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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 1.2×10^{-9} M and 4.1×10^{-9} M, respectively. These performances indicate that the 4-CP-SPE could be considered as an efficient tool for environmental analysis.

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^{-1} [2] and World Health Organization has set 10 μg L^{-1} 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_3COONH_4 (> 99%), H_2SO_4 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^{-1}) 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 $NaNO_2$ from Acros Organics. All solutions were prepared with deionized water (18 MΩ cm^{-1}) from a milli-Q system from Millipore. Solution pH have been adjusted with NH_3 (Prolabo) and CH_3COOH (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^2 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^2. All electrodes were sonicated in H_2SO_4 for 10 min before grafting. SPEs and GCEs were pretreated by cyclic voltammetry (CV) (5 scans at 0.1 V s^{-1} between -0.1 V and -1.0 V) in H_2SO_4 0.1 M. Next, grafting was done by reduction of 4-CPD in H_2SO_4 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_2SO_4 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_3COONH_4 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_2SO_4 (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.

Fig. 1A shows cyclic voltammograms performed on naked SPE and naked GCE in H_2SO_4 (0.1 M) free of active species. This comparative study reveals that the capacitive current is much lower on SPE in comparison to the one generated by GCE (respectively 28 ± 3 nA and 170 ± 15 nA for $E = 0.3$ V).

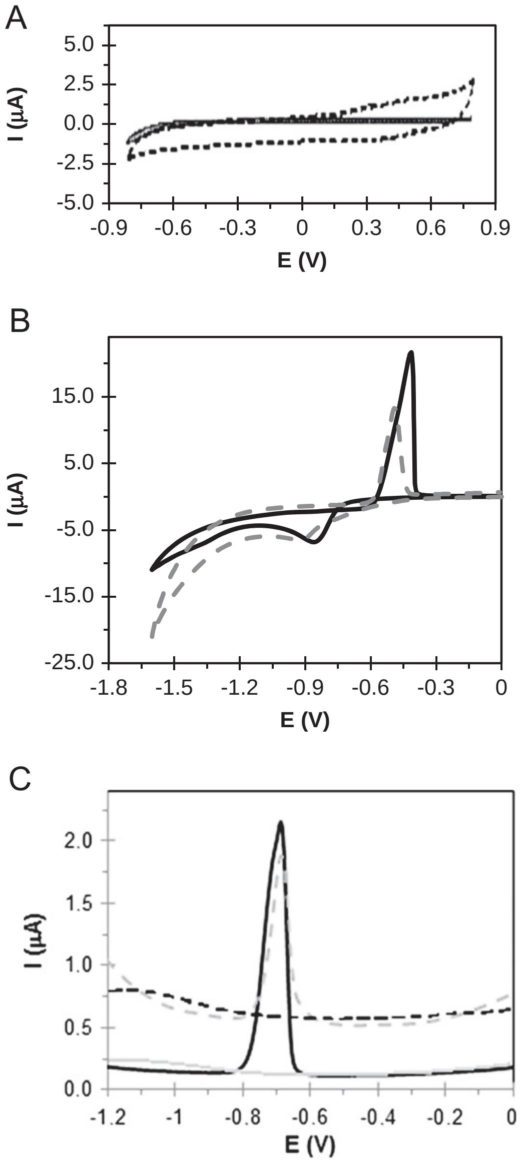


Fig. 1. (A) Cyclic voltammograms on bare SPE (▬) and GCE (- - -) in H_2SO_4 (0.1 M). (B) Cyclic voltammograms on bare SPE (▬) and GCE (- - -) in a 10^{-4} M Pb(II) solution in CH_3COONH_4 (0.05 M) (CV: scan rate 0.1 V/s). (C) SW voltammograms on grafted 4-CP-SPE (▬) and 4-CP-GCE (- - -) in a 5.10^{-8} M Pb(II) solution in CH_3COONH_4 (0.05 M) and the corresponding blank signals in (▬) and (- - -). (DP: −1.4 V during 5 s, SW: pulse amplitude 25 mV; step 4 mV; freq. 25 Hz).

