 mg/L As (curve 2); 0.005 M HCl+0.005 mg/L As+0.5 mg/L Fe(III) (curve 3); 0.005 M HCl+0.01 mg/L As+0.5 mg/L Fe(III) (curve 4). $E_{\text{dep}}=-2.3$ V; $t_{\text{dep}}=40$ s

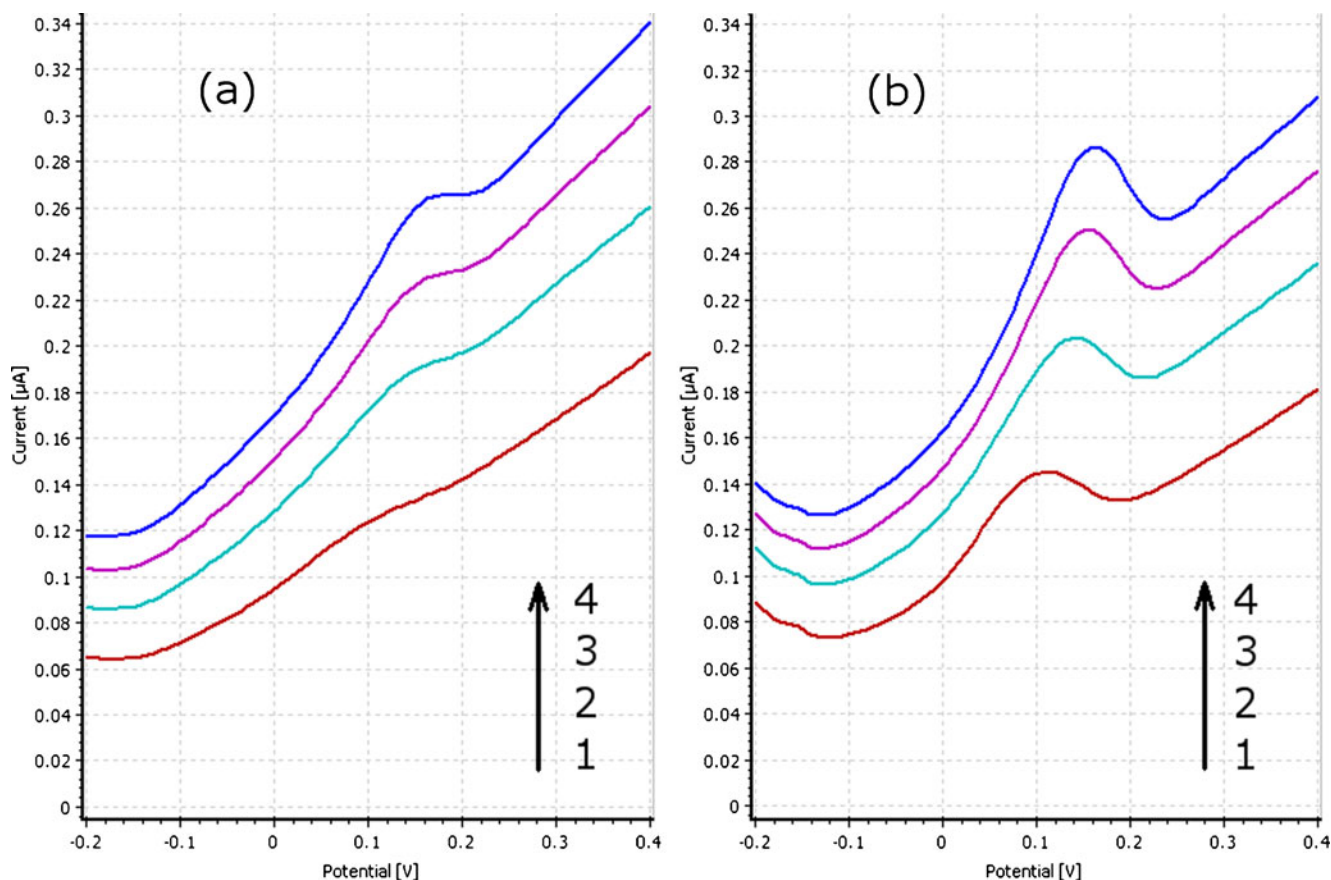


Fig. 4 Voltammograms of **a** As(V) and **b** As(III) on the CB/PE electrode in clean background (curve 1) and with addition of 0.002 M KCl (curve 2); 0.004 M KCl (curve 3); and 0.006 M KCl

(curve 4). Background is 0.005 M HClO₄+0.5 mg/L Fe(III); [As(V)]=0.0050 mg/L; [As(III)]=0.0030 mg/L. $E_{\text{dep}}=-2.3$ V; $t_{\text{dep}}=30$ s

graphite electrode. Increasing the concentration of chlorides in the solution to over 0.005 M causes only a slight variation in the arsenic peak current but at the same time increases the residual current and the signal to noise ratio is thus worsened. Increasing pH over 4 leads to hydrolysis of Fe(III) salts in the solution. Decreasing pH of the solution down to pH<2 does not add to the increase in arsenic peak magnitude, but increases the slope of the voltammogram and considerably shortens the lifetime of the electrodes. Thus, 0.005 M HCl is the optimum background solution for determination of arsenic (V) and arsenic(III) on the CB/PE electrode in the presence of Fe(II, III) ions. Because no difference was found between the effects of Fe(II) and Fe(III) addition, trivalent iron was added to the solution in further studies.

Influence of the deposition potential

In the absence of Fe ions with deposition potential varied from -1.2 to -3 V at the CB/PE, no response for As(V) nor As(III) was obtained. Electrodeposition of arsenic from As(V) or As(III) solutions on the CB/PE electrode in the presence of Fe(III) begins at potentials E_{dep} negative to -1.4

