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ORIGINAL PAPER

Direct reduction of As(V) physically attached to a graphite electrode mediated by Fe(III)

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Abstract As(V) is electrochemically reduced on the surface of a carbonaceous electrode in the presence of hematite and hydrochloric acid 1 M. The influence of other iron oxides (goethite and limonite) was also tested, although they did not provided better results. The potential required to achieve the reduction must be lower than −0.3 V. The anodic voltammograms exhibit a peak at 0.14 V which corresponds to the oxidation of the As° previously generated during the pre-treatment step (−1 V, 5 s) to As(III). Fe(II) generated during the pre-treatment step plays a relevant role in the final reduction to As° which is subsequently reoxidized to As(III) in the anodic scan. This has been applied to the direct detection of 5 mg kg^{-1} of arsenic in a solid sample of compost with high concentration of iron oxides by square wave voltammetry.

Keywords Arsenic · Reduction · Iron oxides · Electrochemistry · Voltammetry

1 Introduction

The electrochemistry of arsenic in acidic aqueous solution is well documented and it is generally accepted that only the redox processes involving the As(III)/As° couple can be observed [1]. Kao et al. have reported that the reduction of As(V) to As(III) is possible at basic pH on a Pt electrode, but through a very complicated process involving the formation of oxides on the electrode surface [2].

Thus, the reduction of As(V) to As° in aqueous media implies its previous reduction to As(III) through different strategies. Several chemical reagents in highly acidic media have been used, like iodide [3], manitol [4], $CuCl_2$ [5] and L-cysteine [6]. Sodium sulphite is one of the most successful, because the total reduction of As(V) to As(III) can be achieved in a heated acidic solution, (1 M acid concentration and 80–100 °C for 20 to 30 min), and the excess of the reagent eliminated as volatile SO_2 [7, 8].

To avoid the addition of chemicals and to simplify the procedures other approaches have been applied. Huang et al. performed the reduction directly onto a gold film electrode at −1.6 V versus Ag|AgCl|1 M HCl, and hydrochloric acid 2.5 M [9]. Huiliang et al. [10] have proposed the direct reduction of As(V) on a gold covered platinum fibre electrode, in a very acidic media (4 M HCl), applying very negative potentials (−1.6 V vs. Ag|AgCl|KCl sat). Gründler et al. have used a heated 25 μm gold microelectrode [11]. The heating enhances the reaction rate as well transport to the electrode surface, which is very useful whenever stirring of the solution is not possible and reagents cannot be added as happens in field analysis; detection limits as low as 0.3 μg l^{-1} were reported.

The extremely negative potentials and acidic pH necessary to reduce As(III) to As° cause two main problems: the generation of hydrogen in the solutions and the reduction of As(III) to AsH_3, producing an increase in the limit of detection. If platinum electrodes are used, the generated hydrogen is adsorbed on the electrodes, facilitating reduction to arsine. This problem can be avoided in the presence of Au(III) because As° is codeposited with Au°; the same effect has been observed with Fe(III) [12].

Arsenic can be found in a number of forms in the environment (e.g., as soluble species in waters, adsorbed onto iron oxides [13, 14] or associated with humic substances

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[15]). In anaerobic conditions As(V) is easily reduced to As(III) [14, 16], a more toxic form, which is more soluble and mobile than As(V), being able to migrate to aquifers, Arsenic can be determined in waters by electrochemical methods with limits of detection low enough to comply with legal regulations. However, to study the fate and occurrence of arsenic in the environment it is necessary to analyse other types of sample (soils, sediments, plants and aquatic animals) [17, 18]. When analysing these solid samples, a previous dissolution treatment is often required which can alter the original distribution of species in the solid sample. The dissolution of the sample can be avoided by using an analytical technique which allows the use of solids, in the voltammetry of immobilized microparticles (VMP). This electroanalytical technique was developed by Sholz in the 1990s to perform the direct determination of the analyte in the sample without any previous treatment [19]. The procedure is very simple; the solid sample is physically attached to the carbonaceous surface of the electrode and afterwards the electrode is connected to the electrochemical cell, where the voltammogram is obtained. Differential pulse-VMP has been applied successfully to the detection of arsenic in contaminated soils [20]. It was observed that the presence of iron oxide was essential for obtaining a useful analytical signal. The aim of this work focuses on explaining the role of the iron oxide on the reduction of arsenic and proposing the general use of VMP for direct solid arsenic monitoring.