Electrochemical reduction of diazonium salt is a simple and versatile method to functionalize carbon; it leads to covalently bound organic groups [42–44]. SPEs and GCEs were modified with 4-carboxy-phenyl functions via electrochemical reduction of the corresponding diazonium salt 2 mM in H_2SO_4 (0.1 M) according to the reaction illustrated in Scheme 1.

The evidence of the carboxy-phenyl grafting on SPEs and GCEs and the stability of the grafted electrodes have been previously described [27,28].

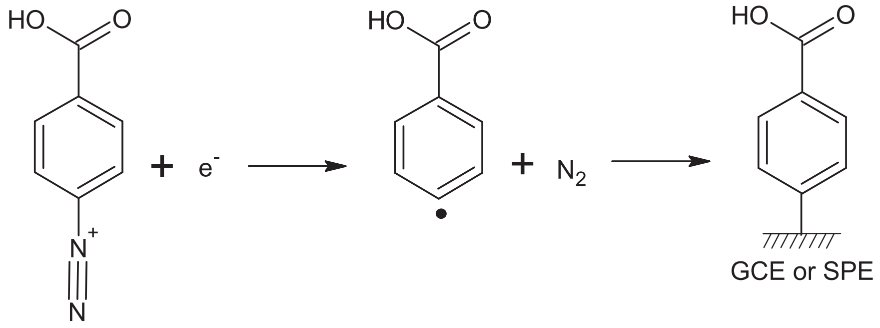
The electrochemical behavior of Pb(II) was studied in a concentrated solution (Pb(II) 10^{-4} M in H_2SO_4 0.1 M) by cyclic voltammetry both on 4-CP-SPE and 4-CP-GCE for comparison. As shown in Fig. 1B, a peak attributed to the reduction of Pb(II) to Pb is observed both on 4-CP-SPE and 4-CP-GCE. But the signal is more intense and the reduction of Pb(II) is less cathodic on 4-CP-SPE than on 4-CP-GCE. These results are explained by the lower capacitive current on SPE and a better electrocatalytic effect of the carbon black of SPE enhanced with electrochemical pretreatment [31].

Then Fig. 1C clearly points out the best electrochemical responses obtained with 4-CP-SPEs: the signal relative to Pb reoxidation with the analytical procedure described in experimental part is better well defined on this type of electrodes.

3.2. Choice of the analytical procedure

In previous works [27,28], Cu(II) and U(VI) analysis were achieved on 4-CP-SPEs following an analytical procedure in two steps: (i) an adsorption step consisting of the electrode immersion in the trace-element solution, (ii) an electrochemical reduction step of the Cu(II) or U(VI) adsorbed by square wave voltammetry. Then, quantitative data were extracted from exploitation of the reduction signal. The feasibility of this analytical procedure for Pb trace analysis should be investigated because Pb(II) reduction occurs in a potential range close to oxygen reduction. Fig. 2 shows voltammograms obtained on 4-CP-SPE and naked SPE in CH_3COONH_4 buffer without Pb(II), with or without preliminary degassing. The electrochemical process in the cathodic domain is due to oxygen in the non-degassed solution. It interferes with Pb(II) reduction signal (Fig. 1B). Analytical procedure based on Pb(II) reduction signal should be discarded. Thus an analytical procedure in three steps was chosen as described in experimental part with a quantification of Pb traces based on the anodic stripping signal.

In a preliminary study, the Pb(II) reduction potential and the corresponding reduction time have been optimized (Figs. S1 and S2 in supplementary data). The optimized chronoamperometric parameters were respectively −1.4 V and 5 s.



Scheme 1. : Electrochemical reduction and grafting of 4-CPD onto GCE or SPE.

