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Article

Electrochemical Detection of Arsenite with Silver Electrodes in Inorganic Electrolyte and Natural System Mixtures

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A detecção eletroquímica de arsenito com eletrodos de fio de prata (SWE) ou de disco de prata (SDE) foi realizada em soluções aquosas inorgânicas, as quais são similares àquelas encontradas em condições naturais. Voltametria cíclica (CV), voltametria de varredura linear (LSV) e voltametria de redissolução anódica (ASV) foram aplicadas. Os fatores investigados foram pH, natureza e concentração do eletrodo de suporte e tempo e voltagem de deposição para ASV. As mudanças de corrente e potencial de pico anódicos de As(III) em soluções padrão (por exemplo, 0,1 mol L^{-1} Na_2SO_4, $NaNO_3$, HNO_3 and H_2SO_4) foram avaliadas. Os meios neutro e básico de sais inorgânicos intensificaram a sensibilidade do eletrodo de prata mais que o meio ácido. Então, foi possível trabalhar em meio alcalino com sensibilidade aumentada para As(III) (limite de detecção de 90 ng L^{-1}). A resposta analítica melhorada fez este sistema comparável a um eletrodo de nanoarranjo. Como o intervalo de uso destes eletrodos era largo, SWE (área de 6,47 mm^2) foi aplicado para monitorar a água de torneira usando 0,1 mol L^{-1} Na_2SO_4 como eletrodo de suporte para detectar quantidades acima de 0,5 µg L^{-1} As(III).

The electrochemical detection of arsenite with silver wire (SWE) or silver disc (SDE) electrodes was carried out in inorganic aqueous solutions, which are similar to those found under natural conditions. Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and anodic stripping voltammetry (ASV) were applied. The investigated factors were pH, nature and concentration of supporting electrolyte and deposition time and voltage for ASV. The changes in the As(III) anodic peak current and potential in standard solutions (*e.g.*, 0.1 mol L^{-1} Na_2SO_4, $NaNO_3$, HNO_3 and H_2SO_4) were evaluated. The neutral and basic media of inorganic salts were found to enhance the silver electrode sensitivity more than the acidic media. Thus, it was possible to work in alkaline medium with increased sensitivity for As(III) (limit of detection of 90 ng L^{-1}). The improved analytical response made this system comparable to a nanoarray electrode. As the range of use of these electrodes was wide, SWE (area of 6.47 mm^2) was applied to monitor tap water using 0.1 mol L^{-1} Na_2SO_4 as supporting electrolyte to successfully detect quantities above 0.5 µg L^{-1} As(III).

Keywords: arsenite electrooxidation, silver electrodes, electrochemical detection, tap water

Introduction

Arsenic is a metalloid that naturally exists in the oxidation states 3+, 5+, 0 and 3−. Its toxicity depends on its complex form, being the organic arsenic less toxic than the inorganic one.[1] Specifically, the inorganic As(III) state is 10 times more mobile and toxic than As(V). The permitted level in water is 10 µg L^{-1} according to World Health Organization (WHO). The mobility of arsenic compounds and their water rejection ability depend on the cations and anions that coexist in the natural media. The As(III) determination at low concentrations in aqueous solutions has been widely performed using electrochemical methods.[2-6]

As(III) traces in natural waters and biological materials were previously determined using a gold disc electrode.[7] However, the sodium chloride concentration must be

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limited when used as supporting electrolyte since the excess causes the formation of two oxidation peaks. Additionally, copper and antimony have been found to produce interference when a gold-film electrode was used to determine As(III) by anodic stripping voltammetry (ASV).[8] These elements, when in seawater, do not significantly interfere with arsenic determination.[7,8]

The use of platinum nanoparticle modified glassy carbon as electrodes for the analytical determination of the As(III) oxidation peak does not suffer from Cu(II) interference, in contrast to other metal surfaces (especially gold) that are typically used to detect arsenic.[9] Contrary to previous studies,[10] it was found that As(III) could be determined by ASV using a gold microwire electrode at any pH (including the neutral pH, typical for natural water). Gold, platinum and silver[11] were also investigated as electrode substrates for arsenic detection via anodic stripping voltammetry. The combination with ultrasound increased the level of arsenic detection (10^{-8} mol L^{-1}). The arsenic determination was optimized using a silver macroelectrode, which is similar to the one in this work, but in acidic media. The authors also studied the copper interference in the determination because it formed intermetallic compounds with arsenic.

Additionally, silver electrodes are nontoxic, the standard potential of the system is high (+0.7991 V)[12,13] and the analytical range of these electrodes is wide (for example, 10^{-1} to 10^{-8} mol L^{-1} for halide).[12] Silver electrodes allow not only anions but also a number of cations and a significant number of organic substances (including high-molecular substances and surfactants) to be quantitatively determined.

The present study targets the electrochemical detection of arsenite species by silver wire electrode (SWE) or silver disc electrode (SDE) with cyclic (CV), linear sweep (LSV) and anodic stripping (ASV) voltammetric methods, studying the produced effect by the nature and concentration of the supporting electrolyte and the pH range. ASV and CV were applied to extend the lower limit of detection. The SWE response was studied for low and high arsenite concentrations in drinking water media. The main advantages of the developed method were simplicity, low cost, no required derivatization, simple instrumentation and the possibility of constructing miniature devices using small electrodes (*e.g.*, silver screen printed electrodes for small sample volumes).

