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Title: Determination of Sb(III) using an ex-situ bismuth screen-printed carbon electrode by adsorptive stripping voltammetry

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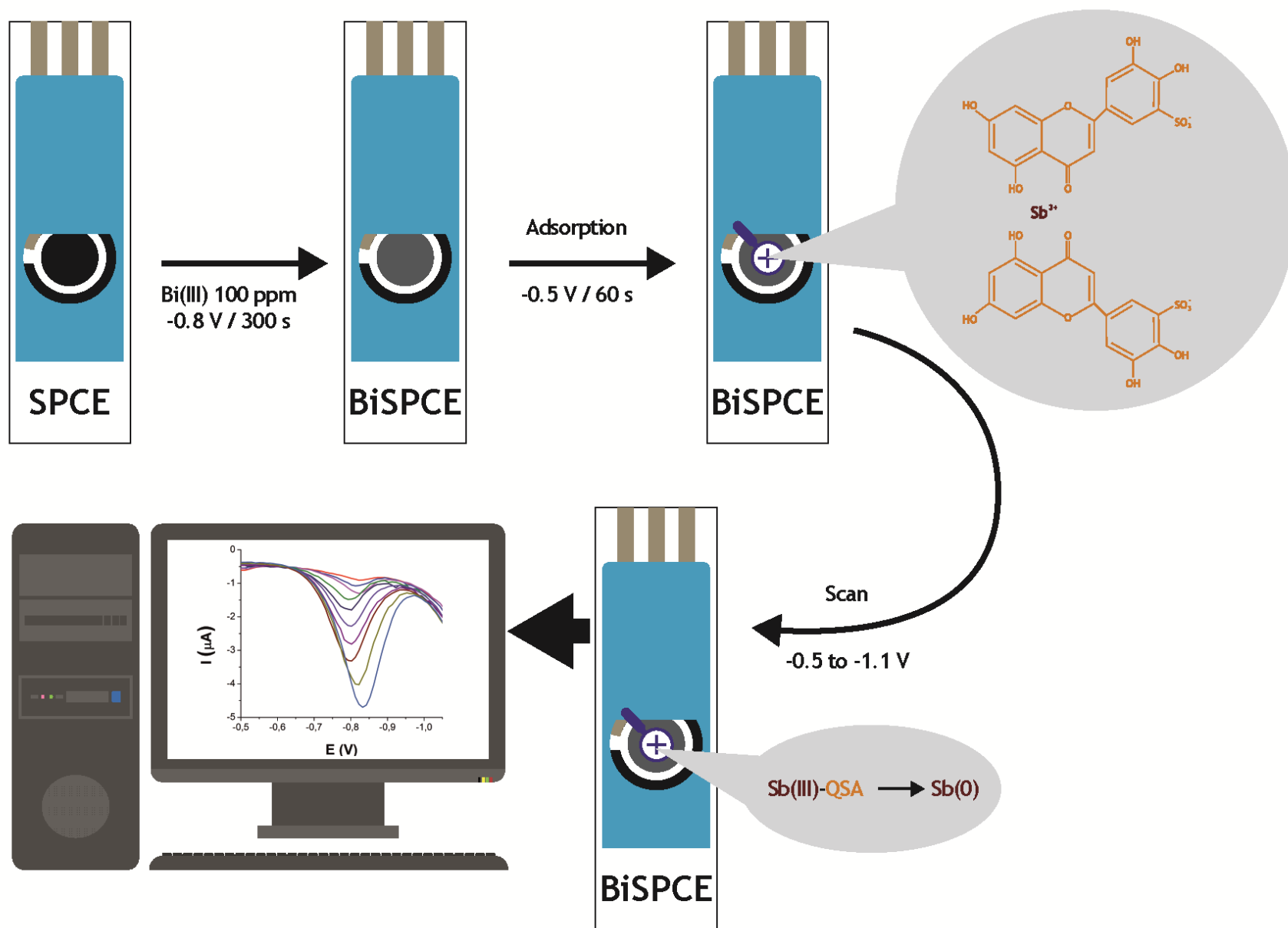
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**Abstract:** The determination of Sb(III) on an ex-situ bismuth screen-printed carbon electrode (ex-situ BiSPCE) by means of adsorptive stripping voltammetry (AdSV) using quercetin-5-sulfonic acid as chelating agent was optimized. The effect of different experimental parameters such pH, ligand concentration (CQSA), accumulation potential (Eacc) and accumulation time (tacc) were studied to obtain a wide linear range, the highest sensitivity and the lowest detection limit. Ex-situ BiSPCE was analytically compared with a sputtered bismuth screen-printed electrode (BispSPE) under optimal conditions. The obtained analytical parameters suggest that ex-situ BiSPCE behaves much better than BispSPE and the first was selected for this study. Optimal parameters were pH= 4.6; CQSA= 10.0 to 20.0 x 10<sup>-6</sup> mol L<sup>-1</sup>; Eacc= -0.5 V and tacc= 60 s. Peak current is proportional to Sb(III) concentration up to 100.0 µg L<sup>-1</sup> (tacc 60 s) and 45.0 µg L<sup>-1</sup> (tacc 120 s) range, with detection limits of 1.2 µg L<sup>-1</sup> (tacc 60 s) and 0.8 µg L<sup>-1</sup> (tacc 120 s). The relative standard deviation for a Sb(III) solution (20.0 µg L<sup>-1</sup>) was 3.9 % for ten successive assays. Thus, the effect of various interfering metal ions was studied and the methodology was validated using a spiked groundwater reference material with very satisfactory results.

# Graphical abstract



**Determination of Sb(III) using an *ex-situ* bismuth screen-printed carbon electrode by adsorptive stripping voltammetry**

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**Abstract**

The determination of Sb(III) on an *ex-situ* bismuth screen-printed carbon electrode (*ex-situ* BiSPCE) by means of adsorptive stripping voltammetry (AdSV) using quercetin-5-sulfonic acid as chelating agent was optimized. The effect of different experimental parameters such pH, ligand concentration ( $C_{QSA}$ ), accumulation potential ( $E_{acc}$ ) and accumulation time ( $t_{acc}$ ) were studied to obtain a wide linear range, the highest sensitivity and the lowest detection limit. *Ex-situ* BiSPCE was analytically compared with a sputtered bismuth screen-printed electrode (Bi<sub>sp</sub>SPE) under optimal conditions. The obtained analytical parameters suggest that *ex-situ* BiSPCE behaves much better than Bi<sub>sp</sub>SPE and the first was selected for this study. Optimal parameters were pH= 4.6;  $C_{QSA}$ = 10.0 to 20.0  $\times 10^{-6}$  mol L<sup>-1</sup>;  $E_{acc}$ = -0.5 V and  $t_{acc}$ = 60 s. Peak current is proportional to Sb(III) concentration up to 100.0  $\mu$ g L<sup>-1</sup> ( $t_{acc}$  60 s) and 45.0  $\mu$ g L<sup>-1</sup> ( $t_{acc}$  120 s) range, with

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4 detection limits of  $1.2 \mu\text{g L}^{-1}$  ( $t_{\text{acc}}$  60 s) and  $0.8 \mu\text{g L}^{-1}$  ( $t_{\text{acc}}$  120 s). The relative standard  
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6 deviation for a Sb(III) solution ( $20.0 \mu\text{g L}^{-1}$ ) was 3.9 % for ten successive assays. Thus, the  
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8 effect of various interfering metal ions was studied and the methodology was validated  
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10 using a spiked groundwater reference material with very satisfactory results.  
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15 **Keywords:** Determination of antimony, Quercetin-5'-sulfonic acid, Screen-printed  
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17 electrode, Bismuth film electrode, Adsorptive stripping voltammetry.  
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## 1 Introduction

Antimony and its compounds have been used in medicine, cosmetics and industry. However, the general population is rarely exposed to antimony. In case of occupational exposure, inhalation and skin contact are the main routes. Antimony trioxide is the most commercially significant form of antimony compounds worldwide. It is primarily used as a flame retardant in rubber, plastics, pigments, adhesives, textiles and paper [1]. Antimony compounds are certainly less toxic than arsenic compounds, but more toxic than bismuth compounds. The toxic effects of antimony compounds resemble those of the corresponding arsenic compounds with the trivalent state being, in general, more toxic than the pentavalent one. Exposure to antimony can produce cellular and organic injury, particularly in the heart, lung, liver and kidney [2].