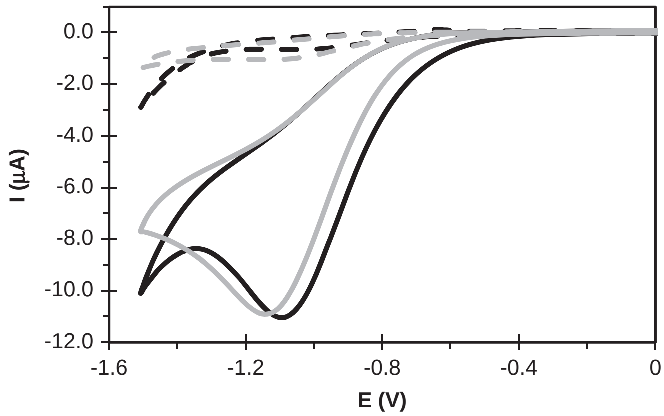


Fig. 2. Naked SPE and grafted 4-CP-SPE under the influence of oxygen removed with argon flow during 1 h (━━: SPE with oxygen; ━ ━ ━: SPE without oxygen; ━━: 4-CPSPE with oxygen ; - - -: 4-CP-SPE without oxygen) (CV: scan rate 0.1 V/s).

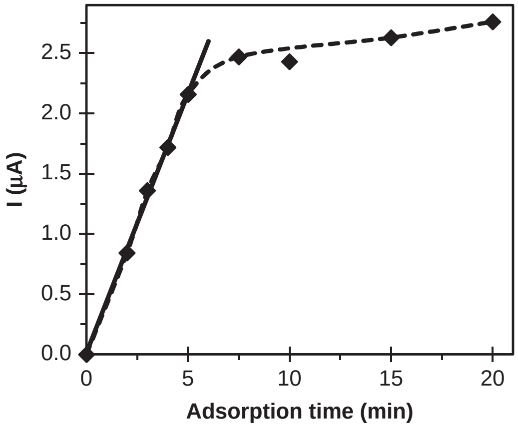


Fig. 3. Influence of adsorption time on the electrochemical response for a 5×10^{-8} M Pb(II) solution in CH_3COONH_4 (0.05 M) (DP: −1.4 V during 5 s, SW: pulse amplitude 25 mV; step 4 mV; freq. 25 Hz).

3.3. *Adsorption time*

The adsorption time is an important factor of the analytical procedure since it will impact the overall time of the analysis. The influence of the adsorption time on the stripping responses (i.e. oxidation peak intensity) in the 0–20 min range was evaluated. Experiments were conducted in CH_3COONH_4 buffer with Pb(II) 5×10^{-8} M. As illustrated in Fig. 3, the Pb oxidation peak intensity increases proportionally with adsorption time in the first 5 min range. This increase is due to the chelation kinetic of the metallic cations by the carboxylate functions grafted on the electrode surface. Beyond 5 min, the thermodynamical equilibrium is almost reached and the current tends to a constant value. Therefore 5 min adsorption time was typically used in this work to obtain the best analytical performances for this study. Indeed, the adsorption time impacts the linearity domain of quantification; the longer the time is, the lower limit of quantification (LOQ) is. Moreover, lower adsorption times lead to less accurate values because monitoring the immersion time is less easy.

3.4. *Influence of adsorption medium pH*

Influence of the adsorption pH medium on the current oxidation values was investigated in the 5–9 pH range for a Pb(II) concentration 5×10^{-8} M. Current values and stripping voltammograms are shown in Fig. 4.

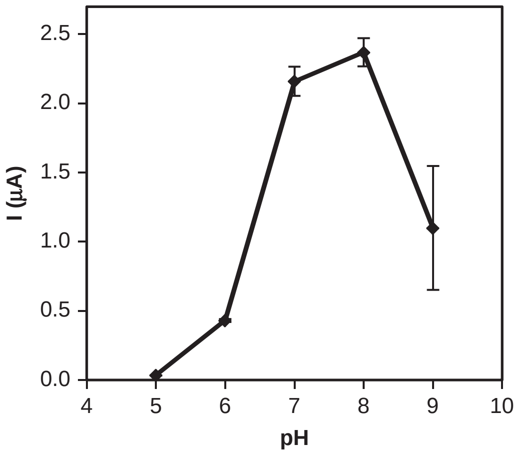


Fig.4. Effect of pH on Pb(II) 5×10^{-8} M detection in CH_3COONH_4 (0.05 M). (A) Intensity response as function of pH (for pH 5 and 6 errors bars are to tiny to be seen, respectively 4.4×10^{-4} and 10^{-2} µA). (B) SW voltammograms obtained with pH 6 (• • •), 7 (━ ━ ━) and 8 (━━) (DP: −1.4 V during 5 s, SW: pulse amplitude 25 mV; step 4 mV ; freq. 25 Hz).

