Talanta 83 (2011) 1428–1435

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of As(III) by anodic stripping voltammetry using a lateral gold electrode: Experimental conditions, electron transfer and monitoring of electrode surface

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ARTICLE INFO

Article history:
Received 30 June 2010
Received in revised form 28 October 2010
Accepted 14 November 2010
Available online 19 November 2010

Keywords:
Arsenic
Anodic stripping voltammetry
Lateral gold electrode
Cyclic voltammetry
Electron transfer

ABSTRACT

The aim of this work is to evaluate the efficiency of the determination of As(III) by anodic stripping voltammetry (ASV) using a lateral gold electrode and to study the modifications of the electrode surface during use. Potential waveforms (differential pulse and square wave), potential scan parameters, deposition time, deposition potential and surface cleaning procedure were examined for they effect on arsenic peak intensity and shape. The best responses were obtained with differential pulse potential wave form and diluted 0.25 M HCl as supporting electrolyte. The repeatability, linearity, accuracy and detection limit of the procedure and the interferences of cations and anions in solution were evaluated. The applicability of the procedure for As(III) determination in drinking waters was tested. Cyclic voltammetry (CV) was used to study the electrochemical behaviour of As(III) and for the daily monitoring of electrode surface. Also scanning electron microscopy (SEM) analysis was used to control the electron surface. Finally we evaluated the possibility to apply the equations valid for flow systems also to a stirred system, in order to calculate the number of electrons transferred per molecule during the stripping step.

1. Introduction

Arsenic is a naturally occurring element which is widely distributed in the earth's crust. It is increasingly being found in drinking water in many parts of the world such as Bangladesh, India, Great Britain, and Thailand, and within the U.S. in California, Oregon, Massachusetts, Maine, and New Hampshire [1–5]. Exposure to arsenic can cause a variety of adverse health effects, including dermal damages, respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic and carcinogenic effects [6].

The predominant arsenic-containing species found in natural waters are inorganic arsenate and arsenite and organic dimethylarsinic and monomethylarsonic acids. The interest in determining the levels of individual compounds of arsenic in environmental samples arises from the recognition that transport, bioavailability, toxicity and possible carcinogenic activity are highly dependent on the chemical form of the element [7]. Inorganic arsenic is more toxic than organic arsenic, and arsenite more toxic than arsenate [8]. However this is a simplification, as the speciation is influenced by ambient conditions and by changes in biologically-mediated redox conditions [9]. It is very important from the analytical point of view to develop sensitive and reliable techniques capable to determine nanogram levels of arsenic [10], since the concentration of arsenic in unpolluted natural waters is at $\mu g\,l^{-1}$ or sub-$\mu g\,l^{-1}$ levels. In addition the guideline value for arsenic in drinking water, indicated both by the US Environmental Protection Agency (EPA) and by the World Health Organization (WHO), is 10 $\mu g\,l^{-1}$ [11,12].

Many techniques to determine such level of arsenic have been proposed, employing atomic absorption spectrometry (AAS) mainly coupled to hydride generation (HG-AAS), electrothermal AAS with graphite furnace (ET-AAS), atomic fluorescence spectrometry (AFS), atomic emission spectrometry (AES) generally with inductively coupled plasma (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), high-performance liquid chromatography coupled to ICP-MS (HPLC-ICP-MS), X-ray fluorescence (XRF), neutron-activation analysis (NAA) and capillary electrophoresis (CE) [13–20]. Such techniques are laboratory-based and time-intensive and can have large costs for instrument purchase and management. Available literature suggests that an attractive and less expensive solution to these problems is represented by electrochemical techniques. In the past the electrochemical technique most commonly used for the determination of As was cathodic stripping voltammetry (CSV) or adsorptive cathodic stripping voltammetry (AdSV) using hanging mercury drop electrode (HMDE) [7,21,22]. Such techniques are still used nowadays [23], but in the last years the analytical use of mercury has been discouraged due to its toxicity. Many kinds of working electrode materials have been reported for the determination of

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doi:10.1016/j.talanta.2010.11.033

arsenic, including platinum [10], gold [12], carbon substrates [20], and boron-doped diamond [24].

New configurations are being studied to increase the performance and to avoid the problems of working with solid electrodes (like the dependence of their response on pre-treatment and the formation of oxide films, which limits sensitivity and reproducibility and, as a consequence, their use for routine applications [25,26]). For example gold-plated screen printed carbon (AuF-SPEs) or carbon paste (AuF-CPEs) electrodes [27,28], gold nanoparticle-modified glassy carbon electrodes (AuNPs-GCE) [29,30], or bismuth film electrodes (BiFEs) [31] have already been reported for the determination of As (III).

In this work we chose to work with a lateral gold electrode for As(III) determination with a view to a future comparison with a AuNPs-GCE that we have recently optimised for the determination of Hg [32,33]. Among the possible substrates for solid working electrodes, gold provides a more sensitive response towards arsenic oxidation than other electrode materials [20,34,35] and has a higher hydrogen overvoltage than platinum [36].

We optimised the conditions for As(III) determination by anodic stripping voltammetry (ASV) and studied the evolution of the electrode surface using cyclic voltammetry (CV) and scanning electron microscopy (SEM). Finally, we evaluated the applicability of the equations commonly used for flow systems [37] to the investigated stirred system.

The findings of this study can be useful for analysts in order to evaluate the real potentialities of the lateral gold electrode and to choose the best conditions for the determination of As(III) by ASV.