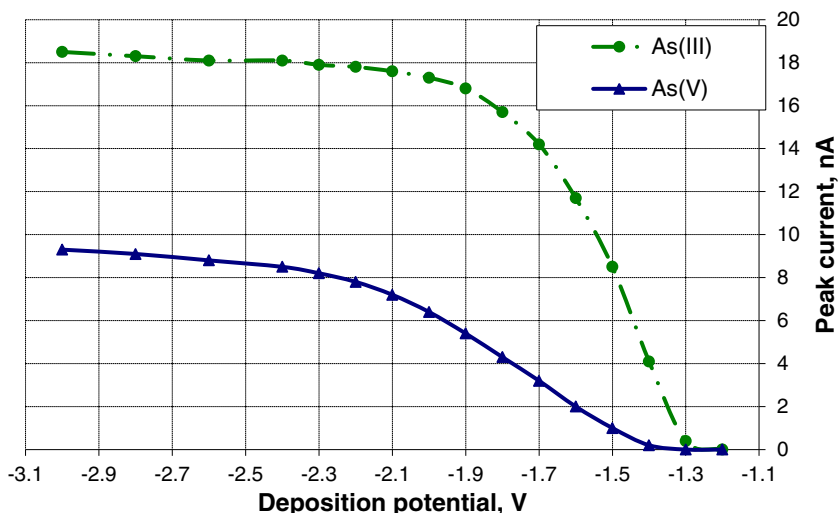
and -1.3 V for As(V) and As(III), respectively (Fig. 5). At potentials lower than -2.2 V, an increase is found not only of the arsenic peak current, but also of the slope of the current baseline as well. It was established that a deposition at potentials negative to -2.3 V impairs the reproducibility of the anodic peak of arsenic and shortens the lifetime of the electrodes between renewals (cut) of their surface.

It should be noted that with gold electrodes [12, 22], the $I(E)$ dependence for As(III) differs greatly from that for As(V). Arsenic(III) is reduced already at -0.4 V, and there is a decrease in current observed at lower potentials probably due to the formation of arsine.

The accumulation of iron on the surface of the CB/PE electrode starts at potentials more negative than -1.5 V (Fig. 6b). In the anodic potential sweep from -0.8 to 0.4 V, an oxidation peak $\text{Fe}^0 \rightarrow \text{Fe}^{2+}$ is recorded at $-0.42 (\pm 0.02)$ V (Fig. 6a). Apparently, arsenic is deposited on the CB/PE surface simultaneously with iron, and if the deposition of iron is hindered, no arsenic is deposited on the electrode.

When the concentration of As(V) or As(III) in the solution is increased (which means a decrease in iron to arsenic ratio), the anodic peak current of iron decreases (left peaks

Fig. 5 Peak current of As(V) and As(III) vs. deposition potential. Background is 0.005 M HCl+0.5 mg/L Fe(III); atmospheric oxygen; [As(V)]=0.010 mg/L; [As(III)]=0.004 mg/L; $t_{\text{dep}}=30$ s



at Fig. 7a). When the Fe(III) to As(V) ratio reaches 1:9 or the Fe(III) to As(III) ratio reaches 1:30, the iron peak at -0.45 V almost disappears. On the contrary, the voltammograms reveal an electrooxidation peak in between the Fe and

As peaks at -0.29 (± 0.02) V (left peaks in Fig. 7b), which increases with increasing the arsenic concentration in the solution. This peak is likely to be due to selective electro-oxidation of iron from the iron–arsenic IMC.

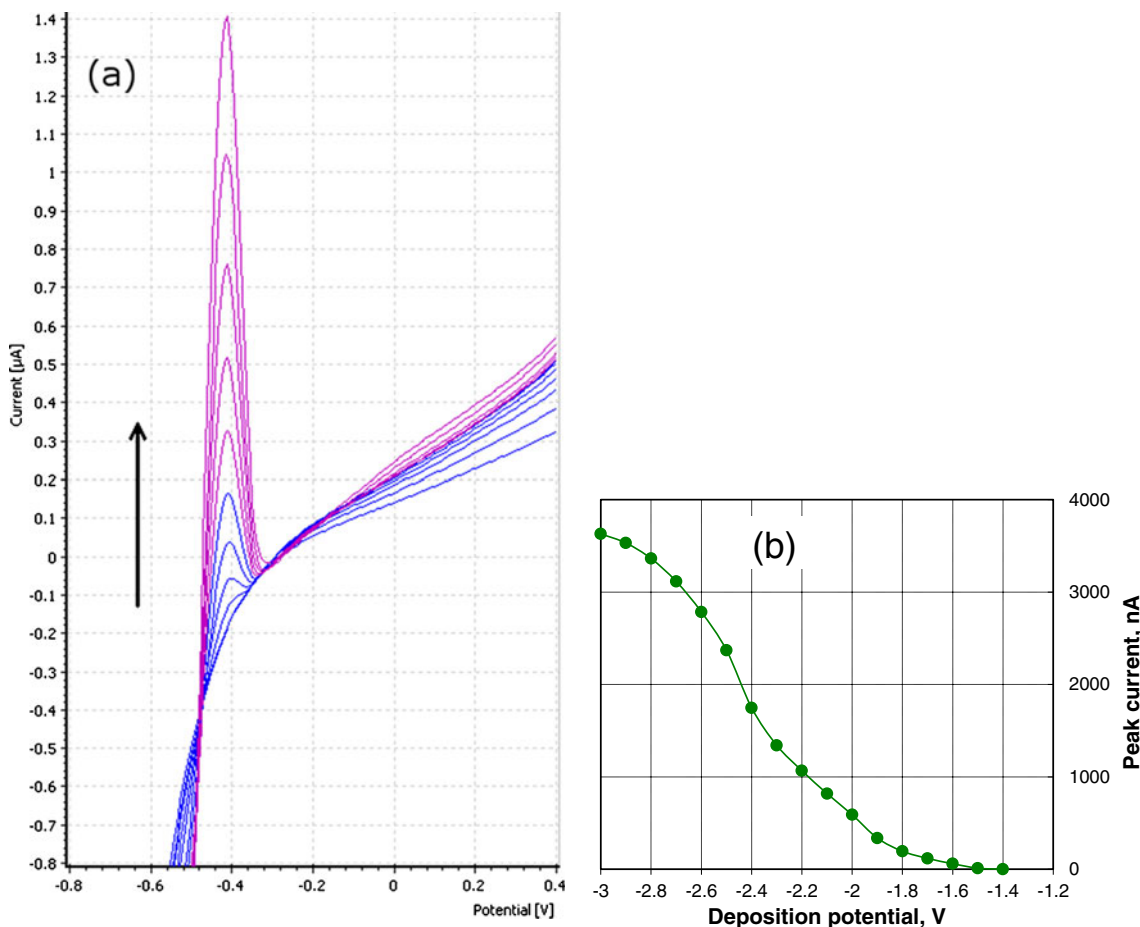


Fig. 6 **a** Voltammograms of Fe(III) on the CB/PE electrode at deposition potentials $-E_{\text{dep}} = 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1,$ and 2.2 V (curves 1–10 from bottom to top). Background is the aerated

