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Talanta 66 (2005) 875–881

Talanta

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Electrochemical screening procedure for arsenic contaminated soils

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Received 1 July 2004; received in revised form 3 November 2004; accepted 17 December 2004
Available online 26 January 2005

Abstract

Voltammetry of immobilized microparticles was used to find arsenic and heavy metals in contaminated soils from areas with long history of industrial development. Traditional sample dissolution and extraction procedures are time consuming and might distort the chemical equilibrium of the sample causing a change in the original physicochemical forms of distribution. A minute amount of sample was physically attached to the carbon paste working electrode surface and an anodic differential pulse voltammogram was obtained without disturbing the original equilibria. The position of the peaks revealed the presence of Pb and Cu and As(V) and As(III) for the most contaminated soils. As(III) was detected when its percentage in soil was more than 0.001% (expressed as As_2O_3). The limit of detectability was strongly dependent on the presence of iron(III) which increased the signal 10 times.

Keywords: Arsenic; Soils; Speciation; Screening; Voltammetry of immobilized microparticles; Direct analysis; Iron oxides

1. Introduction

Arsenic reaches the environment as a by-product of the mining of non-ferrous metals like Pb, Zn, and Au, the biocides used as wood preservatives and pesticides. The toxicity of As is due to its affinity for thiol groups and subsequent inhibition of the enzyme activity causing biological damage in living organisms.

Not all the physicochemical forms have the same toxicity. Inorganic As(III) is more toxic than inorganic As(V) [1] and the toxicity decreases with increasing methylation, being monomethyl and dimethyl arsine the most common forms [2,3]. The percentage of each form is strongly dependent on the pH, redox potential [4] and microbial activity [5] that define the mobility of arsenic and affect the toxicity.

Arsenic can be found in the drinking water, in the air as volatile arsines and in soils where it can concentrate if absorbed on the components of soils. Acid rain, complexation with naturally occurring ligands or from waste waters or biological activity can redissolve it, increasing the health risks and spreading contamination. As(V) in soils is strongly bound to iron(III) oxides specially goethite (α-FeOOH) and amorphous iron oxide [6]. In anoxic conditions As(V) can be redissolved as ferrous arsenate [7] and then it migrates to the aquifers.

All things considered, speciation of As provides more information than total arsenic content. This is a major challenge for analytical chemists since the difficulty lies in the extraction of the species from the sample without disturbing equilibrium and then changing the physical form.

Several extracting agents have been proposed in the literature and also microwave extraction that turned out to be a useful technique. Different analytical techniques are coupled with hydride generation as well as liquid chromatography systems to separate As forms and detect them with atomic absorption spectrometry (AAS) or atomic emission spectrometry (AES), inductively coupled plasma-mass spectrometry (ICP-MS) and electroanalytical techniques [2,8].

All these procedures are time consuming and they cannot be applied when fast analytical and toxicological test methods

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doi:10.1016/j.talanta.2004.12.054

are required to make quick decisions in the case of imminent waste disposal or on site, in contaminated areas. These tests have higher limits of detection than lab standard methods but usually they are adequate for determination in soils, because their As concentration is higher than in water and usually it is not necessary to know the exact concentration but whether the legal limit has been exceeded or not. Field methods for arsenic only provide information about total arsenic, which is not the most valuable to evaluate the contamination of an area. [9].

Electroanalytical techniques have been of great interest in monitoring contamination on site [10,11] due to their versatility, and miniaturization possibilities of the electrodes and instruments. Beside the problem due to sample dissolution or extraction when dealing with solid samples can be overcome with electroanalysis. Solid sample can be added to the electrode material if it does not increase the resistance too much. In this case slow potential scan speed has to be used and the material included in the electrode mass can produce distortion of the voltammograms, due to the increase in the ohmic resistance. All these problems are overcome if voltammetry of immobilized microparticles (VMP) is used.

VMP is an electroanalytical technique developed by F. Scholz that solved the inherent problems of the solid state voltammetry [12] because only a small amount of sample is deposited on the electrode surface. Samples are immobilized on the electrode surface by two different procedures: physically attached by abrasion [13] or entrapped in a polymer film [14].