2. Experimental

2.1. Apparatus and reagents

Voltammetric analyses were performed with a PGSTAT 10 Eco Chemie (Utrecht, The Netherlands) potentiostat coupled to a 663 VA Metrohm (Herisau, Switzerland) stand, equipped with a working electrode (in this study: a lateral rotating solid gold electrode), an Ag/AgCl reference electrode and a glassy carbon counter electrode.

A LEICA-Stereoscan 410 scanning electron microscope was used for SEM investigations.

High purity water (HPW) obtained from a Milli-Q (Millipore, Bedford, MA, USA) apparatus was used throughout. Analytical grade reagents were used. HCl was obtained by sub-boiling distillation in a quartz still. As(III) standard solution (1000 mg l^{-1}) was prepared by dissolving As_2O_3 in 1 M NaOH, then adjusting the pH to about 2 with 1 M HCl. More diluted solutions were prepared daily from the 1000 mg l^{-1} standard.

2.2. Procedures

2.2.1. Electrode pretreatment

The electrode was polished with a suspension of 0.3 mm alumina in HPW for 1 min [26]. Then it was immersed three times into water and into ethanol alternatively to eliminate the remaining Al_2O_3 particles from its surface.

The electrochemical activation of the electrode surface was carried out by CV, with deaerated solutions of 0.5 M H_2SO_4 as supporting electrolyte. The electrode was polarized between 0 and +1.50 V using a scan rate of 100 mV s^{-1}; 10 cycles were applied.

The electrode was kept in 0.1 M NaOH overnight and when not in use; every day it was cleaned three times with water and ethanol alternatively and activated; the activation was repeated halfway through the day; ten voltammograms of the blank were recorded to permit a good stabilization of the background current (7 μA). It is important to take this aspect into account because without these initial steps a gradual decrease of the peak height is observed.

2.2.2. ASV determination of arsenic

20 ml test solutions of supporting electrolyte were delivered into the voltammetric cell and purged with nitrogen. After a deposition step at −0.30 V a voltammetric scan was performed.

A cell containing 5 μg l^{-1} of As(III) was utilized to investigate the effects of the different parameters on the analyte signal. After the optimisation the following conditions were adopted: deposition potential, −0.30 V; deposition time, 80 s; stirring rate, 1500 rpm; supporting electrolyte, 0.25 M HCl, unless otherwise stated. For the values of the scan parameters after optimisation, please refer to Section 3.2.2.

Then, for the evaluation of the performance of the optimised method, after recording the voltammogram of the blank, aliquots of As(III) were added and the corresponding signals were recorded. The detection limit was estimated as three times the standard deviation of the blank signal.

Drinking water was collected from the laboratory tap and filtered through a 0.45 μm cellulose acetate filter. 20 ml of water were transferred into the voltammetric cell, added with 0.4 ml of 12 M sub-boiling HCl and analysed as such and after spiking with 5 μg l^{-1} of As(III).

All experiments were performed in triplicate.

2.2.3. Cyclic voltammetry (CV)

Linear potential sweep CV experiments were performed daily for the electrochemical activation and for the monitoring of the electrode surface, polarizing the electrode between 0 and 1.50 V using a scan rate of 100 mV s^{-1}; the supporting electrolyte was 0.5 M H_2SO_4.

In order to study the electrochemical behaviour of the analyte, CV experiments were also carried out on cells containing 20 μg l^{-1} of As(III) prepared either in 0.5 M H_2SO_4, varying the potential between −0.30 and +1.50 V, or in 0.25 M HCl, varying the potential between −0.30 and +0.30 V.

3. Results and discussion

3.1. Studies on the optimal surface regime

3.1.1. Treatments and CV study of the gold surface

The importance of the pretreatment and activation steps of the active surface of gold electrodes, in order to maintain the electrode surface active and reproducible, is well known [11,25,38,39]. Careful electrode conditioning was found to be essential to enhance the quality and reproducibility of the arsenic signal both in this work and by other authors [12,40,41].

The voltammogram obtained by CV during the activation step (Fig. 1a–d) was also used for the daily monitoring of the electrode surface. The shape of the voltammogram reported in Fig. 1a is well know in literature and identifies a clean gold surface [12,42,43].

The anodic peak at +1.25 V is due to the processes of oxidation at gold surface. The nature of the species that are formed on the surface is not well known: some authors suggest the formation of a monolayer of oxides [29,44], others propose the presence of a thin layer of hydrated oxides or the formation of $Au(OH)_{n,ads}$. Thermodynamic calculations indicated that an hypothetical isolated gold atom (with no lattice stabilization energy) should undergo oxidation in acid solution (to hydrated Au_2O_3) at ca +0.33 V [45]. This value is varied not only by the presence of the crystal lattice, but also by the experimental conditions, such as pH and properties of the supporting electrolyte.

The cathodic peak at +0.90 V is caused by the reduction of the hyphotesized species. Dai et al. observed that the height of the

