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Title: Selenocystine modified screen-printed electrode as an alternative sensor for the voltammetric determination of metal ions

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Keywords: chemically modified electrode; electrochemical grafting; metal determination; stripping voltammetry; selenocystine; L-Cystine

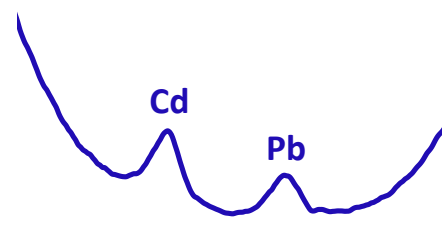
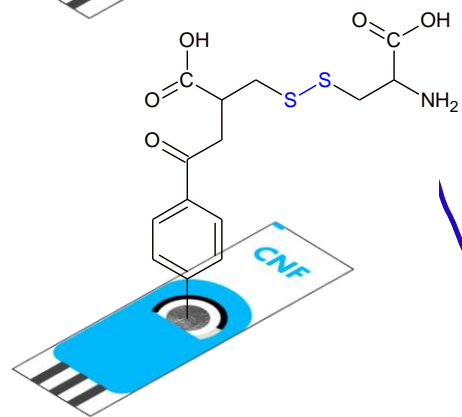
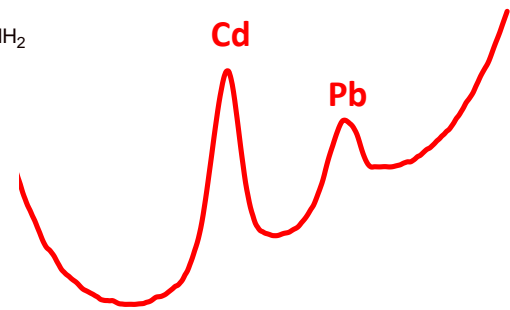
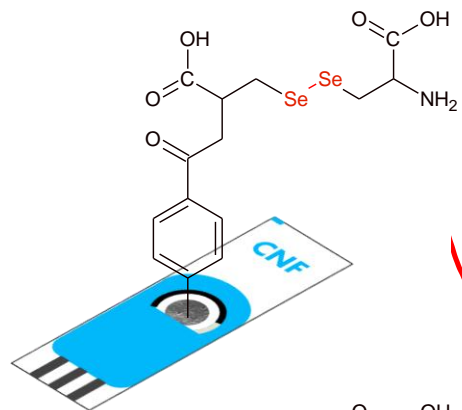
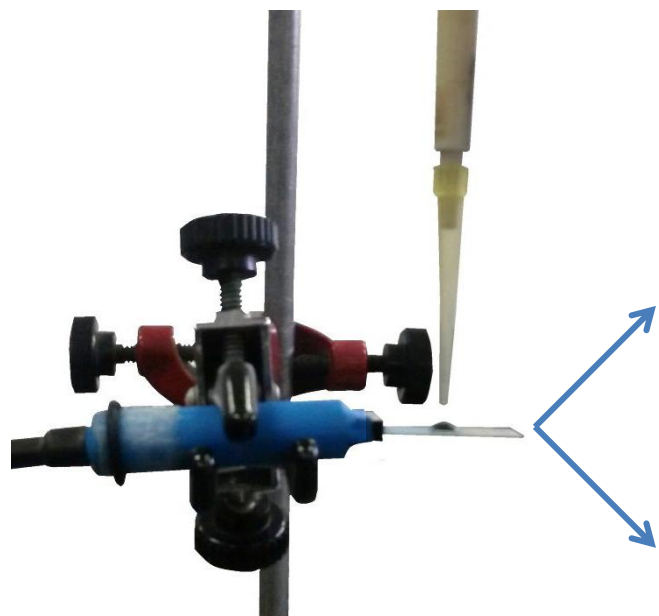
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Abstract: A novel selenium based screen-printed electrode was developed based on the immobilization of selenocystine on aryl diazonium salt monolayers anchored to a carbon-nanofiber screen-printed electrode support (SeCyst-SPCNFE). SeCyst-SPCNFE was analytically compared to a screen-printed carbon nanofiber electrode modified with L-Cystine (Cyst-SPCNFE) for the determination of Pb(II) and Cd(II) by stripping voltammetric techniques. Their analytical performance suggests that SeCyst-SPCNFE could be a much better alternative for metal ion determination at trace levels than Cyst-SPCNFE. The proposed electrode was successfully applied for the simultaneous voltammetric determination of trace Pb(II) and Cd(II) in a wastewater reference material with a very high reproducibility (3.2 %) and good trueness (2.6 %).