The working electrode usually used in VMP is glassy carbon [13] graphite composite electrodes [15] and diamond electrodes [16]. In this work we propose the use of a carbon paste electrode to perform VMP especially useful when the sample is a fine powder with low adhesion to the solid electrode traditionally used. The aim of this work is to develop an easy and friendly-to-use method to evaluate decontamination of a soil with no sample pretreatment. The authors do not try to develop a quantitative method but simply find a straightforward way to decide whether a sample is contaminated or not, and which kind of contamination is present.

2. Materials and methods

2.1. Apparatus

A Perkin-Elmer (Perkin-Elmer, Shelton, CT, USA) microwave oven, model Anton Paar multiwave, was used for closed-vessel high-pressure sample dissolution.

A Perkin-Elmer P-40 inductively coupled plasma atomic emission spectrometer (ICP-AES) was used for the determination of the total arsenic and iron content As(III) was determined using a Perkin-Elmer Model 2380 atomic absorption spectrometer equipped with a flame heated quartz tube atomizer (168 mm length, 2 mm i.d.) (QF–AAS). All these results are shown in Table 3.

All the electrochemical experiments were performed using an AUTOLAB Eco Chemie potentiostat and a three electrode cell with a Ag|AgCl|KCl saturated reference electrode and a Pt wire as auxiliary electrode. All the potentials in this paper are referred to the above mentioned reference electrode.

2.2. Reagents and samples

All reagents were of analytical-reagent grade or higher. As_2O_5 and As_2O_3 were from Fluka; graphite powder, HCl, HNO_3, H_2O_2 and Fe_2O_3 (hematite) were from Merck. Oxalic acid and SiO_2 were purchased from Probus and silicone oil from Aldrich.

Soils from four different areas of Baia Mare were investigated. Soil was sampled at two different depths, 5 and 20 cm in each point, following the Romanian normative STAS 7184/1-84. The sampling points were the Folklore Museum (samples 114 and 115 at 20 and 5 cm depth), the non-ferrous waste disposal dump (samples 125–20 and 122–5 cm), the western industrial area of the city (137–20 and 128–5 cm) and 5 km west of the city (samples 127–20 and 126–5 cm).

The soil samples were dried at room temperature for 2 days and then at 60 °C for 12 h in an oven to constant weight and subsequently milled to obtain a fine powder and sieved. The fraction of 125 μm and less was kept for the total arsenic and iron content, arsenic speciation and voltammetric analysis. For the ICP analysis it was necessary to dissolve the soils. No treatment at all was required for the voltammetric analysis and the voltammetry was performed directly on the powder samples.

An amount of 0.1 g of soil was weighted and transferred to a microwave-adapted vessel. Two mL of H_2O, 3 mL of HNO_3 and 2 mL of H_2O_2 were added and the vessel was closed and placed in the microwave oven.

The digestion procedure followed four steps: 300 W were applied for 4 min, then the power was raised from 400 up to 600 W in 5 min and this power was held constant for 20 min. Finally a resting period of 15 min was elapsed to allow the vessels to cool down and reduce the inner pressure before opening. The samples were transferred to a flask and diluted with Milli Q water to 50 mL.

As(III) was extracted from soils with a solution of 10 M HCl and the hydride was chemically generated, following a procedure described previously in the scientific litterature using L-cysteine as prereductant and conducted to the detection system by a flow injection non-dispersive system [17].

2.3. Electrode preparation

The carbon paste was prepared by careful mixing of 60% graphite with 40% silicone oil. The resulting paste was packed into a PTFE tubing body (1.5 mm i.d.). A copper wire served to pack the paste and to push it to renew the surface, as well as to achieve the electric contact. The electrode was rubbed on a sheet of white paper placed on a tile after each measurement to flatten and clean its surface.

2.4. Electroanalytical measurements

All the experiments were performed by differential pulse voltammetry between −1.1 and 1.1 V at 10 mV/s. All the voltammograms were obtained in 0.1 M oxalic acid solution, pH = 1.3 at room temperature.

