



Antimony film screen-printed carbon electrode for stripping analysis of Cd(II), Pb(II), and Cu(II) in natural samples



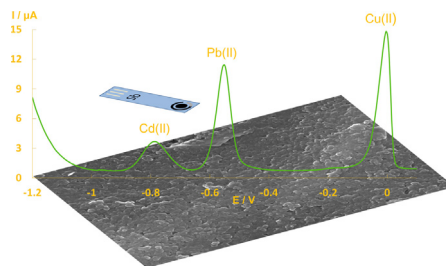
Velia Sosa, Cristian Barceló, Núria Serrano, Cristina Ariño*, José Manuel Díaz-Cruz, Miquel Esteban

Departament de Química Analítica, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, E-08028, Barcelona, Spain

HIGHLIGHTS

- *In-situ* SbSPCEs are used for the determination of Cu(II), Cd(II) and Pb(II) ions.
- Sb electrode is proposed as an alternative to *in-situ* bismuth film electrodes.
- LOD and LOQ at $\mu\text{g L}^{-1}$ levels allow the considered ions determination in natural samples.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 October 2014

Received in revised form 4 December 2014

Accepted 8 December 2014

Available online 10 December 2014

Keywords:

Antimony film electrodes
Screen-printed electrodes
Stripping voltammetry
Metal ions

ABSTRACT

An *in-situ* antimony film screen-printed carbon electrode (*in-situ* SbSPCE) was successfully used for the determination of Cu(II) simultaneously with Cd(II) and Pb(II) ions, by means of differential pulse anodic stripping voltammetry (DPASV), in a certified reference groundwater sample with a very high reproducibility and good trueness. This electrode is proposed as a valuable alternative to *in-situ* bismuth film electrodes, since no competition between the electrodeposited copper and antimony for surface sites was noticed. *In-situ* SbSPCE was microscopically characterized and experimental parameters such as deposition potential, accumulation time and pH were optimized. The best voltammetric response for the simultaneous determination of Cd(II), Pb(II) and Cu(II) ions was achieved when deposition potential was -1.2 V, accumulation time 120 s and pH 4.5. The detection and quantification limits at levels of $\mu\text{g L}^{-1}$ suggest that the *in-situ* SbSPCE could be fully suitable for the determination of Cd(II), Pb(II) and Cu(II) ions in natural samples.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Mercury was used as an electrode material for a long time due to their wide cathodic range. Nevertheless, due to the potentially toxicity of mercury vapors and mercury salts, the research of alternative materials is an area of major concern [1]. In 2000 bismuth film electrodes (BiFE) were introduced as substitutes of mercury electrodes demonstrating their applicability

for electroanalytical purposes [2]. However, some limitations for the determination of Cu(II) were observed using *in-situ* bismuth film electrodes due to the competition of the electrodeposited copper and the bismuth for surface sites [2]. Thus, the presence of Cu(II) interferes on the determination of Pb(II) and Cd(II) decreasing the sensitivity of the bismuth film electrode validating the theory of competition between Cu(II) and Bi(III) ions [3].

With the aim of developing new electrode materials, in 2007, antimony film electrodes (SbFE) were considered for metal ions determination [4,5]. The principal advantages of the SbFE in comparison to the BiFE were the wider useful potential window, and its performance at more acidic media [6]. The general

* Corresponding author. Tel.: +34 93 402 15 45; fax: 34 93 402 12 33.
E-mail address: cristina.arino@ub.edu (C. Ariño).

Sb-coating methods are similar to those used for the preparation of BiFEs: (i) *in-situ* plating method – the electrode is immersed directly into the sample solution containing Sb(III) ions and antimony is electrochemically deposited on the electrode surface during the analysis [4,6–8]; (ii) *ex-situ* plating or preplated method – the electrode is immersed into a Sb(III) solution and, after the application of an appropriate potential, Sb(III) ions are reduced to metallic Sb and electroplated on the electrode surface; later, the SbFE is rinsed carefully with ultra-pure water and then immersed into the sample solution [9,10]; (iii) the “bulk” method – the modification with Sb takes place during the preparation of the electrode and involves the preparation of a mixture of carbon paste and antimony precursor (Sb_2O_3); Sb precursor is later electrochemically reduced to metallic Sb at a selected potential [11]; and (iv) the sputtering method – the thin film of antimony is obtained by the antimony sputtering on a silicon substrate [12].

Glassy carbon and carbon paste are the substrates most commonly used for SbFE. Additionally, gold and platinum disk electrode as well as boron doped diamond (BDD) [13] were also used. Nevertheless, the carbon substrates provided better results than Au and Pt substrates [6].

On the other hand, screen printed technology is a renowned method for the fabrication of sensors and biosensors. Screen-printed electrodes (SPEs) usually include a three electrode configuration (working, counter and reference electrodes) printed on the same strip [14]. Moreover, screen-printed devices present the advantage that they do not need to be polished as the typical glassy carbon electrodes, or be prepared as the carbon paste electrodes. SPEs are well known for their low-cost commercial availability, miniaturized size, and the possibility of connecting them to portable instrumentation. Bismuth screen-printed electrodes (BiSPEs) were successfully used for the determination of different metal ions [13–16] as well as for complexation studies [17].

