IN-SITU MODIFIED ANTIMONY-FILM GLASSY CARBON ELECTRODE FOR METAL TRACE ANALYSIS

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Glassy carbon electrodes (GCE) have been extensively employed for the determination of trace amounts of heavy metals. Lately, modifications of GCE are currently being sought. One way of obtaining better analytical performance compared to GCE is the employment of an *in situ* prepared antimony-film glassy carbon electrode (SbFE). This combination is especially attractive in anodic stripping voltammetry technique which uses square wave excitation signal. This work will report on the optimization of the *in situ* prepared SbFE by employing different deposition potentials. Furthermore, a preliminary study using electrochemical impedance spectroscopy (EIS) was performed at different deposition and measured potentials in order to understand the mechanism of SbFE sensor performance.

Keywords: heavy metal analysis; antimony film electrode; square wave anodic stripping voltammetry.

INTRODUCTION

A growing interest has been shown in the last years on the determination of heavy metals as they are present in different environmental systems as micropollutants (Bansod *et al.*, 2017; Tchounwou *et al.*, 2012). Apart from their natural occurrence in the earth crust as elements the main sources of heavy metals contamination are related among others to industrial applications and waste, mining, atmospheric deposition, cosmetics, agricultural and metal-containing products (Bansod *et al.*, 2017; Tchounwou *et al.*, 2012; Roy, 2010; He *et al.*, 2005; Callender, 2003; Nriagu, 1989). Lead (Pb), chromium (Cr), cadmium (Cd), mercury (Hg) and arsenic (As) are known for their high toxicity. The exposure to even low concentrations (ppb range) can be dangerous not only to the environment, but to the human health as well, leading to multiple organ damage (Cui *et al.*, 2015; Tchounwou *et al.*, 2003; Yedjou and Tchounwou, 2007; Gumpu *et al.*, 2015; WHO, 1996). The high toxicity of these elements combined with the fact that their ions are non-biodegradable further increase the concern on their impact (Bansod *et al.*, 2017; Tchounwou *et al.*, 2012). On the other hand, some heavy metals (like Cu, Fe, Mg, Ni and Zn) are essential to the functioning of the human body (WHO, 1996).

Square wave anodic stripping voltammetry (SWASV) is among the most used electroanalytical techniques in the determination of trace heavy metals (Bansod *et al.*, 2017; Lu *et al.*, 2018). Glassy carbon electrodes (GCE) have presented an excellent alternative to the mercury drop electrodes. The latter's use is restricted due to high mercury toxicity concerns (Lu *et al.*, 2018). In the last years the focus of the research community has been on the modification of the GCE using among others nanomaterials, organic molecules and biomolecules (Bansod *et al.*, 2017; Cui *et al.*, 2015; Lee *et al.*, 2016; Zinoubi *et al.*, 2017; Dahaghin *et al.*, 2018; Sadok and Tyszczuk-Rotko, 2018; Lee *et al.*, 2015; Ariño *et al.*, 2017). Film electrodes, *in situ* or *ex situ* prepared with mainly bismuth, but also of copper, lead and tin, have been also explored (Ariño *et al.*, 2017; Jovanovski *et al.*, 2015, 2017; Economou, 2005; Petovar *et al.*, 2018; Czop, 2011; Korolczuk *et al.*, 2005). Several research groups have also reported on the use of *in situ* and *ex situ* prepared antimony film electrodes (SbFE) for trace heavy metal determination (Serrano *et al.*, 2016) in either 0.01 M HCl solution (Hocevar *et al.*, 2007; Bassie *et al.*, 2013; Ashrafi and Vytřas, 2012; Vasko and Bozidar, 2009) or in 0.1 M acetate buffer (Bassie *et al.*, 2013; Arancibia *et al.*, 2013; Maczuga *et al.*, 2013).