Experimental

Reagents

High purity 0.1 mol L^{-1} sulfuric acid and hydrochloric acid were prepared from suprapure reagents (Merck). The 0.1 mol L^{-1} $NaNO_3$, Na_2SO_4, $NaHCO_3$, NaCl, $CaCl_2$ and Mg_2SO_4 solutions were prepared from solid salts (Merck, analytical grade). A standard solution of 1.5 g L^{-1} As(III) (0.02 mol L^{-1}) was prepared by dissolving the adequate quantity of $NaAsO_2$ (Merck) in deionized water (final pH 9.0) or in a 0.1 mol L^{-1} NaOH solution (Aldrich). All solutions were prepared using milli-Q water from a water purification system (Millipore, MA, USA).

Electrodes, electrochemical cells and instrumentation

All experiments were carried out with a CHI 604C electrochemical analyzer. Standard three-electrode cells were used for analytical experiments. An Ag/AgCl reference electrode in 3 mol L^{-1} KCl (CHI 111) and a platinum wire as counter electrode were used. The silver wire electrode (area of 6.47 mm^2) and silver disc electrode (area of 10.21 mm^2) were polished with 1 µm diamond paste and used for analytical determinations. Cyclic voltammetry was applied in the potential range of 0.1-0.5 V using scan rates of 100, 50, 20 or 10 mV s^{-1}.

As(III) determination

In all cases, 10 mL of aqueous solution containing the electrolyte support of interest or drinking water were used. Standard solutions of 0.1 mol L^{-1} H_2SO_4 and 0.1 mol L^{-1} Na_2SO_4 were used as electrolyte support, with a highly concentrated solution of 20 mmol L^{-1} As(III). The diluted solutions of these standards were assayed under the same conditions. Drinking or tap water containing 0.1 mol L^{-1} Na_2SO_4 solution was prepared and contaminated with known quantities of As(III). The calibration curve at the lowest and highest concentrations was plotted. Linear sweep anodic stripping voltammetry was applied with SWE (6.47 mm^2) in a 15 mL standard solution of 0.003 mol L^{-1} Na_2SO_4 and 0.01 mmol L^{-1} As(III). Additionally, diluted solutions of $NaHCO_3$, NaCl, Na_2SO_4, $MgSO_4$ and $CaCl_2$ were prepared and assayed alone and mixed with As(III).

Results and Discussion

Arsenite oxidation in different supporting electrolytes

The supporting electrolyte effect on the As(III) anodic response on the silver wire and disc electrodes was studied by CV. Among the examined electrolytes (*i.e.*, 0.1 mol L^{-1} Na_2SO_4, H_2SO_4, $NaNO_3$ and HNO_3), Na_2SO_4 and $NaNO_3$ provided the highest well-defined anodic peak currents.

Because any anion can form a complex with As(III), what can modify its electrochemical properties, only

0.1 mol L^{-1} NaOH was used to adjust the pH value. Electrochemical detection of As(III) by silver wire and silver disc electrodes using cyclic voltammetry with the inorganic solutions that was above mentioned was carried out in the pH ranges of 7.0-9.0 and 7.0-13.0. In all cases, the characterized anodic response by As(III) was near 0.3 V.

0.1 mol L^{-1} HNO_3 and $NaNO_3$

The cyclic voltammetric curves of As(III) for SDE (ø = 5 mm) at 100 mV s^{-1} for the range of –0.5-0.5 V in 0.1 mol L^{-1} HNO_3 are shown in Figure 1. A typical assay in blank media (without As(III)) is curve a, while curve b shows a well-defined As(III) reduction wave at –0.3 V and an oxidation wave at 0.24 V, as previously reported for the conversion of As(0) to As(III).[11] The reduction process at 0.4 V was associated with the reduction of the silver in the electrode (curve a) in absence of As(III).

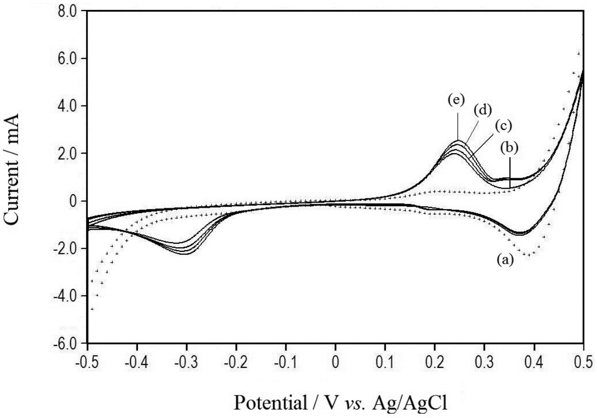

Figure 1. CV curves of SDE (19.3 mm^2) in 0.1 mol L^{-1} HNO_3 at scan rate of 100 mV s^{-1}: (a) in the absence of arsenic, (b) 1.7, (c) 2.6, (d) 3.4 and (e) 4.25 mmol L^{-1} As(III).

