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# Determination of labile trace metals with screen-printed electrode modified by a crown-ether based membrane

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**Abstract**

In this work, we have undertaken the construction of a screen-printed electrode modified by a specific membrane to protect the working surface from interferences during the analysis of trace metals by anodic stripping voltammetry. Different crown-ethers selected for their metals affinity have been incorporated into a membrane then deposed on the working surface of the electrode. Each modified electrode has been first tested in an acidified $KNO_3$ $10^{-1}$ mol $L^{-1}$ solution (pH 2) doped by free $Cd^{2+}$ and $Pb^{2+}$ ions. The response and selectivity of the modified electrodes have been investigated according to different parameters: (i) the substrates (commercial ink or carbon based homemade ink), (ii) the electrode support (polystyrene or transparency film) and (iii) crown-ethers nature (dibenzo-24-crown-8 and tetrathiacyclododecane 12-crown-4). The influence of the substrate on the response of the electrode is clearly demonstrated. Homemade ink appears as the most appropriate substrate to modify the working surface of the screen-printed electrode by a crown-ether based membrane. The effect of the composition of the membrane has been shown too. The best membrane developed showed a detection limit of $0.6 \times 10^{-8}$ mol $L^{-1}$ for Cd and $0.8 \times 10^{-8}$ mol $L^{-1}$ for Pb and a quantification limit of $10^{-8}$ mol $L^{-1}$ for Cd and $2 \times 10^{-8}$ mol $L^{-1}$ for Pb. This method, which integrates the extraction, preconcentration and measurement, was successfully applied to environmental samples without pretreatment.


*Keywords:* Screen-printed electrode; Mercury film; Crown-ether; Anodic stripping voltammetry

## 1. Introduction

In risk assessment, the free metal ion concentration appeared as a key parameter for bioavailability and toxicity of heavy metals to plants and living organisms [1]. In natural systems, exposure to metal ions not only depends on the total metal concentration but also on the speciation and on a number of environmental conditions (e.g. pH, concentration of other ions and concentrations of ligands in solution). Consequently, many analytical techniques have been developed in order to determine the free metal ion concentrations in the raw samples such as diffusive gradients in thin films (DGT) [2] or Donnan Membrane Technique (DMT) [3]. These methods allowed to determine the free metal ion in aqueous system in agreement with speciation models (WHAM or MINTEQ). However, they required a long time of equilibrium, which is not suitable for routine analysis and need of complementary equipments to measure lower concentrations. In summary, a technique is required that can preconcentrate and measure the labile fraction of trace metals without disturb the chemical equilibrium in the solution, the lability concept being defined as the ability of a complex to contribute to the metal flux to plants and living organisms.

Crown-ethers have proved to be an excellent choice in preconcentration techniques because of their ability to complex selectively ions. Crown-ethers can form complexes by fitting of the metal cation into a cage formed by crown structure. Since the cage can be designed to accommodate any ion of a certain size, selective extractions may be possible [4]. Researches have been performed by using this kind of compounds in solid-phase micro-extractions [5,6] or as carrier in supported liquid membrane extractions [7–10] but also in the fabrication of ion selective sensors [8,11–13]. Most of these ion selective sensors offer a good selectivity, a large pH and a wide concentration range but suffer from a lack of sensitivity with a detection limit around $10^{-5}$ mol $L^{-1}$ for the majority of ions.

Because of its high sensitivity, stripping voltammetry was widely used to determine trace levels of metal ions. Moreover, this technique allowed to determine the different forms

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of trace metals: free ions, labile complexes characterized by high rates of association/dissociation and inert complexes. The working electrodes used were mainly mercury electrodes or various kinds of mercury-film electrodes. However, the organic compounds lead to adsorb on the mercury-film coated electrode thus inhibiting the metal deposition or stripping processes [14]. Strategies have been developed for eliminating these interferences including filtering, UV digestion, acidification or mineralization. Chemically modified electrodes (CME) have also attracted considerable interest for a direct analysis of natural water samples, by deliberate modification of the surface or bulk matrix material of the electrode with a selected reagent (monomeric or polymeric). Such manipulation aims at improving sensitivity, selectivity and/or stability requiring for analytical needs. In recent years, determinations of metal ions by various chemically modified electrodes have been reported: overoxidized polypyrrole films [15], graphite working electrode modified by a cellulose-derivative mercury coating [16], Nafion®-coated glassy carbon electrode [17–21] and 1-(2-pyridylazo)-2-naphthol (PAN) [22].