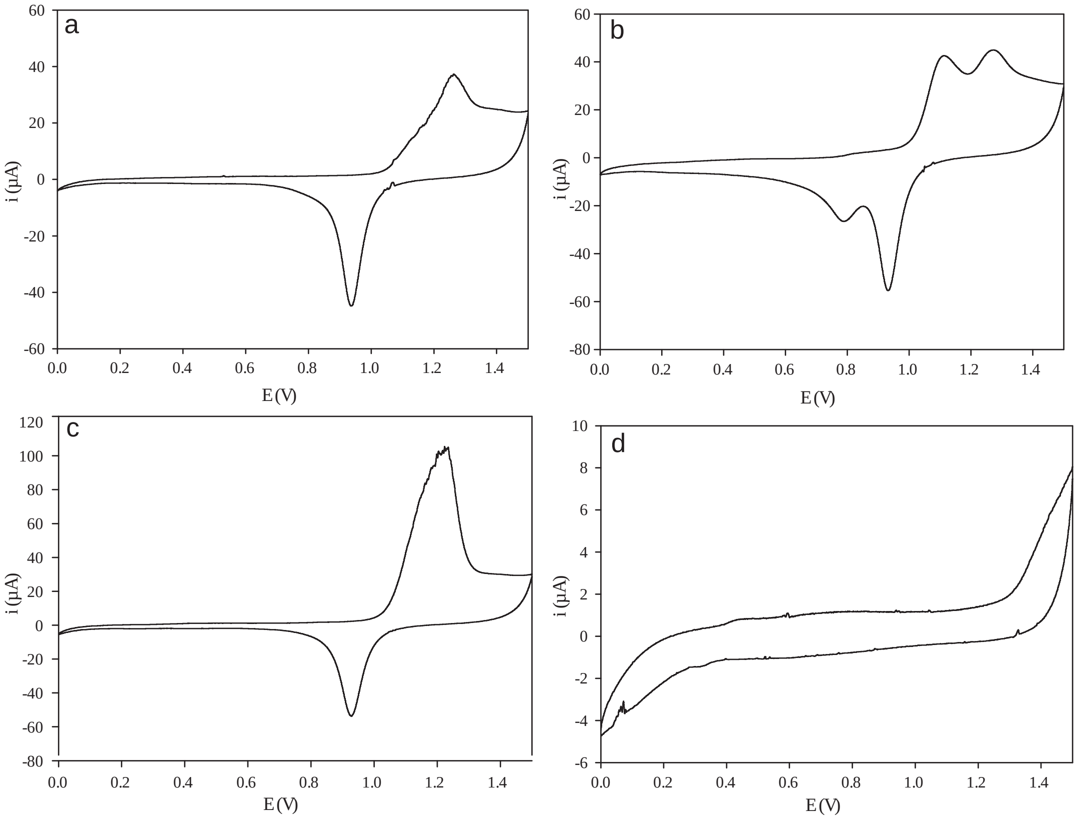

Fig. 1. Cyclic voltammogramms obtained in 0.5 M H_2SO_4 with the lateral gold electrode for (a) a clean surface; (b) the surface in the presence of multilayers of oxides; (c) the surface after the growth of an important oxide layer; and (d) the surface covered by a passivating layer.

cathodic peak varied with the efficiency of the deposition of a gold surface; they identified the value of peak intensity corresponding to the optimum deposition, and used CV in order to evaluate the quality of the deposition [29].

The cyclic voltammogram reported in Fig. 1b was recorded with an electrode which was neither stored in NaOH nor washed with ethanol and water; it shows additional peaks in comparison to Fig. 1a, due to the electrochemistry of gold. Burke and Moran [45] suggested that these peaks are caused by the formation of multilayers of oxides in which gold can exist in different oxidation states ($Au^0/Au^I/Au^{III}$); the presence of these layers causes a worsening of the electrode performance, thus showing the importance of the cleaning steps. After the treatments with NaOH, ethanol and water a cyclic voltammogram like that reported in Fig. 1a is again obtained. We suppose that in the presence of NaOH the surface is covered with a layer of hydroxides, that replace completely or in part the hydration layer; ethanol removes this deposited layer and water removes the traces of ethanol.

Fig. 1c shows another evolution of the electrode surface. The electrode that generated a voltammogram like this gave rise to lower stripping signals of arsenic. In fact the growth of an oxide layer on gold hinders the deposition of the analyte on the surface. Also Feeney and Kounaves showed a similar voltammogramm in their paper: they tested different treatments, but none of them enabled to recover the performances of the electrode. Only the immersion in ethanol temporarily alleviated the problem [42]. We can adfirm that after the cleaning with alumina, and the treatment with NaOH, ethanol and water the electrode worked properly again and the cyclic voltammogram of Fig. 1a was obtained.

When no peaks appear relative to oxidation/reduction of gold (Fig. 1d), the electrode is not working any more. A possible explanation is the formation of many layers of oxides on the electrode surface: they form a passivating layer that prevents an efficient electron transfer, and at the same time inhibits the deposition of the analyte on the conductive layer. After the mechanical and chemical treatment the cyclic voltammogram obtained is again like that reported in Fig. 1a but the sentivity starts to gradually decrease.

3.1.2. SEM investigation

At the beginning of the study, after a few months of extensive work and the end of the life of the electrode, SEM analyses were performed to investigate the status of the gold surface. Fig. 2a shows the SEM image of a brand-new electrode, before any treatment, in which a series of lines are apparent, probably caused by the process of fabrication of the electrode. The surface is also characterised by some defects. Fig. 2b shows the SEM image obtained for the same electrode after a few months of work. The surface is more homogeneous, probably thanks to the mechanical treatments with alumina that permit to level-off the structural defects. Fig. 2c shows the SEM image obtained when the cyclic voltammogram is like Fig. 1d (Section 3.1.1). The electrode presents a spongy surface typical of oxidised metals, probably caused by the presence of chloride in solution (see Section 3.2.1). We can suppose that the use of H_2SO_4 during the activation of the electrode permits to contrast this effect by eliminating the layer of oxides present on the surface, and causing a structural reorganization of gold. Unfortunately, sulphuric acid is unsuitable as a supporting electrolyte for analysis, as shown in Section 3.2.1.