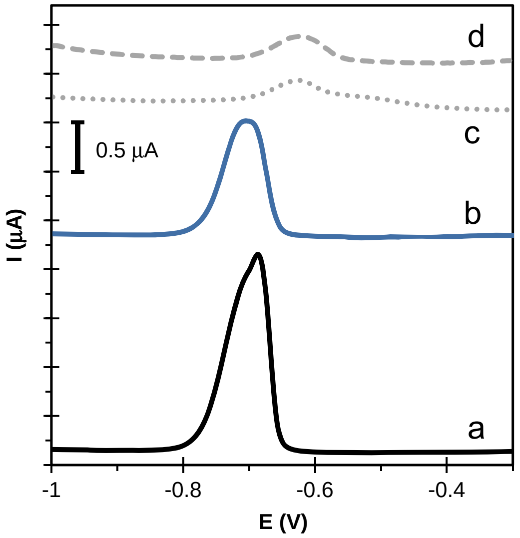


Fig. 5. (a) Standard condition with CH_3COONH_4 (0.05 M) in 3 steps: 5 min adsorption of Pb(II) in a pot and a SW-ASV in the electrochemical cell (DP: −1.4 V during 5 s, SW: pulse amplitude 25 mV; step 4 mV; freq. 25 Hz). (b) Identical to the previous one but the 5 min adsorption of Pb(II) and SW-ASV are made directly in the electrochemical cell. (c) Fan et al. condition [38] with pH 6.1 acetate buffer: SW-ASV in the electrochemical cell (DP: −1.2 V during 120 s under strirring equlibration 15 s, SW: pulse amplitude 40 mV; step 4 mV; freq. 50 Hz). (d) Identical to the previous one but CH_3COONH_4 (0.05 M) is used instead of acetate buffer.

At pH 5, no Pb oxidation peak is observed suggesting the absence of interaction between the grafted functions and Pb(II) at the 4-CP-SPE interface. This result is in accordance with the acidic conditions: the electrode surface is mainly covered by carboxylic functions (pK_a $\phi COOH/\phi COO^- = 4.2$) and is consequently not able to chelate metallic cations. Increase of the current in the 5–8 pH range corresponds to the increase of carboxylate amount at the electrode surface. Then, beyond this pH range, intensity decreases strongly due to the formation of Pb hydroxides, as suggested by chemical species diagrams. This hypothesis of a pH dependent redox system is also supported by a peak potential shift toward more negative values that we observed with increasing pH of the solution.

Fan et al. [40] investigated the determination of Pb(II) using 4-CP-GCEs with a slightly different procedure, where adsorption and electrochemical reduction (−1.2 V for 120 s) steps were

