# Disposable screen-printed electrode modified with bismuth–PSS composites as high sensitive sensor for cadmium and lead determination

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Abstract: Bismuth was incorporated in screen-printed carbon electrodes (SPCEs) modified with polystyrene sulfonate (PSS) and carbon nanopowder (CnP) composites. Different strategies, based on bulk approaches using bismuth oxide particles and bismuth (III) solutions, were assayed. The features of the modified electrodes were evaluated by differential pulse anodic stripping voltammetry (DPASV) of Pb(II) and Cd(II) solutions. The best results were obtained when bismuth was incorporated as bismuth oxide particles during the preparation of the PSS–CnP aqueous suspension used to modify the electrodes. Using this optimal modified sensor, the DPASV measurement conditions for Pb(II) and Cd(II) determination were optimized and their figures of merit were evaluated. Mea- surements were performed using two experimental approaches: the "drop method", by putting the test solution on the surface of the modified SPCE, and the "immersion method" performed by immersing the device in a stirred test solution. The limits of detection (S/N = 3) were 0.27 µg L−1 ($1.3 \times 10^{-9}$ M) for Pb(II) and 0.10 µg L−1 ($9.0 \times 10^{-10}$ M) for Cd(II), using the "drop method", and 0.029 µg L−1 ($1.4 \times 10^{-10}$ M) for Pb(II) and 0.012 µg L−1 ($1.1 \times 10^{-10}$ M) for Cd(II) employing the immersion procedure. The optimal bismuth modified SPCE was used for Pb(II) and Cd(II) determination in natural water samples with successful results.

Keywords: Bismuth bulk modified electrodes Screen-printed electrode, Polystyrene sulfonate composites, Differential pulse anodic stripping voltammetry (DPASV), Cd(II) and Pb(II) determination

## 1. Introduction

The presence of toxic elements, such as Cd(II) and Pb(II), in the environment is of particular concern due to their adverse effects on ecosystems and human health [1,2]. Pollution by these metals has been increasing in the environment and therefore international organisms have established guidelines and quality standards in drinking-water to protect public health [3,4].

Electrochemical techniques can be used for heavy metal determination and, contrary to the most used atomic methodologies, they are portable, low-cost and suitable for *in situ* and real-time analysis [5]. Anodic Stripping Voltammetry (ASV) presents adequate sensitivity for trace heavy metal analysis [6]. In spite of mercury toxicity, mercury electrodes have been traditionally employed for ASV measurements due to their high reproducibility [7]. Bismuth is one of the most used materials to replace mercury-based electrodes due to its environmental-friendly characteristics and its ability to form "fused alloys" with heavy metals [8]. The use of these electrochemical devices for Cd(II) or Pb(II) determination essentially involves formation of a bismuth film onto the electrode surface which is usually performed in three different ways, *ex situ*, *in situ* and *in bulk* [9–12]. In the *ex situ* approach, electroplating of the electrode surface with bismuth is carried out in a Bi(III) solution prior to the introduction of the electrode into the sample solution containing the analyte to perform the measurement. In the *in situ* methodology, an adequate volume of a Bi(III) solution is directly added into the sample solution, and the analyte is accumulated on the electrode surface at the same time that the bismuth film is formed. In the *in bulk* method, different chemical forms of bismuth are incorporated as a modifier of the electrode surface and the bismuth film is formed from these precursors during the measurement process. For instance, bismuth powder [13], bismuth nanostructures [14], bismuth nanoparticles [15], bismuth compounds as $Bi_2O_3$ or $(BiO)_2CO_3$ [16–18] and bismuth salts, as $Bi(NO_3)_3$ or $NH_4BiF_4$ [19–20], have been used as modifiers to develop sensitive sensors for heavy metals. Disposable screen-printed electrodes (SPEs) have been used as platforms to develop bismuth modified devices, employing *ex situ*, *in situ* or *in bulk* modification approaches [12,21–31], taking advantage of the interesting characteristics of SPEs such as their low cost and versatile and easy modification.

In our research group, we have developed composite materials based on polystyrene sulfonate (PSS) as transducers for electrochemical sensors [32]. PSS is a water-soluble polymer in which the negative charged sulfonate groups allow interaction with cationic species, as metal ions, by an ion-exchange mechanism [33]. This property has been exploited in electrochemical methods for heavy metals analysis, using PSS as a coating of the working electrode to favour the metal ions accumulation and as an anti-fouling agent to avoid interference from surfactants or organic matter [34–36]. Sensors based on PSS–carbon nanopowder (CnP) composites maintain the ion-exchange

properties of this polymer and present excellent characteristics for the determination of metals such as Cu(II) [37]. The ion-exchange mechanisms can also be used to incorporate additional components in the PSS composite. In this way, we have introduced $Ni^{2+}$ in a PSS–CnP composite to prepare electrochemical transducers for mercury sensing [38]. Moreover, PSS is a good dispersant of nanomaterials and therefore it is possible to prepare PSS composite materials for sensing purposes in which, in addition to the nanocarbon material, solids such as metal oxides are incorporated to get an adequate analytical performance. For instance, we have proposed a sensor based on a PSS–CnP–NiO composite for fragrance allergens detection [39].

Electrodes based on PSS composites could be modified with bismuth to get sensors with adequate characteristics for ASV metal ions determination. To our knowledge, there are only two bismuth modified sensors reported based on PSS–carbon nanomaterial composites, using carbon nanotubes [40] and graphene [41], respectively. In both cases, a bismuth film was deposited on the electrode surface by an *in situ* procedure.

In the present work, we have evaluated the analytical performance of screen-printed electrodes (SPEs) modified with PSS–CnP composites in which bismuth was introduced by means of three *in bulk* procedures. It was incorporated in the PSS–CnP membrane as $Bi^{3+}$ by an ion-exchange mechanism or it was introduced in the PSS–CnP dispersion used to modify SPCE as bismuth nitrate solution or $Bi_2O_3$ particles. In a previous paper, we have assayed different procedures for the synthesis of $Bi_2O_3$ and carried out preliminary voltammetric studies using the $Bi_2O_3$ particles obtained as modifiers of electrodes. From these studies, it was deduced that the monoclinic $\alpha$-$Bi_2O_3$ phase obtained by sonochemical synthesis route at 30 °C presented the best characteristics to be used as electrode modifier [42]. These $Bi_2O_3$ particles are the bismuth compound employed in one of the *in bulk* modification procedures assayed in the present paper. The features for Cd(II) and Pb(II) determination by differential pulse anodic stripping voltammetry (DPASV) on the bismuth modified electrodes, using the three assayed procedures, have been evaluated. The optimal bismuth modified electrode was used for DPASV determination of Cd(II) and Pb(II) in natural water samples.