2 Experimental

2.1 Instruments and reagents

All the chemicals used in this work were analytical-grade reagents. HCl, Fe(III) oxide (hematite), As_2O_3 and As_2O_5 were purchased from Merck. Paraffin was obtained from Aldrich and pyrolitic graphite rods (diameter: 3 mm diameter, length: 40 mm) from SGL Carbon Group. Limonite was precipitated with NaOH 2 M from a Fe(III) solution and goethite were prepared following the procedure described elsewhere [21].

All electrochemical experiments were performed using an Autolab Eco Chemie potentiostat, a three-electrode cell with a Ag|AgCl|KCl (sat) reference electrode and a Pt wire as auxiliary electrode. The working electrode was a paraffin impregnated graphite electrode (PIGE). Nitrogen was bubbled through the 10 mL solution for 5 min before the working electrode was introduced in the electrochemical cell. Linear sweep voltammetry was used with a scan speed of 10 mV s^{-1}.

The PIGE was prepared by immersing a rod of pyrolytic graphite in paraffin in a closed vessel at low pressure as described elsewhere [19].

2.2 Procedure

Mixtures of 2% (w/w) Arsenic oxides, 2% (w/w) iron oxides and 96% SiO_2 were prepared by grinding in an agate mortar to achieve complete mixing. About 25 mg of the sample were transferred to a filter paper and a line of 2 cm was drawn with the help of a spatula. The PIGE electrode was dragged along the line with gentle pressure on it. A small amount of the sample adhered to the electrode surface. The sample not attached to the surface was removed by rinsing the electrode with ultrapure water.

2.2.1 Influence of the pH on the reduction of As(V)

To observe an electroanalytical signal in the linear sweep-voltammogram for As(V) in the solid it was necessary to apply a pre-treatment potential for at least 5 s. The results are shown in Table 1 and some voltammograms can be seen in Fig. 1A. The voltammograms are noisy due to the dissolution of the iron oxides in the strongly acidic medium. A pre-treatment potential lower than −0.3 or −0.5 V, depending on the pre-treatment time selected, was necessary to reduce As(V) on the electrode. The effect of acidity was also significant, indicating the dependence of the pre-treatment and stripping processes on pH. The peak at 0.6 V was shifted anodically with decreasing acid concentration, but the peak at 0.2 V shifted in the opposite direction. Both peaks disappeared in 0.1 M acetic acid-acetate buffer (pH 5). Several examples of As(V) reduction can be found in the literature; in all instances highly acidic media have been reported. In this work, As(V) has been reduced in milder conditions, 1 M hydrochloric acid and 0.1 M oxalic acid (pH 1.3). This reduction is possible due to the mediation of the redox pair Fe(III)/Fe(II) generated during the pre-treatment step.

2.2.2 Influence of the iron oxide

The influence of the type of iron oxide was also investigated. Limonite, goethite and hematite were selected because they are the most common forms of iron (III) oxide and because they exhibit a different degree of crystallization. Limonite ($Fe(OH)_3$) is an amorphous solid, goethite is a more organized oxo-hydroxide (FeOOH) and hematite is a very stable and organized oxide (Fe_2O_3). The results are shown in Table 2. Voltammograms of solid mixtures of As(V):Fe(III):SiO_2 can be seen in Fig. 1B.