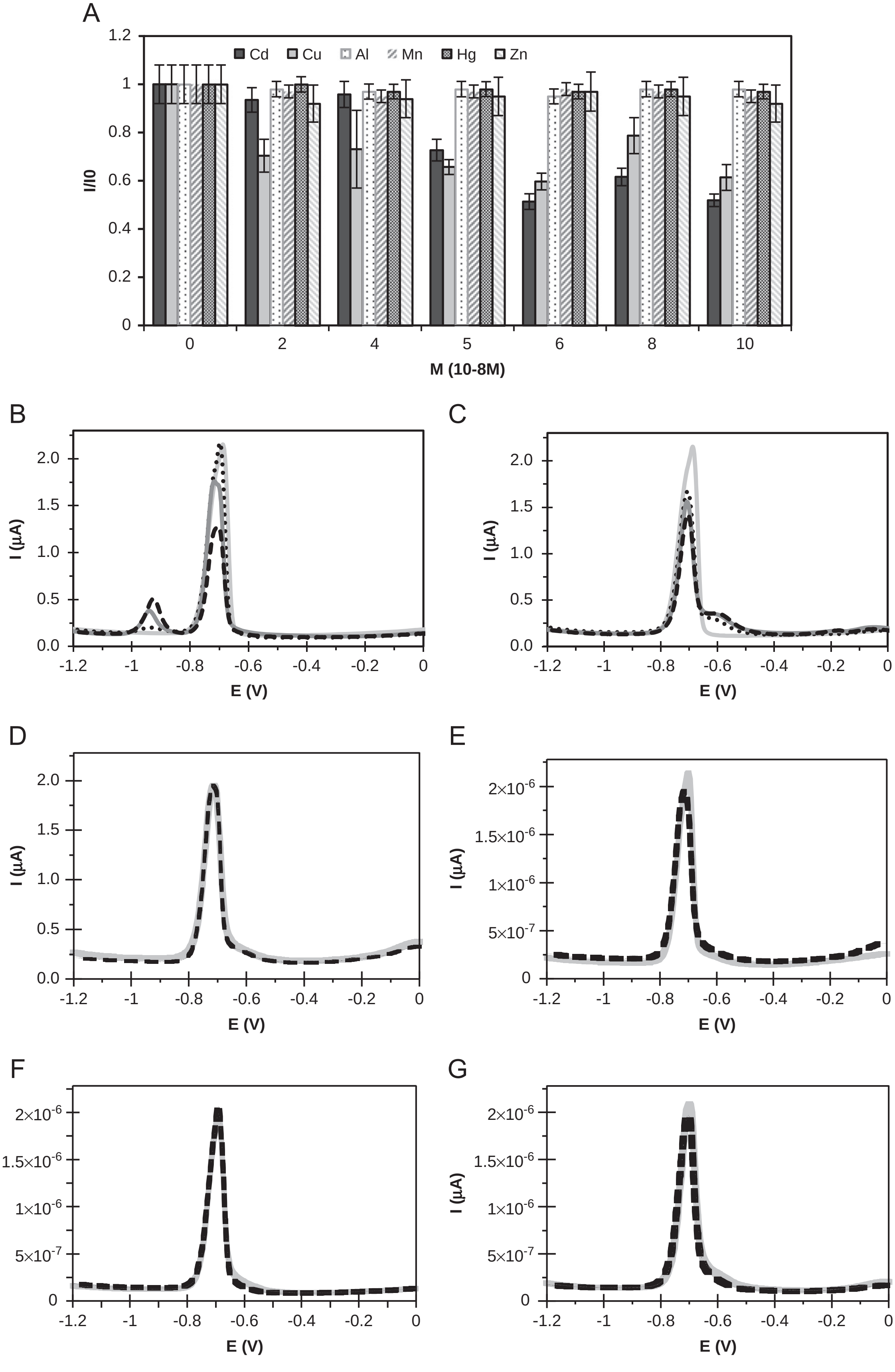


Fig. 6. Influences of the interferents M on the analytical response of 4-CP-SPEs (DP: −1.4 V during 5 s, SW: pulse amplitude 25 mV; step 4 mV; freq. 25 Hz). (A) Pb(II) relative intensity I/I_0 (where I and I_0 are the Pb(II) intensity in the presence and absence of M, versus M concentration). SW voltammograms obtained in the presence of M (▬: without M; ● ● ●: M 2×10^{-8} M; ▬: M 5×10^{-8} M; ▬ ▬ ▬: M 6×10^{-8} M) with (B) M=Cd; (C) M=Cu; (D) M=Al; (E) M=Mn; (F) M=Hg; (G) M=Zn.

achieved simultaneously, at pH 6 (acetate buffer), in the same electrochemical cell. We performed the same procedure on 4-CP-SPEs (Fig. 5) and we quoted that the signal obtained is broader and smaller than our classic one. As described in the influence of adsorption medium pH paragraph, optimum responses have been obtained for pH 7–8, so the same study was carried out in pH 7 CH_3COONH_4 instead of acetic buffer; any improvement have been observed. A comparison with the different procedures proves the need for an adsorption step before the electrochemical reduction.