Different supporting electrolytes were investigated: KNO_3, KCl, NaOH and acetic acid buffer. But only 0.1 M oxalic acid provided a reproducible electroanalytical signal.

Nitrogen was bubbled through the solution for 10 min to avoid the influence of the dissolved oxygen.

The sample was transferred to the electrode before each measurement by gently dragging it on a 2 cm line of sample (5 mg) drawn with a plastic spatula. That way a similar amount of sample was transferred to the electrode each time. The total amount attached to the electrode is within the micrograms range [12], the same line can be used for a whole set of experiments.

3. Results and discussion

3.1. Voltammetry of As_2O_3 and As_2O_5

Pure As_2O_3 and As_2O_5 were deposited on the electrode surface as described in Section 2.4. Differential pulse cathodic voltammetry was performed from 1.1 to −1.1 V, voltammograms are shown in Fig. 1A.

Two peaks appear in the cathodic scan for As(V) and the As(V) + As(III) (1:1 in weight) voltammograms at 0.51 and 0.33 V and no peaks for As(III). Considering that peak potential is close to the formal redox potential, it can be used to explain the electrode process that takes place at the electrode surface. Formal potentials were calculated using the tabulated standard potentials [18]. The observed differences between the calculated values and the experimental data are due to the scan speed used and the fact that solid particles are involved and not only species in solution. Beside, the kinetic aspects of the electrochemical reactions were not considered either. According to this, peak assignment is just orientative.

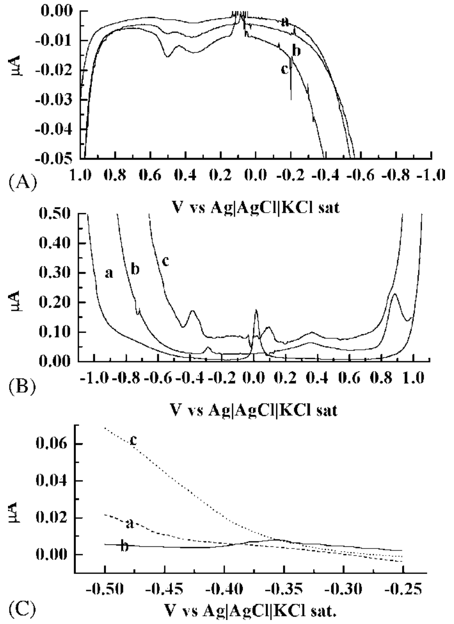

Fig. 1. Voltammetry of arsenic oxides in 0.1 M oxalic acid: (A) cathodic scan; (B) anodic scan (a, voltammogram for As_2O_3; b, voltammogram for As_2O_5; c, 1:1 mixture); (C) anodic scan with pretreatment −1.1 V for 10 s (a, As_2O_3; b, As_2O_5; c, blank).

These peaks correspond to the electrode processes:

$$H_3AsO_4 + 2H^+ + 2e^- \Leftrightarrow HAsO_2 + 2H_2O, \quad E^{0\prime} = 0.355\,\mathrm{V} \quad \text{at} \quad \mathrm{pH} = 1.3 \tag{1}$$

$$As_2O_5 + 4H^+ + 4e^- \Leftrightarrow As_2O_3 + 2H_2O, \quad E^{0\prime} = 0.447\,\mathrm{V} \quad \text{at} \quad \mathrm{pH} = 1.3 \tag{2}$$

The peak at 0.50 V represents the reduction of the external layer of the As_2O_5 particles to As_2O_3. And the peak at 0.35 V is due to the reduction of the hydrated arsenic oxide(V).

No peaks are present in the voltammogram of As(III) because the only electrode process is the reduction to As^0 that takes place at −0.040 V at pH = 1.3.

It is not possible to detect the process As(V)/As^0 because it is an irreversible process and needs potentials lower than −0.6 V [19].