## 2. Experimental

### 2.1. Reagents

All chemicals were of analytical grade, purchased from Sigma-Aldrich and used without further purification. Ultrapure water (resistivity ≥ 18.2 MΩ cm at 25 °C, Ultra Clear TWF UV EDI, Siemens) was used to prepare all aqueous solutions. Bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$, was used to synthesize bismuth oxide particles and prepare Bi(III) solutions. PSS aqueous solutions were prepared from poly (sodium-4-styrene-sulfonate) powder (average $M_W$ 70 000) in ultrapure water. CnP (particle size b 50 nm) were used to prepare the PSS–carbon suspensions. Working stock solutions of Cd(II) and Pb(II) were prepared from 1000 mg $L^{-1}$ atomic absorption standard solutions. Acetate buffer solution (0.2 mol $L^{-1}$, pH 4.5) was used as supporting electrolyte in the voltammetric measurements.

### 2.2. Instruments

Electrochemical measurements were performed using the μSTAT 400 bipotentiostat (DropSens) controlled by the Drop-View software. A specific connector (model DRP-DSC, Drop-Sens) was used to connect SPEs to bipotentiostat.

The morphology of modified working electrode surfaces was studied by Scanning Electron Microscopy (SEM)−Energy-dispersive X-ray spectroscopy (EDX) analysis, using the scanning electron microscope Hitachi S-3000N equipped with an Oxford Instruments X-ray analyser, model INCAx-sight.

An Elmasonic P30H model ultrasonic bath was used to synthesize $Bi_2O_3$ particles and prepare PSS–CnP suspensions.

### 2.3. Preparation of modified electrodes

#### 2.3.1. PSS–CnP modified electrodes

Modified electrochemical sensors were prepared using commercial SPCEs (DRP110D, DropSens) as substrate. These commercial devices consisted of a ceramic substrate strip (3.4 × 1.0 × 0.05 cm) with the electrodes over it. The working (4 mm diameter) and the counter electrodes were made of carbon, whereas the pseudo-reference electrode and the electric contacts were made of silver.

Working electrodes of commercial SPCEs were coated with PSS–CnP composites by micropipette assisted deposition of 4 μL of PSS–CnP aqueous suspension. Homogeneous and stable PSS–CnP coating suspensions (3 wt% in PSS and 0.3 wt% of CnP) were prepared by mixing proper amounts of CnP and PSS with ultrapure water under ultrasonic agitation for 10 min at 80 MHz. These PSS–CnP composite modified SPCEs (hereafter named as PSS–CnP–SPE) were dried overnight at 30 °C.

#### 2.3.2. In bulk bismuth-modified electrodes

Bismuth incorporation in PSS–CnP–SPE was performed by three *in bulk* modification methodologies.

In the first one, Bi(III) was incorporated by an ion-exchange process in the sulfonate groups of the PSS–CnP membrane. In the other two procedures, $Bi_2O_3$ particles or Bi(III) nitrate solution were incorporated during PSS–CnP aqueous suspension preparation. In the ion-exchange method (sensor hereafter named as BiCE–SPE), PSS–CnP–SPEs were immersed in 250 mL of a 100 mg $L^{-1}$ Bi(III) solution for five hours under mechanical stirring at 500 rpm.

Incorporation of bismuth as solid $Bi_2O_3$ was performed by the addition of monoclinic $\alpha$-$Bi_2O_3$ particles in the PSS–CnP aqueous suspension. These particles were synthesized according to our previously optimized sonochemical method [42]. In short, synthesis was carried out by heating, at 30 °C under ultrasonic stirring at 80 MHz and 100 W for 60 min, a mixture of Bi(III) nitrate and Tween 85® with a 4 M NaOH solution. The obtained particles were isolated by centrifugation, rinsed successively with ultrapure water and ethanol and dried out at 60 °C. These $\alpha$-$Bi_2O_3$ particles were incorporated in the PSS–CnP aqueous suspension to form the PSS–CnP–$Bi_2O_3$ suspension (3 wt% PSS, 0.3 wt% $Bi_2O_3$ and 0.3 wt% CnP) used to modify commercial SPCEs by deposition of 4 μL on the working electrode. These electrodes (hereafter named as BiOxP–SPE) were dried overnight at 30 °C.

In the third *in bulk* method assayed, adequate amounts of CnP and PSS were weighted, suspended in 1.0 mL of ultrapure water and mixed with 2.0 mL of $Bi(NO_3)_3 \cdot 5H_2O$ solution, containing 500 mg $L^{-1}$ of Bi(III) in 0.5 M $HNO_3$. Then, 1 M NaOH solution was added dropwise into this suspension until a neutral pH value was achieved. Finally, it was made up to 10.0 mL with ultrapure water to obtain a 3 wt% PSS, 0.3 wt% CnP and 100 mg $L^{-1}$ Bi(III) suspension. The working electrode of SPCEs was modified by deposition of 4 μL of this suspension onto its surface. These electrodes (hereafter named as $Bi^{3+}$–SPE) were dried overnight at 30 °C.

### 2.4. Electrochemical measurements

Analytical performance of bismuth modified screen-printed devices was evaluated by DPASV of Cd(II) and Pb(II) stock solutions. For comparison, Bi(III) oxide modified screen-printed carbon electrodes from DropSens, Ref. DPR-110BI (hereafter named as C−BiOx−SPE) were also used.