0.005 M HCl+1.0 mg/L Fe(III); $t_{\text{dep}}=60$ s. **b** Anodic peak of iron vs. E_{dep} at similar conditions

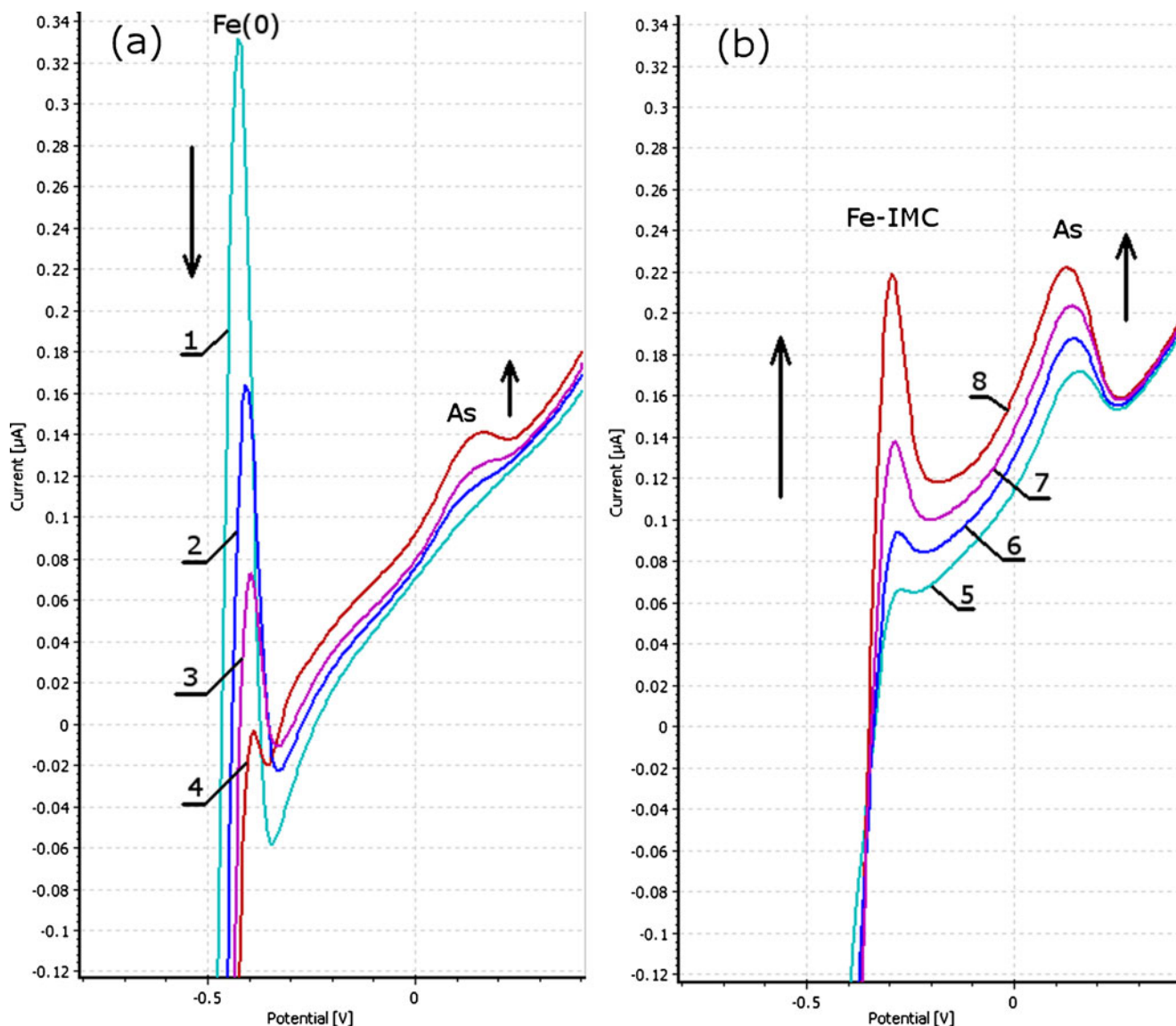


Fig. 7 Voltammograms of As(V) on the CB/PE in 0.005 M HCl + 0.5 mg/L Fe(III) without As(V) (curve a, 1) and with addition of 0.005 (a, 2), 0.01 (a, 3), 0.02 (a, 4), 0.04 (b, 5), 0.06 (b, 6), 0.08 (b, 7), and 0.1 mg/L (b, 8) As(V). $E_{dep} = -2.3$ V; $t_{dep} = 40$ s

Figure 8 shows the peak current variation for elemental iron and iron from an Fe–As IMC (curves 1 and 2) with an increase in As(III) and As(V) concentrations. Due to the more intense deposition of arsenic from As(III)-containing solutions on the electrode, iron is bound into an IMC at much lower As(III) concentrations. For example, the IMC peak at -0.29 V is observed even at 0.01 mg/L of As(III) (Fig. 8a) and 0.05 mg/L of As(V) (Fig. 8b).

Effect of Fe(III) concentration

The arsenic peak current increases as the Fe(III) ion concentration in the solution is increased to a certain value. Further increase of the iron concentration in the solution slightly affects the response of arsenic but increases the

residual current at 0.0 V. The optimum Fe(III) ion concentration in the solution depends on the amount of arsenic deposited on the electrode surface. The higher the arsenic concentration in the solution or the longer the deposition time, the higher should be the iron concentration in order to provide the maximum arsenic peak. The calibration diagrams obtained for the As(V) and As(III) solutions are linear in the limited range of arsenic ion concentration. The linearity range depends on the Fe(III) concentration in the solution (Fig. 9). Because with the same As(V) and As(III) concentrations in the solution, the amount of As(III) reduced on the CB/PE surface is larger, the optimum Fe ion concentration in the solution for determination of As(V) and As(III) at a level of 0.002–0.02 mg/L differs and is 0.5–1.0 mg/L for As(V) and 1.0–1.5 mg/L for As(III).