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4 **Selenocystine modified screen-printed electrode as an**
5 **alternative sensor for the voltammetric determination of metal**
6 **ions**
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32 **ABSTRACT**
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35 A novel selenium based screen-printed electrode was developed based on the
36 immobilization of selenocystine on aryl diazonium salt monolayers anchored to a carbon-
37 nanofiber screen-printed electrode support (SeCyst-SPCNFE). SeCyst-SPCNFE was
38 analytically compared to a screen-printed carbon nanofiber electrode modified with L-
39 Cystine (Cyst-SPCNFE) for the determination of Pb(II) and Cd(II) by stripping
40 voltammetric techniques. Their analytical performance suggests that SeCyst-SPCNFE
41 could be a much better alternative for metal ion determination at trace levels than Cyst-
42 SPCNFE. The proposed electrode was successfully applied for the simultaneous
43 voltammetric determination of trace Pb(II) and Cd(II) in a wastewater reference material
44 with a very high reproducibility (3.2 %) and good trueness (2.6 %).
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6 stripping voltammetry; selenocystine; L-Cystine
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10 11 **1. INTRODUCTION** 12 13

14 In recent years, there has been an increasing ecological and global public health attention
15 associated with environmental contamination by metal ions. Thus, the determination of
16 trace heavy metals with adverse health effects in human metabolism presents obvious
17 concerns due to their persistence in the environment and documented potential for serious
18 health consequences. Therefore, their non-biodegradability and accumulation in organism
19 demand suitable methods for heavy metal monitoring [1,2]. Stripping voltammetric
20 methods are the most efficient electrochemical techniques for trace and species analysis due
21 to their high sensitivity, selectivity and reproducibility, being also suitable for multimetal
22 ion determination in environmental samples with a relatively low cost [3]. The performance
23 of voltammetry is strongly influenced by the working electrode material. For many years,
24 stripping techniques and, in particular anodic stripping voltammetry (ASV), applied to the
25 determination of trace metal ions were associated with the use of working mercury
26 electrodes due to the extensive cathodic potential range [4]. However, the disposal of the
27 mercury containing device and the incorrect handling can lead to the formation of mercury
28 vapours that as solution of soluble mercury salts are toxic and represent a significant health
29 and environmental hazard. This fact, together with the poor versatility of mercury drops as
30 sensing devices, has led to the search for alternative working electrodes that exhibit an
31 analogous electrochemical behaviour but lower toxicity. Indeed, the development of
32 electrochemical sensors for the detection and quantification of metal ions in natural samples
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4 has paid increasing attention to chemically modified electrodes (CME) based on
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6 environmentally friendly supports and modifiers.
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9 The immobilization procedure is a crucial point in the design of CMEs [5]. In this sense,
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11 the immobilization based on aryl diazonium salt electrografting has proven its benefits in
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13 the development of sensors for metal ion determination [6–8]. This immobilization
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15 procedure is based on two main steps: i) the diazonium salt electrografting which is mainly
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17 dependent on both the support and the substrate of the working electrode; and ii) the
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19 covalent immobilization of the ligand via carbodiimide coupling which is affected by the
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21 selected ligand.
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26 Nowadays, the screen-printing technology is a recognized method for the fabrication of
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28 sensors and biosensors for metal ion determination. Its accessible and low-cost character
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30 permits the production of numerous highly-reproducible single-use screen-printed
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32 electrodes (SPEs). SPEs usually include a working electrode (whose surface can be
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34 modified), a counter electrode and a reference electrode printed on the same strip [9–13].
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38 The commercial availability of screen-printed electrodes (SPE) made of different inks,
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40 including also nanomaterial, has largely expanded the field of application of modified
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42 electrodes as substitutes for mercury.
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45 It is well-known the affinity of peptides to different metal ions due to the great number of
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47 potential donor atoms contained in both the backbone of the peptide and the amino acid
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49 side chains[6,14]. Particularly, in the case of thiol rich peptides, the thiol groups as well as
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51 the carboxylate groups and the amino groups play a key role in this respect [15]. Likewise,
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53 electrochemical studies of selenium-containing compounds revealed that selenium groups
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55 are also involved in the chelation of metal ions [5,14,16,17]. Thus, taking into account the
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57 effectiveness of peptides to interact with a great variety of metal ions, the development and
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4 use of peptide modified electrodes for the determination of metal ions in natural media
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6 constitute an issue of major concern [6,14].
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9 In this paper, we present for the first time the development of a selenocystine modified
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11 sensor via electrografting on a screen-printed carbon-nanofiber substrate (SeCyst-
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13 SPCNFE). This sensor will be applied to the voltammetric determination of Cd(II) and
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15 Pb(II) as a model metal ion system and compared to a sensor modified with L-Cystine
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17 (Cyst-SPCNFE) providing a better analytical performance. Finally, the applicability of
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19 SeCyst-SPCNFE will be tested in a certified wastewater sample.
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26 **2. EXPERIMENTAL**

27 **2.1. Chemicals**

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29 4-aminobenzoic acid (ABA), N-hydroxysulfosuccinimide (sulfo-NHS), selenocystine,
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31 certified reference material: wastewater ERM[®]-CA713, sodium hydroxide and sodium
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33 nitrite were provided by Sigma-Aldrich (St. Louis, MO, USA). L-cystine was acquired from
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35 Fluka, 2-(N-morpholino)ethanesulfonic (MES), potassium ferrocyanide
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37 $K_4[Fe(CN)_6] \cdot 3H_2O$, dimethylformamide (DMF), hydrochloric acid, acetic acid and sodium
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39 acetate were purchased from Merck (Darmstadt, Germany). Potassium ferricyanide
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41 $K_3[Fe(CN)_6]$ and ethanol were supplied by Panreac (Barcelona, Spain). N-(3-
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43 dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) was obtained from
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45 AppliChem (Darmstadt, Germany). All reagents were of analytical grade. 10^{-2} mol L⁻¹
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47 stock solutions of Pb(II) and Cd(II) were prepared from $Pb(NO_3)_2 \cdot 4H_2O$ and
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49 $Cd(NO_3)_2 \cdot 4H_2O$ respectively and standardized complexometrically [18]. Ultrapure water
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51 (Milli-Q plus 185 system, Millipore) was used in all experiments.
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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 electrodes respectively. The working electrodes used were a modified L-Cystine (Cyst-SPCNFE) and selenocystine (SeCyst-SPCNFE) electrodes, which were prepared from carbon nanofibers modified screen-printed electrodes with 4 mm diameter provided by Dropsens (Oviedo, Spain) (ref. 110CNF, DS SPCE).