The application of electroanalytical techniques has been a powerful tool for the determination of metals ions in water samples and a wide variety of organic pollutants. Anodic stripping voltammetry (ASV) and adsorptive stripping voltammetry (AdSV) allow the quantification of metal ions in the order of  $\text{ng L}^{-1}$  and  $\mu\text{g L}^{-1}$ . The sensitivity of stripping methods is achieved by a preconcentration step, in which the metal ions are deposited (reduced) in ASV or adsorbed as a complex in AdSV onto the working electrode surface. Electroanalytical methods for antimony determination were reviewed in [3] and, particularly, stripping voltammetric methods have been summarized in [4]. In short, Sb(III) can be determined by both ASV and AdSV, however total antimony (trivalent and pentavalent) is mainly analyzed by ASV. The free mercury stripping voltammetric methodologies developed for Sb(III) quantification are summarized in Table 1.

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4 Unlike ASV, the presence of a chelating agent is required for metal ions determination by  
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6 AdSV, in which the adsorption of the formed complex is one of the more relevant facts to  
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8 obtain a sensitive analytical signal response. However, the ligand could generate an  
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10 undesired decrease of the methodology sensitivity due to adsorption of the free ligand,  
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12 generating quick electrode saturation. This competitive adsorption between free ligand and  
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14 complex could be shifted to a favorable complex adsorption using complexing agents with  
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16 charged groups. In general, more polar species are less easily adsorbed onto electrode  
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18 surface due to its higher solubility or stronger interaction with polar solvents, specifically  
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20 water [17]. In this sense, ligands with sulfonic acid groups in their structure are a suitable  
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22 alternative. Sulfonic acid groups present a small  $pK_a$  value, which increases the solubility  
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24 of ligands in water decreasing their adsorption on the electrode surface owing to  
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26 deprotonation of acid group. Evidence of the positive effect over sensitivity of ligands with  
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28 sulfonic acid group was previously reported. Using an hanging mercury drop electrode  
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30 (HMDE), a high sensitive methodology was described for Sb(III) determination using  
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32 8-hydroxyquinoline-5-sulfonic acid as complexing agent [18] as well as the analysis of ng  
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34  $L^{-1}$  levels of Sb(III) and V(V) with quercetin-5-sulfonic acid as chelating agent was also  
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36 stated [4, 19].  
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45 HMDE is one of the most used electrodes for electroanalytical determination of metal ions  
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47 due to its excellent characteristics. Despite this, the utilization of Hg-based electrodes has  
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49 been questioned for their potential high toxicity if they are not conveniently used. With the  
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51 aim of replace mercury electrodes by more environmentally-friendly ones but with a  
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53 similar electrochemical behavior, different possibilities have been investigated. One of  
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55 them is the bismuth coated carbon electrode, introduced by Wang in 2000 [20] for the  
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57 voltammetric determination of metal ions. Over the years, Bi-based electrodes have  
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4 become a significant alternative to mercury electrodes for electroanalytical determinations  
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6 with great results [21–23]. In the particular case of the bismuth film electrodes (BiFE), the  
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8 deposition of the film can take place in different supports such as glassy carbon, pencil  
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10 lead, carbon paste, screen-printed carbon ink... Nevertheless, taking advantage of the  
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12 progress of the screen-printed technology accomplished in the last years, bismuth film  
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14 coated on screen-printed carbon electrodes (BiSPCE) tend to be used instead of the more  
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16 classical bismuth approaches [23]. Screen-printed electrodes are recognized for their  
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18 low-cost, the commercial availability, their disposable character, the miniaturized size and  
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20 the possibility to adapt them to portable instrumentation. Moreover, unlike bismuth coated  
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22 carbon electrode, BiSPCE do not require any polishing prior to bismuth deposition. On the  
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24 other hand, the durability of the Bi film on every screen-printed platform for a large set of  
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26 measurements enables the voltammetric determination of different metal ions using the  
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28 same unit immersed in the same solution [24–27]. An alternative method for the fabrication  
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30 of bismuth screen-printed electrodes (BiSPE) is based on the sputtering of the Bi on a  
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32 ceramic or a silicon platform giving rise to a thick Bi film working device, which also  
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34 allows the determination of metal ions at trace level behaving in a similar way to the more  
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36 conventional BiSPE approaches without requiring neither a conductive substrate nor the  
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38 Bi(III) plating solution [26–28].  
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48 In this work, a comparative study for Sb(III) determination by means of AdSV using an  
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50 *ex-situ* bismuth screen-printed carbon electrode (*ex-situ* BiSPCE) and a sputtered  
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52 bismuth screen-printed electrode (Bi<sub>sp</sub>SPE) in presence of quercetin-5-sulfonic acid as  
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54 chelating agent is presented. The present work is the first approach to apply high sensitive  
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56 methodologies previously developed on an HMDE using more environmentally-friendly  
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58 electrodes such as Bi-based electrodes.  
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## 2 Experimental Part

### 2.1 Apparatus

The adsorptive stripping voltammograms were obtained on an Autolab System PGSTAT12 (EcoChemie, The Netherlands) attached to a Metrohm 663 VA Stand (Metrohm, Switzerland) and a computer with GPES version 4.9 data acquisition software (EcoChemie).

For experiments, the working electrode was a bismuth film screen-printed carbon electrode (*ex-situ* BiSPCE) prepared from a carbon disk electrode of 4 mm of diameter (ref. DRP-110, DS SPE) or a sputtered thick film bismuth screen-printed electrode (Bi<sub>sp</sub>SPE) of 4 mm of diameter (ref. Bi10, DS SPE), both screen-printed electrodes provided by DropSens (Spain). A flexible cable (ref. CAC, DropSens) is used to connect screen-printed electrodes to the Autolab System. The reference electrode was Ag/AgCl/KCl (3 mol L<sup>-1</sup>) and the auxiliary electrode was a platinum wire.

A Crison micro pH 2000 pH-meter has been used for pH measurements, and all measurements have been carried out in a glass cell at room temperature (20 °C) under a purified nitrogen atmosphere (Linde N50).

### 2.2 Chemicals and reagents

Sb(III) and Bi(III) 1000 mg L<sup>-1</sup> atomic absorption standard solutions and other metal ions standard solutions were purchased from Merck. Quercetin-5-sulfonic acid (QSA) was synthesized and characterized through the procedure reported in [19]. Certified reference material, groundwater (BCR<sup>®</sup>-610) was purchased from Sigma-Aldrich. All other reagents



used were analytical grade from Merck or Fluka. 1.0 and 10.0 mg L<sup>-1</sup> Sb(III) solutions were prepared by dilution of 1000 mg L<sup>-1</sup> standard solution with HCl 0.25 mol L<sup>-1</sup>. 0.25 mol L<sup>-1</sup> KOH solution was used to neutralize the acid addition when stock Sb(III) solution were pipetted into the voltammetric cell. Ultrapure water (Milli-Q plus 185 system, Millipore) was used in all experiments.

### 2.3 Preparation of *ex-situ* BiSPCE

The SPCE, the auxiliary and the reference electrodes were connected to the stand and immersed into 20.0 mL of a 0.2 mol L<sup>-1</sup> acetate buffer solution (pH 4.5) containing 100 mg L<sup>-1</sup> of Bi(III). The solution was purged for 5 min and then was applied for 5 min a deposition potential of -0.8 V with constant stirring (1500 rpm). After bismuth film formation, the three electrodes were rinsed with deionized water and dried with a piece of tissue. Then the Bi(III) solution was replaced by the measurement solution and, previous to ligand or Sb(III) addition, a potential of -1.1 V was applied during 300 s and three voltammograms were recorded as an activation procedure.