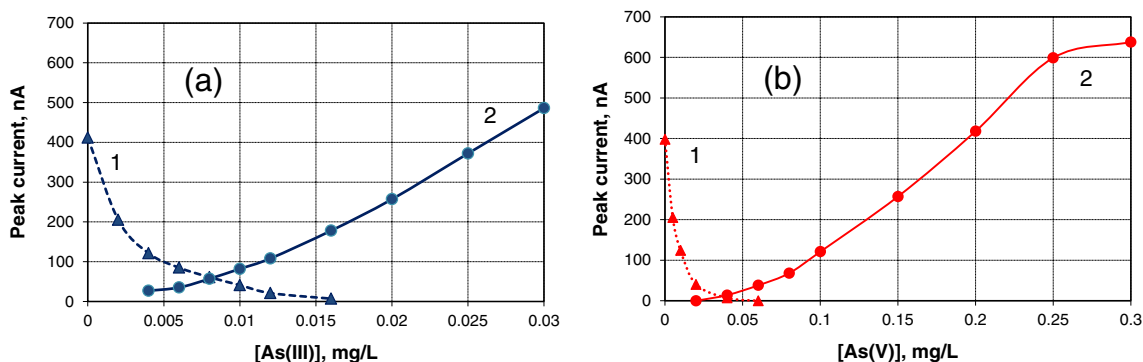


Fig. 8 Dependence of the Fe(0) peak current at $-0.42 (\pm 0.02)$ V (dashed line) and the peak current of Fe IMC at $-0.29 (\pm 0.02)$ V (solid line) both vs. concentration of **a** As(III) and **b** As(V). Background is the aerated 0.005 M HCl+0.5 mg/L Fe(III). $E_{\text{dep}}=-2.3$ V; $t_{\text{dep}}=40$ s

The formation of the AsFe intermetallic compound on the electrode surface gives additional peaks in the voltammogram due to the selective electrooxidation of iron from the compound. This causes a distortion of the arsenic peak and complicates its processing. This effect was diminished as follows: on completion of arsenic and iron deposition, before the potential sweep, a potential more positive than the electrooxidation potential of iron -0.45 V and more positive than the potential of its stripping from the compound with arsenic -0.29 V was applied to the electrode for 3–5 s (Fig. 10). It can be seen from Fig. 10 (curve 6) that the exposure to a potential of $E_{\text{rest}}=-0.1$ V for 5 s (without vibration) causes oxidation of iron, whereupon the voltammogram reveals only the peak of arsenic. The potential sweep was normally started from -0.2 or -0.3 V (iron is not reduced back on the electrode due to high irreversibility). Possible hypotheses of the iron (both Fe ions and atoms) effect in stripping voltammetric determination of arsenic are discussed below.

Optimum conditions for arsenic determination

The following optimum conditions were found for the determination of arsenic(V) and arsenic(III): the background

solution is 0.005 M HCl with an additional concentration of 0.5 mg/L Fe(III) for As(V) determination or 1.0 mg/L Fe(III) for As(III) determination; $E_{\text{dep}}=-2.3$ V; rest potential E_{rest} of -0.1 V for 3–5 s before the potential sweep; potential sweep from -0.2 to $+0.4$ V; scan rate 120 mV/s.

Under these conditions, the calibration plot is linear up to a stripping peak height of 60 nA for As(V) and up to 100 nA for As(III). In the analysis of solutions for arsenic content, the deposition time should be chosen such that the arsenic peak current would not be greater than half of the above values. This allows determination of As(V) by the standard addition method in the range of 0.002 to 0.1 mg/L with $t_{\text{dep}} < 200$ s at the lower end and as low as $t_{\text{dep}}=5$ s for larger concentrations. The As(III) determination is possible in the range of 0.0004 to 0.02 mg/L with the same deposition times. The voltammograms of arsenic stripping after its deposition from As(III) and As(V) solutions are shown in Fig. 11 and the calibration plots are given in Fig. 12.

The solutions with addition of As(III) and As(V) solutions were analyzed under optimum conditions. The obtained results show a good accuracy of stripping voltammetric determination of the ions (within the confidence intervals) at concentration levels below the maximum

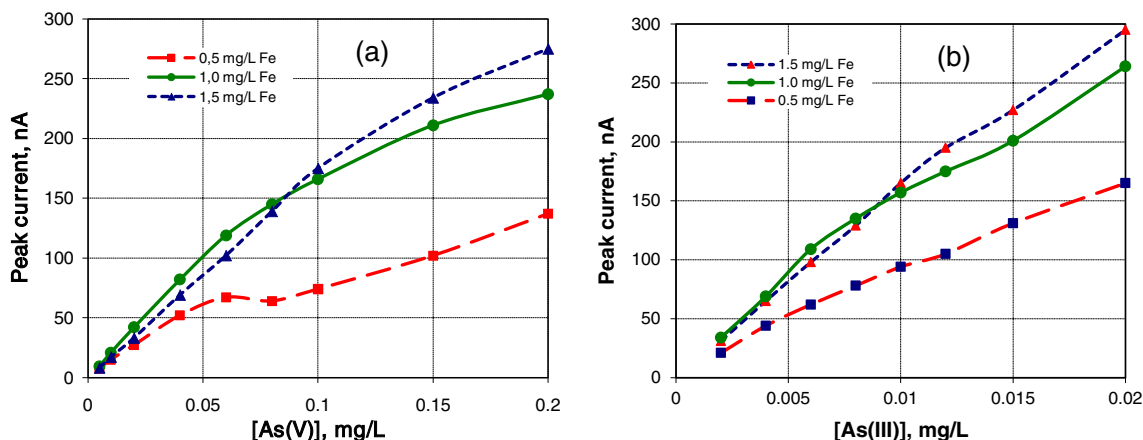


Fig. 9 Dependence of the As peak current on the concentration of **a** As(V) and **b** As(III) for [Fe(III)]=0.5, 1.0, and 1.5 mg/L. Background is the aerated 0.005 M HCl. $E_{\text{dep}}=-2.3$ V; $t_{\text{dep}}=60$ s