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 without oxygen removal.

2.3. Procedures

2.3.1. Preparation of modified SPEs

The preparation of peptide modified SPEs was based on a two-step procedure previously described [19] with slight modifications (Figure 1). A carbon nanofiber modified screen-printed electrode (SPCNFE) was considered as a platform for electrode modification, since it has been reported that its much larger effective surface area provides sensors with a better analytical performance [19–21]

2.3.1.1. Diazonium salt electrografting. Aryl diazonium salt was generated *in situ* by adding 0.2 mmol L⁻¹ of sodium nitrite to a cooled ABA 73 mmol L⁻¹ solution in 1 mol L⁻¹ aqueous HCl. The resulting solution was stirred in an ice bath for about 5 min before the electrochemical grafting process was carried out. For this purpose, 10 µL of the solution were dropped onto the surface of the SPCNFE and 10 cyclic voltammetric (CV) cycles from 0 V to -1 V at 0.2 V s⁻¹ were applied. In

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4 order to remove any physisorbed compounds, the functionalized electrodes were thoroughly rinsed
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6 with Milli-Q water.

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8 *2.3.1.2. Covalent immobilization of peptides via carbodiimide coupling.* 10 μL of a 26 mmol L^{-1}
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10 EDC and 35 mmol L^{-1} sulfo-NHS solution in 100 mmol L^{-1} MES buffer (pH 4.5) were dropped onto
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12 the functionalized SPE and left to incubate for 1 h to activate the carboxyl groups of the
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14 electrografted diazonium salt. The activated carboxyl groups reacted overnight at 4 $^{\circ}\text{C}$ with the
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16 amine terminal groups of peptides by adding 10 μL of a 94 mmol L^{-1} of peptide solution in either
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18 ethanol absolute, NaOH 1 mol L^{-1} , HCl 1 mol L^{-1} or DMF 99.8%.
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22 23 **2.3.2. Voltammetric measurements**

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25 In DPASV measurements using Cyst-SPCNFE and SeCyst-SPCNFE, Cd(II) and Pb(II) were
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27 deposited onto the peptide modified SPEs by applying a deposition potential (E_d) of -1.4 V with
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29 stirring the measuring solution during a deposition time (t_d) of 120 s, and followed by a rest period
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31 (t_r) of 5 s. Determinations were performed by scanning the potential from -1.4 to -0.3 V using pulse
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33 times of 50 ms, step potentials of 5 mV and pulse amplitudes of 100 mV.
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37 Linear calibration plots were obtained by increasing metal ion concentrations in 0.1 mol L^{-1} acetate
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39 buffer solution (pH 4.5).
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41 In the analysis of the certified wastewater sample, a volume of the sample was added to a 0.1 mol L^{-1}
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43 1 acetate buffer (pH 4.5). The resulting solution was placed in the cell and the scan was recorded.
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46 Calibration was performed by the standard addition method. Four aliquots of metal standard
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48 solution were added and the respective curves were recorded.
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50 In the analysis of both calibration and certified wastewater samples, a cleaning step was performed
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52 before each set of measurements by applying a conditional potential (E_{cond}) of -0.3 V for 15 s in 0.1
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54 mol L^{-1} HClO_4 .
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3. RESULTS AND DISCUSSION

3.1 Covalent immobilization of cystine and selenocystine

The modification of carbon electrodes with Cyst and SeCyst was based on the aryl diazonium salt electrografting. This modification strategy has been previously reported for the immobilization of several thiols on carbon substrates [5,7,19,22,23] and it usually includes a final step where the thiol is dissolved in MES buffer so it can react with the carboxylic groups previously generated on the electrode surface. However, the poor solubility of Cyst and SeCyst in MES buffer does not allow this last reaction to take place. For this reason, several alternative solvents such as ethanol, hydrochloric acid, sodium hydroxide and dimethylformamide were tested and the performance of the resulting sensors was evaluated for the simultaneous determination of Cd(II) and Pb(II).

Several electrochemical parameters, such as E_d , t_d and pH, were firstly optimized to ensure the detection of both Cd(II) and Pb(II) ions in the selected concentration range. DPASV measurements of a solution containing $50 \mu\text{g L}^{-1}$ of Pb(II) and Cd(II) were carried out at different E_d and t_d values ranging from -1.2 V to -1.5 V and from 30 s to 300 s respectively, looking for a compromise between peak height and analysis time. In all cases, the compromise conditions were an E_d of -1.4 V applied with stirring for 120 s at pH 4.5 (acetate buffer).