Furthermore, both adsorption and analysis steps have been performed in: (i) the same solution with Pb(II), (ii) in two separate solutions with Pb(II) (for adsorption) and without Pb(II) (for analysis) (Fig. 5). And a better response was obtained for the second (ii) procedure.

In another hand, the use of two solutions proves that the analytical response corresponds only to Pb(II) adsorbed on the 4-CP-SPE. And the transfer of the electrode to a second blank solution for electroanalysis purpose would prevent interference generated from non-adsorbed electroactive species when it comes to real samples analysis.

3.5. *Interference study*

Selective determination of Pb(II) in real samples is a challenging task as other trace elements present in these samples may also be adsorbed, reduced and stripped off under the same conditions. Among the possible interferents, noted M, Cd(II) and Cu(II), Al(III), Mn(II), Hg(II) and Zn(II) are widely found in environmental waters. Their influence on the analytical response of Pb(II) (5×10^{-8} M) was studied and depicted in Fig. 6(A) for a concentration range of 2×10^{-8} to 10^{-7} M. The corresponding stripping voltammograms are presented in Fig. 6(B)–(G). According to the standard errors, none of Al(III), Mn(II), Hg(II) and Zn(II) seemed to affect the 4-CP-SPE sensitivity toward Pb(II). No major interference of these ions is thus expected for the Pb(II) determination in the natural water samples where those trace elements are expected at concentrations lower than 10^{-7} M. Reoxidation of Cd to Cd(II) occurs at -0.9 V. The analytical response increases with the initial Cd(II) concentration. Interference of Cd(II) on the Pb(II) analysis starts only for Cd(II)/Pb(II) ratio superior to one. As Cd(II) concentration in natural water is significantly lower than Pb(II), no major Cd(II) interference is expected for trace Pb(II) analysis. The suggested analytical procedure using 4-CP-SPEs is suitable for drinking water analysis according to the European Standards requirement for both cadmium and lead [45,46] 5 and 10 $\mu g\ L^{-1}$ respectively.

In the presence of Cu(II), the anodic response of lead decreases and presents an extra shoulder at -0.6 V. This shoulder is characteristic of a copper–lead intermetallic compound which is generated during the reduction step [25] and increases with the Cu(II) concentration. Due to the relative high concentration of Cu(II) compared to Pb(II) present in most drinking water, copper interference needed to be solved. Some methods have been proposed in the literature to overcome the interference of the Cu(II) on Pb(II) detection such as the "third element" method [47] or the selective precipitation of CuI [25]. The first method is not friendly for the environment. The addition of KI in the adsorption medium affects the lead sensitivity even for concentrations for which lead iodide could not precipitate. Finally Taps buffer has been chosen as the adsorption medium for its chelating properties and its pH range (pH 8.2). The same analytical procedure described in the experimental section was applied in this study with the adsorption step in the following medium: Pb(II) 10^{-8} M, Cu(II) 10^{-7} M in Taps solution 0.05 M. Fig. 7 shows the obtained lead signals with and without the presence of Cu(II) (10^{-7} M); no peak shoulder was observed at -0.6 V and the sensitivity of the 4-CP-SPE towards Pb(II) was not affected. The selective chelation of Cu(II) by the Taps and/or the selective precipitation of the copper hydroxide can act to avoid the adsorption of the Cu(II) on the 4-CP-SPE. Fig. 7(B) shows the Cu(II) reduction peak on 4-CP-SPE after carrying out the analytical procedure described in [27] along with an adsorption step in both CH_3COONH_4 buffer and in Taps buffer for comparison reasons: the absence of Cu(II) at the electrode surface is obvious in the case of an immersion adsorption step in Taps buffer.