3.2. Effect of operating conditions

3.2.1. Supporting electrolyte

Different supporting electrolytes were tested: 0.25, 0.5 and 0.75 M HCl; 0.1 M H_2SO_4; 0.01 M HNO_3; a mixture of 0.25 M H_2SO_4/0.25 M HCl. The electrolyte solutions were tested working both in DP and in SW modes. HCl was found to be the most suit-

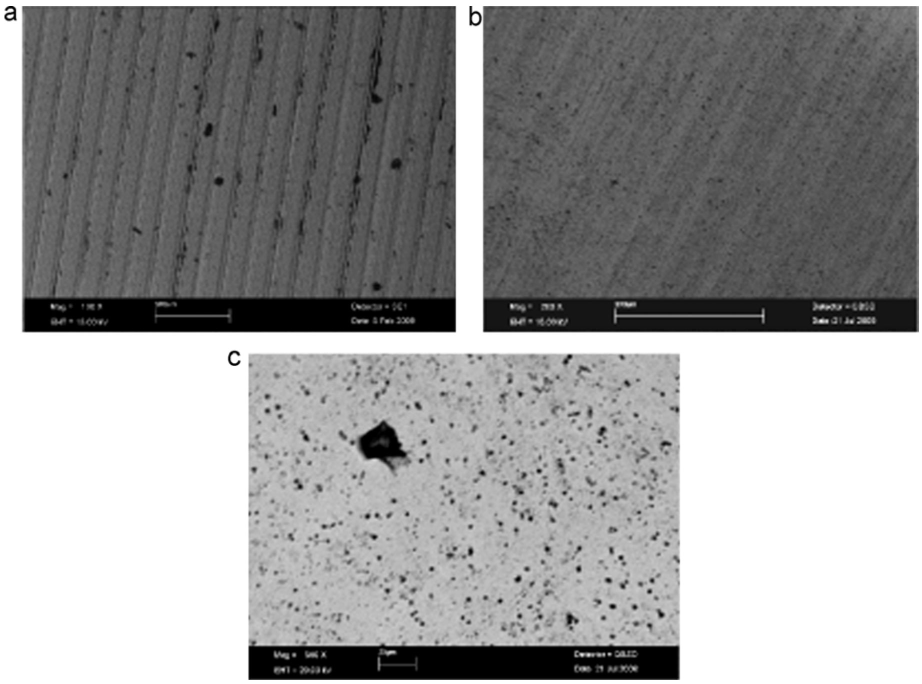

Fig. 2. SEM images of the gold electrode surface: (a) new electrode; (b) after a few months of extensive work; (c) when the surface is oxidised.

able medium, since it provided the highest and narrowest peaks for As(III). This is due to the faster charge-transfer reaction in chloride media [10,42].

High concentrations of HCl can cause the dissolution of the gold surface, owing to the complexation by chloride ions. Gold can be oxidised ($Au \rightarrow Au^{3+} + 3e^-$), and if the chloride ion concentration is high the complex $AuCl_4{}^-$ is formed and gold is dissolved, causing a decrease of the electrode active surface (loss of sensitivity) and of the repeatability [10,35,39]. Using 0.25 M HCl we obtained higher signals than with 0.1 M HCl, and a better repeatability than with 0.5 M HCl. Thus, 0.25 M HCl was chosen as the supporting electrolyte for the next electrochemical experiments.

3.2.2. Instrumental parameters

The effect of the potential scan parameters on the signal of 5 $\mu g\,l^{-1}$ of arsenic was investigated, working both in DP and SW modes, using 30 s as deposition time (for the optimisation of this parameter see Section 3.2.1). Step potential, interval time, modulation amplitude and modulation time were varied in DP mode. Different values of frequency, wave amplitude and step potential were examined working in SW mode.

The trends observed for the arsenic peak following the variation of scan parameters are in agreement with theoretical predictions [46].

Working in DP mode, the signal increased with the increase of the step potential, reflecting the increase of scan rate. An increase of interval time had the opposite effect on the analyte peak owing to a decrease in scan rate. An increase of modulation amplitude caused an increment of the signal intensity, probably due to the larger difference between the current before and after the application of the pulse, and its shift to more positive potentials. The variation of the modulation time had the opposite effect, likely because of the decrease of the faradaic current during long pulses.

As to the SW mode, the signal increased and was shifted to more positive potentials when frequency and step potential were increased, in agreement with the increase in scan rate. Higher values of these parameters caused a distortion of the signal shape. An increase of wave amplitude was responsible for an increase of the peak height, for the same reasons discussed for modulation amplitude above, and no shift of the peak potential was observed.

Both DP [37,40,41,47] and SW [11,35,48] are used in literature for the determination of As(III). SW allowed us to obtain higher signals but it gave rise to a lower repeatability and a greater background signal. For these reasons DP was chosen for the next experiments.

Deaeration with nitrogen was found to be necessary to reduce the background due to oxygen reduction: 120 s or 60 s, working respectively with DP or SW, are sufficient to obtain good results.

We tested the effect of the stirring speed in the range 0–3000 rpm: as expected, the intensity of the signal increased with increasing of electrode rotation rate, and consequently of the extent of mass transfer to the electrode. We choose an intermediate value of 1500 rpm for the next experiments.