Figure 2 shows the voltammograms obtained for a solution containing $100 \mu\text{g L}^{-1}$ Pb(II) and Cd(II) using the resulting SeCyst-SPCNFEs. As it can be observed similar responses, with small and poorly defined peaks, were obtained when SeCyst was dissolved in HCl or NaOH. This poor response could be attributed to the fact that in these media, although

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4 highly soluble, SeCyst is not in its zwitterionic form, which difficult its binding with the
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6 carboxylic groups attached to the electrode surface. Much better defined peaks were
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8 obtained when DMF or ethanol were used and a considerable increase in intensity could be
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10 observed for ethanol, in which SeCyst presented a higher solubility. A similar trend can be
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12 observed when Cyst-SPCNFE is considered. In this case, however, no peaks were observed
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14 for either metal ion using HCl as solvent and the peaks obtained when ethanol was used
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16 were not as intense as the ones obtained with SeCyst-SPCNFE (inset in Figure 2)
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21 Calibration data for the simultaneous determination of Cd(II) and Pb(II) ions using SeCyst-
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23 SPCNFE and Cyst-SPCNFE modified using the four considered solvents are reported in
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25 Table 1. Linear calibration curves were carried out at the optimized conditions by
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27 measuring increasing concentrations of Cd(II) and Pb(II) ranging from 1 to 150 $\mu\text{g L}^{-1}$
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29 (Figure 3). Sensitivities were calculated as the slope of the calibration curve and limits of
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31 detection (LOD) and quantification (LOQ) as 3 and 10 times, respectively, the standard
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33 deviation of the intercept over the slope of the calibration curve. The LOQ was considered
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35 as the lowest value of the linear concentration range. Again, an improvement of the sensors
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37 performance, inferred by the higher sensitivity and the lower LODs, can be observed when
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39 the peptides are dissolved in ethanol. This improvement is particularly high in the case of
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41 SeCyst-SPCNFE. Therefore, ethanol was selected as the optimal solvent for the covalent
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43 immobilization of both Cyst and SeCyst to the carbon electrode surface.
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53 **3.2 Influence of the chosen ligand**

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55 Once the solvent for the covalent immobilization of Cyst and SeCyst was optimized, the
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57 analytical performance of SeCyst-SPCNFE and Cyst-SPCNFE for the simultaneous
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4 determination of Pb(II) and Cd(II) as model metal ions was compared in terms of
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6 repeatability, reproducibility, sensitivity, linear range and LODs.
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9 In order to study the repeatability and reproducibility of SeCyst-SPCNFE and Cyst-
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11 SPCNFE, DPASV measurements of a solution containing $65 \mu\text{g L}^{-1}$ of Cd(II) and Pb(II) in
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13 acetate buffer pH 4.5 were carried out. Repeatability, estimated from 15 repetitive
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15 measurements with the same SeCyst-SPCNFE modified electrode, yielded a RSD% of
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17 6.5% and 9.4% for Cd(II) and Pb(II) respectively whereas Cyst-SPCNFE yielded a RSD%
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19 of 27.4% and 34.9% for Cd(II) and Pb(II) respectively. Reproducibility was calculated
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21 within a series of 10 repetitive measurements from two modified electrodes and yielded a
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23 RSD% of 11.1% for Cd(II) and 9.1% for Pb(II) and 28.5% for Cd(II) and 34.1% for Pb(II)
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25 for SeCyst-SPCNFE and Cyst-SPCNFE respectively. Although both repeatability and
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27 reproducibility are rather poor in the case of Cyst-SPCNFE, SeCyst-SPCNFE presents
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29 good values that are similar to repeatability and reproducibility values previously reported
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31 for electrodes modified with thiols [7,19,22] or crown ethers [8,24] following a similar
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33 strategy. On the other hand, the durability of the SeCyst immobilization on every
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35 screen-printed platform for a large set of measurements (more than 20) without loss of
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37 sensitivity enables the voltammetric determination of metal ions with the same SeCyst-
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39 SPCNFE unit.
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48 The evolution of Cd(II) and Pb(II) ions signals with simultaneously increasing
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50 concentrations using SeCyst-SPCNFE and Cyst-SPCNFE can be observed in Figure 3a and
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52 3b respectively. In all cases, well-defined peaks without splitting were obtained.
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54 Sensitivities, linear ranges and LODs for both SeCyst-SPCNFE and Cyst-SPCNFE are
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56 reported in Table 1. As it can be observed, good linear responses were obtained up to 150
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58 $\mu\text{g L}^{-1}$ in all cases. On the other hand, both electrodes are more sensitive to Cd(II) than
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4 Pb(II) and SeCyst-SPCNFE provides higher sensitivities than Cyst-SPCNFE for both metal
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6 ions. A possible explanation of these facts could be found in the Hard Soft Acid Base
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8 (HSAB) theory of Pearson [25]. In this sense, both selenides and sulfides are considered
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10 soft bases, with selenides being softer, whereas Cd(II) is a soft acid and Pb(II) is borderline.
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12 According to this theory, in which soft bases have more affinity with soft acids, Cd(II)
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14 would react better than Pb(II) and selenides would be more reactive than sulfides.
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18 Good LODs, which allow the detection of both Pb(II) and Cd(II) below the legal limits of
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20 drinking water (10 and 5 $\mu\text{g L}^{-1}$ respectively) [26], were achieved using SeCyst-SPCNFE.
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22 In the case of Cyst-SPCNFE however, slightly higher LODs were obtained and the LOD
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24 for Cd(II) does not allow its detection below the legal limits. The LODs achieved with
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26 SeCyst-SPCNFE are also similar to those reported for Cd(II) and Pb(II) with carbon
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28 electrodes modified following a similar strategy with thiols [7,19,22,23] or crown ethers [8]
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30 (between 1.5 and 3.3 $\mu\text{g L}^{-1}$ for Pb(II) and 1.96 and 4.7 $\mu\text{g L}^{-1}$ for Cd(II)), with antimony
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32 [27], bismuth [28] or mercury [9] films deposited on carbon screen printed electrodes
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34 (between 0.03 and 10 $\mu\text{g L}^{-1}$ for Pb(II) and 0.2 and 8 $\mu\text{g L}^{-1}$ for Cd(II)), with carbon
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36 nanomaterial based electrodes [29] (between 1 and 20.7 $\mu\text{g L}^{-1}$ for Pb(II) and 0.001 and 2.8
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38 $\mu\text{g L}^{-1}$ for Cd(II)) or with metal nanoparticles based electrodes [29] (between 0.2 and 4.9
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40 $\mu\text{g L}^{-1}$ for Pb(II) and 0.9 and 4.9 $\mu\text{g L}^{-1}$ for Cd(II)).
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48 Therefore, the better analytical performance, especially in terms of sensitivity, repeatability
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50 and reproducibility, achieved by SeCyst-SPCNFE, suggest that the immobilization of
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52 selenium based ligands onto carbon electrodes could be much better alternative for the
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54 determination of trace heavy metals ions.
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58 Furthermore, the different analytical response achieved with SeCyst-SPCNFE in
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60 comparison to the one obtained with Cyst-SPCNFE hints that carbon electrodes modified
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4 with selenium based ligands could also be combined with other types of sensors (metal film
5 electrodes, nanomaterial based- electrodes, thiol or crown-ethers modified electrodes...) for
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7 the development of new voltammetric electronic tongues applied to the resolution of
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9 complex metal mixtures.
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15 **3.2 Application to the analysis of a residual water reference material**