In the presence of limonite only a wave at 0.8 V in 1 M HCl was observed. When goethite was used to prepare the mixture a peak at 0.588 V was observed in 4 M HCl and only a wave in 1 M HCl. Hematite produced a

Table 1 Influence of the pre-treatment potential and the media on the stripping peaks potential and number of peaks of a solid sample As_2O_5:Hematite:SiO_2 (2:2:96)

Medium	Pre-treatment potential (V) (5 s)				Pre-treatment potential (V) (10s)			
	−0.1	−0.3	−0.5	−1.0	−0.1	−0.3	−0.5	−1.0
4 M HCl	–	–	0.633 (0.011)	0.633 (0.013), 0.220 (0.013)	–	0.660 (0.020)	0.550 (0.0030)	0.236 (0.009)
1 M HCl	–	–	–	0.868 (0.024), 0.168 (0.017)	–	–	0.748 (0.031)	0.738 (0.040), 0.171 (0.010)
0.1 M Oxalic acid	−0.520 (0.046) 0.042 (0.014)	−0.321 (0.032), 0.115 (0.013), 0.679 (0.038)	−0.420 (0.036), 0.124 (0.011)	−0.409 (0.012), 0.114 (0.006)	–	0.684[a]	0.685[a]	0.685 (0.024), 0.052 (0.006)

Standard deviation is written in brackets. Each value is the mean of five voltammograms. [a] wave. Pre-treatment: −1.0 V for 5 s, scan speed 10 mV s^{-1}

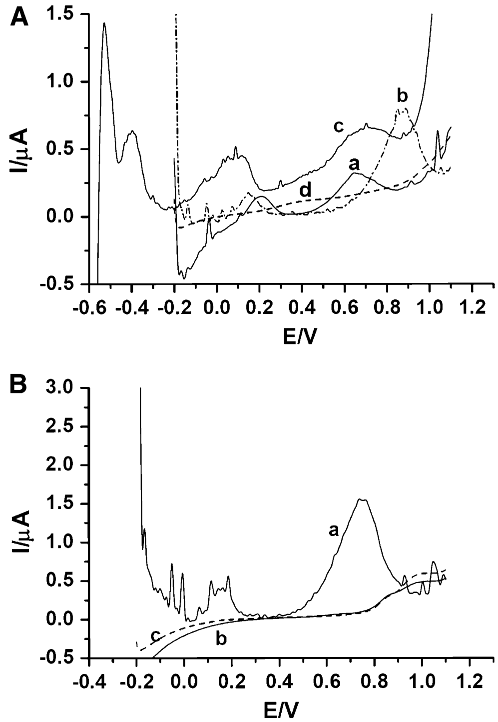

Fig. 1 (**A**) Linear scan voltammograms of a solid mixture of As_2O_5:Hematite:SiO_2 2:2:96 (w/w) in several supporting electrolytes, 4 M HCl (a), 1 M HCl (b), 0.1 M oxalic acid (c) and 0.1 M acetic acid-acetate buffer. Pretreatment: −1.0 V for 5 s. Scan speed: 10 mV s^{-1} (**B**) Linear scan voltammograms of a solid mixture of As_2O_5:iron (III) oxide:SiO_2 2:2:96 (w/w) in 1.0 M HCl obtained with different iron (III) oxides, hematite (a), goethite (b) and Limonite (c). Pretreatment: −1.0 V for 5 s. Scan speed 10 mV s^{-1}

voltammogram with two peaks, at 0.7 and at 0.2 V. The position of the peaks was affected by pH.

An additional peak at 0.9 V was observed in the voltammograms of mixtures containing iron oxides and SiO_2, except in the case of limonite. During the pretreatment electro-dissolution of the iron oxide [22] and its diffusion towards the bulk solution take place. Thus, the peak at 0.9 V corresponds to the process of reoxidation of the electrogenerated Fe(II) during the pre-treatment step. However, the reactivity of the solid depends on its degree of organization, which implies that the well crystallized hematite exhibits slower dissolution kinetics than the amorphous limonite. This explains why no peaks are present in the iron hydroxide voltammogram. The whole process can be described as summarized below:

$$Fe_2O_3 + 2H^+ + 2e^- \Leftrightarrow 2\,FeO + H_2O \quad (1)$$

$$\begin{aligned} &FeO + 2\,H^+ \Leftrightarrow Fe^{2+} + H_2O \\ &Fe^{3+} + 1e^- \Leftrightarrow Fe^{2+} \end{aligned} \quad (2)$$

The peak at 0.2 V is due to the reoxidation of the arsenic deposited on the electrode during the pretreatment

