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## Trace lead analysis based on carbon-screen-printed-electrodes modified via 4-carboxy-phenyl diazonium salt electroreduction

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### ABSTRACT

This paper describes the use of 4-carboxyphenyl-grafted screen-printed carbon electrodes (4-CP-SPEs) for trace lead analysis. These novel and simple use of electrodes were easily prepared by the electrochemical reduction of the corresponding diazonium salt. Pb detection was then performed by a three-steps method in order to avoid oxygen interference: (i) immersion of the grafted screen-printed electrode (SPE) in the sample and adsorption of Pb(II), (ii) reduction of adsorbed Pb(II) by chronoamperometry (CA), and (iii) oxidation of Pb by Anodic Square Wave Voltammetry (SWV). The reoxidation response was exploited for lead detection and quantification.

In order to optimize the analytical responses, the influence of the adsorption medium pH and the adsorption time were investigated. Moreover, an interference study was carried out with Cu(II), Hg(II), Al(III), Mn(II), Zn(II), Cd(II) and no major interference can be expected to quantify Pb(II). The described method provided a limit of detection and a limit of quantification of  $1.2 \times 10^{-9}$  M and  $4.1 \times 10^{-9}$  M, respectively. These performances indicate that the 4-CP-SPE could be considered as an efficient tool for environmental analysis.

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### 1. Introduction

The release of different pollutants into environment has increased noticeably as a result of industrialization, and thereby lowered the quality of the environment. Of such pollutants, heavy and toxic metals considered as major environment hazards because of their non-biodegradability. Among them, lead has extensively been used in industry in the production of pigments, anticorrosion coatings, alloys, batteries, etc. and thus it is widely spread in different areas of the environment (atmosphere, soil, and water). High toxicity of lead is due to chronic poisoning resulting from trace exposure and leads to several organs disruption particularly kidneys and nervous system [1]. Considering its hazardous effects, different world organizations have regulated maximum levels of lead in the environment. The European Union has set the maximum allowable concentrations in food to be from 0.02 to 1 mg L<sup>-1</sup> [2] and World Health Organization has set 10 µg L<sup>-1</sup> for drinkable water [3].

Usually, the presence of trace amounts of heavy metals in environmental samples is determined by sophisticated analytical

techniques such as atomic absorption spectroscopy, inductively coupled plasma–mass spectroscopy or X-ray fluorescence spectroscopy [4]. However, the direct analysis of some complex samples like seawater presents some difficulties due to high salt content, causing matrix interferences and insufficient precision. Therefore, in such cases, a typical dilution of the sample may be necessary before the analysis, which in turns can aggravate the problem and leads to less accurate results.

Efforts are ongoing to develop rapid and inexpensive techniques for metal detection [5]. Among all the conventional heavy metals analysis techniques, electrochemical stripping analysis is one of the simplest and less expensive. However, it remains a technique that provides sensitivity needed for trace metals detection [6,7]. The coupling of disposable screen-printed electrodes (SPEs) with stripping techniques presents an attractive alternative to conventional electrochemical analysis. SPEs are related to a mass production technology based on screening of electroconductive and insulating inks onto planar substrates (plastic, ceramic, etc.) at a controlled thickness [8]. Moreover, SPEs related instruments can be portable which allows the direct monitoring of heavy metal-traces in an in situ control of pollution [9–11].

Stripping voltammetry coupled to SPEs using a variety of electrode designs and experimental protocols has been already proposed for the detection of Pb contained in different matrices

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such as natural waters [9–14], soil extracts [9–10], wastewaters [9–14] and drinkable waters [13,14]. Nevertheless, most of these studies deals with mercury film modified SPE. Although those modified electrodes offer high sensitivity and reproducibility for heavy metal detection [11,15,16], it is highly recommended to find more friendly alternatives giving the high toxicity of mercury. Recently, several materials have been tested for their capacity to replace mercury: bismuth, gold, silver, antimony, many of carbon based materials and boron-doped diamond. In addition, organic or inorganic chemical SPEs' modifications have been evaluated as to their potential application for detecting lead by stripping analysis. Among this extensive literature, the most studied solutions especially concern bismuth film electrodes, and then carbon electrodes and chemically modified electrodes [7]. The alternative provided by bismuth film electrodes, offers several advantages, among which their low toxicity, their ability to form alloys with different metals, their wide cathodic potential ranges, and their low sensitivity to dissolved oxygen [7,17–20]. But their major drawbacks are their limited anodic range and the strong dependence of the electrode performances to the deposition techniques which requires expensive instrumentation and clean-room facilities [18,21–23].

As another alternative, various carbon based electrode materials have been used with a great emphasis to increase the sensitivity and selectivity of the electrode materials toward particular analytes by modifying the surface with selective functionalities having potential affinity toward metal ions. Various forms of carbon materials have been reported as electrode materials for lead detection, such as glassy carbon, graphene, carbon nanotubes, carbon paste, carbon nanospheres and carbon black. Among these carbon electrodes, SPEs offer an attractive way due to their remarkable properties in terms of broad potential range and their easy elaboration and low cost. The sensibility and the selectivity can be improved by chemical modification of the carbon SPEs. This approach involves the chelation of the target analyte ion from solution onto the surface of the modified SPE. Honeychurch et al. [24–26] have used the drop coating technique to modify carbon SPEs by 1-(2-pyridylazo)-2-naphthol or by calix-4-arene compounds. These modified electrodes shown good analytical performance for lead detection [25,26].