SWE (6.47 mm^2) at 50 mV s^{-1} in unbuffered 0.1 mol L^{-1} $NaNO_3$ solution (pH *ca.* 7.0-9.0) showed just one irreversible anodic peak at 0.35 V (Figure 2). A typical assay in blank media was curve a, which did not show anodic peaks in the range of 0.12-0.5 V for silver oxidation. Although the present authors were interested in analyzing the role of silver oxides (*e.g.*, Ag_2O) on the wave oxidation of arsenic, it was not clear that any effect on the As(III) signal (seen as a shoulder in the silver oxidation wave) existed. The increase in the anodic peak currents was proportional to arsenic concentration, and the pH of the solution was increased from 7.0 to 9.0. The net currents (I_c) shown in the inset of Figure 2 were calculated on the basis of the current peak, subtracting the background of the 0.1 mol L^{-1} $NaNO_3$ solution without As(III) (curve a). The linear least square calibration curve over the range of 0.098-1.000 mmol L^{-1} (24 points) was I (µA) = 29.7 $C_{As(III)}$ (mmol L^{-1}) with a correlation coefficient (r^2) of 0.998, indicating that the regression line fit very well the experimental data. Several experiments in the same conditions resulted in linearity ranges of 0.045-1.000 mmol L^{-1} with values of anodic current density in the order of 3.86-4.60 µA mm^{-2} up to 1 mmol L^{-1} As(III). An increase in the SWE area (10.21 mm^2) increased the current density to 5.87-8.12 µA mm^{-2} for a similar linear range of As(III) concentration.

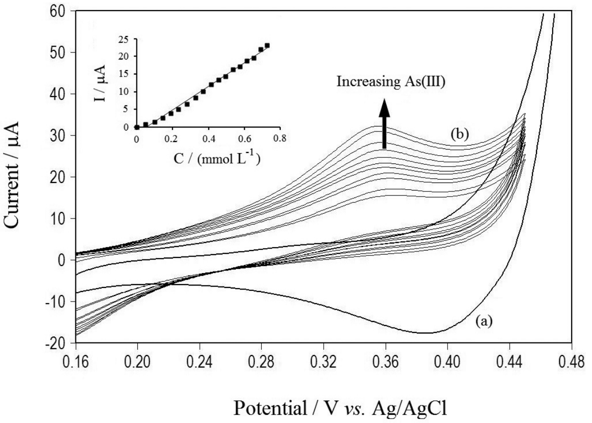

Figure 2. CV curves of SWE (6.47 mm^2) in 0.1 mol L^{-1} $NaNO_3$ at scan rate of 50 mV s^{-1}: (a) in the absence of arsenic and (b) 1 mmol L^{-1} As(III).

0.1 mol L^{-1} Na_2SO_4 and H_2SO_4

The electrochemical behavior of As(III) in Na_2SO_4 solutions was investigated with SWE (6.47 mm^2) by CV, LSV and ASV. CV with a scan rate of 50 mV s^{-1} in 0.1 mol L^{-1} Na_2SO_4 and up to 2 mmol L^{-1} As(III) showed a similar profile to the one in 0.1 mol L^{-1} $NaNO_3$ but with an increase in the anodic peak current values (profile b) at 0.35 V. The calibration curve had a slope of 23.09 µA $mmol^{-1}$ L with a linear correlation factor of 0.988. The calculated current density was 6.2 µA mm^{-2}. In addition, the oxidation potential was independent of the As(III) concentration. The oxidation peak for As(III) occurred at a slightly less positive potential than for the Ag_2O formation at 0.34-0.42 V.[13] In sodium salt electrolytes, it was suggested that some As(III) was adsorbed at the oxide-free Ag electrode surface. Meanwhile, most of the reaction occurred at the As(III) oxidation onset, and the oxide formation simultaneously occurred to produce a peak response at 0.35-0.36 V.

The majority of studies[14-16] reported the use of inorganic acid or salts as supporting electrolytes between the concentrations of 1.0 and 0.1 mol L^{-1}. The dilution effect of the Na_2SO_4 electrolyte support on the current peak was also examined. Figure 3 presents the values of anodic current *vs.* the supporting electrolyte concentration, in which the current of As(III) at each point of the curve was observed to be the result of voltammograms from different applied assays for electrolyte concentrations of 0.001, 0.002, 0.05, 0.01 and 0.1 mol L^{-1}. The reported net current was for 1 mmol L^{-1} As(III) solutions and obtained from the slope of the calibration curve applying linear regression (see Table 1).

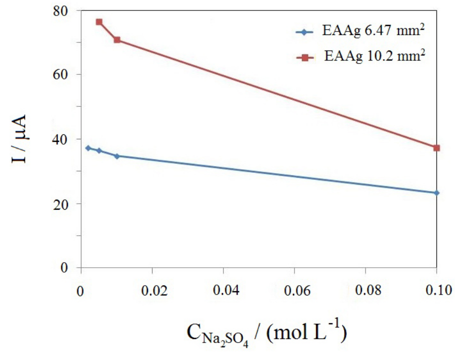

Figure 3. The net current calculated from CV for 1 mmol L^{-1} As(III) *vs.* molar concentration of Na_2SO_4 supporting electrolyte with SWE (6.47 mm^2) and SWE (10.21 mm^2), at scan rate of 50 mV s^{-1} and pH 7.0-9.0.