### 2.4 Voltammetric measurement procedure

100 µL of KCl 3.0 mol L<sup>-1</sup>, 500 µL of Britton Robinson buffer 0.4 mol L<sup>-1</sup> (study of pH effect) or 1 mL of 0.2 mol L<sup>-1</sup> acetate buffer, 10 to 40 µL of QSA 10<sup>-2</sup> mol L<sup>-1</sup>, aliquots of Sb(III) 10.0 mg L<sup>-1</sup> and ultrapure water up to a final volume of 20.0 mL were added to the electrochemical cell. The solution was stirred for 30 s, then a cleaning potential of -1.1 V was applied for 3 s to reduce any Sb(III)-QSA complex adsorbed during the time between measurements obtaining a clean electrode surface for a new adsorption process. An E<sub>acc</sub> of

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4 -0.5 V was applied for 60 s with a constant stirring of 1500 rpm using a rotating PTFE rod.  
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6 After a rest period ( $t_r$ ) of 10 s, voltammograms were recorded, while the potential was  
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8 scanned from -0.5 to -1.1 V using square wave modulation with, unless otherwise  
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10 indicated, a frequency of 8 Hz, 20 mV step amplitude and 10 mV pulse amplitude.  
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13 Validation of the methodology was made using 5.0 mL of certificate groundwater, 100  $\mu$ L  
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15 of KCl 3.0 mol L<sup>-1</sup>, 1.0 mL of 0.2 mol L<sup>-1</sup> acetate buffer, 20  $\mu$ L of QSA 10<sup>-2</sup> mol L<sup>-1</sup>, 60  
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17  $\mu$ L of EDTA 10<sup>-2</sup> mol L<sup>-1</sup>, 190  $\mu$ L of KOH 1.0 mol L<sup>-1</sup> and ultrapure water up to a final  
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19 volume of 20.0 mL. In order to eliminate matrix effects the standard addition method was  
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### 28 **3 Results and Discussion**

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31 Looking for a linear proportionality between metal concentration and analytical response,  
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33 the use of peak height or peak area as analytical response was evaluated during the  
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35 experimental research of this work. The second approach showed a wider range of linearity  
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37 respect to Sb(III) concentration than the peak height. Taking into account that there are also  
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39 in the literature some reports [25-26, 28-29] in which peak area was used as analytical  
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41 response, this approach was used in this study.  
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45 The optimization of the bismuth film formation is one of the most important requirements  
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47 to obtain a sensitive and reproducible methodology for metal ions determination by  
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49 stripping voltammetry. The deposition of a bismuth film via *ex-situ* onto the surface of a  
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51 SPCE was studied and optimized [24]. The procedure detailed in Section 2.3 was used for  
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53 *ex-situ* BiSPCE formation. The reproducibility from 8 different *ex-situ* BiSPCE calculated  
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55 as the relative standard deviation (RSD) of 3 consecutive determinations in independent  
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57 solutions containing 20.0  $\mu$ g L<sup>-1</sup> of Sb(III) was 8.8 %.  
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The effect of experimental parameters (pH,  $C_{QSA}$ ,  $E_{acc}$ ,  $t_{acc}$ ) was studied to obtain the highest signal intensity. However, signal resolution, symmetry and shape must be considered to allow an adequate peak measurement.

### 3.1 Effect of pH

The effect of pH over the peak area of Sb(III)–QSA complex reduction signal was studied in the range of pH 3.0 to 8.5 using 10.0 mmol L<sup>-1</sup> Britton Robinson buffer (Figure 1), which allow the modification of pH conditions without a complete change of supporting electrolyte. Maximal peak area was obtained at pH 4.6. This pH value was chosen as optimal and the peak reduction signal of Sb(III)–QSA complex was observed at -0.80 V. Britton Robison buffer was substituted by 10.0 mmol L<sup>-1</sup> acetate buffer (pH 4.6) to simplify the composition of supporting electrolyte. It has been reported that the dissociation constants of NaQSA in aqueous solution at 20 °C and I = 0.1 are: pK<sub>a1</sub> = 7.43; pK<sub>a2</sub> = 8.16; pK<sub>a3</sub> = 9.24 and pK<sub>a4</sub> = 10.84 (potentiometric method) [30]. At pH 4.6 the net charge of the complex (M:L stoichiometry of 1:2) is -1.

### 3.2 Effect of ligand concentration

The ligand concentration is a very important parameter in AdSV. If the free ligand is adsorbed onto the electrode surface, this generates a competitive adsorption between complex and free ligand, decreasing the electrode surface area available for complex adsorption. Thus, an optimal ligand concentration is required to guarantee the metal ion complexation.

Figure 2 shows the effect of QSA concentration over peak area of the reduction of Sb(III)–QSA complex ( $C_{Sb(III)}$ : 20.0 µg L<sup>-1</sup>). Peak area increases significantly up to QSA

concentration of  $10.0 \mu\text{mol L}^{-1}$ , whereas for QSA concentration higher than  $10.0 \mu\text{mol L}^{-1}$  a slight diminution of peak area was progressively observed.  $10.0 \mu\text{mol L}^{-1}$  of QSA was chosen for further experiments (ratio Sb(III):QSA about 1:63). However, the effect of ligand concentration over sensitivity and linear range was evaluated to define the optimal concentration of QSA (Section 3.4).

### 3.3 Effect of accumulation potential and accumulation time

The effect of accumulation potential over peak area of Sb(III)–QSA complex was evaluated in the range from  $-0.4$  to  $-1.0$  V (Figure 3). More positive potentials were not applied to prevent the oxidation of the bismuth film [24]. The signal area decreases sharply as  $E_{\text{acc}}$  was shifted from  $-0.4$  V to more negatives potentials. Nevertheless, the RSD for 10 measurements of a  $20.0 \mu\text{g L}^{-1}$  Sb(III) solution applying an  $E_{\text{acc}}$  of  $-0.4$  V during the preconcentration step was 32%, whereas a better repeatability was achieved when an  $E_{\text{acc}}$  of  $-0.5$  V was applied (RSD = 4.9%) under the same conditions. Therefore, an  $E_{\text{acc}}$  of  $-0.5$  V was selected for further measurements.

Figure 4 shows the effect of accumulation time on the peak area of the reduction of Sb(III)–QSA complex. Peak area linearly increases with  $t_{\text{acc}}$  until 220 s, where the area stabilizes. A  $t_{\text{acc}}$  of 60 s was chosen as optimal looking for a compromise between the peak area and the time of the analysis.

### 3.4 Repeatability, sensitivity, linear range, detection limit and quantification limit

The analytical response of two types of BiSPEs was compared (*ex-situ* BiSPCE and Bi<sub>sp</sub>SPE) under optimal experimental conditions previously determined using an *ex-situ*

BiSPCE. However, in the case of Bi<sub>sp</sub>SPE, the application of an  $t_{acc}$  of 120 s was required to obtain an enough intense signal for Sb(III)–QSA complex reduction. Therefore, both SPEs were analytically compared applying the same  $E_{acc}$  (–0.5 V) during 120 s.

A solution of 20.0  $\mu\text{g L}^{-1}$  of Sb(III) was measured 10 times using *ex-situ* BiSPCE and Bi<sub>sp</sub>SPE achieving RSDs of 3.9 and 4.5 %, respectively. A stable peak area response was generated in both electrodes.

Calibration plots of Sb(III)–ions by AdSV on both *ex-situ* BiSPCE and Bi<sub>sp</sub>SPE were constructed using a QSA concentration of 10.0  $\mu\text{mol L}^{-1}$  and following the above–mentioned conditions (Figure 5A and 5B, respectively). Table 2 summarizes the analytical parameters obtained using an *ex-situ* BiSPCE and a Bi<sub>sp</sub>SPE. The sensitivity considered from the slopes of calibration plots was 7.0 and 9.0 a.u.  $\mu\text{g}^{-1} \text{ L}$  for *ex-situ* BiSPCE and Bi<sub>sp</sub>SPE, respectively. The linearity was maintained up to 45.0 and 30.0  $\mu\text{g L}^{-1}$ , and detection limits (LOD) calculated using Miller recommendation [31] were 0.8 and 2.2  $\mu\text{g L}^{-1}$  for *ex-situ* BiSPCE and Bi<sub>sp</sub>SPE, respectively. At the view of these results, it could be concluded that sensitivity of the methodology with a Bi<sub>sp</sub>SPE was higher than with an *ex-situ* BiSPCE as working electrode. However, this higher sensitivity is not reflected in the obtained LOD due to a worse linear fitting of peak area versus concentration. Moreover, it should be remembered that using Bi<sub>sp</sub>SPE a longer  $t_{acc}$  is required to obtain an adequate signal response leading to a less symmetrical signal in comparison with the *ex-situ* BiSPCE. Additionally, Bi<sub>sp</sub>SPE presents with respect to the *ex-situ* BiSPCE a shorter linear range, higher detection and quantification limits as well as a higher cost commercial availability. Therefore, in agreement with the better analytical performance of *ex-situ* BiSPCE versus Bi<sub>sp</sub>SPE, *ex-situ* BiSPCE was chosen as working electrode.