A deposition potential of −0.30 V was chosen as it yielded the highest current response with least interference from other reactions. This value is in agreement with the data in literature. Using deposition potentials more positive than −0.40 V the response of As(III) is more reproducible [12], while the deposition efficiency decreases at potentials more negative than −0.35 V, because the reduction of water and the associated production of hydrogen ($H_2O + 2e^- \rightarrow H_2 + 2OH^-$) starts to compete with the reduction of arsenic ($As^{III} + 3e^- \rightarrow As$), blocking the surface and decreasing the current due to the analyte [10,35]. At more negative potentials it is also possible that some elemental arsenic is converted to As^{3-} with the formation of AsH_3 [35]. The response of As(III) after deposition at −1.20 V, the potential commonly used for the determination of As(V), is ten times lower than that obtained using −0.30 V. The optimal values for the parameters for DP and SW are reported in Table 1.

3.3. Repeatability, linearity, detection limit and accuracy

The performance of the analytical method was evaluated using the DP scan mode in the optimal conditions.

The repeatability was evaluated with ten replicates on ten different cells containing 10 $\mu g\,l^{-1}$ of As(III) cleaning the surface between

Table 1
Optimal electrochemical parameters values for As(III) determination.

Parameter	DP	SW
Interval time	0.1 s	
Modulation amplitude	0.15 V	
Step potential	0.018 V	0.035 V
Wave amplitude		0.15 V
Frequency		145 Hz
Scan rate	0.18 V/s	5.07 V/s
Deaeration time	120 s	60 s
Stirring speed	1500 rpm	1500 rpm
Deposition potential	−0.30 V	−0.30 V

Table 2
Slope, intercept and R^2 for the calibration curves obtained in different concentration ranges using different deposition times.

Range (μg l^{-1})	Deposition time (s)	Slope	Intercept	R^2
0.1–1	60	36.89 ± 3.29	0.19 ± 0.71	0.9921
1–5	30	13.31 ± 0.68	−1.04 ± 1.48	0.9974
5–15	10	9.54 ± 0.15	0.75 ± 1.63	0.9997
0.1–15	Variable	9.15 ± 0.22	5.91 ± 1.38	0.9961
0.1–15	30	7.03 ± 0.59	6.60 ± 3.74	0.9534

each determination. The relative standard deviation was 3%. We also evaluated the repeatability for ten consecutive determinations in the same cell without cleaning between experiments: the relative standard deviation was 4% and we noticed a slow decrease of the peak height from 11.5 to 10.5 mA. This behaviour is due to the deposition of chloride on the electrode surface and is in agreement with the results of Salaün et al. [12].

The linearity of the method was investigated in the range 0.1–15 μg l^{-1}. The results obtained are summarized in Table 2. The analytical response strongly depended on the deposition time. Using 30 s as deposition time in all the considered concentration ranges, the peak height increased up to 5 μg l^{-1}, then the response gradually flattened off, yielding a low correlation coefficient ($R^2 = 0.9534$). The decrease in sensitivity at relatively high concentrations of As is caused by a coating of the electrode surface with the deposited As(0) which is non-conductive [49]. On the other hand, longer deposition times permit to acquire better defined peaks at low As concentrations. To obtain a better linearity of response we used 60, 30 and 10 s in the ranges 0.1–1, 1–5 and 5–15 μg l^{-1} respectively ($R^2 > 0.992$).

The limit of detection was estimated as LOD = $3\sigma_B$/slope of the calibration curve for the range 1–15 μg l^{-1} and was found to be 0.060 μg l^{-1}. This value is in good agreement with the LOD reported by Metrohm (0.05 μg l^{-1}) with a lateral gold electrode [41]. Other authors obtained detection limits of 0.015 μg l^{-1} using a gold microelectrode [12] or 0.1 μg l^{-1} with gold ultramicroelectrode arrays [35].

The accuracy of the procedure was tested by analysing solutions containing known concentrations, 2.50 and 0.10 μg l^{-1}, of As(III). The concentrations found were 2.48 ± 0.11 μg l^{-1} (relative error = −1%) and 0.104 ± 0.020 μg l^{-1} (relative error = +4%), using 30 and 60 s as deposition times respectively. Therefore the accuracy of the method can be considered good.

3.4. *Electrode rotation rate*

The sensitivity of stripping voltammetry strongly depends on the amount of substance deposited at the electrode; therefore the rate of substance flux from the bulk of the solution toward the electrode (i.e. the hydrodynamic conditions) is very important [10]. The deposition current (i.e. the current flowing during the deposition step) as well as the stripping peak intensity at a rotating disk electrode is proportional to ω^a (where ω is the rotation rate and a is a constant depending on the hydrodynamic properties of the electrode configuration) [38]. For laminar flow conditions, a usually ranges from 0.3 to 0.5. The equation $i = C\omega^a$, where i is the stripping current, C is the analyte concentration, can be written as $\log(i) = a \log(\omega + \log(c))$. Fig. 3a and b shows the relationship between $\log(i)$ and $\log(\omega)$ found in this work using DP and SW respectively.

We obtained a from the slopes of the two lines. Working in DP mode we found $a = 0.34$ with $R^2 = 0.9495$, while working in SW $a = 0.55$ with $R^2 = 0.998$. In spite of the low R^2 value, the result obtained with DP is in good agreement with that of Sun et al. [10] who found $a = 0.35$ working in DP with a gold film electrode.

The correlation was better in SW and our result was similar to the value frequently found ($a = 0.5$) for a mercury film electrode when a reversible reaction takes place [50].

3.5. *CV Study of As(III) electrochemical behaviour*

Fig. 4 shows the cyclic voltammograms of solutions containing 20 μg l^{-1} of As(III) prepared either in 0.5 M H_2SO_4 varying the potential between −0.30 and +1.50 V (Fig. 4a and b), or in 0.25 M HCl varying the potential between −0.30 and +0.30 V (Fig. 4c and d). The figures also report the voltammograms of the corresponding blanks. It is important to underline that in chloride-containing solutions, the potential should not exceed +0.55 V since at more positive values, the surface of the gold electrode can be altered because of the adsorption of chlorides or formation of an oxide [35]. The potential was varied both in "reverse scan" (from negative to positive potentials and return) (Fig. 4a and c) and in "direct scan" (from positive to negative and return) (Fig. 4b and d).