To further characterize dilution effects, an amount between 0.1 and 2.5 mmol L^{-1}As(III) was added to each Na_2SO_4 solution and then, monitored by CV. The results with SWE (6.47 or 10.21 mm^2) showed that the current slightly increased when the Na_2SO_4 concentration decreased. This effect was increasingly significant with increasing electrode area. The lowest concentration electrolyte did not change or only slightly enhanced the ionic conductivity of the solutions because the ions were too far apart to exert appreciable interionic forces. This poor interionic force reduced the interference on the electrode response and contributed to the good linearity for the lowest supporting electrolyte concentration.

In comparison to the sodium salts, acidic solutions resulted in slower electron transfer kinetics and less

Table 1. Calibration curves, I *vs.* $C_{As(III)}$ (in μA and mmol L^{-1}, respectively), obtained by CV at different supporting electrolyte concentrations (pH 7.0-9.0). J is the current density at 1 mmol L^{-1} As(III)

Electrolyte	E_{ox} / V	SWE (6.47 mm^2) or SDE^a (7.00 mm^2)	SWE (10.21 mm^2)
0.100 mol L^{-1} Na_2SO_4	0.35	$I = 23.09\ C_{As(III)}$, $r^2 = 0.988$ 0.098-1.8 mmol L^{-1} As(III) J = 3.57 μA mm^{-2}	$I = 37.36C_{As(III)}$, $r^2 = 0.996$ 0.061-1.22 mmol L^{-1} As(III) J = 3.66 μA mm^{-2}
0.100 mol L^{-1} Na_2SO_4	0.35	$I^a = 32.20\ C_{As(III)}$, $r^2 = 0.99$ 0.192-1.43 mmol L^{-1} As(III) J = 4.60 μA mm^{-2}	–
0.010 mol L^{-1} Na_2SO_4	0.3	$I = 34.7\ C_{As(III)}$, $r^2 = 0.990$ 0.198-2.6 mmol L^{-1} As(III) J = 5.36 μA mm^{-2}	$I = 70.74C_{As(III)}$, $r^2 = 0.98$ 0.198-2.6 mmol L^{-1} As(III) J = 6.93 μA mm^{-2}
0.005 mol L^{-1} Na_2SO_4	0.28	$I = 36.43\ C_{As(III)}$, $r^2 = 0.99$ 0.198-2.6 mmol L^{-1} As(III) J = 5.63 μA mm^{-2}	$I = 76.28\ C_{As(III)}$, $r^2 = 0.992$ 0.198-2 mmol L^{-1} As(III) J = 7.47 μA mm^{-2}
0.002 mol L^{-1} Na_2SO_4	0.27	$I = 37.25\ C_{As(III)}$, $r^2 = 0.99$ 0.198-1.8 mmol L^{-1} As(III) J = 5.76 μA mm^{-2}	–
0.001 mol L^{-1} Na_2SO_4	0.27	$I = 31.69\ C_{As(III)}$, $r^2 = 0.989$ 0.198-1.8 mmol L^{-1} As(III) J = 4.89 μA mm^{-2}	–
0.100 mol L^{-1} H_2SO_4	0.24	$I = 7.526\ C_{As(III)}$, $r^2 = 0.991$ 0.041-1 mmol L^{-1} As(III) J = 1.16 μA mm^{-2}	$I = 11.15\ C_{As(III)}$, $r^2 = 0.96$ 0.041-1.5 mmol L^{-1} As(III) J = 1.09 μA mm^{-2}
0.100 mol L^{-1} $NaNO_3$	0.35	$I = 30.7\ C_{As(III)}$, $r^2 = 0.998$ 0.098-1 mmol L^{-1} As(III) J = 4.74 μA mm^{-2}	$I = 83.41\ C_{As(III)}$, $r^2 = 0.98$ 0.012-0.55 mmol L^{-1} As(III) J = 8.17 μA mm^{-2}
0.100 mol L^{-1} $NaNO_3$	0.35	$I^a = 29.68\ C_{As(III)}$, $r^2 = 0.982$ 0.049-0.8 mmol L^{-1} As(III) J = 4.24 μA mm^{-2}	–
0.002 mol L^{-1} $NaNO_3$	0.35	$I = 36.6\ C_{As(III)}$, $r^2 = 0.991$ 0.198-2.46 mmol L^{-1} As(III) J = 5.66 μA mm^{-2}	–
0.100 mol L^{-1} HNO_3	0.24	$I = 7.4\ C_{As(III)}$, $r^2 = 0.98$ 0.098-0.83 mmol L^{-1} As(III) J = 1.14 μA mm^{-2}	$I = 11.29\ C_{As(III)}$, $r^2 = 0.993$ 0.049-1 mmol L^{-1} As(III) J = 1.106 μA mm^{-2}

current peak sensitivity. For example, the sensitivity for As(III) with SWE or SDE in 0.1 mol L^{-1} H_2SO_4 was three times lower than that found for the corresponding sodium salts (oxidation potential of 0.29 V for pH 2.2-7.0). CVs for SWE (10.21 mm^2) at 50 mV s^{-1} are presented. The calibration curve was I (µA) = 11.15 $C_{As(III)}$ (mmol L^{-1}) (0.45-1.50 mmol L^{-1} As(III)) with a correlation coefficient of 0.960. The analysis with SWE (6.47 mm^2) indicated I (µA) = 7.526 $C_{As(III)}$ (mmol L^{-1}) and r^2 = 0.991. The obtained results with 0.1 mol L^{-1} HNO_3 were close to those ones with 0.1 mol L^{-1} H_2SO_4 (Table 1).