Then, the effect of QSA concentration was evaluated on *ex-situ* BiSPCE. Table 2 summarizes the analytical parameter obtained on the *ex-situ* BiSPCE at different QSA concentration. For a same applied  $E_{acc}$  and  $t_{acc}$ , an increase of the QSA concentration leads to a decrease of the methodology sensitivity. However, the use of low ligand concentration could be also negative because the presence of others metal ions in real samples could reduce the availability of QSA for Sb(III), which could be solved using an excess of ligand. Hence, a QSA concentration range from 10.0 to 20.0  $\mu\text{mol L}^{-1}$  was chosen as a good compromise between the QSA concentration and the sensitivity of the methodology. Figure 5C shows the adsorptive voltammograms and calibration plot on an *ex-situ* BiSPCE using a QSA concentration of 10.0  $\mu\text{mol L}^{-1}$  and 60 s of  $t_{acc}$ . Similar linear ranges and detection limits were obtained for QSA concentration between 10.0 and 20.0  $\mu\text{mol L}^{-1}$  applying a  $t_{acc}$  of 60s. For  $t_{acc}$  of 120s, the obtained detection limit is slightly lower but the linear range is much restricted than that achieved using a  $t_{acc}$  of 60s. The detection limits obtained for the determination of Sb(III) using QSA as chelating agent with an *ex-situ* BiSPCE are higher compared to those reached with an HMDE (3.6  $\text{ng L}^{-1}$  with 60 s and 1.6  $\text{ng L}^{-1}$  with 180 s) [4]. Similar detection limits were also obtained by ASV with HMDE, 11  $\text{ng L}^{-1}$  with a  $t_{acc}$ = 600 s [32] or 20  $\text{ng L}^{-1}$  with a  $t_{acc}$ = 300 s [33], or by AdSV on HMDE using catechol (24.4  $\text{ng L}^{-1}$ ,  $t_{acc}$ = 180 s) [34] or pyrogallol (12.6  $\text{ng L}^{-1}$ ,  $t_{acc}$ = 407 s) [35] as chelating agent. The main reason for this worsening in the detection limit could be attributed to the applied  $E_{acc}$ , which is different to that applied on HMDE. With HMDE is possible to apply an  $E_{acc}$  of 0 V or even more positive depending on the supporting electrolyte, while with an *ex-situ* BiSPCE these values of  $E_{acc}$  can not be applied due to the oxidation of bismuth of the film [24]. In fact, when in an *ex-situ* BiSPCE the  $E_{acc}$  was shifted 100 mV (from -0.5 to -0.4

V) the peak area increases more than 2 times but with an important loss of repeatability, which made non-viable the application of more positive potentials than  $-0.5$  V. Additionally, the electrode material could also affect the sensibility of the methodology. The complex adsorption seems to be more propitious on a HMDE than onto a BiFE and this fact would be reflected in a lower sensibility when a BiFE is considered. Compared with previous results achieved using other BiFEs, the LOD obtained in this work for Sb(III) is slightly higher than that reported for an *ex-situ* bismuth film plated on a glassy carbon substrate by AdSV in the presence of gallic acid ( $60 \text{ ng L}^{-1}$ ,  $t_{\text{acc}} = 300 \text{ s}$ ) [5] or an *in-situ* bismuth film plated on a graphite substrate by cathodic stripping voltammetry ( $2 \text{ ng L}^{-1}$ ,  $t_{\text{acc}} = 30 \text{ s}$ ) [16]. Nevertheless, it should be pointed out that in the present paper the provided linear range is much wider (until  $100.0 \text{ } \mu\text{g L}^{-1}$  with  $t_{\text{acc}}$  of  $60 \text{ s}$ ) than values obtained in [5] (until  $25 \text{ } \mu\text{g L}^{-1}$  with  $t_{\text{acc}}$  of  $300 \text{ s}$ ) and [16] (until  $0.1 \text{ } \mu\text{g L}^{-1}$  with  $t_{\text{acc}}$  of  $30 \text{ s}$  and until  $12.0 \text{ } \mu\text{g L}^{-1}$  with  $t_{\text{acc}}$  of  $10 \text{ s}$ ). Moreover, determination of the Sb(III) LOD by AdSV on the *ex-situ* BiFE [5] was carried out applying an unpractical  $t_{\text{acc}}$  of  $300 \text{ s}$ . Regarding the determination of Sb(III) with other based-SPEs, SPCE modified with gold [13] or silver [14] nanoparticles, or mercury [36] provide detection limits of  $0.11$ ,  $0.08 \text{ } \mu\text{g L}^{-1}$  and  $1.5 \text{ } \mu\text{g L}^{-1}$  respectively, which are very similar to the LOD obtained in this report with the *ex-situ* BiSPCE but applying longer  $t_{\text{acc}}$  ( $200 \text{ s}$  [13, 14] or even longer  $718 \text{ s}$  [36]).

The World Health Organization and United States Environmental Protection Agency have established up to for antimony in drinking water of  $20$  and  $6 \text{ } \mu\text{g L}^{-1}$  respectively [37, 38]. Therefore the reported calibration data suggests that the *ex-situ* BiSPCE could be fully suitable for the determination of Sb(III) at trace levels in natural samples, since the achieved LOQ value is below the highest level of antimony that is allowed for example in

drinking water, with the addition advantage that the SPCEs which are the basis of the *ex-situ* BiSPCE are commercially available and do not need any polishing prior to the formation of the Bi film. Moreover, the *ex-situ* deposition modality compared to the *in-situ* plating of BiSPCE appears to be a good alternative if the presence of Bi(III)-ions can seriously disturb the metal speciation in the sample.

### 3.5 Interference study

From the study of interferences done using a HMDE [4], the effect of the most relevant interfering metal ions which could interfere on Sb(III)-QSA quantification using an *ex-situ* BiSPCE was evaluated. The criteria applied to decide the maximal concentration of a interfering metal ion was the concentration of interference metal ions which generate a variation on the peak area higher than a  $\pm 10\%$  in the presence of EDTA ( $30.0 \mu\text{mol L}^{-1}$ ). Higher EDTA concentrations generate a progressive decrease of peak area. The results obtained of interferences evaluation are shown in Table 3. It can be concluded that Mo(VI), which forms complex with QSA, is the most important interfering, due to the proximity of the reduction signal of Mo(VI)-QSA complex with the reduction signal of Sb(III)-QSA. In previous reported studies, Cu(II) and Bi(III) using a glassy carbon electrode [8] and Cu(II) and Fe(III) using an *in-situ* BiFE [16] interfere to Sb(III) determination, when these metal ions are present in the same concentration level than Sb(III). Hence, compared with these previous methodologies, in the proposed method for Sb(III)-QSA determination using an *ex-situ* BiSPCE just Mo(VI) interfere while Cu(II), Fe(III) and Bi(III) do not interfere.

### 3.6 Validation



The applicability of an *ex-situ* BiSPCE for the determination of Sb(III) using QSA as chelating agent was validated using a groundwater certified reference material (BCR®-610) spiked with 5.0  $\mu\text{g L}^{-1}$  of Sb(III). It should be pointed out that a spiked sample was necessary because a certified reference material which assures the concentration of antimony as Sb(III) was not available. Sb(III) ion was determined by means of the standard addition method. Then, AdSV measurements following the above mentioned conditions were carried out including the additions of Sb(III). The same *ex-situ* BiSPCE device was used for the AdSV measurements of a complete replicate. Representative adsorptive voltammograms obtained in the analysis of the spiked groundwater using *ex-situ* BiSPCE were shown in Figure 6. A well-defined peak for the Sb(III) ions was obtained. The calibration plot for Sb(III) (Figure 6 inset) shows the good correlations of the representative AdSV measurement achieved on an *ex-situ* BiSPCE. The result of analysis of three replicates of the sample was 4.8  $\mu\text{g L}^{-1}$  (SD: 0.2  $\mu\text{g L}^{-1}$ ) with a recovery of 96%. Thus, it is demonstrated that *ex-situ* BiSPCE can be a convenient and more environmental friendly alternative for mercury electrodes for the determination of Sb(III) at trace levels in samples of environmental interest.