To sum up, the cathodic scan allows to detect the presence of As(V) but nothing can be said about As(III). To get a signal from As(III) an anodic scan was performed from −1.1 to 1.1 V. The voltammograms for pure As(III) and As(V) as well as the 1:1 mixture are shown in Fig. 1B. As(III) gave a sharp peak at 0.013 ± 0.006 V and depending on the amount As_2O_3 of deposited on the electrode a low peak at 0.350 V can be observed. As(V) offered three peaks at −0.281 ± 0.008, 0.355 ± 0.006 and 0.837 ± 0.01 V. The mixture of the oxides gave three peaks at −0.384 ± 0.010, 0.088 ± 0.009 and 0.355 ± 0.010 V and a shoulder at 0.88 V.

To explain these voltammograms it should be kept in mind that the initial potential of the scan is −1.1 V and that the scan speed is slow (10 mV/s), it means that the surface of the microparticles is suddenly covered by a layer of the reduction products of the oxide. But the reduction is not total since it takes place at the moment in which −1.1 V is applied, affecting the surface of the oxide microparticles. That way the surface of the As_2O_5 microparticles is covered by a layer of As_2O_3 that is subsequently oxidized during the anodic scan.

To confirm this point, a pretreatment of −1.1 V for 10 s was applied and a voltammogram between −0.5 and −0.25 V was performed. Only As_2O_5 gave one shallow peak at −0.35 V (see Fig. 1C) because of the slow electron transfer.

The peak at −0.35 V is due to the oxidation in the aqueous medium of the solubilized As^0 to As(III). The half wave for this process in aqueous media is −0.39 V in 1 M HCl [20] which is closed to the values observed in this experiment, specially for the 1:1 mixture:

$$HAsO_2 + 3H^+ + 3e^- \Leftrightarrow As^0 + 2H_2O, \quad E^{0\prime} = -0.026\,V \quad \text{at} \quad pH = 1.3 \qquad (3)$$

or

$$As_2O_3 + 6H^+ + 6e^- \Leftrightarrow 2As^0 + 3H_2O, \quad E^{0\prime} = -0.040 \quad \text{at} \quad pH = 1.3 \qquad (4)$$

This process is strongly dependent on the electrolyte and the surface of the electrode that is why a broad difference is observed between the tabulated and calculated values and the values observed experimentally.

The peak at 0.013 V for As(III) and at 0.088V for the 1:1 mixture can be due to the oxidation of the As^0 formed at the beginning of the potential scan and also to the originally present As(III) to As_2O_5:

$$As_2O_5 + 10H^+ + 10e^- \Leftrightarrow 2As^0 + 5H_2O, \quad E^{0\prime} = 0.155\,V \quad \text{at} \quad pH = 1.3 \qquad (5)$$

This peak current decreased drastically when As_2O_5 is present because the reduction of As(V) to As(III) is easier than the reduction of As_2O_3. It was also observed that concentration of As_2O_3 in the mixture was decisive on the height of this peak. Four mixtures containing As_2O_3 (20, 10, 1 and 0.1%) and SiO_2 were prepared and the voltammograms were recorded following the same procedure. This peak disappeared for mixtures containing less than 10% of As_2O_3. At the same time the peak at 0.35 V becomes clearer but the peak current is still very low.

This might be explained taking into account the initial potential, at which As^0 is produced but in acidic media part of it is reduced to AsH_3 (g). This process starts at −0.64 V for As(V) and −0.4 V for As(III) [19]. As a result part of the As^0 is lost and the signal decreased.

The peak at 0.35 V is related to the oxidation of the As_2O_3 formed on the surface of the As_2O_5 microparticles. This peak is not present in the As(III) voltammogram because almost all the surface of the microparticles is reduced to As^0, unless a bigger amount of As_2O_3 is attached to the electrode.

In the pure As_2O_5 voltammogram a third peak at 0.88 V appeared. It might be related to the oxidative redissolution of the As_2O_3 formed on the surface of the microparticles:

$$2AsO_4^{3-} + 10H^+ + 4e^- \Leftrightarrow As_2O_3 + 5H_2O, \quad E^{0\prime} = 0.881\,V \quad \text{at} \quad pH = 1.3 \qquad (6)$$

or

$$2HAsO_4^{2-} + 8H^+ + 4e^- \Leftrightarrow As_2O_3 + 5H_2O, \quad E^{0\prime} = 0.550\,V \quad \text{at} \quad pH = 1.3 \qquad (7)$$