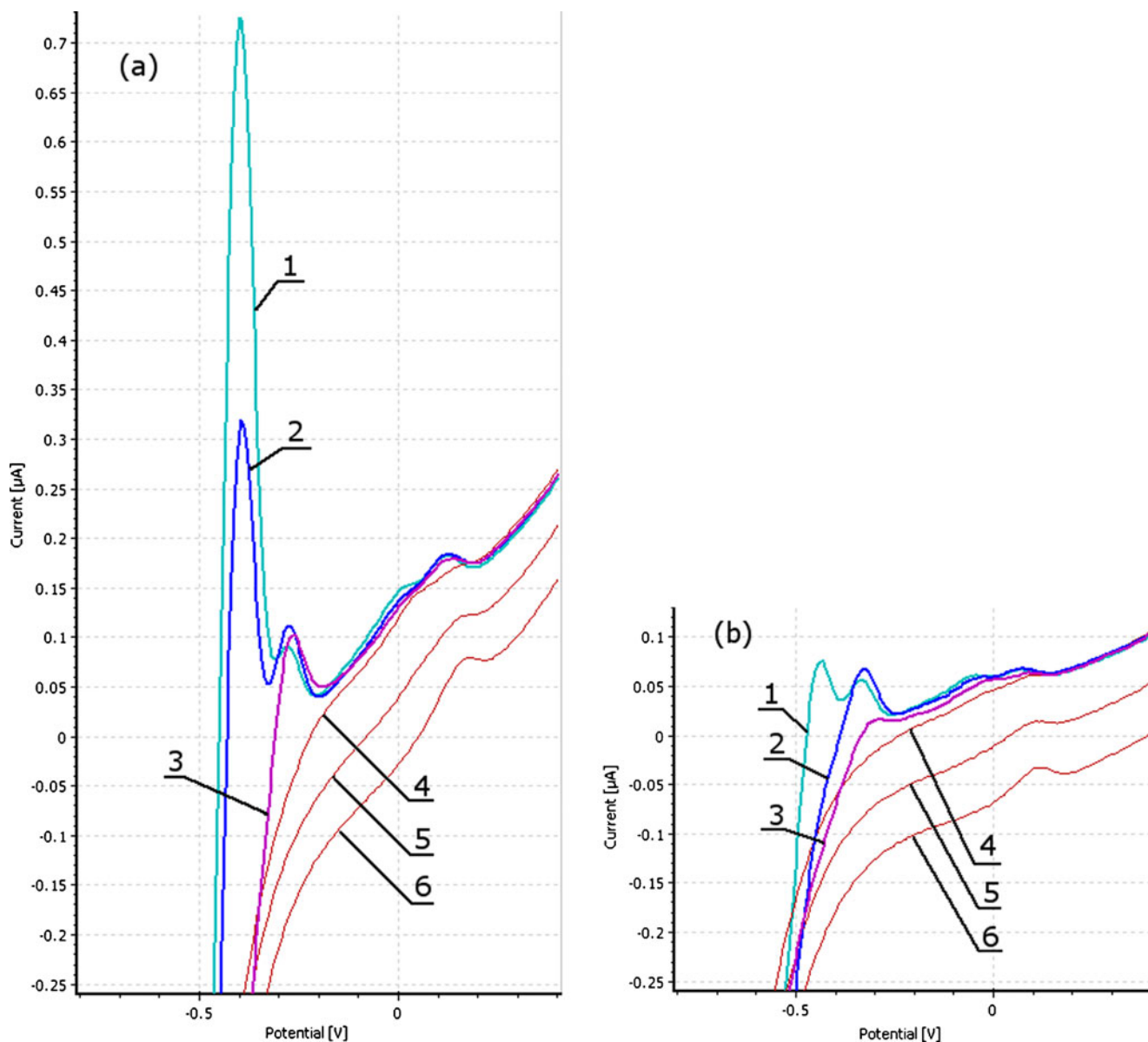


Fig. 10 Voltammograms with the electrode kept before the sweep at various potentials of $-E_{rest}=0.7, 0.6, 0.5, 0.3, 0.2,$ and 0.1 V. The starting sweep potential is -0.8 V. Background is 0.005 M HCl. **a**

b 1.0 mg/L Fe(III); **b** 0.5 mg/L Fe(III). At both figures $[As(III)]=0.0050$ mg/L; $E_{dep}=-2.3$ V; $t_{dep}=60$ s

concentration limit (0.01 mg/L) on the Fe-modified CB/PE electrodes (Table 1).

The practical minimum $[As(III)]$ at $t_{dep}=120$ s is 0.0003 mg/L; LOD= 0.00016 mg/L (3σ).

The practical minimum $[As(V)]$ at $t_{dep}=120$ s is 0.0015 mg/L; LOD= 0.0008 mg/L (3σ).

Influence of other elements

Electrolysis at potentials less than -2.0 V reduces most of the known metals, which interact with each other and with iron. In the present work, we did not undertake the task to

study the influence of all metals; it was more important to find a way to eliminate the influence of the most widespread metals under the conditions chosen for arsenic determination on the CB/PE electrode. We measured the response of As(V) at 0.01 mg/L and As(III) at 0.002 mg/L in 0.005 M HCl + 1 mg/L Fe(III) in the presence of oxygen and the tested interfering metals. It was found that the introduction of an additional rest step at $E_{rest}=-0.1$ V for $3-5$ s, i.e., at a potential more positive than the oxidation potentials of impurities but more negative than the oxidation potential of arsenic (0.15 V), makes it possible to eliminate the influence of most of the tested metals. Zinc, cadmium, lead,