#### 4 Conclusions

The proposed method for the determination of Sb(III) is the first approach using BiSPCE and using a ligand with a sulfonic acid group. Particularly, the analytical behavior of both *ex-situ* BiSPCE and Bi<sub>sp</sub>SPE was compared concluding that *ex-situ* BiSPCE has a much better performance than Bi<sub>sp</sub>SPE for the determination of Sb(III) ions by AdSV using QSA

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4 as chelating agent. Thus, *ex-situ* BiSPCE appears to be an environmentally safe alternative  
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6 to mercury electrodes for the analysis of Sb(III) below  $\mu\text{g L}^{-1}$  level. *Ex-situ* BiSPCE  
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8 produces well-defined peaks in all the concentration range applying a short accumulation  
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10 time (60 s) and providing a linear range much wider than those reported previously for other  
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12 BiFEs. Moreover, *ex-situ* BiSPCE represents a remarkable improvement as compared to  
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14 other BiFE approaches since any polishing prior to the deposition of the film is required. In  
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16 addition, *ex-situ* BiSPCE can be applied for large number measurements without signs of  
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18 loss of sensitivity. *Ex-situ* BiSPCE has also the special features of screen-printed  
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20 electrodes such as the low-cost commercial availability, potential portability, disposable  
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22 character as well as the good reproducibility. Finally, the viability of the proposed method  
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24 using *ex-situ* BiSPCE for the determination of Sb(II) using QSA as chelating agent was  
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26 demonstrated using a spiked groundwater certified reference material with very high  
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28 reproducibility inferred by the SD.  
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## 55 **References**

- 56  
57  
58 [1] M. De Boeck, M. Kirsch-Volders, D. Lison, *Mutat. Res.* 533 (2003) 135-152.  
59  
60 [2] A. Léonard, G.B. Gerber, *Mutat. Res.* 366 (1996) 1-8.  
61  
62  
63  
64  
65

- 1  
2  
3  
4 [3] K.E. Toghill, M. Lu, R.G. Compton, *Int. J. Electrochem. Sci.* 6 (2011) 3057–3076.  
5  
6 [4] C. Rojas, V. Arancibia, M. Gomez, E. Nagles, *Sens. Actuators B* 185 (2013)  
7 560–567.  
8  
9 [5] J. Su, S. Zhong, X. Li, H. Zou, *J. Electrochem. Soc.* 161 (2014) H512–H516.  
10  
11 [6] A.V. Kolliopoulos, J.P. Metters, C.E. Banks, *Anal. Methods* 5 (2013) 3490–3496.  
12  
13 [7] D. Afzali, M. Padash, F. Fathirad, A. Mostafavi, *Ionics* 21 (2015) 565–570.  
14  
15 [8] P. Surmann, H. Channaa, *Electroanalysis* 27 (2015) 1726–1732.  
16  
17 [9] H. Vardar Sezgin, H. Ismet Gökcel, Y. Dilgin, *Sens. Actuators B* 209 (2015)  
18 686–694.  
19  
20 [10] P. Salaun, K.B. Gibbon–Walsh, G.M.S Alves, H.M.V.M. Soares, C.M.G. van den  
21 Berg, *Anal. Chim. Acta* 746 (2012) 53–62.  
22  
23 [11] J.R. Santos, J.L.F.C. Lima, M.B. Quinaz, J.A. Rodriguez, E. Barrado,  
24 *Electroanalysis* 19 (2007) 723–730.  
25  
26 [12] N.S. Gadhari, B.J. Sanghavi, A.K. Srivastava, *Anal. Chim. Acta* 703 (2011) 31–40.  
27  
28 [13] O. Dominguez–Renedo, M.J. Arcos–Martinez, *Anal. Chim. Acta* 589 (2007)  
29 255–260.  
30  
31 [14] O. Dominguez–Renedo, M.J. Arcos–Martinez, *Electrochem. Commun.* 9 (2007)  
32 820–826.  
33  
34 [15] S.B. Khoo, J. Zhu, *Anal. Chim. Acta* 373 (1998) 15–27.  
35  
36 [16] P. Zong, Y. Nagaosa, *Microchim. Acta* 166 (2009) 139–144.  
37  
38 [17] J. Barek, K. Peckova, V. Vyskocil, *Curr. Anal. Chem.* 4 (2008) 242–249.  
39  
40 [18] C. Rojas–Romo, V. Arancibia, *Electroanalysis* 27 (2015) 1262–1267.  
41  
42 [19] C. Rojas–Romo, V. Arancibia, D. Moreno–da Costa, R.A. Tapia, *Sens. Actuators B*  
43 224 (2016) 772–779.  
44  
45  
46  
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- 1  
2  
3  
4 [20] J. Wang, J. Lu, S.B. Hocevar, P.A.M. Farias, B. Ogorevc, *Anal. Chem.* 72 (2000)  
5  
6 3218–3222.  
7  
8  
9 [21] J. Wang, *Electroanalysis* 17 (2005) 1341–1346.  
10  
11 [22] A. Economou, *Trends Anal. Chem.* 24 (2005) 334–340.  
12  
13 [23] N. Serrano, A. Alberich, J. M. Díaz–Cruz, C. Ariño, M. Esteban, *Trends Anal.*  
14  
15 *Chem.* 46 (2013) 15–29.  
16  
17 [24] N. Serrano, J. M. Díaz–Cruz, C. Ariño, M. Esteban, *Electroanalysis* 22 (2010)  
18  
19 1460–1467.  
20  
21 [25] N. Serrano, J. M. Díaz–Cruz, C. Ariño, M. Esteban, *Anal. Bioanal. Chem.* 396  
22  
23 (2010) 1365–1369.  
24  
25 [26] V. Sosa, N. Serrano, C. Ariño, J. M. Díaz–Cruz, M. Esteban, *Talanta*, 119 (2014)  
26  
27 348–352.  
28  
29 [27] C. Barceló, N. Serrano, C. Ariño, J. M. Díaz–Cruz, M. Esteban, *Electroanalysis* 28  
30  
31 (2016) 640–644.  
32  
33 [28] V. Sosa, N. Serrano, C. Ariño, J. M. Díaz–Cruz, M. Esteban, *Electroanalysis* 26  
34  
35 (2014) 2168–2172.  
36  
37 [29] C. Locatelli, *Microchem. J.* 110 (2013) 99–106.  
38  
39 [30] J. Magdalan, A.Szelag, E. Chlebda, A. Merwid-Lad, M. Trocha, M. Kopacz, A.  
40  
41 Kuzniar, D. Nowak, *Pharmacol. Reports* 59 (2007) 210–218.  
42  
43 [31] J.N. Miller, *Analyst* 116 (1991) 3–14.  
44  
45 [32] F. Quentel, M. Filella, *Anal. Chim. Acta* 452 (2002) 237–244.  
46  
47 [33] A. Postupolski, J. Golimowski, *Electroanalysis* 3 (1991) 793–797.  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
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65

- 1  
2  
3  
4 [34] G. Capodaglio, C.M.G. Van den Berg, G. Scarponi, J. Electroanal. Chem. 235  
5  
6 (1987) 275–286.  
7  
8  
9 [35] M.J.G. Gonzalez, O. Dominguez–Renedo, M.J. Arcos–Martinez, Talanta 71 (2007)  
10  
11 691–698.  
12  
13  
14 [36] O. Dominguez–Renedo, M.J. Gómez González, M.J. Arcos–Martínez. Sensors 9  
15  
16 (2009) 219–231.  
17  
18  
19 [37] World Health Organization (WHO); Guidelines for Drinking-Water Quality, 4th  
20  
21 ed., WHO Library Cataloguing-in-Publication Data: Geneva, 2011.  
22  
23  
24 [38] [http://www.epa.gov/your-drinking-water/table-regulated-drinking-water-](http://www.epa.gov/your-drinking-water/table-regulated-drinking-water-contaminants#Inorganic)  
25  
26 [contaminants#Inorganic](http://www.epa.gov/your-drinking-water/table-regulated-drinking-water-contaminants#Inorganic). accessed on february 19, 2016.  
27  
28  
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**Table 1.** Free mercury stripping voltammetric methods developed for Sb(III) determination.