Table 1
Composition of the synthetic soils in % in grams

Sample	As_2O_5	As_2O_3	SiO_2	Fe_2O_3
1	0.0	8.0	89.2	2.8
2	0.0	10.6	80.9	8.5
3	0.0	15.4	81.8	2.8
4	0.0	1.5	61.3	37.2
5	0.0	2.1	87.4	10.5
6	0.0	0.0	99.0	1.0
S	0.0	0.0		
S + 3		0.5		
7	5.6	0.0	85.8	8.6
8	11.6	0.0	86.3	2.0
9	10.2	0.0	88.9	0.9
10	1.2	0.0	90.8	8.0
11	1.6	0.0	87.1	11.3
S + 4	0.8			
12	4.2	0.6	94.2	1.0
13	10.2	1.6	87.2	1.0
14	10.0	1.5	97.5	1.0
15	1.0	0.4	97.6	1.0
16	1.3	1.8	96.0	1.0
S + 5	2.6	0.6		

S, S + 3, S + 4, S + 5 are the uncontaminated soil and the spiked soils with As_2O_3, As_2O_5 and As_2O_3+As_2O_5, respectively; the percentage in table represents the spiked amount of toxic component.

3.2. *Synthetic soils*

Soil is a very complex matrix with electroactive and non-electroactive components. The main non-electroactive component is silica (50–60%) and clays (20%). Iron oxides and hydroxy-oxides (mainly hematite and goethite) are associated to clays and constitute the main electroactive component (usually 3–5%). To study the influence of the main components in a soil on the electrochemistry of arsenic oxides, several synthetic soils were prepared. Their composition is listed in Table 1. Iron oxide was introduced as hematite. Anodic scan was applied to study the samples because it provided well-resolved peaks and allowed the authors to distinguish As(III) from As(V). The voltammograms are shown in Fig. 2 and the peak potentials are listed in Table 2.

The presence of iron oxide introduced an important change in the voltammograms for all the mixtures. A 10-fold increase in the peak current was observed for all the peaks and also the peak corresponding to process (5) appears also for As_2O_5 containing mixtures but at a position strongly dependent on the As_2O_5:Fe_2O_3 ratio.

These changes are caused by the presence of iron in the synthetic samples. When the initial potential is applied for a few milliseconds a reduction takes place on the carbon electrode with embedded microparticles originating As^0, Fe^0 and As(III). The peaks corresponding to the oxidation of Fe^0 and As^0 will be definetly influenced by the alloy produced and that is why the peak potential is shifted from the positions on the voltammograms of the iron(III) free mixtures [13,21]. The increase of the peak current is also caused by the presence of iron(III). This effect has been observed with Au(III).

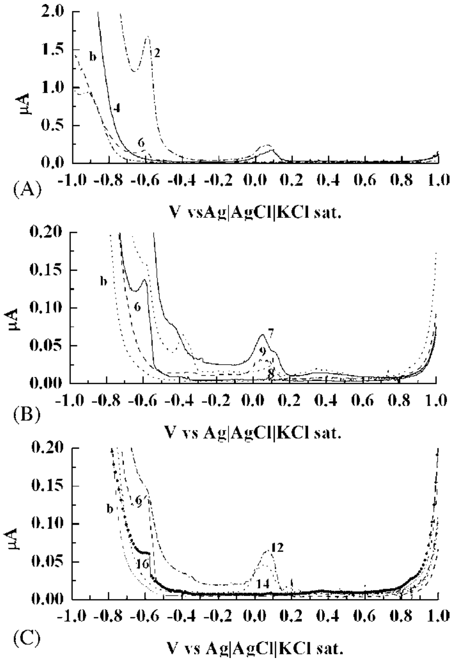

Fig. 2. Voltammetry of synthetic soils in 0.1 M oxalic acid, numbers indicate the sample label, synthetic soils with: (A) As_2O_3; (B) As_2O_5; (C) As_2O_3 and As_2O_5; (b) blank 0.1 M oxalic acid.