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18 At the view of the above results, given the better repeatability and reproducibility, the
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20 higher sensitivity and the lower LODs provided by SeCyst-SPCNFE, this electrode was
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22 selected as a better option to study its applicability for the simultaneous determination of
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24 trace Pb(II) and Cd(II) in a wastewater reference material (ERM[®] - CA713) by means of
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26 the standard addition method. It should be pointed out though, that since Cd(II)
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28 concentration in this available reference material was below the LOQ, only Pb(II) could be
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30 determined. Thus, DPASV measurements using the above optimized conditions were
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32 carried out including four additions of Pb(II). Representative voltammograms obtained in
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34 the analysis of the wastewater samples using SeCyst-SPCNFE are shown in Figure 4a. As it
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36 can be observed, Pb(II) behaves in a similar way to that observed in the calibration
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38 samples. Also, as it can be observed in Figure 4b, a good correlation of the representative
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40 stripping measurements was observed for Pb(II). It should be mentioned that the presence
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42 of other metal ions in the reference material such as As, Cr, Cu, Fe, Hg, Mn, Ni or Se does
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44 not seem to interfere in the Pb(II) determination.
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53 The obtained metal concentration data from three replicates of the certified wastewater
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55 material using SeCyst-SPCNFE are reported in Table 2. As it can be observed, a good
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57 concordance between the Pb(II) concentrations from the three replicates, as well as with the
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59 certified metal value, was obtained. These good results confirm the applicability of SeCyst-
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4 SPCNFE for the determination of Pb(II) in the presence of Cd(II) in natural samples.
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6 Therefore, the use of selenium based sensors for the determination of trace metal ions can
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8 be a valuable alternative to other ligands like thiols or crown ethers, since they provide a
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10 distinctive response that could be really useful in the development of new voltammetric
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12 electronic tongues.
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15 16 17 18 **4. CONCLUSIONS** 19

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22 In this work, the possibility of using selenium based sensors for the determination of trace
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24 metal ions was studied through the development of a selenocystine modified screen-printed
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26 carbon nanofiber electrode (SeCyst-SPCNFE) and its application to the simultaneous
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28 voltammetric determination of Pb(II) and Cd(II) as a model system. Furthermore, the
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30 performance of the resulting sensor was compared to that of an electrode modified with
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32 cystine (Cyst-SPCNFE).
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36 First of all, the solvent used for the covalent immobilization of both ligands was optimized
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38 and, out of all the solvent tested, the best results were achieved using ethanol. In
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40 comparison with Cyst-SPCNFE, SeCyst-SPCNFE provided better repeatability and
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42 reproducibility as well as higher sensitivities and lower LODs. These good results
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44 demonstrate that selenium based sensors can be successfully used for metal ion
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46 determination as an alternative to more conventional thiol rich peptide modified electrodes.
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48 Moreover, the distinctive response provided by SeCyst-SPCNFE compared to Cyst-
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50 SPCNFE, makes selenium based sensors good candidates to be included in voltammetric
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52 electronic tongues applied to the resolution of complex metal mixtures.
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4 Finally, the applicability of SeCyst-SPCNFE for the analysis of real samples was
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6 successfully proven by the determination of Pb(II) in a certified wastewater reference
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8 materials, in which good reproducibility and high trueness inferred by the low relative
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10 standard deviation (3.2%) and relative error (2.6%) were achieved.
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22 grant.
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Table 1. Calibration data for the simultaneous determination of Pb(II) and Cd(II) on Cyst-SPCNFEs and SeCyst-SPCNFEs modified using different solvents. DPASV were carried out at E_d of -1.4 V, t_d 120 s and pH 4.5.