In this work we first discuss the analytical performance of the antimony film electrode (SbFE) that was formed *in situ* in 0.01 M HCl containing 0.5 ppm of Sb(III), in the

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determination of Pb(II) and Cd(II) using the SWASV technique. Next, electrochemical impedance spectroscopy (EIS) measurements for the studied systems were performed at different deposition and measured potentials and the response of the bare GCE was compared with SbFE with and without additions of the tested analytes. Finally, based on the preliminary EIS results the SbFE performance is discussed.

EXPERIMENTAL

The electrochemical measurements were performed in a three-electrode electrochemical cell using GCE (Cat. No.6.1204.300) as working electrode, Ag/AgCl(saturated KCl) as reference electrode, and a Pt counter electrode. All potentials in this work refer to Ag/AgCl (saturated KCl) reference electrode. These electrodes and the electrochemical cell were provided by Metrohm (Herisau, Switzerland). Before the measurements the working electrode was polished using Al_2O_3 powder (Buehler, Illinois, USA) and thoroughly washed with ultrapure water. Then the electrode was also cleaned under the ultrasound for 5 minutes in ultrapure water.

A system containing 10 mM potassium hexacyanoferrate(III) (Sigma Aldrich, St. Louis, Missouri, USA) in 1.0 M KCl solution was used to test the electrode reversibility. The tests were performed using cyclic voltammetry at different sweep rates, where the electrode response needed to fit into specific criteria. HCl and KCl were supplied by Carlo Erba Reagents (Val de Reuil, France). The atomic absorption standard stock solutions (1000 mg L^{-1}) of Cd(II), Pb(II) and Sb(III) were purchased from Merck (Darmstadt, Germany). These standards were diluted as required. All the solutions were prepared using ultrapure water with a resistivity of 18.2 MΩ cm that was obtained with a Milli-Q system (Millipore Corporation, Massachusetts, USA).

The *in situ* SbFE was formed in 0.01 M HCl where 0.5 mg/L of Sb(III) alongside the Pb(II) and Cd(II) analytes were present. SWASV was performed at different deposition potentials, *i.e.* –1.2, –1.1, and –1.0 V *vs*. Ag/AgCl. These are sufficiently negative deposition potential that three elements deposit on the surface – analytes preconcentration step alongside SbFE formation. All the methods were performed at 60 s deposition time. Before and after the measurement the electrode was electrochemically cleaned by applying a potential of 0.3 V *vs*. Ag/AgCl for 30 s. This potential is positive enough to oxidize all the employed metals. Before the measurements a period of 15 s equilibration time was employed. The measurements were performed with SW excitation signal with positive-going potential scan between –1.2 V (or –1.1 V or –1.0 V) and 0.6 V *vs*. Ag/AgCl. During the preconcentration step the solution was stirred at about 300 rpm, whereas during the equilibration and measurement steps the solution was not stirred.

EIS measurements were performed with the same electrodes as used for the method validation procedure and the same 60 s preconcentration step was used. The EIS response was obtained at two different potentials, *i.e.* E_{meas} and E_{oc} (open circuit potential). Measurements were performed in the $5 \cdot 10^4$–0.05 Hz frequency range, with 5 points per decade and 10 mV amplitude of the excitation signal. All the electrochemical measurements were performed with a PalmSens3 EIS potentiostat/galvanostat controlled by PSTrace 4.7 software (PalmSens, Houten, the Netherlands).

RESULTS AND DISCUSSION

Analytical Performance of the SbFE

In order to evaluate the analytical performance of the prepared SbFE first the selectivity of the method was proven. Then, the linearity of the method was determined, followed by the determination of the accuracy and the precision of the method.

Selectivity of the Method

Fig. 1 shows voltammograms measured after the preconcentration step at three different deposition potentials, *i.e.* –1.2, –1.1, and –1.0 V *vs.* Ag/AgCl. The stripping signals for Cd(II), Pb(II) and Sb(III) are located at approximately –0.75, 0.50, and 0.00 V *vs.* Ag/AgCl, respectively. The peaks are well separated indicating method selectivity towards Pb(II), Cd(II), and Sb(III).