Electrode	Method	Ligand	Linear range ( $\mu\text{g L}^{-1}$ )	Limit of Detection ( $\text{ng L}^{-1}$ )	$t_{\text{acc}}$ (s)	Ref.
BiFE	SWAdSV	Gallic Acid	2 – 25	60	300	5
SPGE	LSASV	----	2 – 6 9.1 – 80	1200	125	6
MWcnsCPE	DPAdASV	Bromopyrogallol red	0.01 – 14	3.3	180	7
HGDE	DPASV	----	NR	$6.0 \times 10^6$	90	8
GCE	DPAdASV	Rivastigmine	0.06 – 61	9.0	120	9
AuMWE	DPASV	----	----	120	600	10
GTE	DPASV	----	1 – 10	190	600	11
HT18C6–RH–CPE	PSA	----	0.008 – 1.7	2.5	90	12
Au-nps-SPCE	DPASV	----	12 – 111	116	200	13
Ag-nps-SPCE	DPASV	----	12 – 111	83	200	14
PPG–GCE	DPASV	----	0.6 – 12.2	50	600	15
<i>In-situ</i> BiFE	SWCSV	----	0.01 – 0.1 0.1 – 1.0	2.0	30	16

Ag-nps-SPCE: Screen-Printed Carbon Electrode modified with Silver Nanoparticles; AdASV: Adsorptive Anodic Stripping Voltammetry; AdSV: Adsorptive Stripping Voltammetry; ASV: Anodic Stripping Voltammetry; AuMWE: Gold Microwire Electrode; Au-nps-SPCE: Screen-Printed Carbon Electrode modified with Gold Nanoparticles; BiFE: Bismuth Film Electrode; DP: Differential Pulse; GCE: Glassy Carbon Electrode; GTE: Gold Tubular Electrode; HGDE: Hanging Galinstan Drop Electrode; HT18C6–RH–CPE: Hexathia 18C6 and Rice Husk

modified Carbon Paste Electrode; LS: Linear Sweep; MWcnsCPE: Multi-Walled Carbon-nanotube-modified Carbon Paste Electrode; NR: Not Reported; PPG-GCE: Poly(Pyrogallol) Film modified Glassy Carbon Electrode; SPGE: Screen-Printed Graphite Electrode; SW: Square Wave; SWCSV: Square Wave Cathodic Stripping Voltammetry.

**Table 2.** Analytical parameters obtained with *ex-situ* BiSPCE and Bi<sub>sp</sub>SPE. The standard deviations are denoted by parenthesis.

<i>ex-situ</i> BiSPCE						
C <sub>QSA</sub> ( $\mu\text{mol L}^{-1}$ )	Sensitivity (SD) <sup>a</sup> (a.u. L $\mu\text{g}^{-1}$ )	Intercept (SD) (a.u.)	Linear range <sup>b</sup> ( $\mu\text{g L}^{-1}$ )	R <sup>2</sup>	Detection Limit ( $\mu\text{g L}^{-1}$ )	t <sub>acc</sub> (s)
5.0	6.16 (0.05)	−10 (2)	4.2–100.0	0,999	1.3	60
10.0	5.18 (0.04)	7 (2)	3.9–100.0	0,999	1.2	60
15.0	4.24 (0.03)	−0.5 (1)	4.0–100.0	0,999	1.2	60
20.0	4.45 (0.01)	6 (5)	3.9–100.0	0,999	1.4	60
10.0	7.0 (0.2)	4 (2)	2.7–45.0	0.999	0.8	120
Bi <sub>sp</sub> SPE						
C <sub>QSA</sub> ( $\mu\text{mol L}^{-1}$ )	Sensitivity (SD) <sup>a</sup> (a.u. L $\mu\text{g}^{-1}$ )	Intercept (SD) (a.u.)	Linear range <sup>b</sup> ( $\mu\text{g L}^{-1}$ )	R <sup>2</sup>	Detection Limit ( $\mu\text{g L}^{-1}$ )	t <sub>acc</sub> (s)
10.0	9.0 (0.4)	2 (7)	7.4–30.0	0.996	2.2	120

<sup>a</sup> Sensitivity was considered from the slope of the calibration curve.

<sup>b</sup> The lowest value of the linear range was considered from the LOQ.



**Table 3.** Tolerance level of interfering metal ions in the presence of Sb(III) and QSA (pH 4.6) in the presence of 30  $\mu\text{mol L}^{-1}$  of EDTA.

<b>Maximum concentration of metal ions. (<math>\Delta\text{Area} &lt; 10\%</math>)</b>	
<b>Metal ion</b>	<b>Level (<math>\mu\text{g L}^{-1}</math>)</b>
Mo(VI)	5
Tl(I)	100
Bi(III)	150
Cu(II), Fe(III), Zn(II)	200
As(V)	500
Be(II), Al(III)	600
Cd(II), Pb(II)	1000

## Figure captions

Fig. 1. Effect of pH on the peak area of Sb(III)–QSA complex signal. Conditions:  $C_{\text{Sb(III)}}$ :  $20.0 \mu\text{g L}^{-1}$ ;  $C_{\text{QSA}}$ :  $15.0 \mu\text{mol L}^{-1}$ ;  $E_{\text{acc}}$ :  $-0.50 \text{ V}$ ;  $t_{\text{acc}}$ :  $60 \text{ s}$ .

Fig. 2. Effect of ligand concentration on the peak area of Sb(III)–QSA complex signal. Conditions: pH:  $4.6$ ;  $C_{\text{Sb(III)}}$ :  $20.0 \mu\text{g L}^{-1}$ ;  $E_{\text{acc}}$ :  $-0.50 \text{ V}$ ;  $t_{\text{acc}}$ :  $60 \text{ s}$

Fig. 3. Effect of accumulation potential on the peak area of Sb(III)–QSA complex signal. Conditions: pH:  $4.6$ ;  $C_{\text{Sb(III)}}$ :  $20.0 \mu\text{g L}^{-1}$ ;  $C_{\text{QSA}}$ :  $10.0 \mu\text{mol L}^{-1}$ ;  $t_{\text{acc}}$ :  $60 \text{ s}$ .

Fig. 4. Effect of accumulation time on the peak area of Sb(III)–QSA complex signal. Conditions: pH:  $4.6$ ;  $C_{\text{Sb(III)}}$ :  $20.0 \mu\text{g L}^{-1}$ ;  $C_{\text{QSA}}$ :  $10.0 \mu\text{mol L}^{-1}$ ;  $E_{\text{acc}}$ :  $-0.50 \text{ V}$ .

Fig. 5. Adsorptive voltammograms and calibration plots (inset) of Sb(III)–QSA system. Conditions: (A) Electrode: *ex-situ* BiSPCE; pH:  $4.6$ ;  $C_{\text{QSA}}$ :  $10.0 \mu\text{mol L}^{-1}$ ;  $E_{\text{acc}}$ :  $-0.50 \text{ V}$ ;  $t_{\text{acc}}$ :  $120 \text{ s}$ . (B) Electrode: Bi<sub>sp</sub>SPE; pH:  $4.6$ ;  $C_{\text{QSA}}$ :  $10.0 \mu\text{mol L}^{-1}$ ;  $E_{\text{acc}}$ :  $-0.50 \text{ V}$ ;  $t_{\text{acc}}$ :  $120 \text{ s}$ . (C) Electrode: *ex-situ* BiSPCE; pH:  $4.6$ ;  $C_{\text{QSA}}$ :  $10.0 \mu\text{mol L}^{-1}$ ;  $E_{\text{acc}}$ :  $-0.50 \text{ V}$ ;  $t_{\text{acc}}$ :  $60 \text{ s}$ .

Fig. 6. Adsorptive voltammograms and calibration plot (inset) of the methodology validation. Conditions: Electrode: *ex-situ* BiSPCE; pH:  $4.6$ ;  $C_{\text{QSA}}$ :  $20.0 \mu\text{mol L}^{-1}$ ;  $E_{\text{acc}}$ :  $-0.50 \text{ V}$ ;  $t_{\text{acc}}$ :  $60 \text{ s}$ ;  $C_{\text{EDTA}}$ :  $30 \mu\text{mol L}^{-1}$ .