For the DPASV measurement, the bismuth film formation in all assayed electrodes was performed simultaneously to Cd and Pb electrodeposition. For this purpose, 180 μL of Cd(II) and Pb(II) solution in acetate buffer were placed onto the electrodes and a potential of −1.2 V was applied for 420 s. After that, the reoxidation sweep from −1.2 V
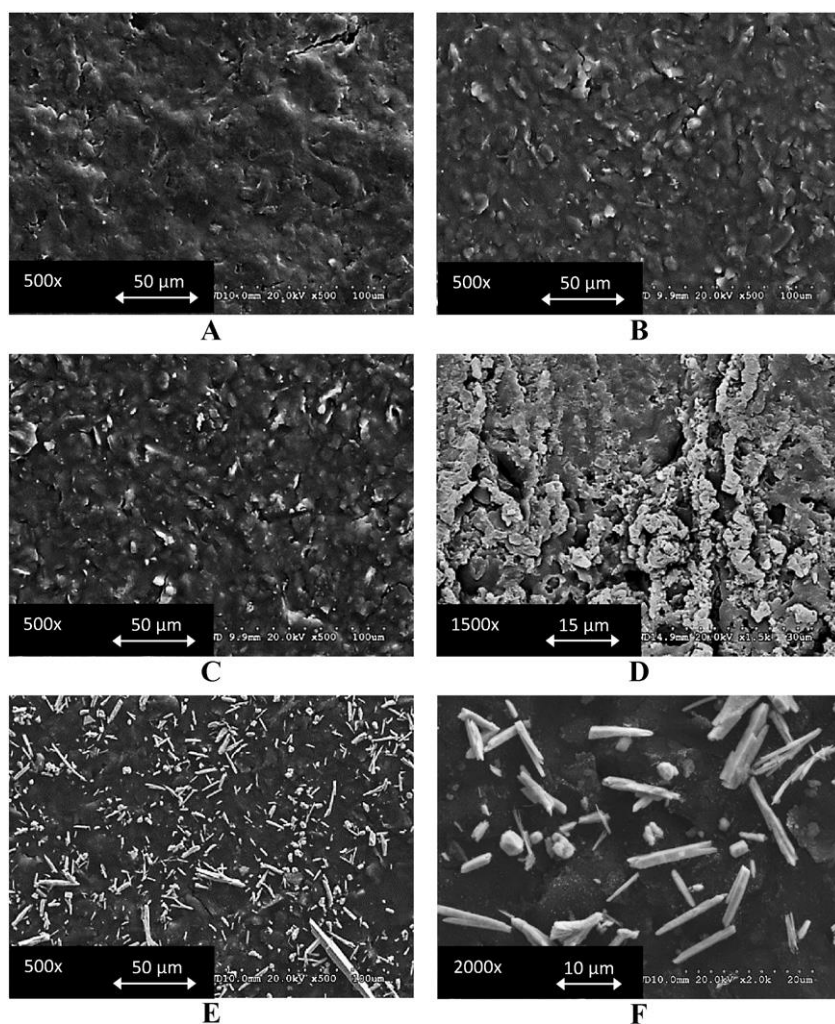
Fig. 1. SEM images of the working electrode surface of PSS−CnP−SPE (A), C−BiOx−SPE (B), BiCE−SPE (C), Bi³⁺−SPE (D) and BiOxP−SPE (E and F) devices.

to 0.2 V was performed at 50 mV s⁻¹ scan rate, 2 mV potential step, 5 ms pulse time and 100 mV pulse amplitude. All measurements were carried out at room temperature using 0.2 mol L⁻¹ acetic acid−sodium acetate buffer solution at pH 4.5 as supporting electrolyte.

For the C−BiOx−SPE, to obtain the best results in heavy metal detection, the manufacturer recommends the bismuth oxide electrochemical reduction to bismuth before starting to work with it, employing as pre-treatment conditions a reduction potential of −1.2 V in 0.1 M KOH. Electrochemical signals for Pb(II) and Cd(II) on these commercial devices were compared when bismuth film formation was performed by following this procedure or using the procedure indicated above for the *in bulk* bismuth-modified electrodes prepared in this work, that is based on bismuth film formation simultaneously to Cd and Pb electrodeposition. Given that voltammetric responses obtained were similar employing both approaches and for a better comparison of all bismuth-based screen-printed devices, the procedure herein proposed (−1.2 V in 0.2 mol L⁻¹ acetate buffer) was also applied for the commercial devices.

All reported potential values in this work are referenced to the Ag pseudo-reference electrode of the commercial screen-printed devices.

## 3. Results and discussion

### 3.1. Morphological characterization of bismuth modified electrode surface

The surface of the working electrode of bismuth modified screen-printed devices was characterized by SEM. Fig. 1 shows the SEM images

of BiCE−SPE, BiOxP−SPE and Bi³⁺−SPE modified electrodes and the images of the non-containing bismuth PSS−CnP−SPE and the commercial C−BiOx−SPE. As can be observed in Fig. 1, C−BiOx−SPE and PSS−CnP−SPE present a homogeneous and quite smooth surface. The surface appearance of BiCE−SPE, C−BiOx−SPE and PSS−CnP−SPE devices was similar, although more fissures were observed in the surface of BiCE−SPE probably due to a slight deterioration of the composite membrane caused during the bismuth incorporation process. The Bi³⁺−SPE showed the most heterogeneous surface with a lot of fissures and holes that can be attributed to salt deposits formed during the drying step of the device, after the bismuth incorporation process. The BiOxP−SPE surface presented the appearance of a smooth membrane with a homogeneous distribution of bismuth oxide particles. According to these findings, preliminary inferences could be drawn about the possible analytical performance of these bismuth modified devices. A priori, those electrodes with a more homogeneous surface that can be easily reproduced, as BiOxP−SPE, would be the best candidates as electrochemical sensors. The surface of the electrodes will be heterogeneous and scarcely reproducible when holes and fissures are formed easily (as it was observed for Bi³⁺−SPEs) and therefore these devices will be the least suitable electrodes for the DPASV measurements.

### 3.2. Comparison of electrochemical features of bismuth modified electrodes

In order to select the electrode with the best analytical features, sets of at least three SPCEs were modified according to each of the assayed

bismuth incorporation procedures and the electrochemical responses of Cd(II) and Pb(II) on the bismuth modified electrodes were evaluated by DPASV. A volume of 180 µL of a solution containing Cd(II) and Pb(II) in 0.2 mol L$^{-1}$ acetate buffer was placed onto the surface of the modified SPE covering the three electrodes. DPASV measurements were performed by applying a deposition potential of −1.2 V for 420 s. Fig. 2A shows the DPASV voltammograms obtained on the different bismuth modified electrodes for a solution containing 4 µg L$^{-1}$ ($3.8 \times 10^{-8}$ M) of Cd(II) and 4 µg L$^{-1}$ ($1.9 \times 10^{-8}$ M) of Pb(II). As can be seen, responses for BiOxP−SPE and BiCE−SPE devices were more sensitive than those observed for the C−BiOx−SPE commercial device. In addition, among the non-commercials devices, the worst response was obtained for the Bi$^{3+}$−SPE.