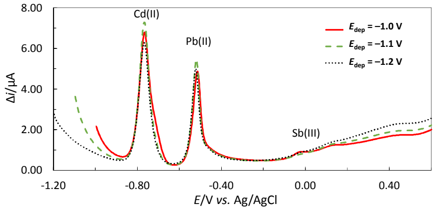

Figure 1. Voltammograms measured at three different deposition potentials using SbFE in 0.01 M HCl

Linearity of the Method

The method linearity was determined at three different deposition potentials, *i.e.* at –1.2, –1.1, and –1.0 V *vs.* Ag/AgCl respectively, as shown in Fig. 2. The current response Δ*i* *vs.* mass concentration γ was fitted using a least squares linear regression. Method linearity was accepted when the square of the correlation coefficient was higher than 0.99 ($R^2 > 0.99$). The linearity of the method for Cd(II) determination was found to be in the concentration range from 14.6 to 100.0 µg/L, using all three deposition potentials (Fig. 2a–c). On the other hand, in the case of Pb(II) determination at the same deposition potentials, the method was found to be linear in the mass concentration range from 24.4 to 100.0 µg/L (Fig. 2d–f).

Accuracy and Precision

The accuracy of the method was evaluated based on the calculated recovery value as shown in equation 1:

$$\text{recovery [\%]} = \frac{\text{(determined concentration)}}{\text{(theoretical concentration)}} \cdot 100 \qquad (1)$$

The accuracy was tested at four different concentrations of Pb(II) and Cd(II), *i.e.* 15 and 40 µg/L. The method was considered accurate when the recovery was in the range from 80.0 to 120.0%.

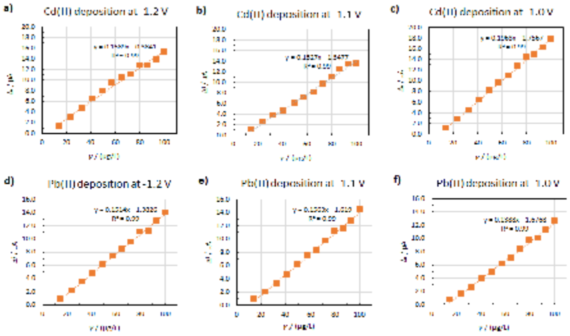

Figure 2. Linearity of the method for (a, b, c) Cd(II) and (d, e, f) Pb(II) determination at different deposition potentials. The accumulation time was 60 s.

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The accuracy was tested at three different deposition potentials *i.e.* –1.2, –1.1, and –1.0 V *vs.* Ag/AgCl. The best recovery value (the closest to 100.0%) was obtained at E_{dep} = –1.1 V *vs.* Ag/AgCl.

Precision was evaluated based on the relative standard deviation (RSD). In order for a method to be considered precise, a RSD value lower than 20.0% needs to be obtained. All the methods at three different deposition potentials provided values lower than 20.0%, indicating that they are precise.

Electrochemical Impedance Spectroscopy (EIS) Measurements

Fig. 3a–c and 4a–c present the EIS measurements (Nyquist plots) obtained in 0.01 M HCl solution containing 0.5 mg/L of Sb(III) with and without additions of the analytes (*i.e.* 15 or 40 µg/L of Pb(II) and Cd(II)). The EIS spectra of the bare GCE in 0.1 M HCl solution with and without additions of the analytes are given in each case (Fig. 3d–f and Fig. 4d–f) for comparison. Fig. 3 shows measurements performed at the same potential as the deposition potential (E_{meas} = E_{dep}), while the measurements in Fig. 4 are obtained at the open circuit potential (E_{meas} = E_{oc}).