	Cyst-SPCNFE		SeCyst-SPCNFE	
	Cd(II)	Pb(II)	Cd(II)	Pb(II)
EtOH absolute				
Sensitivity (nA μg^{-1} L)	14.2 (0.3)	7.6 (0.1)	32.4 (0.4)	14.3 (0.2)
R^2	0.997	0.999	0.999	0.999
Linear range ($\mu\text{g L}^{-1}$)	19.1 – 150.0	15.1 – 150.0	10.7 – 150.0	10.8 – 150.0
LOD ($\mu\text{g L}^{-1}$)	5.7	4.5	3.2	3.2
HCl 1 mol L⁻¹				
Sensitivity (nA μg^{-1} L)	---	---	4.8 (0.2)	2.8 (0.1)
R^2	---	---	0.995	0.996
Linear range ($\mu\text{g L}^{-1}$)	---	---	46.7 – 150.0	37.9 – 150.0
LOD ($\mu\text{g L}^{-1}$)	---	---	14.0	11.4
DMF 99.8%				
Sensitivity (nA μg^{-1} L)	10.2 (0.5)	7.0 (0.3)	6.1 (0.2)	3.05 (0.09)
R^2	0.994	0.992	0.997	0.996
Linear range ($\mu\text{g L}^{-1}$)	49.2 – 150.0	45.3 – 150.0	29.9 – 150.0	31.2 – 150.0
LOD ($\mu\text{g L}^{-1}$)	14.7	13.6	9.0	9.4
NaOH 1 mol L⁻¹				
Sensitivity (nA μg^{-1} L)	8.3 (0.4)	3.6 (0.2)	4.8 (0.1)	3.84 (0.09)
R^2	0.993	0.993	0.996	0.998
Linear range ($\mu\text{g L}^{-1}$)	51.8 – 150.0	43.4 – 150.0	30.8 – 150.0	25.1 – 150.0
LOD ($\mu\text{g L}^{-1}$)	15.5	13.0	9.2	7.5

Table 2 Total concentrations of Pb(II) and Cd(II) determined in certified wastewater (ERM[®]- CA713) by stripping voltammetry on SeCyst-SPCNFE by standard addition calibration method applying an E_d of -1.4 V and t_d of 120 s at pH 4.5

	Lead (II)			Cadmium (II)	
	c ($\mu\text{g L}^{-1}$)	RSD (%)	Relative error (%)	c ($\mu\text{g L}^{-1}$)	RSD (%)
SeCyst-SPCNFE	51.0	3.2	2.6	n.q.	—
Certified metal value	49.7	3.4	—	5.09	3.9

n=3 for RSD (%); n.q. not quantified.

Caption to figures

Figure 1. Scheme of the preparation of SeCyst-SPCNFE and Cyst-SPCNFE by electrochemical grafting.

Figure 2. DPASV measurements of $100 \mu\text{g L}^{-1}$ Pb(II) and Cd(II) at pH 4.5 and applying an E_d of -1.4 V and t_d of 120 s on SeCyst-SPCNFE modified using NaOH, HCl, ethanol and DMF. Inset: Comparison of the performance of SeCyst-SPCNFE and Cyst-SPCNFE modified with ethanol.

Figure 3. Stripping voltammetric measurements of increasing concentrations of Pb(II) and Cd(II) ranging from 1 to $150 \mu\text{g L}^{-1}$ on SeCyst-SPCNFE (a) and Cyst-SPCNFE (b) at pH 4.5 applying an E_d of -1.4 V and t_d of 120 s.

Figure 4. a) Stripping voltammetric measurements in a wastewater sample by using a SeCyst-SPCNFE at pH 4.5 with E_d of -1.4 V during a t_d of 120 s; and, b) Pb(II) standard addition plot.