Table 2 Influence of the type of iron (III) oxide in different media on the stripping peak number and position of a solid sample As_2O_5:Hematite:SiO_2 (2:2:96)

Medium	Limonite peak pot (V)	Goethite peak pot (V)	Hematite peak pot (V)	
4 M HCl	–	0.588 (0.027)	0.636 (0.013)	0.220 (0.013)
1 M HCl	0.80[a]	0.80[a]	0.868 (0.024)	0.168 (0.017)
0.1 M Oxalic acid	–	–	0.685 (0.024)	0.052 (0.011)

[a] wave. Standard deviation is shown in brackets. Each value is the mean of four voltammograms. Pre-treatment: −1.0 V for 5 s, scan speed 10 mV s^{-1}

step. This potential and the influence of pH on it suggest the oxidation of As° to As(III):

$$HAsO_2 + 3e^- + 3H^+ \Leftrightarrow 2As^\circ + 2H_2O \qquad (3)$$

The assignation of a process for the peak at 0.6 V is not clear. It may be due to the reduction of iron complexes, specially in oxalic acid medium, but a solid sample containing only hematite did not produced a peak at this potential. This may represent the direct oxidation of the remaining As_2O_3 to As_2O_5:

$$H_3AsO_4 + 2H^+ + 2e^- \Leftrightarrow HAsO_2 + 2H_2O \qquad (4)$$

2.2.3 The process of As(V) reduction

The reduction of As(V) starts at −0.3 V in highly acidic medium when hematite is present in the solid mixture (Table 1). The peak at 0.2 V in the anodic scan indicates that As(V) has been reduced in the pretreatment step. There is no association between the As_2O_5 and the Fe_2O_3 in the solid mixture, because they were just physically mixed, and the explanation for this fact must involve the solubilization of some of the components, which are able to interact with the remaining solid and achieve reduction of As(V).

Several studies have been published showing the redox relationship between the couples Fe(III)/Fe(II) and As(V)/As(III) [14, 16, 23]. It has been observed that Fe(III) can oxidize As(III) to As(V) but Fe(II) is also able to reduce As(V) to As(III) if high As(V) concentration is present at low pH. To explain the voltammograms of the As(V) in the presence of hematite, voltammograms of As_2O_5 inmobilized on the electrode surface were obtained in 1 M HCl containing dissolved Fe(III) or Fe(II) 0.01 M. The corresponding voltammograms obtained after a pretreatment step (−1.0 V for 5 s) are shown in Fig. 2.

The voltammogram of aqueous Fe(III) obtained with a clean electrode showed a peak at 0.913 ± 0.014 V corresponding to the reoxidation of the dissolved Fe(II) generated during the pretreatment step, as described in process (2). When As(V) was deposited on the electrode surface this peak disappeared and a peak at 0.140 ± 0.001 V was observed (see Fig. 2A). When the supporting electrolyte contained Fe(II) 0.01 M, the peak related to process (2) appeared at 0.922 ± 0.003 V. In the presence of solid As(V) on the electrode, a pretreatment step had to be applied (−1.0 V for 5 s) to obtain a peak at 0.134 ± 0.006 V (see Fig. 2A), otherwise no peak was observed. This behaviour suggests that As(V) is reduced by the aqueous Fe(II) generated during the pretreatment due to the pH and reducing conditions used, and afterwards the As(III) is reduced on the electrode to As° following the process (3) which is stripped on the anodic scan.