It has been observed that the presence of Au(III) in the solution favours the reduction of As(V) and (III) to As^0, at the same time it is supposed to deposit on the electrode surface creating a sort of net that entraps As^0 preventing it from reduction to AsH_3 [19] increasing the oxidation current when stripping takes place. A similar situation can be claimed here to explain the presence of the peak at 0.07–0.10 V corresponding to a As^0 oxidation as well as the shifting of this peak with As_2O_5:Fe_2O_3 ratio and the 10-fold increase in the peak current.

Table 2
Peak potentials for the synthetic soils and spiked soils (S, S + 3, S + 4, S + 5)

Sample	Molar ratio	$E_{\mathrm{p\,Fe}}$ (V)	$E_{\mathrm{p\,1As}}$ (V)	$E_{\mathrm{p\,2As}}$ (V)	$E_{\mathrm{p\,3As}}$ (V)
As_2O_3:Fe_2O_3					
1	0.03	−0.585	–	0.070	–
2	0.16	−0.580	–	0.070	–
3	1.00	−0.580	–	0.079	–
4	2.60	–	–	0.079	–
5	4.30	–	–	–	–
6	0.00	−0.600	–	–	–
S	0.00	−0.600	−0.393	–	–
S + 3	0.14	–	−0.382	0.004	–
As_2O_5:Fe_2O_3					
7	0.10	–	–	–	0.353
8	0.11	−0.594	–	0.055	0.353
9	0.45	–	−0.370	0.074	0.348
10	3.95	–	−0.350	0.109	–
11	8.06	–	−0.365	0.026	–
S + 4	0.17	−0.560	−0.380	0.089	0.350
As_2O_5:As_2O_3					
12	6.10	−0.600	−0.380	0.063	0.365
13	5.70	–	−0.340	0.072	0.360
14	4.60	–	−0.343	0.054	0.360
15	1.90	–	–	0.095	0.365
16	0.60	−0.580	−0.379	0.082	0.365
S + 5	1.20	−0.560	−0.383	0.089	0.350

Each data is the mean of three values, the standard deviation is in all instances less than 0.010 V.

Finally an uncontaminated soil was spiked with As_2O_3, As_2O_5 and $As_2O_3 + As_2O_5$ and the corresponding anodic scan differential pulse voltammograms were obtained and compared with the synthetic soils to test the application on arsenic contaminated soils. The amount of arsenic added to the uncontaminated soil (S) is listed in Table 1 and the peak potentials are shown in Table 2.

No contaminated soils have 5–10 mg/kg of As, mainly as As(V) and an iron content of 3–5% as Fe_2O_3. This low concentration is detected and the presence of As(V) is marked by the peak at −0.393 V. Iron oxide gave a peak at −0.600 V as in the case of the sample 6. The spiked soil samples S + 3, S + 4 and S + 5 offered peaks at similar positions as the respective synthetic soils. The peak potential corresponding to process (5) is the more sensitive to the As_2O_5:Fe_2O_3 molar ratio.

3.3. Contaminated soils

Anodic scan dp-voltammetry was applied to contaminated soils from Baia Mare (Romania) following the same procedure. Baia Mare is a town from north-western Romania, close to the Ukraine border. It has suffered from an important industrial activity for 150 years, which produced a heavy metal contamination due to old tailing ponds, copper smelters and a sulfuric acid plant. The soil was sampled in different points scattered in the town to know whether the contamination was located in defined points or it was spread all over the city. The total iron and arsenic of these samples as well as the peak potentials found in the voltammograms are shown in Table 3. In Fig. 3 the voltammograms for all the samples can be compared.

The voltammograms of the soil samples are more complicated than the synthetic soils because there are more electroactive components, which are also reduced. This can explain the shifting of the arsenic peaks. The iron peak does not appear in any voltammogram, due to the different halotropic forms present in these soils. Synthetic soils have been prepared with hematite and natural soils might contain goethite, which does not show any peak at −0.60 V. This is consistent with the fact that arsenic and heavy metals are fixed in soils onto goethite and amorphous iron hydroxide particles [22]. To confirm the presence of hematite or goethite, dp-voltammograms in 0.1 M oxalic acid were obtained for pure hematite (α-Fe_2O_3), goethite (α-FeOOH), maghemite (γ-Fe_2O_3) and lepidocrocite (γ-FeOOH) and compared to the soil ones. Only goethite exhibits a behavior similar to the contaminated soils.