Diazonium electrochemical grafting is an easy method to obtain covalently bound organic coating. In previous works, we showed the interest of the 4-carboxyphenyl-SPE grafted via electroreduction of the corresponding diazonium salt, for the trace analysis of Cu(II) [27] and U(VI) [28]. In this paper, we report opportunities offered by 4-carboxyphenyl-SPE grafted for the detection of lead in water at nanomolar level. The analytical procedure is based on the adsorption of the metal cation on the electrode surface enhanced by the complexation of Pb(II) by the carboxylate grafted ligand following by a SW-ASV analysis. The same analytical procedure will be applied to 4-carboxyphenyl-grafted glassy carbon for comparison. Metallic cations interferences are also studied: Al(III), Hg(II), Zn(II), Mn(II), Fe(II), Cu(II) and Cd(II).

## 2. Materials and methods

### 2.1. Chemicals and reagents

CH<sub>3</sub>COONH<sub>4</sub> (> 99%), H<sub>2</sub>SO<sub>4</sub> standard solution (1 M) and tetrafluoroboric acid were purchased from Fluka; 4-aminobenzoic acid, N-[Tris(hydroxymethyl)methyl]-3-aminopropanesulfonic acid (Taps) from Aldrich; suprapur standard solutions (1 g L<sup>-1</sup>) in nitric acid of Pb(II), Hg(II), and Cu(II) from JT Baker; Al(III), Mn(II) and Zn(II) from Fluka; Cd(II) from Sigma Aldrich; and NaNO<sub>2</sub> from Acros Organics. All solutions were prepared with deionized water (18 MΩ cm<sup>-1</sup>) from a

milli-Q system from Millipore. Solution pH have been adjusted with NH<sub>3</sub> (Prolabo) and CH<sub>3</sub>COOH (Fluka).

### 2.2. Electrode fabrication

4-Carboxyphenyldiazonium tetrafluoroborate (4-CPD) was synthesized as previously described [29]. Working electrodes were carbon-based screen-printed electrodes (SPEs) or 7 mm<sup>2</sup> glassy carbon electrodes (GCEs) (purchased from Tokai). SPEs were prepared by a printing process which consists of the deposition of a thin layer of a commercial conducting ink (Electrodag PF-407A purchased from Circuit Imprimé Français (CIF)) on a polystyrene support, through a screen supplied by CIF, then followed a drying step (1 h at room temperature) and a curing step (30 min at 90 °C), the working disk area was of 9.6 mm<sup>2</sup>. All electrodes were sonicated in H<sub>2</sub>SO<sub>4</sub> for 10 min before grafting. SPEs and GCEs were pretreated by cyclic voltammetry (CV) (5 scans at 0.1 V s<sup>-1</sup> between -0.1 V and -1.0 V) in H<sub>2</sub>SO<sub>4</sub> 0.1 M. Next, grafting was done by reduction of 4-CPD in H<sub>2</sub>SO<sub>4</sub> by chronoamperometry (-0.6 V/SCE during 300 s) at room temperature. Once grafted, electrodes were rinsed, sonicated for 2 min and stored in H<sub>2</sub>SO<sub>4</sub> 0.1 M before use.

### 2.3. Apparatus

Experiments were performed with an Autolab (low current PGSTAT12, Metrohm) in a classical electrochemical cell with Pt as counter electrode and saturated calomel electrode (SCE) as reference electrode as already mentioned [30]. All the potentials reported in this work are relative to SCE.

### 2.4. Procedure for lead electrochemical analysis

Lead detection consists of an adsorption step in Pb(II) solution followed by an electrochemical analysis in two steps in a lead free solution. Adsorption step (5 min, with stirring) was achieved by immersing the grafted electrodes into 10 mL of the analyzed solution (CH<sub>3</sub>COONH<sub>4</sub> 0.05 M, pH 7 with Pb(II)). For some interference experiments, another buffer (TAPS) was used for the adsorption step. Electrodes were then transferred to the electrochemical cell containing the same buffer free from trace-element in order to perform (i) a reduction of Pb(II) adsorbed onto 4-CP-SPEs by chronoamperometry (CA), (potential -1.4 V, time 5 s) followed by (ii) an oxidation of Pb by Square Wave Voltammetry (SWV), (pulse amplitude: 25 mV, step: 4 mV, frequency: 25 Hz). Solutions were deoxygenated with argon for 20 min and blanketed with an argon atmosphere during analysis. After use, electrodes were rinsed with milli-Q water and stored in H<sub>2</sub>SO<sub>4</sub> (0.1 M). All experiments were conducted at room temperature.

## 3. Results and discussion

### 3.1. Electrode materials and functionalization

In recent literature, SPEs have been reported as reliable tool for trace metal analysis more specifically mercury and bismuth thin film modified SPEs [24,31]. Only few papers mentioned the use of SPEs grafted via the reduction of diazonium salt [27,28,32–34] and are usually focused on biosensor applications [35–37]. On the contrary, many studies have reported the functionalization of GCEs by reduction of diazonium salt and their applications as electrochemical sensors for trace-element [38–41]. In this work, we first present a brief study of the electrochemical behavior of both SPEs and GCEs was conducted to guide the choice of our sensor material.

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