Another approach consists to modify the working surface of a screen-printed electrode. This technology has been already developed in other fields such as electrochemical immunoassays or immunosensors [23,24]. This kind of sensors has the advantages to definitely solve problems related to contamination between samples. Moreover, their surface can be easily modified and therefore different improvements of the final sensor, such as enhanced selectivity and/or sensitivity, can be achieved. Finally, screen-printing is a simple and fast method for large-scale production of reproducible disposable low-cost electrochemical sensors. However, few works have exploited these sensors in the trace metal analysis.

The objective of this study was therefore to modify a thin-film mercury-coated screen-printed carbon electrode by a crown-ether based membrane in order to quantify the different forms of Cd and Pb (free ions, labile complexes or inert complexes) in environmental samples such as soil solutions. Two crown-ethers have been chosen, the dibenzo-24-crown-8 (DB24C8) and a thiacrown-ether, the tetrathiacyclododecane 12-crown-4 (TT12C4). Optimum experimental parameters have been examined and application to trace metal determinations in environmental samples is described.

## 2. Experimental

### 2.1. Reagents

Dibenzo-24-crown-8 (DB24C8) and tetrathiacyclododecane 12-crown-4 (TT12C4) were obtained from Aldrich Chemicals, USA. Tetrahydrofuran (THF), Mesitylene, potassium tetrakis(4-chlorophenyl borate) (KTCPB), all from Aldrich, were of the highest purity available and used without any further purification. Potassium nitrate (99.997% metal basis) was obtained from Alfa Aesar. Nitric acid of the Suprapur grade and Mercury(II) nitrate for atomic absorption standard was obtained from J.T. Baker. Polystyrene support was obtained from Sericol. Commercial ink (electrodag PF-407A) was purchased from Acheson Colloids. The carbon powder used in the homemade ink is a porous graphitic carbon provided by Thermo Electron Corporation. Polystyrene used in the membrane conception was taken from packing. The divalent metal ion solutions were prepared from cadmium nitrate (Normapur) and lead nitrate (Normapur) obtained from VWR International. Working solutions were prepared by the dilution of a $10^{-2}$ mol $L^{-1}$ solution in milli-Q water (resistivity of 18 MΩ cm) and stored in polyethylene containers.

### 2.2. Sensors

#### 2.2.1. Electrode preparation

The electrodes were screen-printed on two different supports: flexible polyester films (transparency films for copiers) and 1 mm-thick polystyrene plates. Two different inks were used to screen-print electrodes. The first is a commercial ink used as received. A manual screen-printer was used to produce an array of six electrodes, by forcing the conductive ink to penetrate through the mesh of a screen stencil [23]. After a drying step (1 h at room temperature) and a curing step (1 h in an oven at 60 °C), an insulator layer was spread manually over the conductive track, leaving a working disk area of 9 $mm^2$ and an electrical contact.

The second ink is a homemade ink based on a porous graphitic carbon powder. The conductive carbon ink was prepared by thoroughly hand-mixing the carbon mixture and a polystyrene/mesitylene mixture as previously described [25]. The same screen-printing process was used except the curing step.

#### 2.2.2. Membrane preparation

The ionophores (DB24C8 or TT12C4) were dissolved in a mixture of THF (1.5 mL) and mesitylene (1 mL) and then mixed with KTCPB and polystyrene according to the proportion given in Table 1. The mixture was vigorously shaken. A drop of the mixture (3 μL) was deposited on the electrode working surface and dried at 30 °C during one night.

#### 2.2.3. Mercury film deposition

Thin-film mercury-coated screen-printed carbon electrodes consist of a very thin film layer of Hg atoms adsorbed onto the electrode surface. The Hg film was deposited at −1 V for 300 s from a stirred solution of $KNO_3$ 0.1 mol $L^{-1}$–$HNO_3$ 0.2 mol $L^{-1}$ containing 2 mL of a 1000 mg $L^{-1}$ $Hg(NO_3)_2$ solution. Before using, each mercury-coated electrode is pretreated by applying −1 V for 300 s with stirring, then, differential pulse voltammetric scans were carried out three times in order to stabilize the background current.

### 2.3. Analytical parameters

All the experiments were carried out using Autolab PGSTAT12 potentiostat (Eco Chemie, The Netherlands). A volume of 10 mL of the sample solution was transferred into the voltammetric cell. $Cd^{2+}$ and $Pb^{2+}$ concentrations were determined by linear scan anodic stripping voltammetry (LSASV).