The peak at −0.50 V present in all the voltammograms for contaminated areas is due to Pb reoxidation in presence of

Table 3
Contaminated soils; a total arsenic expressed as As_2O_5, arsenic(III) as As_2O_3 and iron as Fe_2O_3 in contaminated soils expressed in % of the oxide

Soil	As_2O_3[a] (%)	As_2O_5[b] (%)	Fe_2O_3[c] (%)	$E_{p\,Pb/Cu}$ (V)	$E_{p\,As1}$ (V)	$E_{p\,As2}$ (V)	$E_{p\,As3}$ (V)
114	0.000	0.000[d]	5.1	−0.560/–	−0.406	–	–
115	0.001	0.000[d]	4.8	−0.555/–	–	–	–
122	0.009	0.290	8.8	−0.505/0.000	−0.350	–	–
125	0.005	1.350	24.6	−0.530/−0.022	−0.373	0.110	–
126	0.001	0.026	3.7	−0.497/−0.039	–	0.098	
127	0.002	0.019	3.7	−0.508/−0.080	−0.401	–	0.388
128	0.003	0.015	5.2	−0.510/−0.022	−0.368	–	–
137	0.002	0.018	5.9	−0.510/−0.039	−0.362	–	0.339

Standard deviation is always less than 0.015 V.

[a] Standard deviation less than 0.0001, peak potentials.

[b] Standard deviation less than 0.003, peak potentials.

[c] Standard deviation less than 0.1, peak potentials.

[d] Below detection limit.

0.1 M oxalic acid:

$$PbO_x + 2e^- + 2H^+ \Leftrightarrow Pb^0 + O_xH_2, \quad E_p^{0\prime} = -0.612\,V \quad \text{at} \quad pH = 1.3 \qquad (8)$$

The potential for this process in 0.1 M oxalic acid, pH = 1.3 is −0.582 V. Lead has been qualitatively determined in all the samples by its reaction with dithizone [23].

The peak at −0.02 to −0.08 V is caused by the reoxidation of copper to CuO, with a standard potential of −0.078 V.

$$CuO + 2e + 2H^+ \Leftrightarrow Cu^0 + H_2O, \quad E^{0\prime} = -0.165\,V \quad \text{at} \quad pH = 1.3 \qquad (9)$$

Copper was identified in all the samples but in 114 and 115 by its reaction with α-benzoinoxime [23].

The peak $E_{p\,1As}$ was found for all the samples but for 115 and 126. The peak $E_{p\,3As}$ was clear for samples 127 and 137. The peak characteristic for As(III), $E_{p\,2As}$ was found for samples 125 and 126. The ratio of As(III) to As(V) in the contaminated soils was very low and that is why the total arsenic percentage was expressed in Table 3 as As_2O_5. This implies that only in the samples with higher As content can be possible to detect As(III) but only if it is present in an electroactive chemical form.

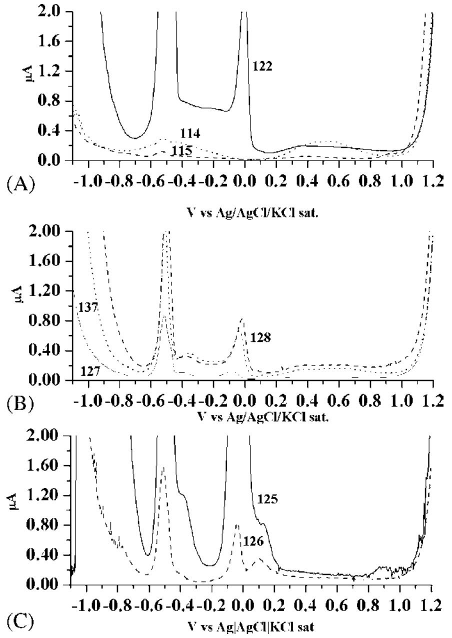

Fig. 3. Voltammograms of contaminated soils in 0.1 M oxalic acid, numbers indicate the label sample.

