



# Can bismuth film screen printed carbon electrodes be used to study complexation?

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## ABSTRACT

*Ex situ* bismuth film on commercial screen-printed carbon electrodes (BiSPCE) has been used for the first time for the analysis of the complexation of  $\text{Cd}^{2+}$  by thiol containing compounds as glutathione (GSH) and phytochelatin ( $(\gamma\text{-Glu-Cys})_2\text{-Gly}$  ( $\text{PC}_2$ )).

Reproducibility of data is quite satisfactory and allows their treatment by multivariate curve resolution by alternating least squares (MCR-ALS). Unitary voltammograms and concentration profiles provided by MCR-ALS confirm the formation of 1:1 and 1:2  $\text{Cd}^{2+}$ :GSH and 1:2  $\text{Cd}^{2+}$ : $\text{PC}_2$  complexes. These results are in agreement with those previously obtained by mercury electrodes, and allow us to propose the use of BiSPCE for further studies on complexation.

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## 1. Introduction

Glutathione ( $\gamma\text{-Glu-Cys-Gly}$ , denoted usually as GSH) and its oligomers named phytochelatins ( $(\gamma\text{-Glu-Cys})_n\text{-Gly}$ , denoted usually as  $\text{PC}_n$ , where  $n$  generally ranges from 2 to 6) are thiol rich peptides which are synthesized enzymatically by plants in response to an excessive uptake of certain heavy metal ions [1–4]. The great affinity of the thiol group for heavy metals makes important the complexation by these thiol containing peptides not only for heavy metal detoxification but also for phytoremediation purposes [5–7].

The complexation of metals as  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  with GSH [8–10], mixtures of GSH and SeCyst [11], and  $\text{PC}_n$  [8–10,12–19] has already been studied by voltammetric methods in Hg electrodes. The resulting voltammetric data have been analyzed by chemometric methods as multivariate curve resolution by alternating least squares (MCR-ALS) [8–10,14–18] and/or gaussian peak adjustment (GPA) [11,19] and a complexation sequence has been proposed for most of the analyzed systems. However, certain metal-thiol peptides systems present the difficulty that thiol favors the electroodic oxidation of the mercury of the electrode. This process generates anodic signals that are strongly overlapping with those related with the metal ion to be studied, making the analysis of these systems even more complicated [20,21]. By the other hand, a policy against the use of mercury as electroodic material has appeared in the last years due to its potential toxicity.

In the last decade bismuth electrodes have been postulated as a valuable alternative to mercury electrodes for the analysis of traces of heavy metals in environmental samples [22]. Despite the lower

toxicity of the bismuth electrodes and their versatility and diversity in use, only a significantly small number of papers is devoted to the heavy metal complexation by voltammetric techniques [23,24]. Particularly, in one of these previous works, the complexation of Pb(II) by GSH has been studied by differential pulse voltammetry (DPV) on an *ex situ* bismuth film electrode (BiFE), achieving a better resolution of the signals than on a mercury drop electrode (SMDE), and allowing a qualitative analysis of the complexation process (not possible on SMDE). In contrast, it was found that because of the more complex shape of the signals obtained for the Pb(II)–GSH system on BiFE, the DPV/MCR-ALS analysis could not be successfully applied and was unable to provide essential information on complex composition [24].

In this work, the study of the complexation of Cd(II)–GSH and Cd(II)– $\text{PC}_2$  on an *ex situ* bismuth film on commercial screen-printed carbon electrodes (BiSPCE) was carried out. Taking into account that BiSPCE increasingly gained advantage over the most conventional BiFE due to the improvement of many aspects, such as the disposable character, the minimised splitting of the metal peaks, their sensitivity and their linearity ranges [25–28], the aim of the present work is the evaluation of the applicability of the BiSPCE in the study of the Cd(II)–GSH and Cd(II)– $\text{PC}_2$  systems, and the subsequent treatment with MCR-ALS or GPA of the obtained data, allowing us the establishment of the stoichiometry of the possible complexes formed.

## 2. Experimental

### 2.1. Chemicals

A standard Bi(III) solution  $1.000 \text{ g L}^{-1}$ , atomic absorption standard solution, was purchased from Fluka. All others reagents used

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were Merck analytical grade. Cd(II) stock solution  $10^{-2}$  mol L $^{-1}$  was prepared from Cd(NO $_3$ ) $_2 \cdot 4$ H $_2$ O and standardized complexometrically. Glutathione (GSH), in the reduced form, was provided by Merck. ( $\gamma$ -Glu-Cys) $_2$ Gly (PC $_2$ ), in lyophilized form with a purity >95%, was provided by Genosphere Biotechnologies France. Tris (hydroxymethyl) aminomethane, HCl buffer solution 0.1 mol L $^{-1}$  (pH 7.5 and pH 8.5) and KNO $_3$  0.01 mol L $^{-1}$  were employed as supporting electrolyte. Ultrapure water (Milli-Q plus 185 system, Millipore) was used in all experiments.

## 2.2. Apparatus and measurements

Differential pulse voltammetric (DPV) measurements were performed on a bismuth screen printed carbon electrode (BiSPCE) 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.

The working electrode was a BiSPCE prepared from a commercial screen-printed carbon disk electrode of 4 mm diameter (ref. 110, DS SPCE) provided by DropSens (Spain) and connected to the Autolab by means of a flexible cable (ref. CAC, DropSens). A new BiSPCE was used for each voltammetric titration [25].

*Ex situ* bismuth coated method was selected in order to prevent the side reactions that can take place between Bi $^{3+}$  -ions and ligands.