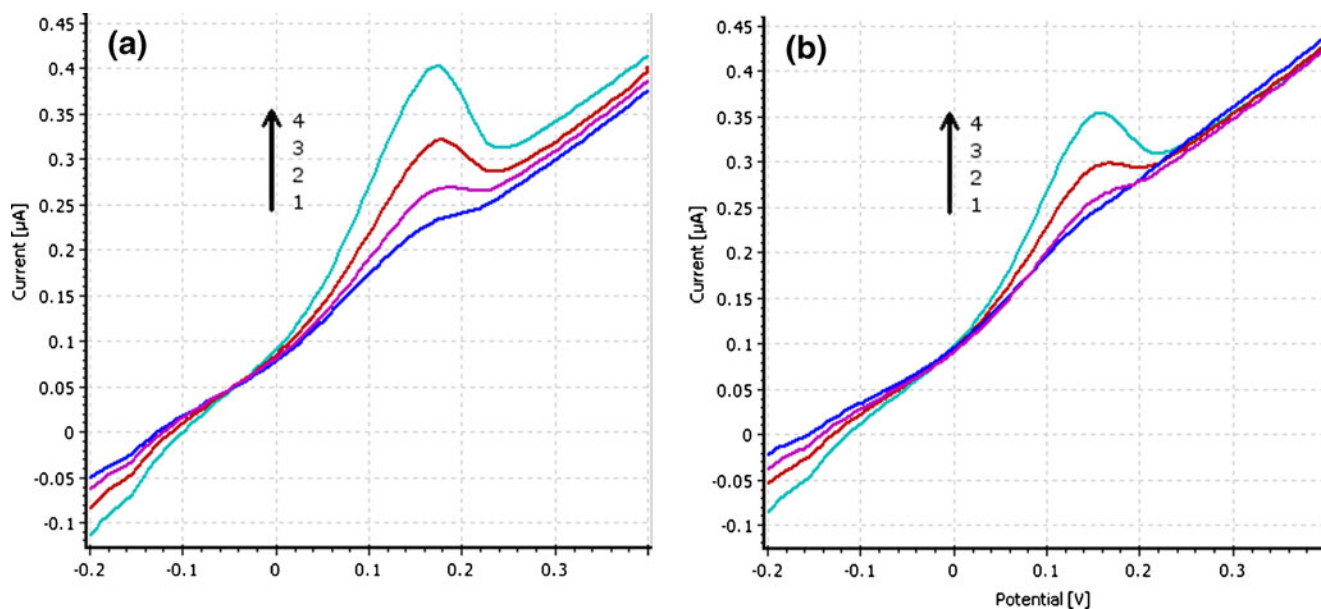


Fig. 11 Voltammograms of As at **a** As(III) concentrations of 0.00050, 0.0010, 0.0020, and 0.0040 mg/L and **b** at As(V) concentrations of 0.0020, 0.0040, 0.0080, and 0.016 mg/L. Background is the aerated 0.005 M HCl. $E_{\text{dep}} = -2.3$ V; $t_{\text{dep}} = 120$ s

cobalt, and nickel did not affect the arsenic peak at 1 mg/L. Introduction of 0.1 mg/L copper and antimony(III) did not interfere in the arsenic determination ($E_{\text{p,Cu}} = -0.25$ V; $E_{\text{p,Sb}} = 0.0$ V). Antimony(V) was not reduced under the experimental conditions. Small copper additions up to 0.005 mg/L even increased the magnitude of the arsenic signal—an effect which probably can be exploited in further studies.

Not only the interference by other elements was of interest, but also the possibility to record the anodic peak of arsenic in the presence of other ions, besides Fe ions. Ga(III) and In(III) cations introduced in the absence of iron did not allow the detection of arsenic under our conditions. However, it was found that nickel and cobalt at a concentration of 0.1 to 0.5 mg/L without Fe(III) or Fe(II) in a 0.01-mg/L As(V) solution are deposited together with arsenic on the CB/PE electrode. On the voltammogram ($E_{\text{rest}} = -0.8$ to -0.5 V), a cobalt peak at $E_{\text{peak}} = -0.24$ V was detected, and at 0.15 V, an anodic peak of arsenic appeared, but its magnitude was smaller than that with iron. In stripping voltammetric determination of arsenic, nickel gives an anodic peak at -0.03 V. At a concentration higher than 0.1 mg/L, this peak conceals the anodic peak of arsenic. Interestingly, the deposition of Fe, Co, and Ni on the CB/PE surface occurs with high overvoltage (at -1.5 V) as the deposition of arsenic (at -1.5 V) in their presence does. This confirms the probability that these metals form an alloy or intermetallic compound with arsenic. Thus, the addition of Fe ions in the solution is best suited for the determination of arsenic(V) and arsenic(III), and the exposure of the electrode to a rest potential $E_{\text{rest}} = -0.1$ V eliminates the influence of most of the metals during the electrooxidation of the precipitate.

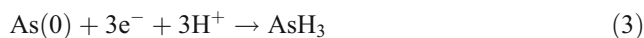
Discussion of the results

A closer look at the electrochemical reactions involved in the ASV determination of arsenic(V) and arsenic(III) clarifies the role of iron at the different stages of this process.

Electroreduction of As(III) or As(V) on the electrode (M) at potentials of -1.8 to -2.8 V:



Under certain conditions, further reduction of arsenic with the formation of hydride is possible:



Electrochemical hydride formation serves for producing arsenic hydride (and arsenic as target products) [23], for removal of toxic arsenic from water solutions [24], and for determination of arsenic impurities by hydride generation atomic absorption spectrometry [25], hydride generation mass spectrometry [26], and voltammetry [27]. Chemical generation of AsH_3 has also been used as a separation step for a follow-up determination of As by differential pulse voltammetry [28]. The formation of AsH_3 or As(0) and their amount depends on the substrate material, current density, and solution composition.

In stripping voltammetry, elemental arsenic is deposited on different electrodes in solutions at pH values of 1–3 and oxidized at potentials of $+0.2$ to $+0.1$ V according to

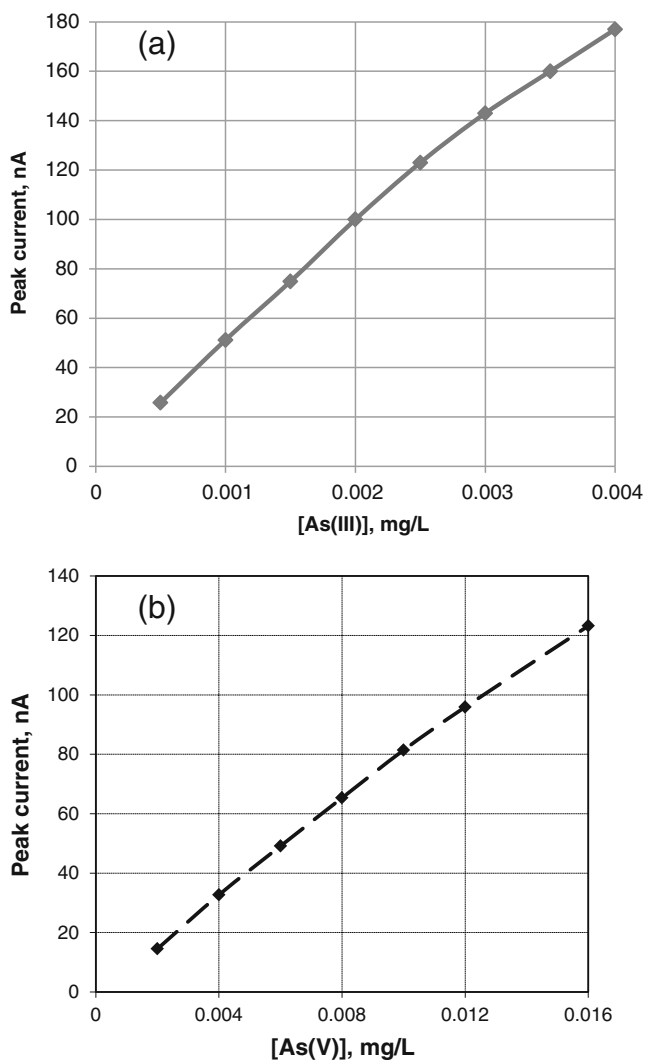
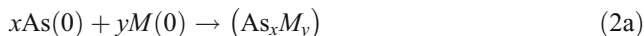