Studies devoted to the application of Sb electrodes for the simultaneous determination of Cu(II) with others metals ions such as Cd(II) and Pb(II), or the single determination of Cu(II) are really scarce [18,19]. A tentative study using an antimony film microelectrode (SbFME) for the determination of Cd(II), Pb(II) and Cu(II) [18] was carried out and, although the simultaneous determination of the three metals was not successfully achieved, it demonstrated the possibilities of Sb electrodes for the determination of Cu(II). Regarding the applicability of antimony screen printed electrodes (SbSPE) for the analysis of metal ions, only few studies are published using modified SbSPE for the determination of Pb(II) [20,21], for the determination of Hg(II) [21], and for the simultaneous determination of Cd(II) and Pb(II) [22]. Nevertheless, the applicability of an *in-situ* antimony screen-printed carbon electrode (*in-situ* SbSPCE) for the single determination of Cu(II) or for the simultaneous determination of this metal ion with other metal ions such as Cd(II) and Pb(II) was not investigated yet.

Thus, in the present work, an *in-situ* antimony electrode obtained from the modification of a commercial screen printed carbon electrode (*in-situ* SbSPCE) were microscopically and analytically studied for the determination of Pb(II), Cd(II) and Cu(II) using differential pulse anodic stripping voltammetry (DPASV). Moreover, *in-situ* SbSPCE were applied for the first time for the simultaneous monitorization of Pb(II), Cd(II) and Cu(II) ions in a certified groundwater sample.

2. Experimental

2.1. Chemicals

A Sb(III) 1000 mg L⁻¹ atomic absorption standard solution was purchased from Merck. Certified reference material, groundwater (BCR[®]-610), and ultrapure potassium nitrate were purchased from

Sigma–Aldrich. All other reagents used were Merck or Fluka analytical grade. Daily standard solutions of Cd(II), Pb(II) and Cu(II) were prepared by appropriate dilution of stock solutions 10⁻² mol L⁻¹, prepared from Cd(NO₃)₂·4H₂O, Pb(NO₃)₂·4H₂O and Cu(NO₃)₂·3H₂O respectively, and standardized complexometrically. 0.01 mol L⁻¹ solutions of hydrochloric acid (pH 2.0), maleic acid/maleate buffer solution (pH 6.8) and acetate buffer solution (pH 4.5) were used for pH control. 0.01 mol L⁻¹ KNO₃ was employed as supporting electrolyte. Ultrapure water (Milli-Q plus 185 system, Millipore) was used in all experiments.

2.2. Apparatus

Differential pulse anodic stripping voltammetric (DPASV) measurements were performed in an Autolab System PGSTAT12 (EcoChemie, The Netherlands) attached to a Metrohm 663 VA Stand (Metrohm, Switzerland) and a personal computer with GPES version 4.9 data acquisition software (EcoChemie).

The reference electrode (to which all potentials are referred) and the auxiliary electrode were Ag/AgCl/KCl (3 mol L⁻¹) and Pt wire, respectively.

In all the experiments, the working electrode used was an *in-situ* SbSPCE prepared from a commercial screen-printed carbon disk electrode of 4 mm of diameter (ref. DRP-110, DS SPE) provided by DropSens (Spain).

All measurements were carried out in a glass cell at room temperature (20 °C) under a purified nitrogen atmosphere (Linde N50).

Unless otherwise indicated, a pulse time of 40 ms, step potential of 2 mV, and pulse amplitude of 50 mV were applied in the stripping step. The optimized deposition potential (E_d) was applied with stirring during the optimized accumulation time (t_{acc}), and a rest period (t_r) of 30 s was maintained between deposition and stripping step.

The surface morphology characterization was carried out by a scanning electron microscope JSM 7100FE from JEOL (Japan).

2.3. Experimental procedure

2.3.1. In-situ preparation of SbSPCE

For the antimony *in-situ* modification of SPCE, a 0.5 mg L⁻¹ Sb(III) ion solution was directly added to the sample solution and electrochemically deposited with the target metal ions (cadmium, lead and copper) on the electrode surface during the analysis.

2.3.2. Procedure

The linear calibration plots for the simultaneous determination on an *in-situ* SbSPCE by DPASV of Pb(II) and Cu(II), and of Pb(II), Cd(II) and Cu(II), at E_d of -0.7 V and -1.20 V respectively, were obtained increasing metal concentrations at pH 4.5 acetate buffer and 0.01 mol L⁻¹ ionic strength.

In the analysis of the certified groundwater sample, voltammetric analysis started by placing in the cell a volume of the sample (BCR[®]-610) in 0.01 mol L⁻¹ acetate buffer (pH 4.5) and 0.01 mol L⁻¹ KNO₃. Then, the sample was deaerated with pure nitrogen for 15 min, to avoid the effect of oxygen in voltammetric measurements, and the voltammetric scan was recorded. In the case of calibration by standard addition, four aliquots of Cd(II), Pb(II) and Cu(II) standard solutions, applying a E_d of -1.2 V, and five aliquots of Pb(II) and Cu(II) standard solutions, applying a E_d of -0.7 V, were further added and the respective curves were recorded. All solutions were deaerated and mechanically stirred for 30 s after each standard addition. In order to prevent changes in ionic strength, the solutions to be added contained 0.01 mol L⁻¹ KNO₃.

In both, linear calibration plots and analysis of the certified groundwater sample, before each measurement a cleaning

Download English Version:

<https://daneshyari.com/en/article/1163542>

Download Persian Version:

<https://daneshyari.com/article/1163542>

[Daneshyari.com](https://daneshyari.com)