The above section summarizes the calibration curves, which were calculated from CV for the respective Na_2SO_4, H_2SO_4, $NaNO_3$ and HNO_3 solutions with both electrode types. Differences in the current densities were found between 0.100 and 0.002 mol L^{-1} $NaNO_3$ supporting electrolyte.

Preconcentration and limit of detection (LOD)

The anodic stripping voltammetry was applied to determine the lowest detectable As(III) concentration with the 6.47 mm^2 silver wire electrode in 0.003 mol L^{-1} Na_2SO_4 solution and 0.01 mmol L^{-1} As(III) at pH 9.0. A study of time and voltage deposition was performed to optimize the conditions. Negative reduction voltages of –0.4, –0.6 and up to –0.8 V with longer times of 300, 900, 1000, 1500 and 2000 s were assayed (see Table 2). The –0.6 V and 2000 s were the selected parameters for the best LOD. The limit of detection was determined by measuring eleven samples at the lowest concentration (3.3 nmol L^{-1} (250 ng L^{-1})) and calculating $3\sigma/m$ (σ = standard deviation of eleven determinations (in nmol L^{-1}) and m = slope of the calibration curve).[9] The selected value of –0.6 V was the same as the selected one by Compton *et al.*[11] (data not shown). The found limit of detection was less than the reported LOD by Compton *et al.*[11] by one order of magnitude because of the large accumulation time for arsenic and low scan rate, which decreased the background noise in the determination by ASV (see Figure 4). The mechanism in accordance with ASV indicated that As(III) was reduced on the silver electrode according to:

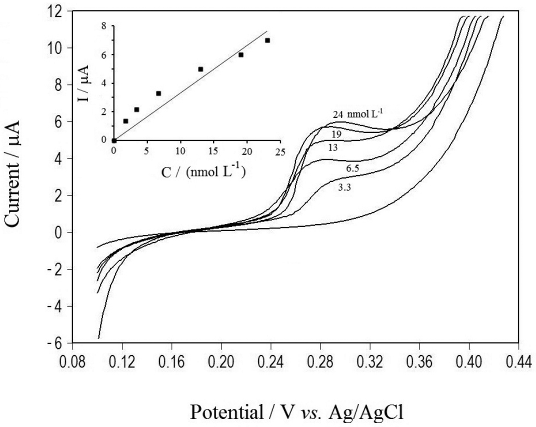

Figure 4. Anodic stripping voltammetry (E_{acc} = –0.6 V, t_{acc} = 2000 s) of SWE (6.47 mm^2) in 0.0033 mol L^{-1} Na_2SO_4 and scan rate of 10 mV s^{-1}.

$$As(III) + 3e^- \rightarrow As(0)$$

Figure 4 presents the calibration curve in the range of 3.33-33.2 nmol L^{-1} and shows a slope (sensitivity) of 0.4 µA nmol L^{-1}. Eleven determinations at 1.4 µg L^{-1} (18.68 nmol L^{-1}) for the reproducibility gave a standard deviation of 0.22 µA, corresponding to 3% RSD (relative standard deviation). LOD of 90 ng L^{-1} (1.2 nmol L^{-1}) was calculated as three times the standard deviation over the calibration curve slope. This value was lower than those ones that were reported using a Ag electrode (0.63 µmol L^{-1}) in HNO_3 solution at –0.6 V deposition potential at times of 120 s.[11] This LOD was much lower than those ones obtained with a Pt electrode (7.5 mg L^{-1}) (0.1 mmol L^{-1}),[3] a hanging mercury drop electrode (0.6 µg L^{-1}) (8 nmol L^{-1}),[5] a Pt electrode in flow injection analysis (5 µg L^{-1}) (66.7 nmol L^{-1})[6] and an Au electrode (0.15 µg L^{-1}) (2 nmol L^{-1}). This LOD was higher than that one found for the glassy carbon electrode modified with gold nanoparticles (15 ng L^{-1}) (0.2 nmol L^{-1}),[4]

Table 2. Anodic stripping voltammetry (ASV) in 0.0033 mol L^{-1} Na_2SO_4 with SWE (6.47 mm^2)

Volume As(III) / µL	$C_{As(III)}$ / (mmol L^{-1})	Deposition potential / V	Deposition time / s	Peak current / µA	Anodic potential / V
5	1.00	–0.4	900	1.500	0.300
1	1.00	–0.4	1500	3.500	0.280
1	1.00	–0.4	2000	2.648	0.310
1	1.00	–0.6	2000	6.330	0.286
10	0.01	–0.6	2000	4.990	0.272
10	0.01	–0.8	2000	3.440	0.325
10	0.01	–0.6	2000	7.219	0.272
5	0.01	–0.6	2000	3.523	0.270

however, most likely due to the gold nanoparticles behaving like an electrode nanoarray. Considering the low limit that was found, the regression equation could be used to determine unknown samples at concentrations below the required limit by WHO for drinking or tap water. Simple linear voltammetry with SWE (6.47 mm^2) at 10 mV s^{-1} determined a linear range of 1.33-13.33 µmol L^{-1} for As(III) when using 0.005 mol L^{-1} Na_2SO_4 as supporting electrolyte (see Figure 5).