Fig. 12 Calibration plots for determination of **a** As(III) and **b** As(V) at CB/PE electrode. Background is the aerated 0.005 M HCl. Fe(III) addition was **a** 1.0 mg/L or **b** 0.5 mg/L. $E_{dep} = -2.3$ V; $t_{dep} = 120$ s



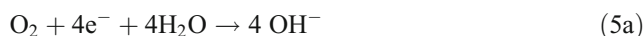
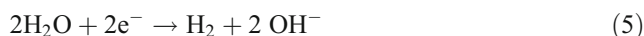
The above pattern of reactions is very simplified. Reaction (1) cannot only proceed as an electrochemical reaction,

but also as a chemical reaction, e.g., as a reduction of As(V) by electrolysis products like hydrogen *in status nascendi*. The deposited arsenic (reaction (2)) can form an alloy or intermetallic compound with the substrate material (M):



In electrooxidation of an intermetallic compound with an element more electronegative than arsenic, the electronegative metal is first selectively oxidized, and then the remaining arsenic is stripped by reaction (4).

Reactions (1) and (2) can proceed in parallel with the release of hydrogen from weak acids and water, and also with discharge of oxygen molecules attended by alkalization of the near-electrode layer:



The fact that the signal of As(0 → III) is impossible to obtain in stripping voltammetry on carbon electrodes or CB/PE (reaction (4)) can be explained by several reasons: First, formation of arsine by reaction (3) is possible, so that no As(0) remains on the electrode surface. Second, strong binding of arsenic to carbon could prevent its oxidation. A third reason may be an electrochemical inactivity of arsenic on carbon under our test conditions (low current densities and low arsenic current yield). Unfortunately, the amount of arsenic (arsine) detected by stripping voltammetry (this amount can be estimated from the area beneath its anodic peak) is too small to experimentally verify the foregoing hypotheses.

Table 2 presents the arsenic–substrate binding energy (ϵ_{As-M}) calculated for various substrate materials by the Pauling equation [29]. These data suggest that the As–C binding energy is higher than that of As–metal, making the As chemisorption at carbon a less probable process.

Let us consider the possible positive effects of iron or its ions on different stages of the complex process of arsenic reduction and anodic oxidation (reactions (1)–(4)):

Table 1 Results of determination of As(III) and As(V) in model/pure solutions ($n=6$; $p=0.95$)

As(III)			As(V)		
Added (mg/L)	Found (mg/L)	Recovery (%)	Added (mg/L)	Found (mg/L)	Recovery (%)
0.0025	0.0028±0.0005	112	0.00044	0.0051±0.0012	120
0.0042	0.0037±0.0007	88	0.00084	0.0092±0.0018	110
0.0050	0.0045±0.0008	90	0.0012	0.0014±0.0002	116
0.0086	0.0084±0.0012	98	0.0024	0.0028±0.0005	116
0.010	0.011±0.002	110	0.0056	0.0049±0.0009	88
0.020	0.022±0.002	110	0.0078	0.0077±0.0011	99
0.034	0.034±0.003	100	0.012	0.013±0.006	108

Table 2 Arsenic–substrate metal binding energy

Substrate metal (M)	C	Au	Fe	Cu	Ga	In	Mn
$\varepsilon_{\text{As-M}}$ (kJ/mol)	632.2	436.6	394.9	370.8	274.7	260.3	254.7

Possible effect of Fe ions

The presence of Fe ions at the electrode–solution interface under our test conditions (at pH=2–3, $\text{Fe}(\text{OH})^{2+}$ ions dominate) can assist reaction (1):

- The excess (100-fold) amount of positively charged Fe^{2+} and Fe^{3+} ions shields the negative charge of the cathode, reducing the repulsion of hydroarsenate anions. Multiply charged Ga(III), In(III) ions are bound to produce the same effect, but their influence did not promote As detection at CP/PE without the addition of Fe ions in the solution. Besides, Fe(II) ions behave in the same way as Fe(III) ions such that the contribution from eliminated repulsion is likely to be small.
- At the stage of electrodeposition ($E < -2$ V), hydrated iron forms are produced near the surface (simultaneously with OH^- ions) that can adsorb As(V) or As(III) anions/molecules. This increases the rate of reaction (1) and hence the amount of deposited As(0). Adsorption of As ions on Fe hydroxides is widely used in water purification from arsenic(V) and arsenic(III) contamination [19]. For determination of As(V) and As(III), the optimum solution acidity is pH=2–3. Acidification of the Fe(III) solution to pH<2 decreases the positive effect of Fe on the peak height. This effect can be also attributed to the decrease in deposited iron fraction with increasing the hydrogen current yield.

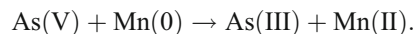
Probable effect of Fe(0)

- Chemical reaction of As(V) with Fe(0)

At potential between -1.4 and -2.3 V, metallic iron can be deposited on carbon electrodes (for $\text{Fe}^{2+}/\text{Fe}^0$, $E^\circ = -0.44$ V vs. SHE or -0.66 V vs. Ag/AgCl). As can be seen from Fig. 6a and b, the anodic peak potential of iron (transition $0 \rightarrow 2$) is -0.45 V. Actually, modification of the electrode surface with iron takes place. The obtained electrode is most likely to be an Fe microelectrode array similar to a gold microelectrode array as shown in Fig. 4. However, modification of the CB/PE electrode with iron is efficient only with Fe ions introduced into the solution, i.e., in situ. If iron is deposited ex situ, particles of elemental iron are rapidly oxidized and no arsenic signal is detected. The high reducing ability of the $\text{Fe}^{2+/0}$ system (compared to $\text{As}^{(5+/3+)}$, $E^\circ = 0.55$ V vs. SHE) provides a thermodynamic possibility of the chemical reduction of arsenic(V). And taking into account the negative potential of electrodeposition, Fe(II) will be reduced to Fe(0), thus

providing the (electro)catalytic effect with Fe(0) as a redox mediator [30] according to $\text{As}(\text{V}) + \text{Fe}(\text{0}) \rightarrow \text{As}(\text{III}) + \text{Fe}(\text{II})$.