Sample 125 exhibits a peak at 0.110 V and a high total As percentage, 1.350% of As (expressed as As_2O_5). Sample 122 was taken at the same place, the non-ferrous waste disposal dump, but the arsenic content 0.290%. Sample 125 was extracted at 20 cm and 122 close to the surface at 5 cm. The external layer of the soil is exposed to weathering that causes the oxidation of As(III) as well as the dissolution and transport of the arsenic species to other areas by rain water. As(V) is less soluble than As(III) and it is absorbed on the surface of goethite fixing it and avoiding its transport, but in anoxic conditions the reduction of the ferric-arsenate is possible to ferrous-arsenate which is a more soluble form [2,5]. The iron oxides content is greater for these samples than for the rest of them, increasing their capacity to immobilize and accumulate arsenic. It seems to be a controversy with the concentration of As(III) because sample 122 has greater percentage of it than 125 but only the latest gave a peak for As(III). This means that electroactive species of As(III) accumulate in a deeper layer of the soil were the redox potential might be less oxidant and non-electroactive As on the superficial layer [24].

The non-ferrous waste disposal dump shows also the higher peak current for the heavy metal peaks, being the most superficial sample the less contaminated due to the washing effect of the rain. These samples showed the highest content of As(III) but only sample 125 gave a peak for As(III).

Samples 126 and 127 correspond to an area 5 km away from downtown. In this case the superficial sample 126, exhibits the highest percentage of As, and a peak at 0.098V indicating the presence of As(III). The external sample showed less content of As(III) than the inner sample but as it happened for samples 122 and 125 signal for As(III) is observed for the less concentrated sample, indicating that the elctroactive form concentrate on the surface. It can be due to a recent contamination with As(III) from other areas or to the weathering of minerals like pyrite and arsenopyrite, associated to the sulfuric acid production. In this area a high content of Pb and Cu was also detected, especially in sample 126 taken at 5 cm depth.

Samples 137 and 128 belong to a western part of the city. The sample collected at 20 cm has a slightly higher content of As, mainly as As(V) as can deduced from the peaks $Ep_{1\mathrm{As}}$ and $Ep_{3\mathrm{As}}$. No mark for As(III) was observed, indicating that the physicochemical forms present in the area are mainly non-electroactive species or below detection limit. In these soil samples Pb and Cu are present. Both have a similar content of copper but sample 137 has a greater amount of Pb than 128, as can be deduced by the corresponding peak heights.

Finally samples 114 and 115 from the town museum do not suffer from severe arsenic contamination but their voltammograms show a peak for Pb.

4. Conclusions

Direct voltammetry of solid arsenic oxides is possible and their voltammograms are different enough to allow differentiation among the two oxidation states.

The presence of solid iron(III) increases the signal for As(III) and favors the process As(V)/As^0 facilitating the identification of this species in the solid sample. The content of iron(III) in the sample is a relevant factor.

The total content of As in soils is related to iron percentage due to its ability to immobilize arsenic(V).

If the concentration of total arsenic is greater than 0.02 it is possible to identify As(III).

Two different kinds of As(III) can be detected, the electroactive physicochemical forms, mainly inorganic species and non-electroactive physicochemical forms as for instance metilated species.

Three contaminants were identified in the soils. A classification of the soils is possible observing the peak currents of the heavy metals present in the samples.

VMP is a promising tool to classify contaminated soils in order to save time and allows the researcher to design more adequately to the concentration, the experimental procedure. Only 4 min are necessary to impregnate a carbon paste electrode with the soil sample and obtain the voltammogram and information about four species is soil is obtained.

Acknowledgments

Finantial support of the DGICYT, project number BQW 2003/01993 is gratefully acknowledged. N. Alexa was on leave form Babes-Bolyai University at the University of Zaragoza thanks to an Erasmus grant (50554-IC-5-2001-1-R0-ERASMUS). The authors want to thank María Pilar Górriz Ramón for her help with the microwave soils dissolution and to Antonio López Ciriano from the Area of Mineralogy and Christalography of the Faculty of Sciences of the University of Zaragoza for his geological advice about arsenic minerals and their weathering.

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