



Short communication

## Performances of carbon-based screen-printed electrodes modified by diazonium salts with various carboxylic functions for trace metal sensors

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## ABSTRACT

The electrochemically induced functionalization of carbon-based screen-printed-electrodes (SPEs) by phenyl groups, having one or two carboxylic functions, was achieved by reduction of *in situ* generated diazonium salts in aqueous media. The corresponding diazonium cations of 4-aminobenzoic acid, 4-aminophthalic acid, 3-(4-aminophenyl) propionic acid, 3-(4-aminophenyl)-2-propenoic acid and 5-aminoisophthalic acid were generated *in situ* with sodium nitrite in aqueous H<sub>2</sub>SO<sub>4</sub>. The electrochemical detection of Pb(II) with the grafted SPEs was investigated using Pb(II)  $5 \times 10^{-8}$  M solutions. The performances of the grafted SPEs were found to be dependent on the number of carboxylic groups, on their position on the phenyl ring, on the olefinic or the aliphatic character of the chain bearing the carboxylic group. The performances of mono-4-carboxyphenyl and 3,5-dicarboxyphenyl grafted SPEs for Cd(II) and Cu(II) trace detection were tested and compared.

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## 1. Introduction

The discharge of heavy trace metals into the aqueous environment has become a global problem since continuous exposure of organisms to their low concentrations may result in bioaccumulation and transfer to man through the food chain [1]. The usual systems used to monitor the quality of water require on-site sampling followed by analyses carried out in the laboratory using heavy and costly techniques so that a restricted number of tests are generally done. It results that there is currently an urgent need to find on-site and fast solutions to monitor micro-pollutants in water and able to meet the requirements imposed by the standards of the European Water Directive both for drinking and natural waters [2–4].

Electrochemical methods and among them stripping methods are the most suitable for on-site continuous trace analysis as they can be performed using small-size portable devices based on screen-printed electrodes (SPEs) [5,6]. Adsorptive-stripping-voltammetry (ASV), involving the non-Faradaic accumulation of target analytes prior to performing a voltammetric stripping analytical procedure, has been applied to the detection of many chemical species of environmental interest [7–9] and especially of trace metals. This technique allows pushing the limits of quantification [10–12]. Thereafter, functionalization of electrodes by selective groups that bound target species has been developed [13].

Among the grafting methods, electrochemical diazonium salt reduction is currently most commonly used to reach strong covalent modifications. Stable grafted organic layers bearing a wide range of functional groups are obtained by this method on many conductive or semi-conductive surfaces [11–17].

Our previous studies were devoted to the detection of Cu(II), Pb(II) or U(VI) using carbon SPEs functionalized with 4-carboxyphenyl diazonium salt [18–20]. The limits of quantification were respectively  $10^{-8}$ ,  $5 \times 10^{-9}$  and  $2 \times 10^{-9}$  M. The method is based on the adsorption of trace elements by the carboxylate layer followed by their electrochemical detection.

The aim of this paper is to investigate the influence of the carboxylic diazonium salt structure electro-grafted on the SPEs on their analytical performances. The carboxylic groups differ in their number, in their aromatic, aliphatic or olefinic character or in their position on the aromatic ring.

## 2. Experimental

## 2.1. Chemicals and reagents

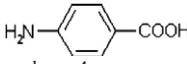
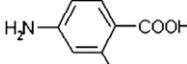
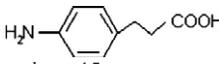
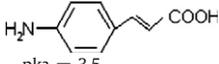
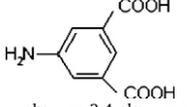
CH<sub>3</sub>COONH<sub>4</sub> (>99%), H<sub>2</sub>SO<sub>4</sub> standard solution (1 M) and HCl (1 M) were purchased from Fluka, 4-aminobenzoic acid, 4-aminophthalic acid, 3-(4-aminophenyl) propionic acid, 3-(4-aminophenyl)-2-propenoic acid and 5-aminoisophthalic acid from Aldrich; suprapur standard solutions (1 g L<sup>-1</sup>) of Pb(NO<sub>3</sub>)<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> from JT Baker, NaNO<sub>2</sub> (suprapur) from Acros Organics. All solutions were prepared with deionized water (18 MΩ cm) from a Millipore milli-Q system.

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**Table 1**

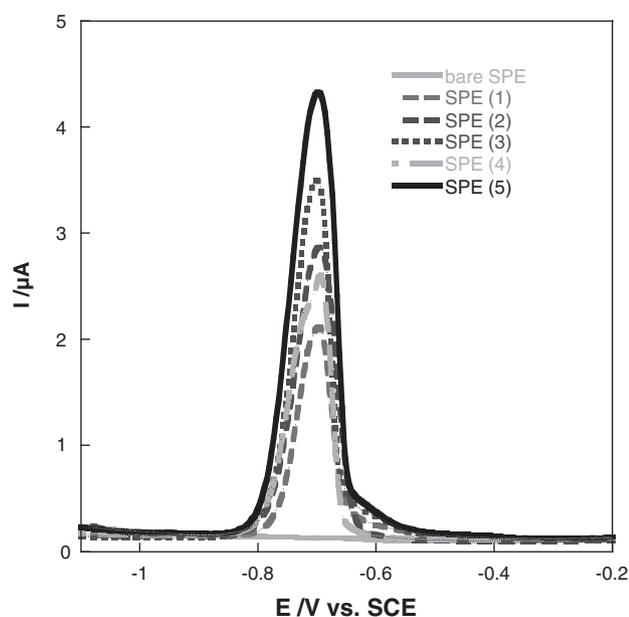
Structure of amines used for *in situ* diazonium salt reduction, reduction potentials of the corresponding diazonium salts ( $E_p$ ) and charges engaged during the reduction ( $Q_{\text{grafting}}$ ) at  $-0.7$  V during 300 s, peak intensities ( $I_p$ ) relative to the Pb signal on SW-ASV voltammograms.