Figure 1

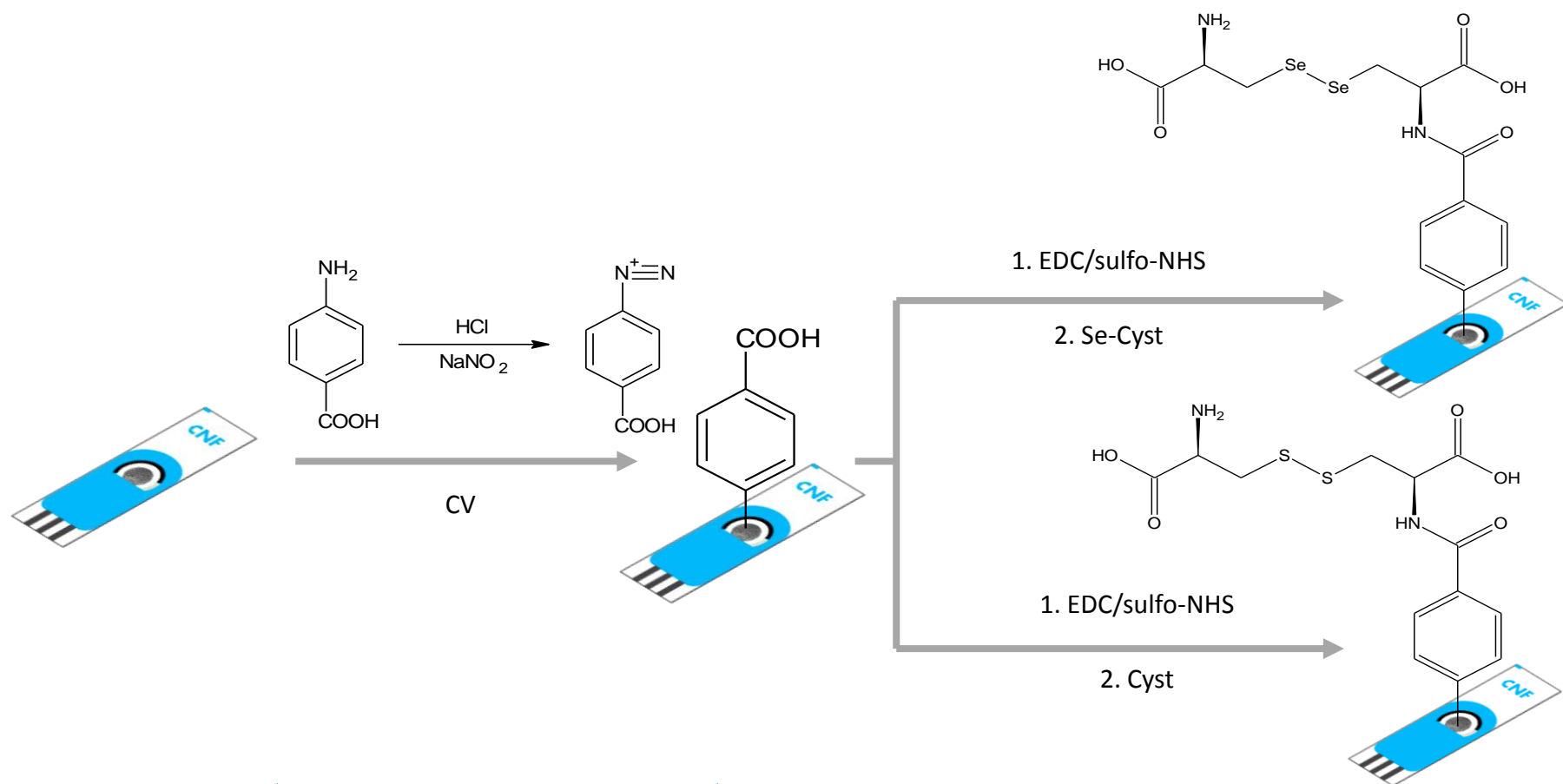


Figure 2

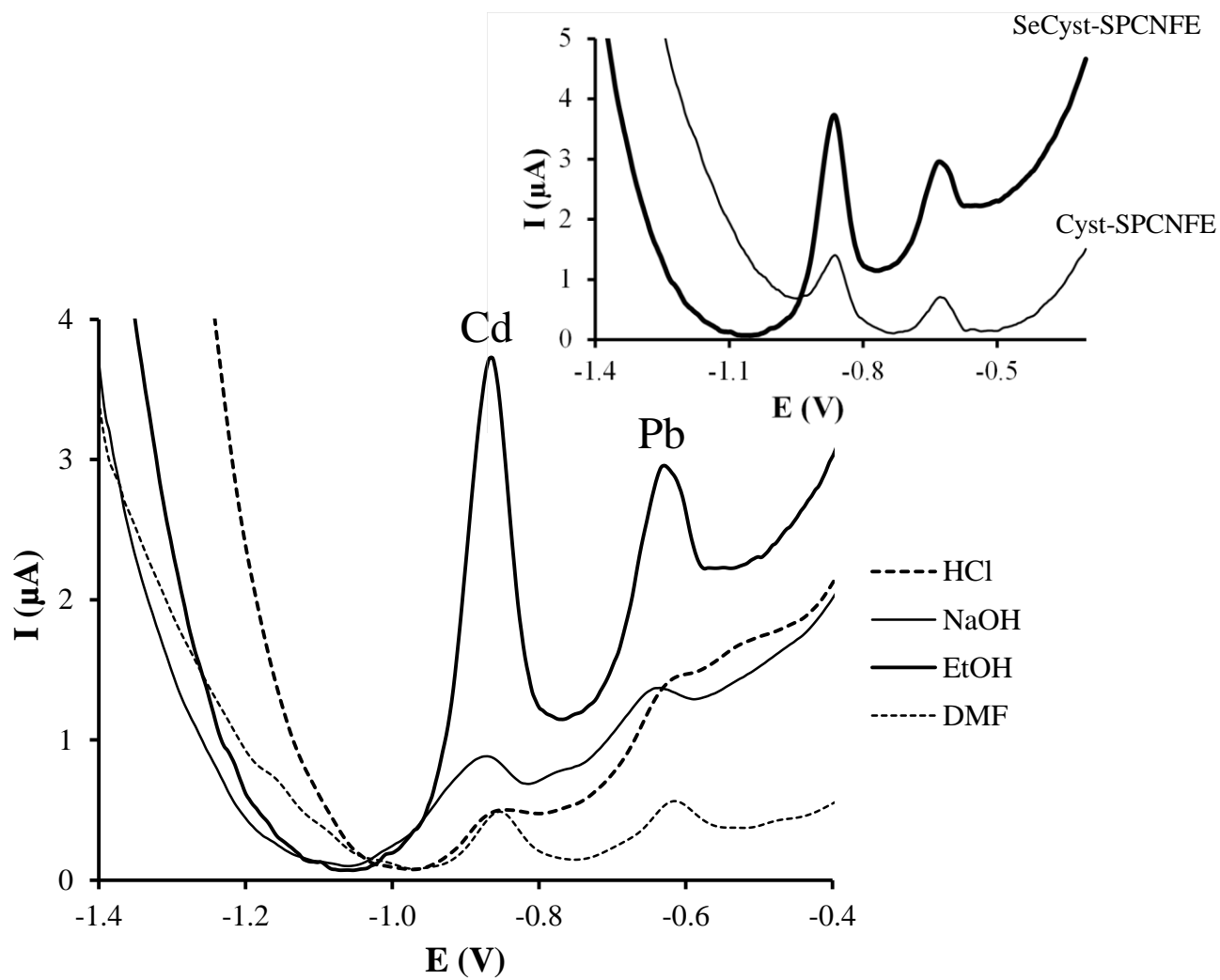