Figure 1

Figure 1

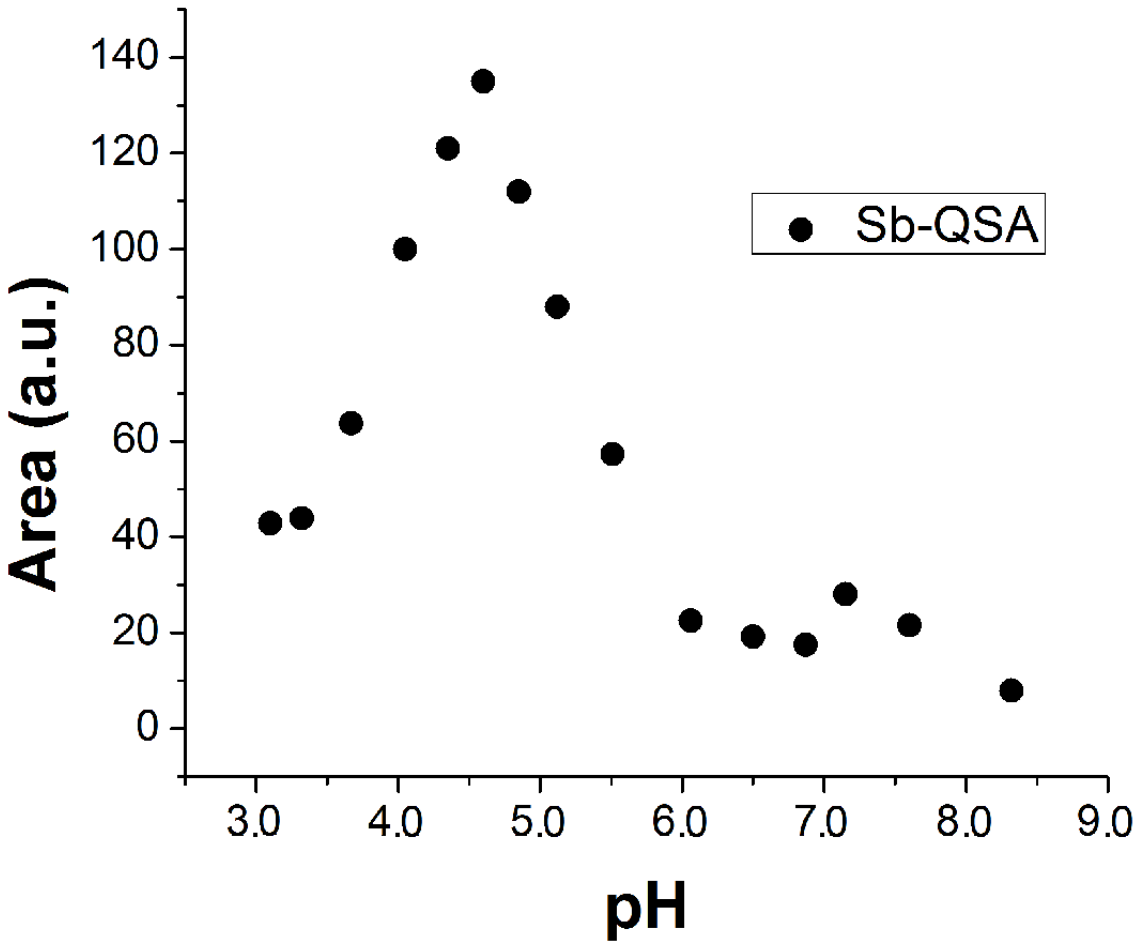


Figure 2

Figure 2

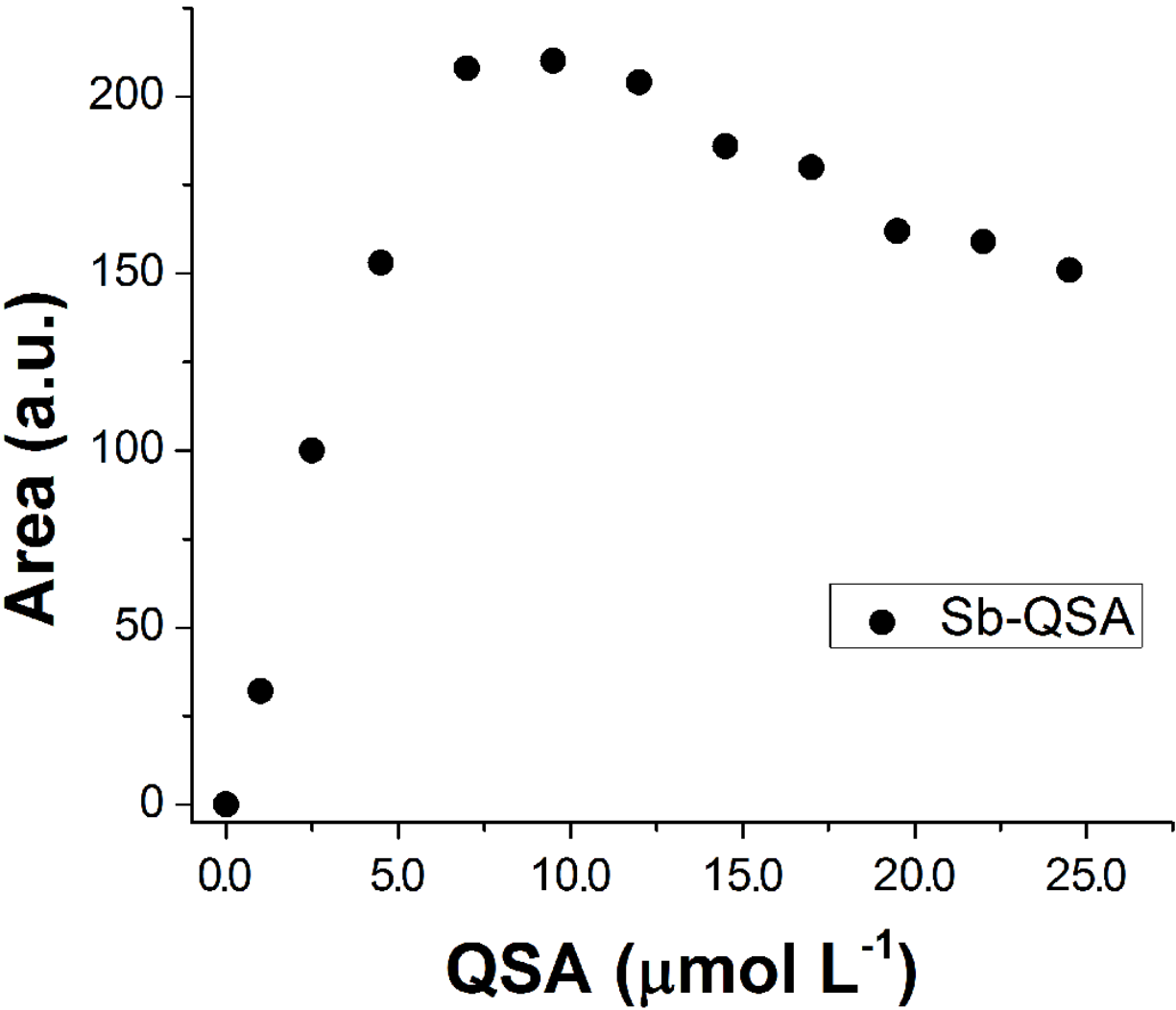


Figure 3

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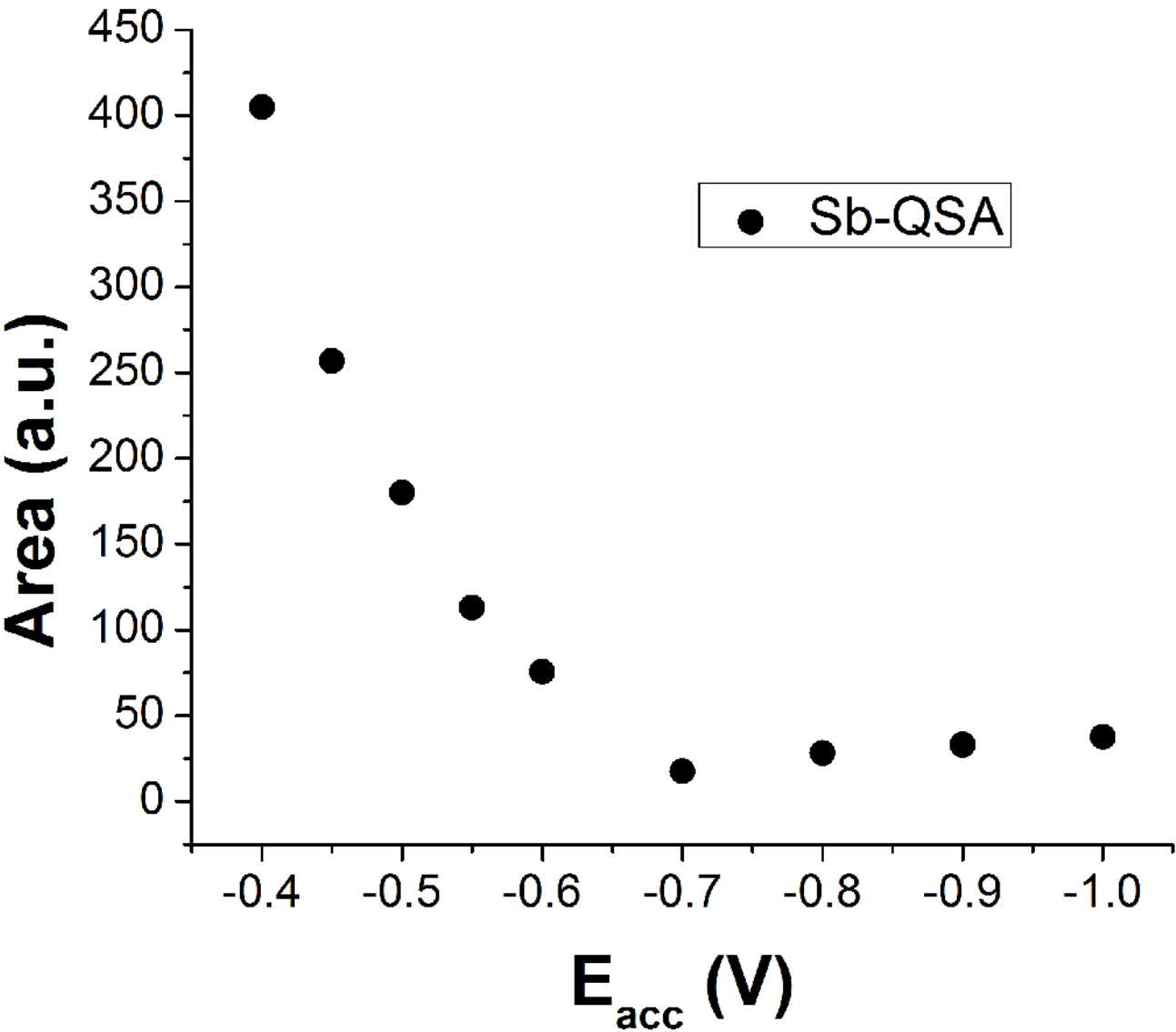