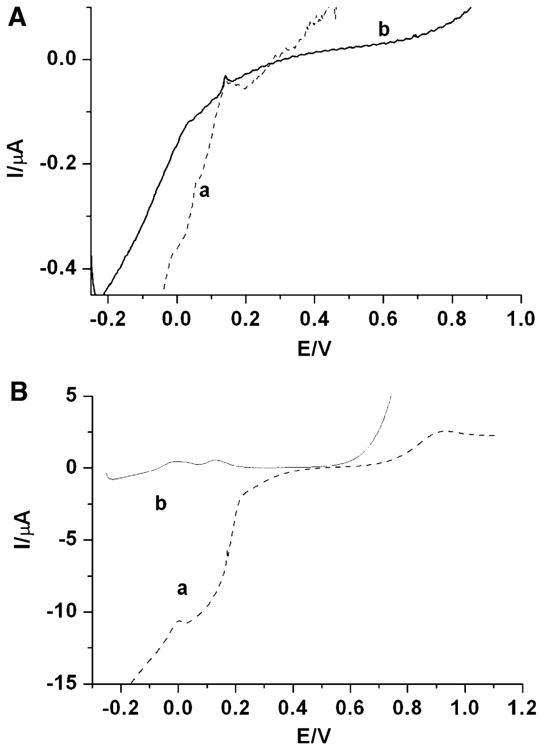

Fig. 2 (**A**) Linear scan voltammograms of As_2O_5:SiO_2, 2:98 (w/w), immobilized on the electrode surface and 0.01 M Fe(III) + 1 M HCl as supporting electrolyte (a) and 0.01 M Fe(II) + 1 M HCl as supporting electrolyte (b). Pretreatment: −1.0 V for 5 s. Scan speed: 10 mV s^{-1} (**B**) Linear scan voltammograms of As_2O_3:SiO_2, 2:98 (w/w), immobilized on the electrode surface and 0.01 M Fe(III) + 1 M HCl as supporting electrolyte (a) and 0.01 M Fe(II) + 1 M HCl as supporting electrolyte (b). Pretreatment: −1.0 V for 5 s. Scan speed: 10 mV s^{-1}

When As(III) was attached to the electrode, the electrochemical pretreatment was applied, and Fe(II) or Fe(III)

Table 3 Influence of the type of iron (III) oxide and the media on the position of the stripping peak when As_2O_3:iron (III) oxide:SiO_2 (2:2:96) was deposited on the electrode surface

Medium	Limonite peak pot (V)	Goethite peak pot (V)	Hematite peak pot (V)	
4 M HCl	0.55[a]	0.588 (0.027)	0.798 (0.058)	0.198 (0.019)
1 M HCl	–	–	0.813 (0.054)	0.137 (0.006)
0.1 M HAc/Ac$^-$	−0.111[b](0.014)	−0.131 (0.014)	−0.145 (0.006)	

Each value is the mean of four voltammograms, standard deviation is shown in brackets. Scan speed: 10 mV s^{-1}, pre-treatment: −1.0 V for 5 s. [a]wave. [b] the pre-treatment potential was applied for 10 s

were present in the supporting electrolyte, two peaks were observed at 0.912 ± 0.014 V and 0.003 ± 0.006 V (see Fig. 2B). In the case of Fe(II), a third peak was also observed at 0.134 ± 0.006 V as in the case of As(V). We do not know the process associated with the peak at 0.003 V but it is probably related to the presence of As(III) in the solid. More studies are necessary to clarify this.

A mixture of 2% of As_2O_3, 2% Fe_2O_3 and 96% SiO_2 was prepared following the same procedure and voltammograms in 4 and 1 M HCl, 0.1 M acetic acid/acetate buffer and 0.1 M oxalic acid were obtained. The results are summarized in Table 3. It is clear that the processes are the same in both cases indicating that As(V) and As(III) are reduced to As° and they are stripped following the same process.

The type of iron oxide had the same effect on the voltammograms of As(III) as in the case of As(V). Only hematite provided peaks for arsenic redissolution. The effect of pH was also similar, a cathodic shift with increasing pH was observed for the peak at 0.2 V. In this case no peak was observed in oxalic acid medium, but a peak at −0.1 V was observed in acetic buffer for all the iron (III) oxides tested. The suppression of the stripping peak is due to the generation of AsH_3 at the electrode during the reduction step which is favoured at high H^+ concentration.

Since the As(V) containing samples do not offer the arsenic redissolution peak in acetic buffer (pH 5) it can be said that the pH required for the reduction of As(V) is definitely acidic.

It is clear that the kind of iron oxide also has some relevance for the reduction of arsenic (III). This can be explained by the change in the chemical conditions of the solution close to the electrode due to the different kinetics of the redissolution of the iron oxide.