3.6. *Stability of the 4-CP-SPEs*

The stability of the electrochemical response of 4-CP-SPEs with time was also studied in CH_3COONH_4 buffer with Pb(II) 5×10^{-8} M. Between two successive analysis, 4-CP-SPEs were stored in the dark in H_2SO_4 solution (0.1 M) at room temperature to ensure the desorption of reoxidized Pb(II) that would remain on the electrode surface. Pb signal obtained on a freshly grafted 4-CP-SPE loses only

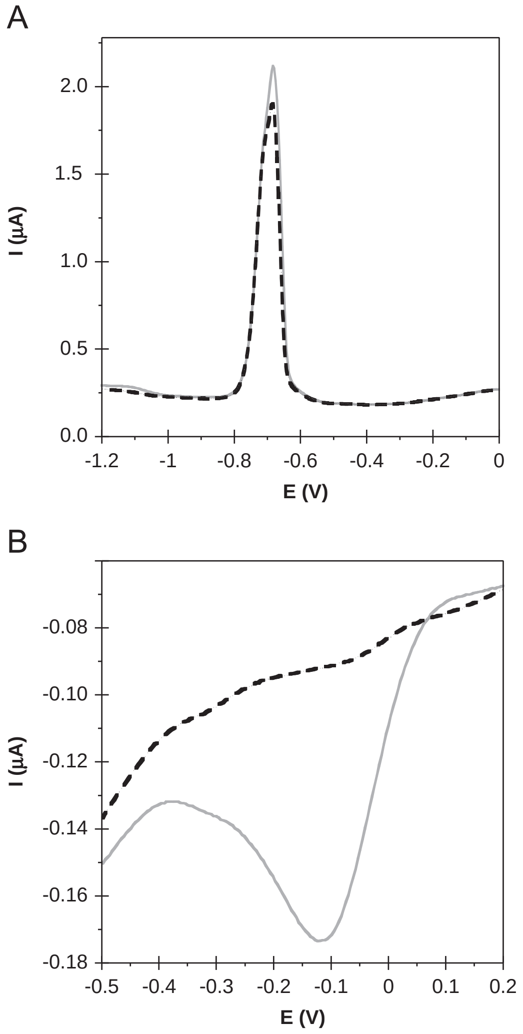


Fig. 7. Influence of the immersion media on the Cu(II) interference (A) SW voltammograms on grafted 4-CP-SPE obtained after 5 min of immersion in 5×10^{-8} M Pb(II) solution in Taps buffer (0.05 M) without Cu(II) (– – –); in the presence of Cu(II) 10^{-7} M (━━); Electrochemical analyze in CH_3COONH_4 (0.05 M) (DP: -1.4 V during 5 s, SW: pulse amplitude 25 mV; step 4 mV; freq. 25 Hz); (B) SW voltammograms on grafted 4-CP-SPE obtained after 5 min of immersion in 10^{-7} M Cu(II) solution in CH_3COONH_4 (0.05 M) (━━) Taps buffer (0.05 M) and in Taps buffer (0.05 M) (– – –); Electrochemical analyze in CH_3COONH_4 (0.05 M) (SW: pulse amplitude 25 mV; step 4 mV; freq. 25 Hz).

