



Glutathione modified screen-printed carbon nanofiber electrode for the voltammetric determination of metal ions in natural samples



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ABSTRACT

This work reports the development of a glutathione modified electrode via electrografting on a screen-printed carbon nanofiber substrate (GSH-SPCNFE). GSH-SPCNFE was compared to a classical screen-printed carbon electrode modified with glutathione (GSH-SPCE) for the simultaneous voltammetric determination of Cd(II) and Pb(II). Their electrochemical characterization and analytical performance suggest that SPCNFE could be a much better support for GSH immobilization. The applicability of GSH-SPCNFE for the determination of low concentration levels of Pb(II) and Cd(II) ions in environmental samples was successfully tested in a certified wastewater reference material by means of stripping voltammetry with a very high reproducibility and good trueness.

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1. Introduction

The great variety of natural and anthropogenic sources of heavy metals, as well as their inability to be degraded, results in concerning levels of contamination of the environment. This, coupled to these metals being a serious threat to human health, makes necessary to have proper methods for their determination [1]. In this sense, stripping techniques and, in particular anodic stripping voltammetry (ASV), are especially suitable for trace heavy metal ions determination in natural samples because they provide excellent detection limits and high reproducibility and sensitivity and they are capable of multielement determination with a relatively low cost [2]. Traditionally, stripping techniques were connected to the use of mercury-based working electrodes due to their high reproducibility and wide cathodic potential range [3]. However, concerns about mercury toxicity have led to focus on the development of more environmentally friendly working electrodes. In this area, chemically modified electrodes are of great interest. In the design of these electrodes, many different strategies for designing recognition interfaces can be followed. In recent years, though, monolayers strategies, dominated by alkanethiol self-assembled monolayers (SAMs), have become increasingly popular. However, alkanethiols SAMs present some limitations including a narrow potential range for metal ion determination as

well as poor long term stability [4]. Another viable strategy for molecule immobilization that can overcome these limitations and has proven its usefulness in the development of metal ion sensors is based on aryl diazonium salt monolayers anchored on the electrode surface [4–6]. This strategy leads to stable electrodes that can be used for a wide number of measurements without signs of degradation [7–9] and allows to incorporate a wide range of functional groups to the electrode surface [10].

Peptides are known as effective, and often specific, ligands for metal ions. Their ability to bind metals is a consequence of the great number of donor atoms not only in their peptide backbone but also in their aminoacid side chains [11–13]. Particularly, the complexation of heavy metals with thiol rich peptides like glutathione (GSH) or its fragments has been largely studied by electroanalytical techniques (Table 2 in [13]). Thus, thiol rich peptides and related structures can be an interesting choice as recognition molecule in metal ion sensors [7,8].

The modification of electrodes with aryl diazonium salts has been applied to many sorts of carbon surfaces including glassy carbon [7,14,15], graphite [8,9], diamond [16,17] and screen-printed carbon electrodes [18–20] among others. Great advancements have been achieved in the last years in the field of screen-printed electrodes (SPEs) allowing the mass production of reproducible, economical and disposable devices. The whole electrode system, including reference, auxiliary and working electrodes, is usually printed on the same strip. Other important features of these SPEs are related to its miniaturized size and their capability to be

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connected to portable instrumentation, which makes them suitable for on-site analysis. Furthermore, SPEs offer the possibility to use many different compositions of printing inks that can strongly influence their performance [21,22]. This versatility in printing inks composition also allows the incorporation of nanomaterials like carbon nanotubes or carbon nanofibers to the SPEs, which are ideal for sensor application since they are conductive, easily functionalized and possess very large surface areas. In particular, carbon nanofibers are unique in the fact that their whole surface area can be activated [23]; recent studies have shown that they can be a great choice of substrate in sensors design, enabling to achieve better analytical performances [24,25].

In this paper, all the above-mentioned benefits have been considered for the first time in the development of a glutathione modified electrode via electrografting on a screen-printed nanomaterial substrate leading to a glutathione modified screen-printed carbon nanofiber electrode (GSH-SPCNFE) which will be compared to a classical screen-printed carbon electrode modified with glutathione (GSH-SPCE) in terms of their electrochemical characterization and their analytical performance in the simultaneous determination of Cd(II) and Pb(II) as a model metal ion system. Taking advantage of the better analytical performance of the GSH-SPCNFE, its applicability has been tested through the simultaneous determination of Pb(II) and Cd(II) ions in a certified wastewater reference material.