2.2.4 An analytical application

A sample with a high content of iron oxide was selected to develop an application based on the effect of the iron oxide in the reduction of solid As(V) that allowed the detection of the presence of arsenic easily. Compost is a complex sample with a high content of iron oxides (15,000–17,000 mg kg^{-1} of iron) which may contain arsenic. Compost Agromat CP-1 is a reference material which has a certified value of 5.5 mg kg^{-1} of total arsenic and 17,500 mg kg^{-1} of iron. Linear sweep voltammetry cannot detect such a low concentration of arsenic and a more sensitive technique has to be used. Square wave voltammetry was chosen in this case.

A synthetic compost was prepared by mixing SiO_2 (40%) and starch (60%) and 1,600 mg kg^{-1} of iron as hematite and spiked with 5 mg kg^{-1} of As as As_2O_5 to find the optimal conditions for the detection of arsenic. The supporting electrolyte was 1 M HCl.

The resulting optimal conditions were, frequency 150 Hz, step potential 8 mV, amplitude 40 mV. The pre-treatment potential was −1.0 V applied for 100 s. The anodic scan was performed from −0.2 to 1.0 V. Arsenic offered one peak at −0.010 ± 0.010 V (the peak potential is the mean value of five voltammograms). The shifting of the peak potential for arsenic is due to the extremely different electroanalytical technique used in this case. No interferences from other components of the solid sample are expected since they are not in solution.

Voltammograms of the Agromat CP-1 and the reference material spiked with 5 mg kg^{-1} of As as As_2O_5 can be compared in Fig. 3. The peak at −0.018 V ± 0.011 corresponds to the arsenic present in the sample.

3 Conclusions

In the presence of hematite As(V) can be reduced on a carbonaceous electrode under mild conditions, lower acid concentration (1 M HCl) and moderate reducing potentials (−1.0 V). Other iron (III) oxides do not exhibit the same behaviour. It is related to the kinetics of their reductive dissolution. The iron oxide is reduced on the electrode and the formed FeO is dissolved, then a high aqueous Fe(II) concentration is achieved in the solution close to the electrode surface and due to the reductive conditions As(V) is reduced to As(III) which is subsequently electrochemically reduced to As°. Goethite and limonite dissolve quickly due to their less organized crystalline structure and

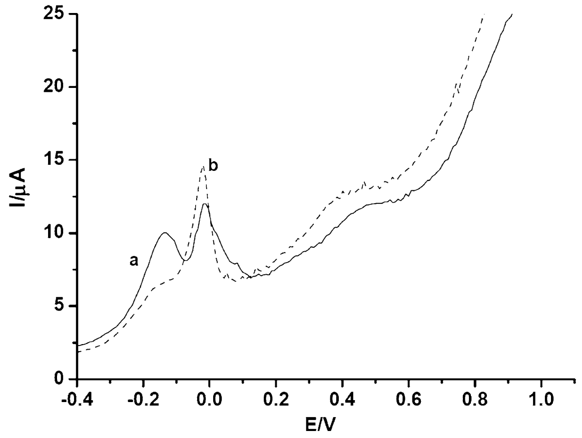

Fig. 3 Square wave voltammograms of a reference material (a) and the same reference material spiked with 5 mg kg^{-1} of As (b) in 1 M HCl. 150 Hz, amplitude 40 mV, step potential 8 mV, pretreatment potential −0.8 V for 100 s

hence the concentration of Fe(II) on the electrode is insufficient to reduce As(V).

The arsenic (III) oxide is also reduced in the presence of iron oxide to As° when hematite is present. The stripping peak appears at the same position as in the case of As(V) and is affected in the same way by pH and the kind of iron oxide. At pH 5 this peak is observable, but not when As(V) is present in the mixture, indicating that the reduction of arsenic (V) oxide is only possible at pH lower than 5.

The detection of total arsenic based in the effect of iron oxide is possible in a solid material using square wave voltammetry. If the sample contains a high concentration of iron oxides it is possible to detect 5 mg kg^{-1} directly in the solid.

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