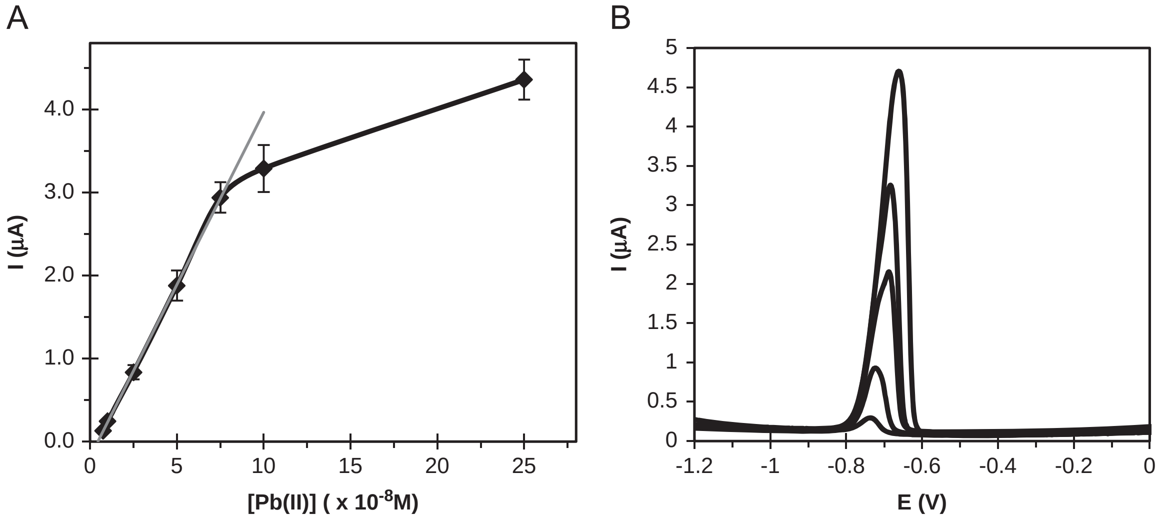


Fig. 8. (A) 4-CP-SPE Pb(II) calibration curve obtained in CH_3COONH_4 (0.05 M). (B) SW voltammograms for Pb(II) 1×10^{-8}, 2.5×10^{-8}, 5×10^{-8}, 7.5×10^{-8}, 25×10^{-8} mol L^{-1} (DP: −1.4 V during 5 s, SW: pulse amplitude 25 mV; step 4 mV; freq. 25 Hz).

50% of its intensity after 20 tests and 8 days of storage. This suggests that 4-CP-SPEs can be reusable for Pb(II) detection.

3.7. Analytical performances

The calibration curve (Fig. 8A) is obtained from experiments that have been conducted in the ammonium acetate buffer with Pb(II) in the range 0–2.5×10^{-7} M. The relative stripping voltammograms are presented in Fig. 8B. The sensitivity, based on the slope of the calibration curve, is determined from the calibration curve obtained from six concentration levels; its value is 41.5 A/M. The calibration plot is found to be linear between 7.5×10^{-9} M and 7.5×10^{-8} M and obeys to the following relation: $I = 41.5$ [Pb(II)]-1.7×10^{-8} ($r^2 = 0.9998$).

The Limits Of Detection (LOD) and Quantification (LOQ) that have been calculated statistically [48] are 1.2×10^{-9} M and 4.1×10^{-9}M respectively. These performances are slightly better than those observed with gold screen printed sensor [49] and similar to mercury coated screen printed carbon electrode [50,51].

Repeatability was evaluated after seven analysis replicates of Pb(II) 5×10^{-8} M solution with a single electrode. Well shaped voltammograms were obtained for all experiments: the calculated relative standard deviation is 13%. Reproducibility of the procedure was evaluated by performing a series of analysis with six different electrodes. The obtained relative standard deviation is 8%. These results indicate that 4-CP-SPEs are reliable tools for Pb(II) detection and quantification.

3.8. Applications

To assess the applicability of the 4-CP-SPEs experiments were conducted in a standard primary drinking water metals spiked sample (from High Purity Standard) diluted in CH_3COONH_4 buffer (pH 7) with the following composition (in ppb): As, 10; Cd, 5; Pb, 10; Se, 5; Ba, 5; Cr, 10; Hg, 2; Ag, 1. After five measurements, we quantified Pb concentration in solution at 10 ± 0.3 ppb value. These results indicate that the suggested analytical procedure using 4-CP-SPEs is suitable for the determination Pb(II) in drinking water according to the European Standards regulations and World Health Organization regulations [3].

4. Conclusions

In this paper, the detection of Pb(II) was carried out on 4-carboxyphenyl grafted SPE functionalized via diazonium reduction. The carboxylate functions of the grafted layer chelate Pb(II) and thus allows a preconcentration of Pb(II) close to the electrode interface. The grafted SPE were able to analyze Pb(II) in nanomolar concentration with good reproducibility and repeatability. The functionalization of surfaces by diazonium salts is a versatile and efficient method. Resulting layers are robust. Ongoing investigations are carried out to identify the nature of the grafted function in order to increase its selectivity and in turn improve the performances of these novel Pb(II) sensors.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.01.021.

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