Bismuth content in the electrode surface was evaluated from the peak areas of the bismuth reoxidation signal for each bismuth-modified device used in this work. As can be seen in Fig. 2B, C—BiOx−SPE and BiOxP−SPE devices present higher bismuth contents and a better reproducibility of peak area values than those observed for BiCE−SPE and Bi$^{3+}$−SPE. From these data and the voltammetric signals for Cd(II) and Pb(II) on each device (Fig. 2A) it could be deduced that the sensitivity of voltammetric responses does not depend directly on the bismuth content in the electrode surface. On the other hand, the bismuth film formation process during the reduction step and the thickness of this film have an influence on voltammetric signals of Cd(II) and Pb(II). High bismuth content can result in an increase of the film thickness and a more difficult reoxidation of metals and accordingly a decrease of the voltammetric signals could be observed [21,43,44].

The differences in sensitivity of the voltammetric responses on the bismuth modified electrodes proposed in this work and the commercial bismuth-based device could be explained by taking into account the electrode composition and the modification mode. As it was indicated in the introduction, sulfonic groups of PSS present in the composite membrane could favour accumulation of metal ions on electrode surface and therefore, an increase in DPASV peak currents should be observed on electrodes modified with PSS composites [37]. Voltammograms obtained for a solution containing Cd(II) and Pb(II) on a commercial SPCE and a modified PSS−CnP−SPE are shown in Fig. 3. An increase in Cd(II) and Pb(II) voltammetric signals can be observed for the device modified with the PSS composite. This effect can be appreciated when voltammetric signals on BiOxP−SPE and BiCE−SPE are compared to those obtained on the commercial C−BiOx−SPE (Fig. 2A). The presence of PSS in BiOxP−SPE and BiCE−SPE produces an increase in the voltammetric signals for Cd(II) and Pb(II). However, Cd(II) and Pb(II) peak currents on Bi$^{3+}$−SPE are similar to those obtained on the C−BiOx−SPE although Bi$^{3+}$−SPE is also a device based on a PSS composite. This fact could be attributed to the bismuth incorporation process in Bi$^{3+}$−SPE. The salt deposits formed in the drying process could produce that part of the composite material was separated from the electrode surface and therefore, there could be lesser amount of available PSS for the interaction with metal ions in this device than in BiOxP−SPE and BiCE−SPE.

The reproducibility of voltammetric responses for Pb(II) and Cd(II) strongly depended on the procedure performed for bismuth-modified electrode preparation. Relative standard deviation values (RSD) were obtained from the voltammetric measurements of a solution containing Cd(II) and Pb(II) in acetate buffer carried out on different electrodes (n = 3) for each modification procedure. The lowest RSD values (about 7%) were obtained with the BiOxP−SPE. The reproducibility for this device was similar or even better than the calculated value from measurements performed with C−BiOx−SPE (RSD values about 10%). The RSD values were about 30% for BiCE−SPE. The worst reproducibility of voltammetric responses was shown on the Bi$^{3+}$−SPE with RSD values higher than 45% for both metals. These differences in reproducibility values could be related to the surface morphology observed in the SEM studies and to the variability of the amount of bismuth available on the electrode surface (Fig. 2B). The surface of BiOxP−SPE was homogeneous, whereas holes and fissures were observed on BiCE−SPE surface and unstable amounts of salt deposit were shown on Bi$^{3+}$−SPE surface. According to these results, the addition of α-Bi$_2$O$_3$ particles in the PSS−CnP suspensions can be considered as the best procedure to incorporate bismuth in the modified electrodes. For this reason, the BiOxP−SPE was selected as the most adequate bismuth modified electrode for Cd(II)
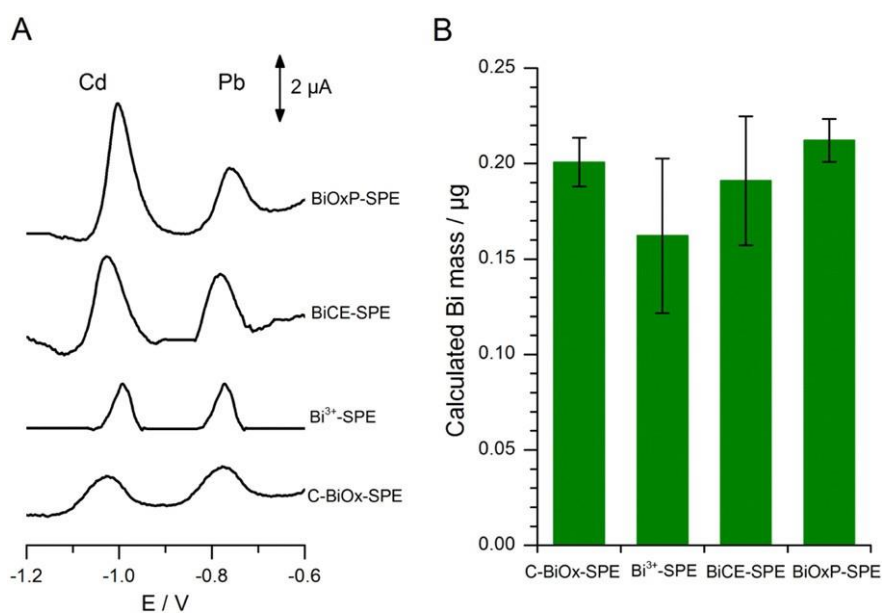


Fig. 2. (A) DPASV voltammograms for a solution containing 4.0 µg L$^{-1}$ ($3.8 \times 10^{-8}$ M) of Cd(II) and 4 µg L$^{-1}$ ($1.9 \times 10^{-8}$ M) of Pb(II) in 0.2 M acetate buffer at pH 4.5 on the bismuth modified electrodes. Conditions: −1.2 V deposition potential for 420 s and reoxidation sweep from −1.2 V to −0.6 V at 100 mV s$^{-1}$ scan rate, 2 mV potential step, 40 ms pulse time and 50 mV pulse amplitude. Measurements were carried out by adding 180 µL of the solution onto the electrodes. (B) Calculated masses of bismuth of the modified SPE.
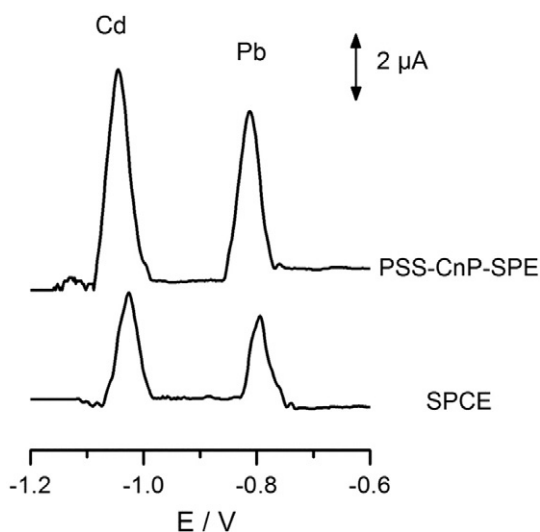
Fig. 3. DPASV voltammograms for a solution containing 40 μg L$^{-1}$ (3.8 × 10$^{-7}$ M) of Cd(II) and 40 μg L$^{-1}$ (1.9 × 10$^{-7}$ M) of Pb(II) in 0.2 M acetate buffer at pH 4.5 on the commercial SPCE and on the PSS–CnP–SPE device. Experimental conditions as in Fig. 2.

and Pb(II) determination and all subsequent studies were carried out with this sensor device.