The figures show that the arsenic peak intensities are higher in H_2SO_4 (Fig. 4a and b) than in HCl (Fig. 4c and d). The difference between the anodic and cathodic peak heights in voltammograms recorded in HCl is caused by the fact that the system is not completely reversible [51]. This difference is more evident in H_2SO_4 due to the different potential ranges: for both solutions (Fig. 4a

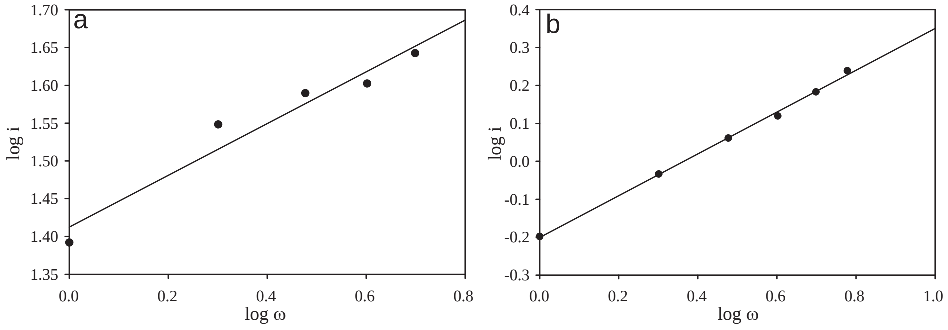

Fig. 3. The relationship between $\log(i)$ and $\log(\omega)$ at the lateral gold electrode in the presence of 1 μg l^{-1} of As using (a) DP and (b) SW.

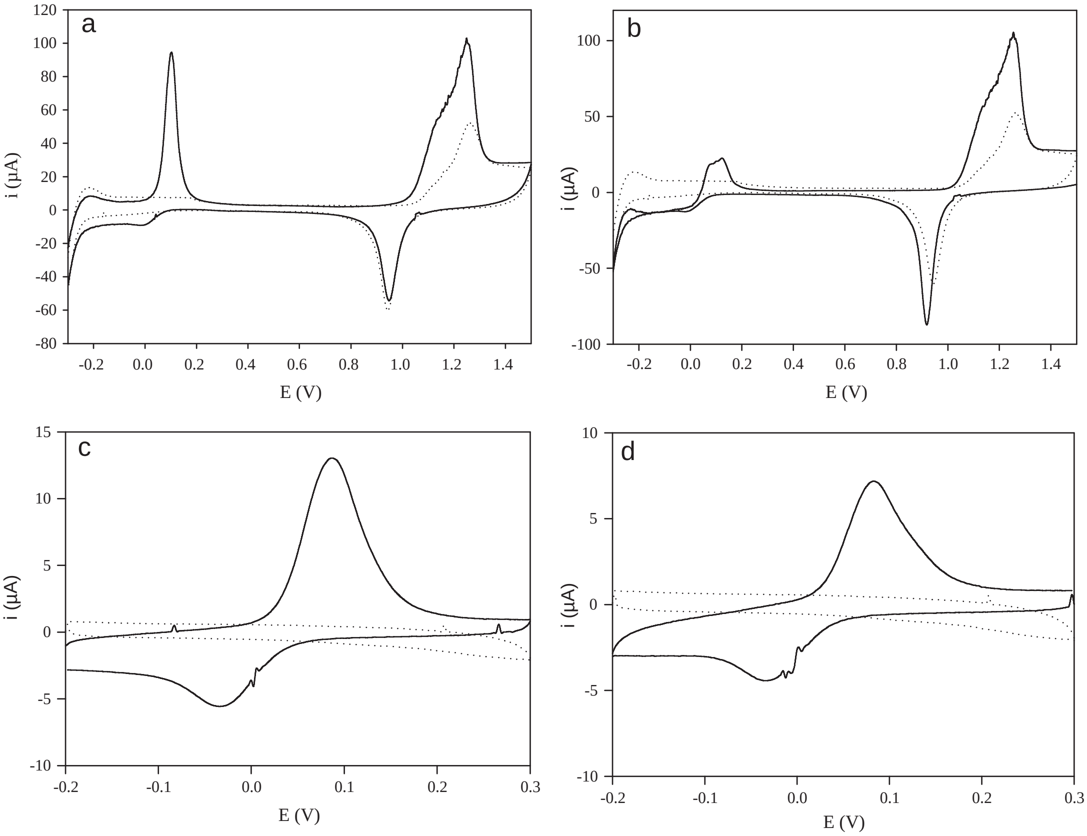

Fig. 4. Voltammograms of blanks (. . .) and of 20 µg l^{-1} of As(III) solutions (—) obtained working in (a) reverse scan in 0.5 M H_2SO_4; (b) direct scan in H_2SO_4; (c) reverse scan in 0.25 M HCl; (d) direct scan in HCl.

and c) arsenic is present as As(0) at −0.30 V and it is oxidised to As(III) at +0.10 V, but in HCl the scan stops at +0.30 V while in H_2SO_4 it continues until +1.50 V. In these conditions As(III) is easily oxidised to As(V), which is considered electroinactive except in extreme conditions of high acid concentrations or at very negative potentials like −1.20 V [12,37,52]; for this reason it is not reduced back to As(III) in the inverse scan. The cathodic peak is caused by the residual fraction of As(III) that was not reduced to As(0). The same considerations are valid for the voltammograms in Fig. 4b and d. Some authors observed the reduction peak of As(III) at −0.30 V, while we found it very close to 0 V. According to Brusciotti and Duby [53], the peak at −0.30 V is not caused by the reduction of As(III), but by the development of hydrogen from the solution. Sun et al., working in 2 M HCl, found the oxidation peak at +0.15 V and the reduction peak at 0 V, in agreement with our observations [10].