All the measurements were carried out in a glass cell at room temperature (20 °C) under a purified nitrogen atmosphere (Linde N50) in order to prevent the possible oxidation of the thiol compounds.

Unless otherwise indicated, a pulse of 50 mV and a potential step of 2 mV were applied.

## 2.3. Ex situ preparation of BiSPCE

The SPCE, the reference, and the auxiliary electrodes were connected to the stand and immersed into 20 mL of a 0.2 mol L $^{-1}$  acetate buffer solution (pH 4.5) containing 100 ppm Bi(III). After deaeration of the solution for 10 min, a deposition potential of  $-0.80$  V was applied for 300 s with solution stirring, followed by a rest period (without stirring) of 20 s.

Once the bismuth film was deposited, the three electrodes were rinsed carefully with water and the Bi(III) solution was replaced in the cell by the one to be measured. This methodology was previously tested, and results showed a very high repetitivity and reproducibility [25].

## 2.4. Procedure

Voltammetric titrations of Cd(II) with ligand (direct titrations) started by placing in the cell 20 mL of  $1 \times 10^{-5}$  mol L $^{-1}$  Cd(II) solution in 0.1 mol L $^{-1}$  Tris (hydroxymethyl) aminomethane, HCl buffer solution and 0.01 mol L $^{-1}$  KNO $_3$ . Then, the sample was deaerated with pure nitrogen for 20 min and a DPV curve was recorded. Aliquots containing  $4 \times 10^{-4}$  mol L $^{-1}$  of ligand solution were added and, after purging and mechanically stirring the solution for 1 min, the respective DPV curves were recorded. Voltammetric titrations of 20 mL of  $1 \times 10^{-5}$  mol L $^{-1}$  ligand solution with  $4 \times 10^{-4}$  mol L $^{-1}$  of Cd(II) solution (reverse titrations) were also performed following the same procedure.

## 2.5. Data treatment

The DPV curves were smoothed, base line corrected, and converted into data matrices by means of homemade programs implemented in Matlab [29]. The application of MCR-ALS [30] and GPA [31] methods to the analysis of matrices constituted by voltammetric data have been described elsewhere. MCR-ALS and GPA analyses were carried out through several programs implemented in MATLAB (some of them available at <http://www.ub.edu/mcr/html> and [http://www.ub.edu/dqaelc/programas\\_eng.html](http://www.ub.edu/dqaelc/programas_eng.html)).

## 3. Results and discussion

### 3.1. Cd(II)–GSH system

The complexation study of the Cd(II)–GSH system was carried out on BiSPCE at pH values of 7.5 and 8.5. Titrations of  $1 \times 10^{-5}$  mol L $^{-1}$  Cd(II) solution with GSH (direct titration) until a GSH:Cd $^{2+}$  ratio value of 3, and those of  $1 \times 10^{-5}$  mol L $^{-1}$  GSH solution with Cd(II) (reverse titration) until a Cd $^{2+}$ :GSH ratio value of 2.25, were done. In both cases the obtained voltammograms were arranged in a data matrix with as many rows as different [GSH]/[Cd(II)] or [Cd(II)]/[GSH] ratios were considered, and as many columns as the number of registered potentials.

Fig. 1 shows the voltammograms obtained in both direct (Fig. 1a) and reverse (Fig. 1b) titrations at pH 7.5. MCR-ALS and GPA analyses were applied to both voltammetric titrations. At a first inspection several components can be observed in all cases, being every component interpreted as every single electrochemical process which contributes to the measured signal [32]. Thus, component 1 is

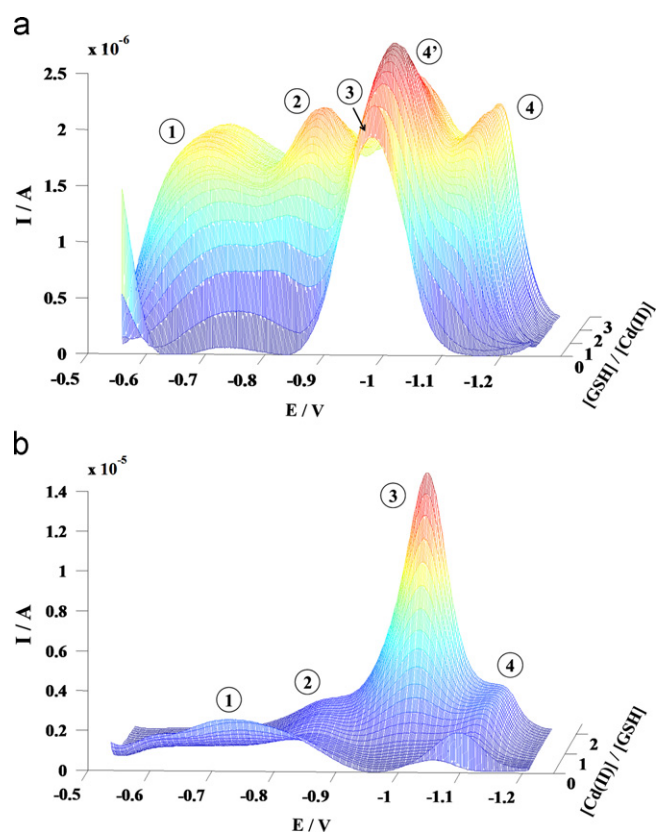


Fig. 1. Experimental data matrix of a  $1 \times 10^{-5}$  mol L $^{-1}$  Cd(II) solution titrated with GSH (a) of a  $1 \times 10^{-5}$  mol L $^{-1}$  GSH solution titrated with Cd(II) (b); both titrations were performed at pH 7.5 and ionic strength 0.01 mol L $^{-1}$  KNO $_3$ .

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