To evaluate the influence of Bi$_2$O$_3$ content in the composite on the voltammetric responses obtained on BiOxP–SPE, sets of modified electrodes (n = 3) were prepared using PSS–CnP–Bi$_2$O$_3$ suspensions containing 0.15, 0.3 and 0.6 wt% of α-Bi$_2$O$_3$ particles. DPASV measurements for a solution containing Cd(II) and Pb(II) were carried out using the BiOxP–SPE sensors with the different percentages of Bi$_2$O$_3$. The bismuth mass on the electrode surface was calculated from the peak area of bismuth reoxidation signal. As can be expected, an increase in bismuth mass was obtained as the amount of Bi$_2$O$_3$ in the composite was increased (Fig. 4) and non-significant differences in RSD values (between 2.8 and 3.3%, n = 3) were observed for the percentages of bismuth oxide particles assayed. This indicated that PSS–CnP–Bi$_2$O$_3$ suspensions are sufficiently homogeneous and stable to get good reproducibility in sensor preparation. Regarding the influence of bismuth
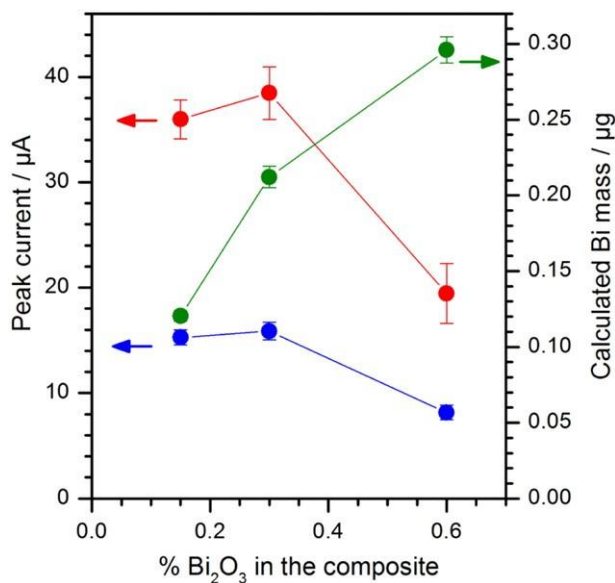


Fig. 4. Influence of Bi$_2$O$_3$ percentage in the composite on the bismuth mass on the electrode surface (●) and on the peak currents for Cd(II) (●) and Pb(II) (●) obtained from DPASV measurements for a solution containing 40 μg L$^{-1}$ (3.8 × 10$^{-7}$ M) of Cd(II) and 40 μg L$^{-1}$ (1.9 × 10$^{-7}$ M) of Pb(II) in 0.2 M acetate buffer at pH 4.5 on BiOxP–SPE devices. Experimental conditions as in Fig. 2.

amount on voltammetric signals for Cd(II) and Pb(II) (Fig. 4), similar peak currents were obtained on bismuth devices that contain up to 0.3% Bi$_2$O$_3$. A noticeable diminution in peak currents was observed on electrodes modified with bismuth amount higher than 0.3% Bi$_2$O$_3$ in the PSS–CnP–Bi$_2$O$_3$ suspension. In previous studies reported in the bibliography, this behaviour has been attributed to a decrease in the conductivity of the electrode surface at high percentages of Bi$_2$O$_3$ [19,21]. This diminution in peak current of Cd(II) and Pb(II) has been also attributed to mass transfer limitations in the metal diffusion out of bismuth film during the stripping step, because high Bi$_2$O$_3$ percentages in the electrode provide a great thickening of the bismuth film formed in the reduction step [43,45,46]. According to these results, a 0.3 wt% of α-Bi$_2$O$_3$ was selected as optimal to prepare the modified BiOxP–SPE devices and to carry out the optimization of the method for Cd(II) and Pb(II) determination.

### 3.3. Conditions for Cd(II) and Pb(II) determination

An acetate buffer at pH 4.5 was used as supporting electrolyte [41, 47–52]. The concentration of supporting electrolyte was optimized by DPASV measurements of a solution containing 40 μg L$^{-1}$ (3.8 × 10$^{-7}$ M) of Cd(II) and 40 μg L$^{-1}$ (1.9 × 10$^{-7}$ M) of Pb(II) in 4.5 pH acetate buffer solution. The peak currents for cadmium and lead increased as the concentration of the supporting electrolyte was risen up to 0.2 M acetate buffer concentration. For electrolyte concentrations higher than 0.2 M, a diminution of the peak currents for both metals was observed. This fact could be due to the accumulation of metal ions is favoured by an ion-exchange process on the active sites of PSS on the electrode surface, but in solutions with a high electrolyte concentration, a competition is produced between sodium ions and cadmium and lead ions for the PSS active sites of the electrode surface and consequently the voltammetric signals diminish [32]. According to these results, a 0.2 M acetate buffer at pH 4.5, was selected as the optimal supporting electrolyte solution.

In order to choose an adequate value of deposition potential, both stability of PSS membranes and required potential values for effective Cd(II) and Pb(II) reduction were considered. In previous studies [32] we have observed that PSS–CnP membranes can be used in a working potential window between − 1.2 V and + 1.0 V. Deterioration and even rupture of the PSS membrane were observed at potential values lower than −1.2 V, so this potential value was selected as deposition potential. The deposition time was evaluated from DPASV signals for a solution containing 40 μg L$^{-1}$ (3.8 × 10$^{-7}$ M) of Cd(II) and 40 μg L$^{-1}$ (1.9 × 10$^{-7}$ M) of Pb(II) in acetate buffer at pH 4.5. A deposition potential of −1.2 V was applied for 120, 300 and 420 s. A pronounced increase in peak currents was observed when the deposition time was increased from 120 to 300 s, whereas this increase was only very slight when the deposition time was increased from 300 to 420 s. This behaviour could indicate that the saturation of electrode surface is achieved for deposition times longer than 420 s at these experimental conditions. In order to perform voltammetric measurements with high sensitivity and using not very long measurement times, a deposition time of 420 s was chosen as the optimal value.