Figure 3

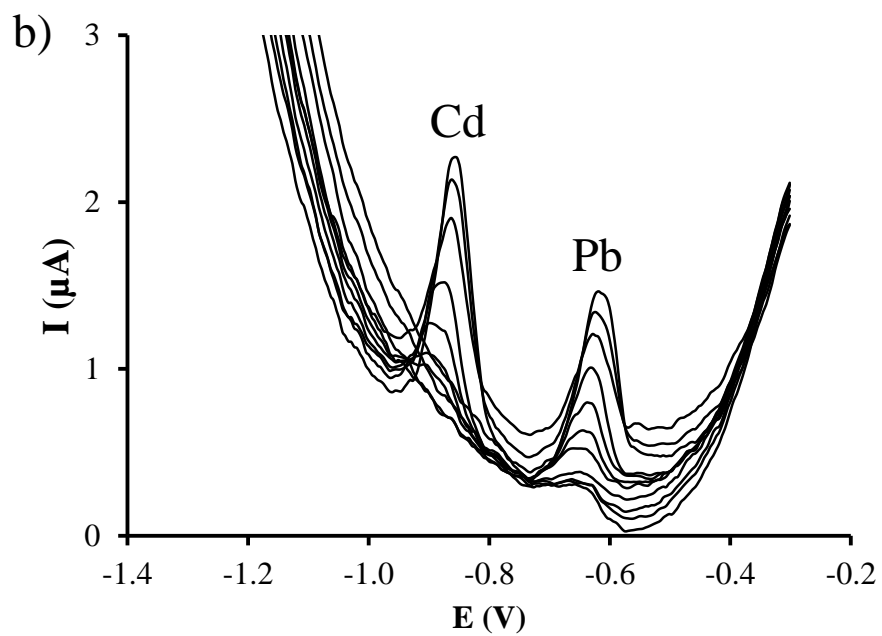
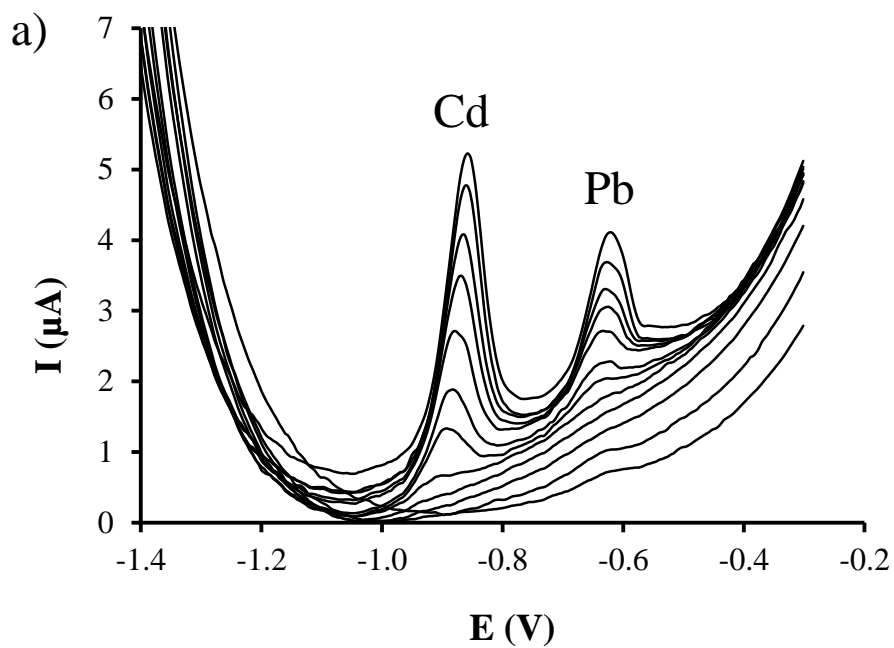


Figure 4