Amine	Grafting				Pb(II) detection
	Corresponding diazonium salt naming	$E_p$ (V/ECS)	$Q_{\text{grafting}}$ ( $\mu\text{C}$ )	Corresponding grafted SPE naming	$I_p$ ( $\mu\text{A}$ )
 $pK_a = 4$ <b>Am (1)</b> : 4-aminobenzoic acid	<b>Diazo (1)</b>	$-0.3$	$23 \pm 5$	<b>SPE(1)</b>	$2.10 \pm 0.06$
 $pK_{a1} = 2.8$ $pK_{a2} = 5$ <b>Am (2)</b> : 4-Aminophthalic acid	<b>Diazo (2)</b>	$-0.4$	$28 \pm 2$	<b>SPE(2)</b>	$2.84 \pm 0.08$
 $pK_a = 4.5$ <b>Am (3)</b> : 3-(4-Aminophenyl) propionic acid	<b>Diazo (3)</b>	$-0.7$	$27 \pm 1$	<b>SPE(3)</b>	$3.23 \pm 0.09$
 $pK_a = 3.5$ <b>Am (4)</b> : 3-(4-Aminophenyl)-2-propenoic acid	<b>Diazo (4)</b>	$-0.4$	$29 \pm 2$	<b>SPE(4)</b>	$2.35 \pm 0.07$
 $pK_{a1} = 3.4$ $pK_{a2} = 4.3$ <b>Am (5)</b> : 5-Aminoisophthalic acid	<b>Diazo (5)</b>	$-0.3$	$25 \pm 4$	<b>SPE(5)</b>	$4.10 \pm 0.1$

## 2.2. Electrode fabrication

Working electrodes were carbon-based screen-printed electrodes (SPEs) and were prepared as described previously [18].

Modification of SPEs by electrochemical reduction of *in situ* generated diazonium salt was achieved according to a method already described in the literature [21]. 400  $\mu\text{L}$  of 0.1 M  $\text{NaNO}_2$  (final concentration of 2 mM) was added to 20 mL of 0.5 M HCl solution containing 2 mM amine, under stirring. The diazonium salt reduction was carried out at  $-0.7$  V/SCE during 300 s.



**Fig. 1.** SW-ASV voltammograms obtained at bare SPE and SPEs grafted with different diazonium salts, in  $5 \times 10^{-8}$  M Pb(II) solution.

## 2.3. Apparatus

All electrochemical methods were performed with an Autolab (low current PGSTAT12, Metrohm) in a classical electrochemical cell with the Pt wire as counter electrode and saturated calomel electrode (SCE) as reference electrode as already mentioned [18–20]. Potentials reported are given with respect to SCE.

## 2.4. Procedure for metal electrochemical analysis

Analysis consisted of an adsorption step (OCP, 5 min, with stirring) in 10 mL of the analysis solution ( $\text{CH}_3\text{COONH}_4$  0.05 M, pH7, M(II)). Electrodes were then rinsed with deionized water before the detection step undertaken in the same buffer free from trace-elements. Adsorbed Cu(II) was analyzed by reduction using square-wave-voltammetry (SWV), (pulse amplitude: 25 mV, step: 4 mV, frequency: 25 Hz) with a potential scan from 0.4 to  $-0.5$  V. Adsorbed Pb(II) or Cd(II) was previously reduced ( $-1.4$  V during 5 s) and SW adsorptive-stripping-voltammetry (ASV) with the same parameters fixed for SWV associated to a potential scan from  $-1.4$  to 0.4 V was then performed. Experiments were conducted in deoxygenated solutions (argon bubbling for 20 min) at room temperature. Each analysis was replicated five times.

## 3. Results

### 3.1. *In situ* SPE grafting

Table 1 describes amines used in this study for *in situ* diazonium salt generation; they bear one or two carboxylic functions linked either directly or indirectly to the phenyl ring via an aliphatic or olefinic substituent chain. The  $pK_a$  of the acidic functions [22] are shown in Table 1. The latter gives also the reduction peak potential ( $E_p$ ) of each diazonium salt deduced from voltammetric curves (not presented here) and the charge engaged in the reduction of the *in situ* generated diazonium salt ( $Q_{\text{grafting}}$ ) at  $-0.7$  V during 300 s. Carboxylic function is electro-donor by inductive effect and electro-withdrawing by mesomeric effect.

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