DPV parameters were also optimized to obtain well-defined DPASV signals with high and narrow peaks. The best results were obtained using 50 mV s$^{-1}$ of scan rate, a 2 mV of step potential, 5 ms of pulse time, and 100 mV of pulse amplitude.

### 3.4. Calibration and analytical parameters

The calibration curves for Cd(II) and Pb(II) determination were obtained using the BiOxP–SPE sensor under two experimental procedures. In the first one, the DPASV measurements were carried out by putting 180 μL of the test solution onto the surface of the BiOxP–SPE. In the second procedure, the BiOxP–SPE was immersed in 25.0 mL of the assayed solution under stirring at 800 rpm in the deposition step. The
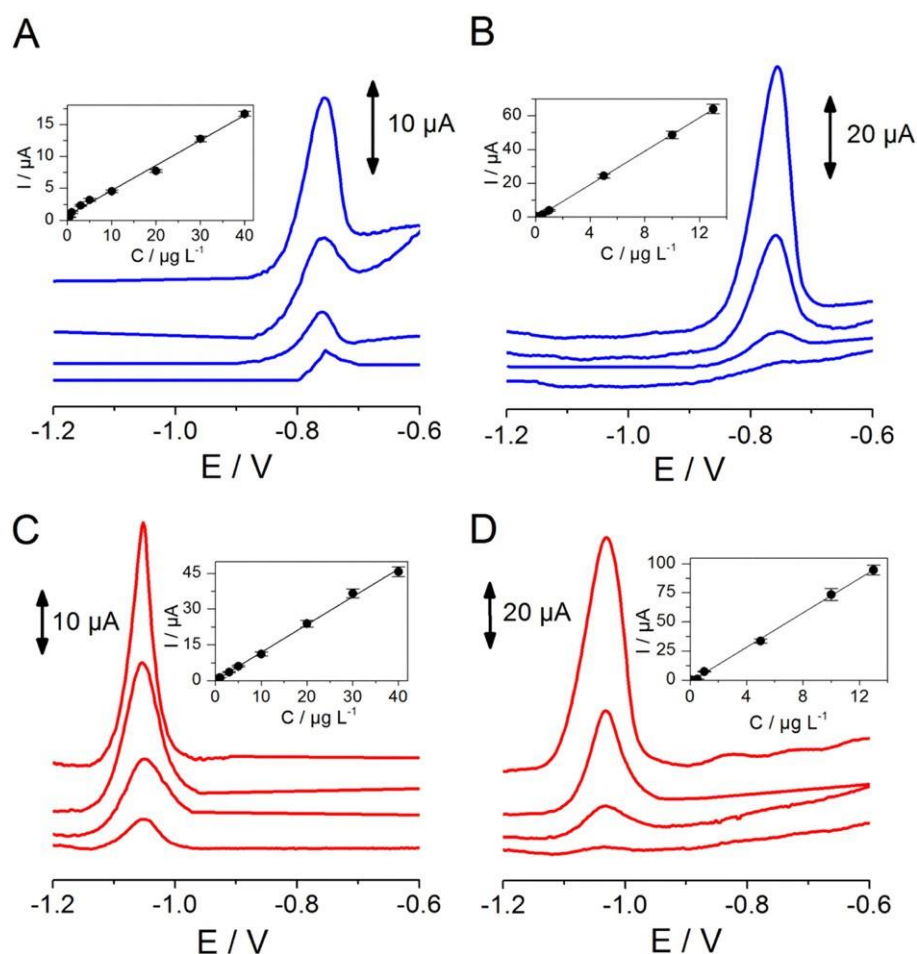
**Fig. 5.** DPASV voltammograms and calibration plots obtained using the "drop on sensor" method (A and C) in 5.0, 10.0, 20.0 and 40.0 μg L$^{-1}$ (2.4 × 10$^{-8}$, 4.8 × 10$^{-8}$, 9.6 × 10$^{-8}$ and 1.9 × 10$^{-7}$ M) Pb(II) solution (A) or 5.0, 10.0, 20.0 and 40.0 μg L$^{-1}$ (4.5 × 10$^{-8}$, 9.0 × 10$^{-8}$, 1.8 × 10$^{-7}$ and 3.6 × 10$^{-7}$ M) Cd(II) solution (C) and the "sensor immersion" method (B and D) in 0.5, 1.0, 5.0 and 10.0 μg L$^{-1}$ (2.4 × 10$^{-9}$, 4.8 × 10$^{-9}$, 2.4 × 10$^{-8}$ and 4.8 × 10$^{-8}$ M) Pb(II) solution (B) or 0.5, 1.0, 5.0 and 10.0 μg L$^{-1}$ (4.5 × 10$^{-9}$, 9.0 × 10$^{-9}$, 4.5 × 10$^{-8}$ and 9.0 × 10$^{-8}$ M) Cd(II) solution (D). Measurement conditions: in 0.2 mol L$^{-1}$ acetate buffer at pH 4.5; −1.2 V deposition potential and reoxidation sweep from −1.2 V to −0.6 V at 50 mV s$^{-1}$ scan rate, 2 mV potential step, 5 ms pulse time and 100 mV pulse amplitude.

voltammograms for different Pb(II) and Cd(II) concentrations using both procedures are shown in Fig. 5.

The principal analytical figures of merit obtained for Pb(II) and Cd(II) determination using both procedures are shown in Table 1. The upper limit of the linear range was graphically calculated as the concentration at which the deviation from the ideal linearity plot is greater than 5% (±5% window around the ideal linearity plot) [53]. The limits of detection (LOD) were calculated using a signal-to-noise ratio of 3:1 from the standard deviation of the peak current for a Pb(II) or Cd(II) standard solution with concentration close to the limit of detection. The limits of quantification (LOQ) were similarly calculated using a signal-to-noise ratio of 10:1. The reproducibility was calculated using relative standard deviation of Pb(II) or Cd(II) DPASV signals obtained with different electrodes on different days.