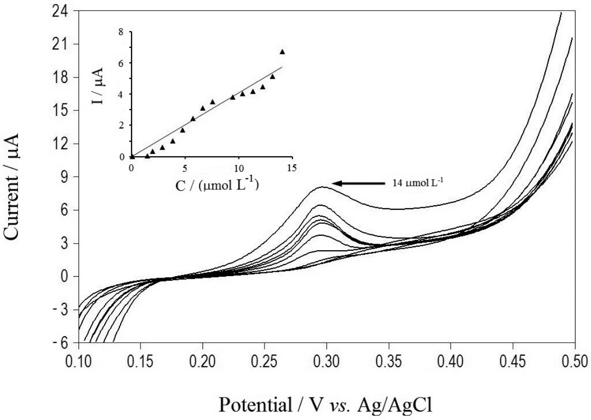

Figure 5. Linear voltammetry with SWE (6.47 mm^2) in 0.005 mol L^{-1} Na_2SO_4.

Effect of enhancement for solution alkalinity

Because the supporting electrolytes in the above cases were unbuffered inorganic salts, the pH of the solutions varied between 7.0 and 9.0 when the added analyte was As(III) at pH 9.0. The arsenite detection was also performed in strongly alkaline conditions using the standard As(III) solutions at pH 13.0 to investigate the pH effect. Figure 6 shows CV on SWE (6.47 mm^2) in 0.1 mol L^{-1} Na_2SO_4 solution at a scan rate of 20 mV s^{-1} and Figure 7 shows CV at 50 mV s^{-1}. When comparing Figure 7 with CV of SWE (6.47 mm^2) and As(III) at pH 9.0 in a 0.1 mol L^{-1} Na_2SO_4 at a scan rate of 50 mV s^{-1}, the As(III) oxidation potential decreased to 0.29 V with a better resolution of maximum definition and a higher current density. The process progressively becomes more irreversible, and at a high voltage scan rate, the slope of the calibration curve (inset Figure 7) was greater than the reported one in Table 1 at lower pH. This phenomenon is the basis of As(III) tritations[18] because E°' for As(V)/As(III) varies with E° – 0.059 × pH. (E°' = secondary potential).

The decrease in the scan rate to 20 mV s^{-1} affected the resolution, and two oxidation waves were found for the most concentrated arsenic solutions. When the solution was at pH 11.0, a shoulder appeared at 0.36-0.39 V. The process occurring on the silver electrodes in alkaline solutions was previously reported,[17,18] and the simplest mechanism that was estimated for a silver electrode in this media would involve a single hydroxyl. Furthermore, the silver electrodes in 1 mol L^{-1} NaOH showed an anodic current peak near 360 mV, which could be ascribed to the electroformation of a multilayer of Ag_2O.[19] This process has been previously reported to occur via nucleation and growth according to:

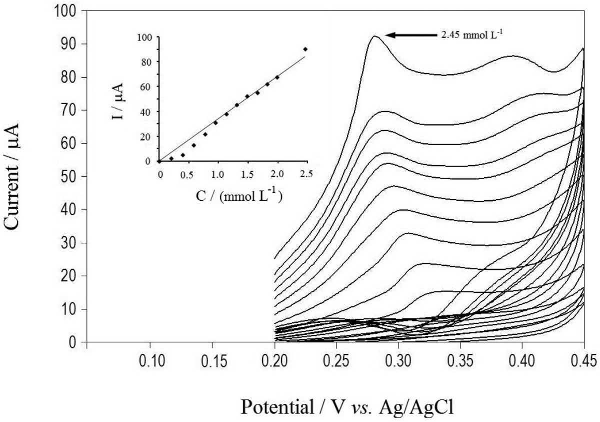

Figure 6. Cyclic voltammograms of SWE (6.47 mm^2) in 0.1 mol L^{-1} Na_2SO_4 with As(III) at pH 13.0 and scan rate of 20 mV s^{-1}.