2. Experimental

2.1. Chemicals

2-(N-morpholino)-ethanesulfonic acid (MES), potassium ferrocyanide $K_4[Fe(CN)_6] \cdot 3H_2O$, hydrochloric acid, sodium acetate, acetic acid and glutathione (GSH), in the reduced form, with purity greater than 99% were purchased from Merck (Darmstadt, Germany). *N*-hydroxysulfosuccinimide (sulfo-NHS), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC), 4-aminobenzoic acid (ABA), perchloric acid, potassium dihydrogen phosphate, sodium nitrite, sodium monophosphate, methanol and certified reference material, wastewater ERM[®]-CA713, were supplied by Sigma-Aldrich (St. Louis, MO, USA). Potassium ferricyanide $K_3[Fe(CN)_6]$ was provided by Panreac (Barcelona, Spain). All reagents were of analytical grade. Pb(II) and Cd(II) stock solutions $10^{-2} \text{ mol L}^{-1}$ were prepared from $Pb(NO_3)_2 \cdot 4H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ respectively and standardized complexometrically [26]. Ultrapure water (Milli-Q plus 185 system, Millipore) was used in all experiments.

2.2. Apparatus

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) was used for stripping measurements.

Ag/AgCl/KCl (3 mol L^{-1}) and Pt wire (Metrohm, Switzerland) were used as reference and auxiliary electrode respectively. The working electrode was a modified glutathione electrode prepared from carbon screen-printed electrode (GSH-SPCE) or carbon nanofibers modified screen-printed electrode (GSH-SPCNFE), both with 4 mm diameter and provided by Dropsens (Oviedo, Spain) (ref. 110, DS SPCE and 110CNF, DS SPCE respectively).

Screen-printed electrodes were connected to the Autolab System by means of a flexible cable (ref. CAC, DropSens).

A Crison micro pH 2000 pH-meter was used for pH measurements.

All measurements were carried out in a glass cell at room

temperature (20°C) without oxygen removal.

2.3. Procedures

2.3.1. Preparation of modified SPEs

Glutathione modified SPEs were prepared based on a two-step procedure previously described [7] with slight modifications.

2.3.1.1. Diazonium salt electrografting. Aryl diazonium salt was generated *in situ* by adding 2 mmol L^{-1} of sodium nitrite to a cooled solution of 73 mmol L^{-1} of ABA in 1 mol L^{-1} aqueous HCl. The resultant solution was allowed to stir in an ice bath for about 30 min before the electrochemical grafting process [27] was conducted. For this purpose, the SPE was immersed in 20 mL of the diazonium salt solution and 15 cyclic voltammetry (CV) cycles from 0 V to -1 V at 0.2 V s^{-1} were applied. In order to remove any physisorbed compounds the functionalized electrodes were thoroughly rinsed with Milli-Q water and methanol.

2.3.1.2. Covalent immobilization of glutathione via carbodiimide coupling. $10 \mu\text{L}$ of a 26 mmol L^{-1} EDC and 35 mmol L^{-1} sulfo-NHS solution in 100 mmol L^{-1} MES buffer (pH 4.5) were dropped onto the functionalized SPE and left to incubate for 1 h to activate the carboxyl groups of the electrografted diazonium salt. The activated carboxyl groups reacted overnight at 4°C with the amine terminal groups of glutathione by placing $10 \mu\text{L}$ of a $2.9 \text{ mg}/100 \text{ mL}$ glutathione solution in 0.1 mol L^{-1} MES buffer (pH 4.5).

2.3.2. Voltammetric measurements

In stripping voltammetric measurements of Cd(II) and Pb(II) using a GSH-SPE, target metal ions were deposited for a deposition time (t_d) of 120 s at a deposition potential (E_d) of -1.4 V , applied with stirring. Deposition was followed by a rest period (t_r) of 5 s and determinations were done by scanning the potential from -1.4 to -0.45 V using pulse times of 50 ms, step potentials of 5 mV and pulse amplitudes of 50 mV.

Linear calibration plots were obtained by increasing metal ion concentrations in 0.1 mol L^{-1} acetate buffer (pH 4.5) solution.

In the analysis of the certified wastewater sample, a volume of the sample in 0.1 mol L^{-1} acetate buffer (pH 4.5) was placed in the cell and the scan was recorded (dilution factor 10/17). Calibration was performed by the standard addition method, five aliquots of metal standard solutions were further added and the respective curves were recorded.

In both linear calibration plots and analysis of the certified wastewater sample, a cleaning step was performed before each set of measurement by applying a conditioning potential (E_{cond}) of -0.3 V for 15 s in 0.1 mol L^{-1} $HClO_4$.

3. Results and discussion

3.1. Electrochemical characterization

Electrochemical characterization of both GSH-SPCE and GSH-SPCNFE was performed at each functionalization step by CV using ferrocyanide/ferricyanide as redox probe in 100 mmol L^{-1} phosphate buffer (pH 7.4). The potential was scanned between -0.6 V and 0.6 V at 100 mV s^{-1} without stirring. As expected, bare CNF resulted in more intense peaks than bare SPCE (Fig. 1), which can be attributed to its enhanced surface area. In both electrodes, a current decrease could be observed after electrografting (Fig. 1) due to the formation of a blocking layer [28]. There is not a clear agreement about the number of CV cycles that should be performed during the electrografting process. In fact, values ranging from 1 to 200 cycles can be found in the literature [29,30]. In this

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