The separation between the anodic and cathodic peaks for a reversible reaction is expressed by the equation $\Delta E = \left|E_{\mathrm{an}} - E_{\mathrm{cat}}\right| = 59/n$ [46]. Assuming the approximation that the couple As(III)/As is reversible, we obtained $n = 0.48$, 0.47, 0.48 and 0.49 from voltammograms a, b, c, d respectively. Our results confirm that obtained by Feeney and Kounaves: they studied the electrochemical behaviour of As(III) in 2 M HCl with a mercury drop electrode and found $n = 0.4$ instead of the theoretical value of 3 (deposition step: $\mathrm{As^{III}} + \mathrm{Au} + 3\mathrm{e}^- \rightarrow \mathrm{As} + \mathrm{Au}$; stripping step: $\mathrm{As} + \mathrm{Au} \rightarrow \mathrm{As^{III}} + \mathrm{Au} + 3\mathrm{e}^-$) [37]. Moreover they demonstrated that the electron-transfer process is slow and approaches electrochemical irreversibility. Since elemental arsenic is a very poor conductor of electricity, the oxidation peak current was found to be limited when the active surface of the electrode was fully covered with elemental arsenic [35].

Furthermore, the current in a semi-reversible process is lower than that expected from a reversible process, because it depends also on the coefficient of electronic transfer (α), whereas the current does not depend on this parameter for a reversible process.

Jia et al. using a Au (1 1 1) single crystal electrode in a phosphate solution at pH = 1.0 containing $NaAsO_2$, calculated the cathodic transfer coefficient (α) of the rate-determining step with Tafel's law $\eta = E_{\mathrm{eq}} - E = RT/\alpha nF \log i/i_0$. They found $\alpha = 0.42$, a value that reflects a semi-reversible process [51].

3.6. *Interferences*

The interference of several cations, namely Al(III), As(V), Bi(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Hg(II), Mn(II), Mo(II), Ni(II), Pb(II), Sn(IV), Zn(II), and of some anions (BO_3^{3-}, Br^-, CH_3COO^-, CO_3^{2-}, F^-, $HCOO^-$, I^-, PO_4^{3-}, S^{2-}, Sb(V) as $[Sb(OH)_6]^-$, Se(IV) as SeO_3^{2-} and Te(IV) as $[Te(OH)_5]^-$ and $[Te(OH)_4]^{2-}$) was evaluated.

Voltammograms of a solution with 5 µg l^{-1} of As(III) were recorded in the presence of each species (added into the polarographic vessel in 1:1 and 1:2 concentration ratios with respect to arsenic). The presence of most cations (Bi(III), Cd(II), Cr(III), Cu(II), Fe(III), Hg(II), Mn(II), Mo(II), Ni(II), Sn(II), Zn(II)) gives rise to a decreasing of the intensity of arsenic peak.

Regarding the considered cations we observed that:

- Cd(II), Cu(II), Hg(II) and Pb(II) gave rise to another peak at +0.2 V, +0.35 V, +0.38 V and −0.18 V respectively.
- The effect of Cu(II) on the determination of As(III) is widely discussed in literature [10,35]. In fact, it is well known that Cu forms an intermetallic compound with As [10,29] that causes the decrease of the analyte signal. Some researchers, working with mercury electrodes, added copper to promote the deposition of As on the electrode surface [37]. In the presence of Cu(II), we noticed

a strong memory effect, that remained for long time, even after some cleaning steps.
- Hg(II) caused a decrease in the analyte peak height. This element can interfere with the determination of arsenic, due to the competition for the sites on the gold surface [29,35].

Regarding the anions we observed in particular that:

- An addition of Br^-, F^- and I^- caused a decrease of the peak height. This is due to the high affinity of arsenic for the halogens.
- Adding Sb(V) in ratio 1:1 the analyte signal apparently increased. This is caused by the fact that antimony produces a peak at the same potential as that of As(III) [12].
- After the addition of S^{2-}, Se(IV) and Te(IV) the signal of As(III) decreased. This is probably caused by the formation of intermetallic compounds (e.g. As_2S_3, As_2Te_3) [54,55].
- The addition of As(V) did not cause changes in the As(III) peak, showing that the present method can be used to study the speciation of arsenic.

3.7. Applicability to a real sample

Preliminary measurements about the applicability of the procedure to the analysis of drinking water were made. No As(III) peak was observed in the sample, therefore the water was spiked with $5\ \mu g\ l^{-1}$ of As(III). The concentration was determined with the standard additions method. The result obtained was $4.12 \pm 0.04\ \mu g\ l^{-1}$ ($n = 3$). Although the concentration was underestimated (−18%) and further optimisation is necessary to increase the accuracy of this determination, we think that this result represents a good starting point because it shows that the procedure is able to determine As(III) at concentrations lower than the maximum admissible level of $10\ \mu g\ l^{-1}$ set by EPA and WHO [56].