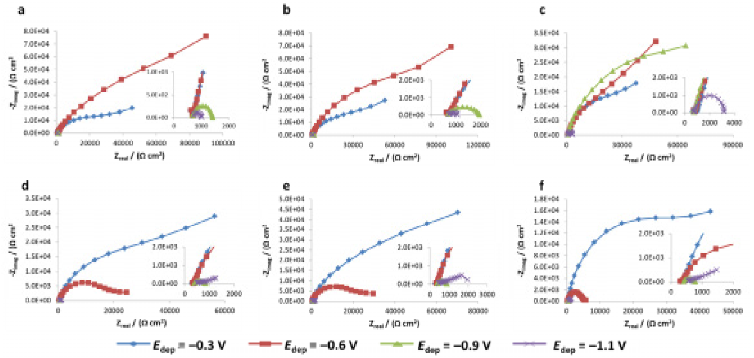

Figure 3. The EIS spectra of the SbFE (a–c) and bare GCE (d–f), recorded in 0.01 M HCl solution at the same potential as the deposition potential, with (a, d) 15 µg/L, (b, e) 40 µg/L and (c, f) without additions of analytes

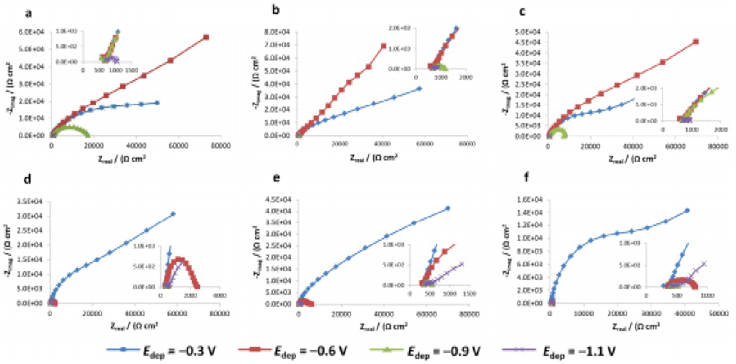

Figure 4. The EIS spectra of the SbFE (a–c) and bare GCE (d–f), recorded in 0.01 M HCl solution at open circuit potential, with (a, d) 15 µg/L, (b, e) 40 µg/L and (c, f) without additions of analytes

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Two distinguished patterns of the EIS measurements can be observed from Fig. 3 and 4. First, the EIS measurements obtained at more negative potentials (*i.e.* at –1.1 and –0.9 V *vs*. Ag/AgCl), independently of the addition of the analytes, present depressed semi-circular shape indicating charge-transfer-controlled reaction (kinetic control). However, it can be seen in Fig. 3 and 4 that the impedance of both the bare GCE and the SbFE increases with the presence and concentration of the analytes. The EIS response of the SbFE measured at E_{dep} is an exception from the above mentioned observation. Meanwhile at more positive potentials (*i.e.* at –0.6 and –0.3 V *vs*. Ag/AgCl) the measured curve in the Nyquist spectrum deviates from the Z_{real} axis indicating diffusion-controlled reaction. Second, in all the studied systems the impedance is found to be significantly reduced when moving towards more negative potentials. The lower the polarisation resistance the higher the sensitivity of the method (Petovar *et al*., 2018). Fig. 3 and 4 show no significant change in the impedance of the bare GCE and the SbFE at –1.1 V *vs*. Ag/AgCl.

CONLUSIONS

In this work the analytical performance of an *in situ* antimony-modified glassy carbon electrode in 0.01 M HCl solution containing 0.5 mg/L Sb(III), is presented. In addition a preliminary electrochemical impedance spectroscopy (EIS) study was performed at different deposition and measured potentials with and without additions of analytes, *i.e*. 15 and 40 µg/L of Pb(II) and Cd(II).

It was shown that at deposition potentials of –1.2, –1.1, and –1.0 *vs*. Ag/AgCl, for the determination of Pb(II) the method linearity was in the range from 24.4 to 100.0 µg/L, while for Cd(II) determination in the range from 14.6 to 100.0 µg/L. The accuracy and precision of the measurements was proven as shown by the recovery and relative standard deviation (RSD) values.

A preliminary EIS study indicated that at –1.1 and –0.9 V *vs*. Ag/AgCl the system is under kinetic control, while at more positive potentials (*i.e.* at –0.6 and –0.3 V *vs*. Ag/AgCl) the system is under both kinetic and diffusion control.

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