A similar chemical reaction mechanism was offered for Mn(II)/Mn,Au by Gibbon-Walsh et al. [15] at the gold microelectrode, but it was not considered to have an electrocatalytic nature:



The product of this reaction Mn(II) is thought to be diffused into the bulk solution under vibration.

But there is a difference in the nature of Fe(II)/Fe(0),C and Mn(II)/Mn(0),Au effect on the ASV of arsenic. The addition of Fe ions is required for reduction of both As(V) and As(III) forms into As(0) deposit at the carbon electrode, whereas the addition of Mn at Au-doped electrode is not required for reduction of As(III). This fact make us search for other mechanisms of Fe effect on electrodeposition of As ions at carbon-based electrode.

- Modification of electrode surface with Fe

Particles of Fe(0) deposited by electrolysis may become electrocatalytic sites for easier reduction of arsenic ions. Simultaneous deposition of Fe(0) and As(0) on the electrode surface (at $E_{\text{dep}} < -1.4$ V) can form an intermetallic compound (Fe IMC). The Fe–As phase diagram exhibits three compounds: Fe_2As , FeAs , and FeAs_2 [31]. Addition of excess arsenic (Fe/As=1:9 and higher) and subsequent stripping voltammetric analysis decrease the electrooxidation peak of Fe(0) and result in additional peaks (Fe IMC) due to selective electrooxidation of iron from its IMC with arsenic (Figs. 7 and 8). The residue of arsenic is dissolved from the electrode at a potential of (0.12 ± 0.05) V.

Cobalt and nickel have similar positive effect on As deposition onto the CB/PE electrode; however, electrooxidation peaks of Co (-0.3 V) and Ni (0.0 V) are very close to the arsenic peak and mask the latter. Stripping of Fe(0) occurs near -0.45 V, which allows for registration of arsenic peak at $E^\circ = 0.1$ V even in the presence of excess iron.

- Fe as inhibitor of AsH_3 evolution reaction

Deposition of Fe(0) on the electrode is bound to impede the As(III) hydride formation, a reaction which can decrease the amount of As(0) on the electrode. It is known that transition metals like Cu, Fe, Ni, Co, etc. inhibit the formation of AsH_3 [32–34]. According to Denkhaus et al. [32], only metal cathodes with high hydrogen overvoltage provide a high arsenic yield. The hydrogen overvoltage on iron, gold, and copper is average (about -0.7 V); on mercury,

lead, cadmium, and glassy carbon, the overvoltage is high (more than -1 V); and on platinum, palladium, etc., overvoltage is low. In considering various hypotheses of the possible effects of iron on the anodic peak of arsenic, we come to the conclusion that iron displays a complex of electrochemical properties the combination of which is favorable for the stripping voltammetric determination of arsenic. At the stage of electrolysis, iron is deposited at potentials less than -2.0 V simultaneously with arsenic in the form of IMC (As–Fe). During the stripping stage, the more electronegative iron is dissolved from the electrode before the stripping potential of As(0) and does not mask the arsenic peak. Electrochemically inactive arsenic on the carbon-containing substrate becomes active on the new in situ Fe-modified sensor based on a carbon microelectrode array. Thus, the conditions found for simultaneous deposition of arsenic and iron are basic to the new technique of stripping voltammetric determination of both arsenic(III) and arsenic(V).

The proposed stripping voltammetric technique fails to distinguish between As(III) and As(V) in the solution, but allows the determination of total arsenic from any of its forms. An analyst can choose a way of arsenic reduction to one of its forms (i.e., sample preparation) according to the purposes of analysis. If very sensitive determination of arsenic is required (at a level of 0.1 $\mu\text{g/L}$), it is more beneficial to use As(III); in this case, the preparation is longer and requires chemical reagents. If simpler and express determination of arsenic is important (at a level of 1 μg), it is more advantageous to reduce the total arsenic to As(V); the sample preparation for oxidation (e.g., with ozone) is simpler, takes a short time (5–10 min), and requires no chemical reagent. This, in view of the high stability of arsenic(V), makes the second method more attractive than the As(III) determination.

Conclusion

Stripping voltammetric signals of arsenic(V) and arsenic(III) at the level of microgram per liter were obtained for the first time on carbon-based electrodes in the presence of Fe ions in the solution without removal of oxygen. Various hypotheses of the effects of Fe(III) ions were considered. The most probable role of iron consists in simultaneous deposition with arsenic on the carbon electrode with the formation of an alloy or intermetallic compound. Similar properties are displayed by other metals of the Fe group; however, in the presence of cobalt, the arsenic response is lower, and the peak potential of nickel is nearly coinciding with the anodic peak potential of arsenic. Thus, carbon in situ modified with iron is a new sensor for determination of arsenic(V) or (III). The factors that affect the magnitude of analytical signals of

arsenic in stripping voltammetry were studied. The operating conditions were the following: 0.005 M HCl background solution in the presence of oxygen and 1 mg/L Fe(III), and the deposition potential is -2.3 V. An interfering action of certain metals was found and was eliminated by exposure of the electrode to a potential of -0.1 V for 3–5 s before the anodic potential sweep.

The proposed sensor and the new technique of stripping voltammetric determination of arsenic on the Fe-modified carbon composite electrode allow the determination of As(III) with a LOD of 0.16 $\mu\text{g/L}$ (3σ) and As(V) with a LOD of 0.8 $\mu\text{g/L}$ (3σ) in the range of concentrations from 0.3 to 100 $\mu\text{g/L}$ and from 1.5 to 300 $\mu\text{g/L}$, respectively. The new method of determination of As(III) and As(V) differs from known analogues (at gold electrodes) by its simplicity, low cost, and availability of the electrode material.

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