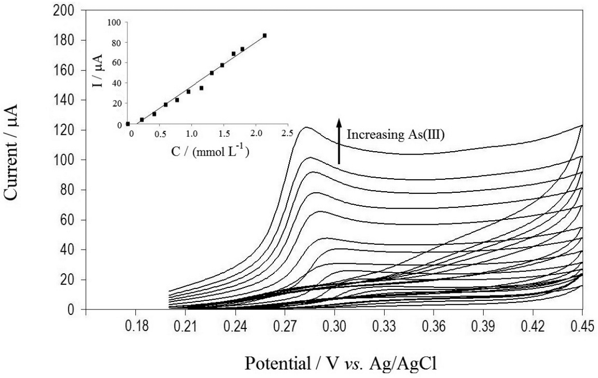

Figure 7. Cyclic voltammograms of SWE (6.47 mm^2) in 0.1 mol L^{-1} Na_2SO_4 with As(III) at pH 13.0 and scan rate of 50 mV s^{-1}.

$$2Ag + 2OH^- \rightarrow Ag_2O + H_2O + 2e^-$$

The high OH^- concentration would be a factor in determining the peak resolution of the voltamperogramm for arsenite detection, considering the reports on the effect of alkaline concentration on silver electrodes.[19] The authors revealed that the rates of both hydrogen and oxygen evolutions were enhanced with increased NaOH concentration. Additionally, the involved charge in the electroformation of the oxide layer increased with increasing alkali concentration. Furthermore, the anodic and cathodic peak current densities increased with increasing NaOH concentration and shifted to slightly more negative values. The effects that were caused by the increasing NaOH concentration could be interpreted on the basis of the enhanced solubility of silver oxides at a more alkaline pH.[20] Moreover, the Ag_2O layer that was generated on the silver electrode surface by the anodic sweep could serve as an intermediate in the arsenic anodic oxidation:

$$3Ag(I) + As(0) \rightarrow 3Ag(0) + As(III)$$

Synthetic mixtures

The effect of various ions which are usual components of natural water on arsenite detection (as well as the possible interferences in the electrode response) were evaluated by CV. The standard As(III) solution was prepared at pH 9.0. The interferences occurring at the same oxidation potential of As(III) would increase the peak current of the arsenic signal, minimizing its resolution. This phenomenon was attributed to the oxidation wave of arsenic and the occurrence of interference at the surface electrode, making anodic oxidation of arsenic more reversible. In this case, As(III) was detected using supporting electrolyte solutions with Na, Ca and Mg salts in similar compositions to potable water. The effect of HCO_3^- was analyzed alone and together with other anions in water, including SO_4^{2-} and Cl^-. SWE (6.47 mm^2) was assayed in 0.002 mol L^{-1} NaCl, corresponding to 50 mg L^{-1} Na^+ (2 mmol L^{-1}) and being the typical Na^+ content in tap water. The CV curves of As(III) at pH 10.0 and scan rate of 20 mV s^{-1} contained a wide maximum at 0.36 V, with peak current increasing with As(III) content. A simple CV did not show the double peak at low salt concentration used. At this potential, the calibration curve had a r^2 of 0.996 and a slope of 31.46 µA $mmol^{-1}$ L, very similar to the reported results for 0.1 mol L^{-1} $NaNO_3$ and Na_2SO_4.

In comparison with chloride anions, low bicarbonate anion concentrations had a more pronounced effect on the As(III) resolution at pH 9.0 with a silver wire electrode (6.47 mm^2). The pH range was 7.0-9.0. Solutions were prepared in milli-Q water with 0.7 and 1.0 mmol L^{-1} of $NaHCO_3$, analyzed at 20 mV s^{-1} and presented double voltage peaks (0.33 and 0.4 V) for the highest As(III) concentration (1.13 mmol L^{-1}). It was likely that the HCO_3^-/CO_3^{2-} equilibrium had an effect. The electrochemical behavior of polycrystalline silver electrodes in a highly concentrated Na_2CO_3 solution (0.5-1.5 mol L^{-1}) was previously reported.[21] It was found that the most probable electrooxidation reactions for Ag in aqueous Na_2CO_3 solution could be ascribed to the successive establishment of Ag/Ag_2O (344 mV) and Ag/Ag_2CO_3 (477 mV) systems on the electrode surface. In our case, the peak potentials slightly shifted and the resolution of the current peak maximum decreased with increasing carbonate and arsenic concentrations. This behavior might be explained in terms of interferent effects between the anodic oxidation with the increasing solubility of Ag_2O and Ag_2CO_3 at basic pH.

In our work, it was observed the effect of hard water on the As(III) detection with SWE by adding basic salts of Ca and Mg. Aqueous solutions of Ca^{2+} and Mg^{2+} salts were used as supporting electrolytes in compositions which were similar and in excess of tap water. For example, the SWE (6.47 mm^2) response in a $CaCl_2$ solution of 7.92 mg L^{-1} Ca^{2+} (0.2 mmol L^{-1}) showed an irreversible enhancement of the current in the pH range of 7.0-11.0 for As(III) with broadened peaks, but was linear in the range of 0.093-1.33 mmol L^{-1} As(III). Similar results were obtained over magnesium sulfate at 1.2 mg L^{-1} Mg^{2+} (0.05 mmol L^{-1}). A solution with 6.9 mg L^{-1} Ca^{2+} (0.17 mmol L^{-1}) and 2.27 mg L^{-1} Mg^{2+} (0.10 mmol L^{-1}) showed $I = 39.09\ C_{AsIII}$ (µA $mmol^{-1}$ L) and a linear factor of 0.952. Alkaline divalent cation salts likely produced greater fouling of the surface of the electrode, decreasing the measurement resolution.