The LODs and LOQs obtained for both metals with the sensor immersion procedure (0.029 μg L$^{-1}$ or 1.4 × 10$^{-10}$ M for Pb(II) and 0.012 μg L$^{-1}$ or 1.1 × 10$^{-10}$ M for Cd(II)) were about one order of magnitude lower than those calculated for the drop on sensor method (0.27 μg L$^{-1}$ or 1.3 × 10$^{-9}$ M for Pb(II) and 0.10 μg L$^{-1}$ or 9.0 × 10$^{-10}$ M for Cd(II)). The upper limits of the linear range calculated for the drop on sensor method were higher than for the sensor immersion method. These results can be explained considering that, in the drop on sensor procedure, metal ions reach the electrode surface by diffusion from the bulk of the drop, whereas in the sensor immersion method the mass transport of Pb(II) or Cd(II) takes place by convection, from the stirred solution to the electrode surface. In this second method, the mass transport is faster and more efficient, so higher amounts of metal ion than those for the drop method can be accumulated in a

Table 1
Figures of merit for Pb(II) and Cd(II) DPASV determination using the BiOxP–SPE.

| Measurement procedure | LOD[a], μg L$^{-1}$ | | LOQ[b], μg L$^{-1}$ | | Sensitivity, μAL μg$^{-1}$ | | UELR[c], μg L$^{-1}$ | | R$^2$ | | Reproducibility RSD, %[d] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cd(II) | Pb(II) | Cd(II) | Pb(II) | Cd(II) | Pb(II) | Cd(II) | Pb(II) | Cd(II) | Pb(II) | Cd(II) | Pb(II) |
| Drop | 0.10 | 0.27 | 0.35 | 0.91 | 1.17 | 0.39 | 45 | 45 | 0.9978 | 0.9928 | 7.2 | 5.6 |
| Immersion | 0.012 | 0.029 | 0.043 | 0.098 | 7.39 | 4.95 | 15 | 15 | 0.9986 | 0.9997 | 6.9 | 5.8 |

[a] LOD: limit of detection.
[b] LOQ: limit of quantification.
[c] UELR: upper end of linear range.
[d] Metal ion concentration 10 μg L$^{-1}$ (n = 3).

Table 2

Comparison of different ASV methods for determination of Cd(II) and Pb(II) using bismuth-based screen-printed electrodes.

| Electrode material | Technique[a] | Measurement procedure | UELR µg L⁻¹ | | LOD µg L⁻¹ | | Deposition time, s | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | Pb | Cd | Pb | Cd | | |
| SPE−CNT *in situ* bismuth plating | SWASV | Immersion | 100 | 100 | 1.3 | 0.7 | 300 | [23] |
| SPE−MWCNTs−Nafion *ex situ* bismuth plating | SWASV | Immersion | 8 | 8 | 0.2 | 0.2 | 120 | [31] |
| SPE−Bi$_2$O$_3$ paste on GC paste | SWASV | Immersion | 100 | 100 | 2.3 | 1.5 | 300 | [25] |
| SPCE−Bi nanoparticles | SWASV | Immersion | n.i. | n.i. | 1.7 | 1.3 | 120 | [24] |
| SPE−Bi nanopowder−Nafion on carbon surface | SWASV | Immersion | 60 | 60 | 0.16 | 0.09 | 600 | [54] |
| SPE−Bi$_2$O$_3$−graphite-ink | DPASV | Immersion | 300 | − | 20 | − | 120 | [26] |
| SPE−Graphene−PSS. Bi *in situ* deposition | DPASV | Immersion | 120 | 120 | 0.089 | 0.042 | 120 | [41] |
| SPE−Bi sputtered film[b] | DPASV | Immersion | 19.8 | 12.3 | 0.16 | 0.10 | 360 | [52] |
| SPE−Bi$_2$Q [c] | DPASV | Immersion | 12 | 9 | 0.16 | 0.10 | 45 | [52] |
| SPE−Bi sputtered film[b] | DPASV | Immersion | 16.9 | 10.6 | 0.18 | 0.10 | 360 | [27] |
| SPE-reduced GO on ionic liquid-graphite ink. Bi *in situ* deposition | SWASV | Immersion | 80 | 80 | 0.10 | 0.08 | 120 | [51] |
| SPE−Bi$_2$O$_3$ (Bi spark discharge on graphite) | SWASV | Immersion | 12 | 12 | 0.2 | 0.2 | 120 | [29] |
| SPE−Bi nanoribons deposition on SPCE | SWASV | Immersion | 50 | 50 | 0.104 | 0.145 | 200 | [30] |
| SPCE−Bi$_2$O$_3$−PSS−CnP membrane | DPASV | Immersion | 15 | 15 | 0.03 | 0.01 | 420 | This work |
| SPE−Bi$_2$O$_3$−graphite carbon ink | CCSCP | Drop | 300 | 300 | 8.0 | 16 | 120 | [21] |
| SPCE−Bi$_2$O$_3$−PSS−CnP membrane | DPASV | Drop | 45 | 45 | 0.3 | 0.1 | 420 | This work |

n.i.: not indicated in the paper.

[a] DPASV: differential pulse anodic stripping voltammetry; SWASV: Square wave anodic stripping voltammetry; CCSCP: constant current stripping chronopotentiometry.

[b] Commercial device.

[c] Commercial device denoted as C−BiOx−SPE.

short time. For the same deposition time, the saturation of the electrode surface in the sensor immersion procedure is achieved with Cd(II) or Pb(II) concentrations lower than those to achieve the electrode saturation using the drop on sensor method. Good linearity of calibration graphs (values of correlation coefficients close to 1) and reproducibility values (less than 7.2%) were obtained for Pb(II) and Cd(II) using both methods.

Some features of Pb(II) and Cd(II) determination using the BiOxP−SPE are compared in Table 2 to those of other ASV methodologies published in the last years for the determination of these metals using bismuth-based screen-printed electrodes. The analytical characteristics of both BiOxP−SPE sensor methods have been also compared with those obtained for other electrodes modified with bismuth (Table S1 in Supplementary Information). As can be seen in Table 2 (and Table S1), the methodologies developed in this work present excellent characteristics. Using the BiOxP−SPE in the immersion procedure, the LOD values are lower than the reported ones for other SPE even when some of them employ longer deposition times [54] than the proposed device in this work. Employing the drop procedure, the here reported LOD values are lower, about one order of magnitude, than those obtained for other bismuth modified SPEs using this measurement procedure.