Figure 4

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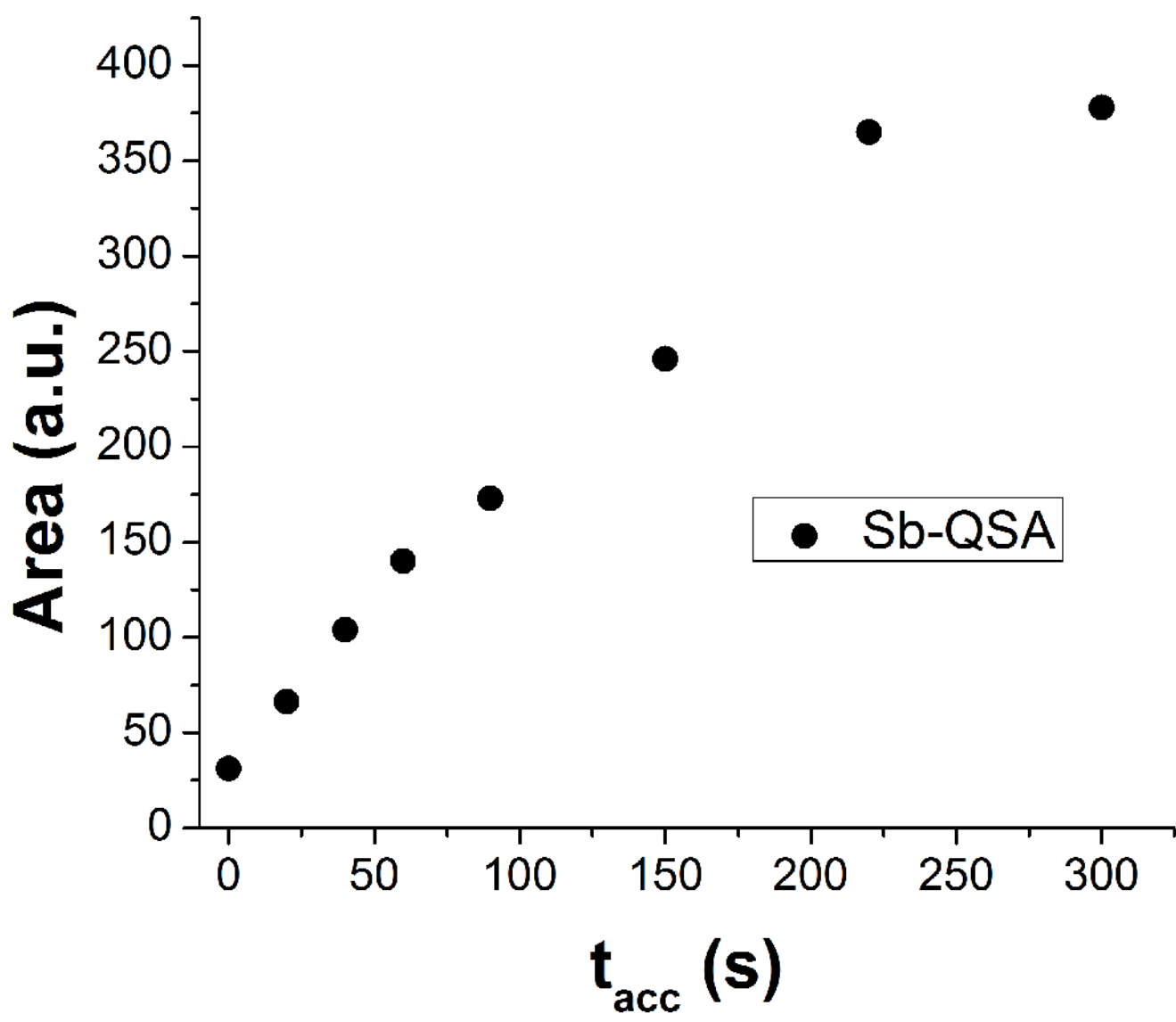


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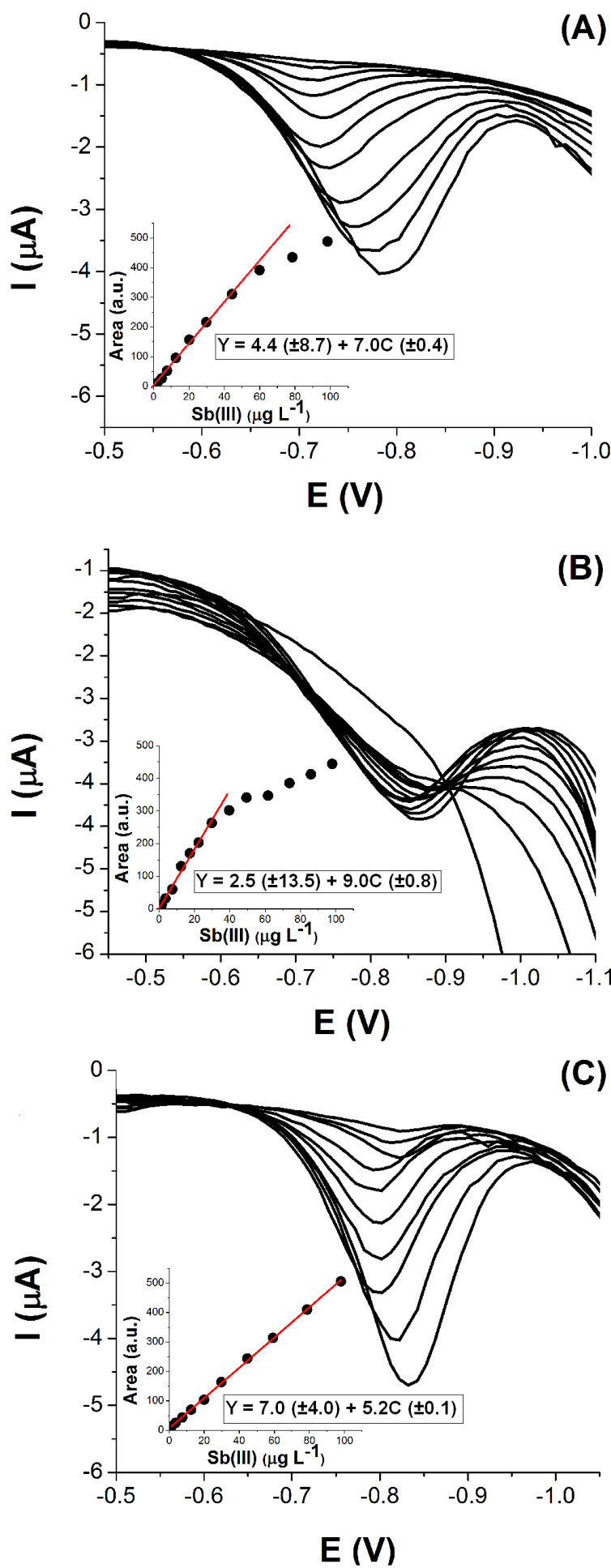


Figure 6

Figure 6