Tap or drinking water

The SWE electrodes were used for analytical assays of tap water. A mixture of supporting electrolyte (0.2 mol L^{-1} Na_2SO_4) and tap water was prepared to contain 0.1 mol L^{-1} Na_2SO_4. The cyclic voltammograms of SWE (6.47 mm^2) in tap water samples at a scan rate of 20 mV s^{-1} were performed at different As(III) concentrations and monitored between 200 mg L^{-1} (2.67 mmol L^{-1}) and 25 µg L^{-1} (0.3 µmol L^{-1}) As(III). The standard As(III) solution in both cases was adjusted to pH 13.0.

The stripping mode with a 600 s of deposition time and potential of –0.6 V was applied for the lowest As(III) concentration. Figure 8 shows the linear sweep voltammetry and the calibration curve between

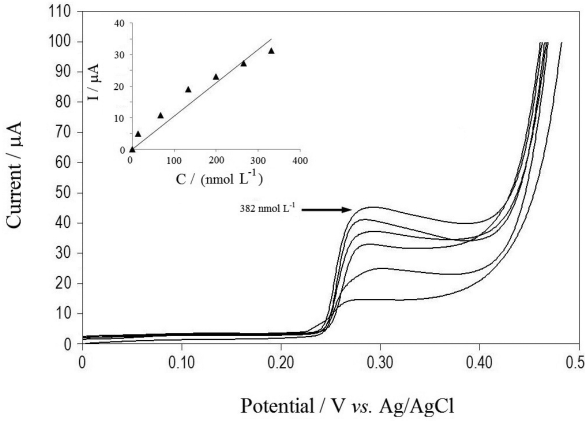

Figure 8. Linear sweep voltammograms of SWE (6.47 mm^2) in a drinking water sample with 0.1 mol L^{-1} Na_2SO_4 between 13 and 380 nmol L^{-1} As(III) at pH 13.0 and scan rate of 20 mV s^{-1}.

1-28.5 µg L^{-1} (13.34-380 nmol L^{-1}) As(III), which included values deemed acceptable by the WHO for drinking water. The slope was 1.2 µA $µg^{-1}$ L (0.1 µA $nmol^{-1}$ L) with a correlation coefficient of 0.960. Figure 9 shows CV in which the highest As(III) concentration was added (200 mg L^{-1} (2.67 mmol L^{-1})). The oxidation potential in these experiments was 0.3 V. The calibration curve had a slope of $I/C_{As(III)}$ = 0.51 µA mg^{-1} L (38.37 µA $mmol^{-1}$ L). This was coincident with measurements that were made in 0.1 mol L^{-1} Na_2SO_4 under similar conditions.

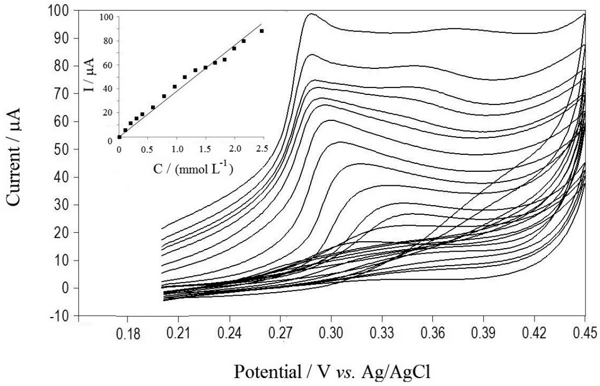

Figure 9. Cyclic voltammograms of SWE (6.47 mm^2) in a drinking water sample up to 2.67 mmol L^{-1} As(III) and scan rate of 20 mV s^{-1}.

The importance of this experiment is its possible use for monitoring water because As(III) could be detected at the pH of natural and seawater samples. Additionally, the results indicated that the silver electrode could be used to detect both the highest and the lowest assayed As(III) concentrations as a mixture with As(V).

Conclusions

To determine As(III) with SWE or SDE, inorganic solutions, such as 0.1 mol L^{-1} Na_2SO_4, $NaNO_3$ and H_2SO_4, may be used as the supporting electrolyte. The oxidation potential in this case was low, between 0.25 and 0.3 V. The variation in the supporting electrolyte concentration did not significantly influence the detection resolution or the sensitivity. The wide linear range for different class of electrodes suggested a good possibility that the regression equation in each case could be used to determine unknown concentrations. The lowest LOD (90 ng L^{-1} (1.2 nmol L^{-1})) indicated that SWEs could be used to detect trace quantities of arsenic in both basic and neutral media. Arsenic in tap water with 0.1 mol L^{-1} Na_2SO_4 could be monitored across a wide concentration range (from 1.8 µg L^{-1} (24 nmol L^{-1}) to 200 mg L^{-1} (2.67 mmol L^{-1})).

Many ions (such as Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-}, HCO_3^- and Cl^-) are components of the natural water and could interfere with the electrode response even at the lowest analyzed concentrations. As such, a doubling effect of the voltage peak with bicarbonate was found.

The importance of these experiments lies in the demonstrated detection of As(III) at the typical pH of both natural and seawater samples, being convenient for monitoring purposes. The developed method showed linearity intervals higher than those ones that were previously reported with platinum and gold electrodes. Furthermore, it increased the sensitivity when applied to strongly alkaline conditions, and complex sample preparations were not necessary. Additionally, the results suggested that the silver electrode could be used to detect both high and low As(III) concentrations in a mixture with As(V).

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