## 3.5. Interference study

The interference study was performed by adding various potentially interfering ions at different concentrations into a standard solution containing 20 µg L⁻¹ (9.6 × 10⁻⁸ M) Pb(II) and 20 µg L⁻¹ (1.8 × 10⁻⁷ M) Cd(II) in 0.2 M acetate buffer at pH 4.5. The interfering ions were added up to a foreign ion to analyte µg L⁻¹ concentration ratio of 100:1. The results from these studies are presented in Table 3. In this table, interfering ion to Pb(II) or Cd(II) molar concentration ratio are also included. No significant modification (peak current values into the RSD for this concentration level) of the voltammetric responses for Cd(II) and Pb(II) was observed when the following ions were in excess: Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Fe$^{3+}$, NO$_3^-$, and SO$_4^{2-}$. A slight variation of the expected peak current values for Cd(II) and Pb(II) was observed in the presence of phosphate ions at 100:1 µg L⁻¹ concentration ratio. The voltammetric signals for Pb(II) and Cd(II) were significantly reduced when Cu(II) was in the test solution even at 1:1 µg L⁻¹ concentration ratio. This influence of copper on the stripping responses on bismuth electrodes has been usually reported. This effect has been attributed to

the competition between electrodeposited bismuth and copper for surface sites on the electrode [8] as well as the formation of intermetallic compounds between copper and metal ions [11,22,25,54]. The interfering effect of copper can be significantly reduced, even avoided, by adding ferrocyanide ions into the test solution to complex with Cu(II) [22,55].

The influence of Cd(II) on Pb(II) response and *vice versa* was evaluated in solutions containing a constant concentration of one metal ion (10 µg L⁻¹) and increasing concentrations of the other one (up to 20 µg L⁻¹). Interference of Cd(II) on Pb(II) determination was not observed at any of the assayed concentrations. Therefore, no significant modification of peak current values for Pb(II) was observed in the presence of Cd(II) ions at a 2:1 µg L⁻¹ concentration ratio (3.69:1 M concentration ratio). However, a diminution in peak current of Cd(II) was observed as Pb(II) concentration was increased. For the same concentration (10 µg L⁻¹) of both metal ions (1:1 µg L⁻¹ concentration ratio or 0.54:1 M concentration ratio) the voltammetric signal of Cd(II) diminished about 20% compared to that obtained in the absence of Pb(II). This interfering effect has been reported in other papers that deal with simultaneous ASV determination of Cd(II) and Pb(II) [50].

Table 3

Relative signals obtained with BiOxP−SPE for Cd(II) and Pb(II) in the presence and absence of foreign ions. Concentrations of Cd(II) 20 µg L⁻¹ (1.8 × 10⁻⁷ M) and Pb(II) 20 µg L⁻¹ (9.6 × 10⁻⁸ M). Deposition time: 420 s.

| Interfering ion | µg L⁻¹ concentration ratio[a] | Molar concentration ratio[a] | | Relative signal[b] | |
|---|---|---|---|---|---|
| | | Cd(II) | Pb(II) | Cd(II) | Pb(II) |
| Na$^+$ | 100 | 489 | 901 | 0.99 | 0.98 |
| K$^+$ | 100 | 288 | 530 | 1.01 | 1.01 |
| Ca$^{2+}$ | 100 | 280 | 517 | 1.04 | 1.05 |
| Mg$^{2+}$ | 100 | 463 | 853 | 1.00 | 1.02 |
| Cu$^{2+}$ | 1 | 1.77 | 3.26 | 0.58 | 0.74 |
| Fe$^{3+}$ | 100 | 201 | 371 | 0.95 | 1.07 |
| NO$_3^-$ | 100 | 181 | 334 | 0.96 | 0.98 |
| SO$_4^{2-}$ | 100 | 117 | 216 | 1.01 | 1.00 |
| PO$_4^{3-}$ | 100 | 118 | 218 | 0.87 | 0.88 |

[a] Calculated as ratio between foreign ion concentration and analyte concentration.

[b] Expressed as ratio between peak currents for the metal in the presence and in the absence of the foreign ion.

**Table 4**
Results for Cd(II) and Pb(II) determination in real water samples.

| Sample | Cd(II) concentration, µg L$^{-1}$ | | | | Pb(II) concentration, µg L$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|
| | Present | Added | Found[a] | Recovery % | Present | Added | Found[a] | Recovery % |
| Mineral water | bLOD | 1.0 | 0.97 ± 0.05 | 97 ± 5 | bLOD | 1.0 | 0.96 ± 0.05 | 96 ± 5 |
| River water | bLOD | 1.0 | 0.97 ± 0.03 | 97 ± 3 | bLOD | 1.0 | 1.08 ± 0.09 | 108 ± 9 |

[a] Average values ± standard deviation (n = 3).

### 3.6. Application

The BiOxP–SPE was used to determine Pb(II) and Cd(II) in a commercial mineral water with a low mineralization (Bezoya, trademark, Spain) and a natural water sample from headed Manzanares River in Madrid (Spain). For this purpose, 5.0 mL of 1.0 mol L$^{-1}$ acetate buffer at pH 4.5 were added to 20.0 mL of the water sample and the DPASV measurement was performed by the immersion method previously described. Cd(II) and Pb(II) concentrations were below LOD values in both water samples. The samples were fortified with 1.0 µg L$^{-1}$ of target analytes, and these spiked water samples were analysed in triplicate. The recovery values for both spiked samples are shown in Table 4. The good and adequate recoveries obtained for Pb(II) and Cd(II) in both water samples indicate the suitability of the proposed BiOxP–SPE sensor to determine these heavy metals at low concentration levels.

## 4. Conclusions

In this work, a comparative study between different methods for *in bulk* incorporation of bismuth in SPCE has been performed. Among the different assayed methods, electrodes modified with a PSS–CnP composite membrane where bismuth was incorporated as α-Bi$_2$O$_3$ particles (BiOxP–SPE sensor) exhibited the most reproducible electrochemical responses to Cd(II) and Pb(II). The features showed for this sensor could be attributed to the homogeneous bismuth distribution on the membrane used to modify the electrode surface. The proposed BiOxP–SPE device can be considered as a low-cost and disposable electrochemical sensor for Cd(II) and Pb(II) determination at low concentration levels. The LOQ values for both metals are below the parametric values for Pb(II) and Cd(II) in waters according to European and Spanish Drinking Water Directives (5.0 µg L$^{-1}$ and 10 µg L$^{-1}$ for Pb(II) and Cd(II) respectively). In fact, this electrochemical device has been successfully used to determine Cd(II) and Pb(II) traces in real samples of mineral and river water.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/XXX.

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