3.8. Approximation of a stirred system to a flow system

The behaviour of flowing solutions is well described by some laws. The current measured by an electrochemical detector is governed by the convective diffusion towards the electrode surface and hence by the hydrodynamic conditions of the flow. A general equation for the limiting current is $i_l = knFC^*D(Sc)^{\beta}b(Re_x)^a$, where k is a dimensionless constant, n the number of electrons transferred per molecule, F the Faraday constant (96485,3399 C/mol), C^* the bulk concentration of the electroactive species, D its diffusion coefficient, Sc the dimensionless Schmidt number (νD^{-1}, ν being the kinematic viscosity), b a measure for the electrode width, Re_x the dimensionless Reynolds number ($\upsilon l_x \nu^{-1}$, υ being the mean linear velocity of the fluid and l_x the characteristic length of the electrode). The values of β and a are determined by the specific characteristics of the hydrodynamic conditions. The values of k, b, and l_x depend on the cell geometry [57].

We entered our data in the equation in order to estimate the number of electrons involved in the considered process ($n = i/kbFCD(Sc)^{\beta}(Re)^a$). We adapted some terms of this equation to our particular system. Briefly we considered that:

- i is the peak height (μA);
- $k = 2$ for a rotating disk electrode [58];
- b in this case is the radius of the electrode, $b = 0.35$ cm;
- F is Faraday's constant;
- $D = k_bT/6\pi r_i \eta$, where k_b is the Boltzmann's constant ($1.3806505 \times 10^{-23}\ J\ K^{-1}$), T is the absolute temperature (272.15 K), r_i the ionic radius of the considered species (for As(III), $r_i = 5.8 \times 10^{-11}$ m), η the viscosity coefficient of the solution (for 0.25 M HCl, $\eta = 1.050 \times 10^{-3}$ Pa s): we obtained $D = 3.528 \times 10^{-5}\ cm^2\ s^{-1}$;
- $Sc = \eta/\rho D = \nu/D$, where ρ is the density of the solution (for 0.25 M HCl, $\rho = 1.004\ kg\ l^{-1}$), $D = 3.528 \times 10^{-9}\ m^2\ s^{-1}$: we obtained $Sc = 297$;
- $Re = \nu\rho L/\eta = \upsilon L/\nu$. We considered υ as the average velocity of a particle present in cell at a mean distance from the electrode ($\upsilon = 2\pi r f x$, where r is the average distance of a particle from the electrode, 9.5×10^{-3} m (estimated taking into account the cell size); f is the minimum value of the stirring rate which can be set with the instrument utilized, 3 Hz; x is a multiplicative coefficient of f, such that xf is the stirring rate adopted during the experiments ($x = 3$)); L is a length that depends on the nature and on the geometry of the cell (we assumed that L could be interpreted as either (i) the width of the cell in correspondence of the active surface (L_1), or (ii) the mean distance that a species has to travel to reach the electrode (L_2); we obtained $L_1 = 0.03$ and $L_2 = 0.032$ respectively): we obtained $Re_1 = 15{,}400$ and $Re_2 = 16{,}427$.
- β and a are two constants determined by the hydrodynamic characteristics of the system: for a rotating disk electrode $\beta = 1/3$ [57,58] and from the calculations reported in Section 3.5 $a = 0.34$.

A cell containing $100\ \mu g\ l^{-1}$ ($1.334\ mmol\ cm^{-3}$) of As(III) was used to collect the data for this calculation. The measurement was carried out without deposition, which would influence the intensity of the current. The number of electrodes obtained is $n_1 = 0.48$ or $n_2 = 0.48$ working in DP and $n_1 = 0.46$ or $n_2 = 0.45$ working in SW.

Even if the application of this equation on our system is a constrainment, the number of electrons found with this approach is in good agreement with the values obtained with CV, demonstrating that it is possible to apply the equations generally applied to the flow systems also to this type of stirred system.

4. Conclusions

The results obtained showed the efficiency of the lateral gold electrode for the determination of low concentrations of As(III) by anodic stripping voltammetry. The repeatability, sensitivity and accuracy are good.

We observed that the presence of some cations and anions in solution interfered with the determination of As(III), in particular Cu(II), Hg(II), Br^-, F^- and I^-.

We underline the importance to repeat the electrochemical conditioning step every day and to perform the mechanical cleaning when necessary in order to maintain the electrode surface active and reproducible. We showed that the voltammogram obtained by CV during the activation step can be also used for the daily monitoring of the electrode surface. CV can be an alternative to SEM, which is not available in many analytical laboratories, to check the status of the gold layer and decide about the need of a mechanical treatment or even the substitution of the electrode. To our knowledge, this is the first paper which reports monitoring of the electrode surface with both CV and SEM and gives detailed suggestions on electrode storage and maintenance.

We demonstrated that it is possible to apply the equations generally used for flow systems to the investigated stirred system: the number of electrons involved in the electron transfer process calculated with this approach was in good agreement with that obtained by CV and with literature data. As far as we know, this approach has not previously been reported in the literature in this context.

The use of a gold nanostructured or film-plated electrode would permit to overcome some problems encountered with the traditional solid gold electrode. In fact the possibility to work with a freshly renewable surface would permit to reduce the decreasing of the response sensitivity in time, the memory effects and some interferences. In particular, the use of a gold nanoparticle-modified electrode would allow to obtain lower detection limits thanks to the larger active surface [29,55].

Acknowledgements

We thank Prof. Ghiotti and Dr. Morandi, Department of Inorganic, Physical and Materials Chemistry, University of Torino, for the SEM analyses.

We thank the Italian Ministry of University and Research (MIUR, PRIN, Rome) for financial support.

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