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Short communication

Sputtered bismuth screen-printed electrode: A promising alternative to other bismuth modifications in the voltammetric determination of Cd(II) and Pb(II) ions in groundwater

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A B S T R A C T

A commercially available sputtered bismuth screen-printed electrode ($Bi_{sp}SPE$) has been pioneeringly applied for the simultaneous determination of Cd(II) and Pb(II) ions in a certified groundwater sample by means of differential pulse anodic stripping voltammetry (DPASV) as an alternative to more conventional bismuth screen-printed carbon electrodes (BiSPCEs). $Bi_{sp}SPEs$ can be used for a large set of measurements without any previous plating or activation. The obtained detection and quantification limits suggest that $Bi_{sp}SPEs$ produce a better analytical performance as compared to In-situ BiSPCE for Pb(II) and Cd(II) determination, but also to Ex-situ BiSPCE for Cd(II) determination. The results confirm the applicability of these devices for the determination of low level concentrations of these metal ions in natural samples with very high reproducibility (0.7% and 2.5% for Pb(II) and Cd(II) respectively), and good trueness (0.3% and 2.4% for Pb(II) and Cd(II) respectively).

1. Introduction

Nowadays a recognized method for the fabrication of sensors and biosensors for the determination of metal ions in industrial, environmental and biomedical applications is based on the screen-printing technology which permits production of numerous highly-reproducible single-use screen-printed electrodes (SPEs) [1]. SPEs usually include working, counter and reference electrodes printed on the same holding. Its accessibility, low cost character, miniaturized size, and the possibility of connection to portable instrumentation make these devices very suitable for on-site determination of target analytes. Many research laboratories possess screen printing machines and they have developed prototype devices from commercial or self-made inks and applied them to a wide variety of application samples [1–3]. Nowadays, different types of SPE can also be commercially purchased from different electrochemical firms (e.g., Dropsens, PalmSens Electrochemical Sensor Interface, Pine Research Instrumentation, eDAQ, Metrohm, Micrux Technologies, etc.).

In the last decade bismuth-based electrodes have become a valuable alternative to mercury electrodes for the analysis of traces of heavy metals in environmental samples [4–6]. Particularly, Bi-coated screen-printed electrodes (BiSPEs) have been gaining advantage over the more conventional Bi-film electrodes (BiFEs) and have been widely used for analytical purposes [7]. The screen-printed three-electrode configuration is based in most cases on a carbon working electrode, a carbon counter electrode, and a silver/silver chloride reference electrode. Although, these BiSPE can be used as working electrodes in a conventional electrochemical cell with external counter and reference electrodes [8–11]. The method of coating the substrate with bismuth has to be taken into consideration in designing a Bi electrode [6,7]. Three general methods are well-known: (i) Ex-situ plating or preplated method: the SPE is immersed into a Bi(III) solution and, after the application of an appropriate potential, Bi(III) ions are reduced to metallic Bi and electroplated on the electrode surface. Then, the BiSPE is relocated in the sample solution for measurements, (ii) In-situ plating method: Bi(III) ions are directly added to the sample solution and electrochemically deposited on the electrode surface during the analysis, (iii) "Bulk" method: the modification with Bi takes place during the SPE production and lies in the preparation of a mixture between the graphite ink and a determined amount of a bismuth precursor before the printing procedure. Later, the bismuth precursor is electrochemically reduced at a selected potential to metallic Bi [7,12]. An alternative method for the fabrication of a BiSPE is based on the sputtering of the bismuth on a silicon or ceramic substrate leading to a thick Bi film working electrode. This approach simplifies the fabrication process since neither the Bi(III) plating solution nor a conductive substrate is required. Moreover, these sputtered BiSPE are applicable to media covering a wide pH range [13,14].

In the present work, sputtered BiSPEs ($Bi_{sp}SPEs$) were applied for the first time for the simultaneous determination of Pb(II) and Cd(II) ions in a certified groundwater sample, as an example of their applicability for the analysis in environmental samples.

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Moreover, Bi_{sp}SPEs were microscopically and analytically compared with In-situ, Ex-situ and Bi_2O_3-bulk BiSPCEs as working electrodes.

2. Experimental

2.1. Chemicals

A standard Bi(III) 1.000 g L^{-1} atomic absorption standard solution was purchased from Fluka. Certificated reference material, groundwater (BCR®-610) and potassium nitrate trace metals basis were purchased from Sigma Aldrich. All other reagents used were Merck and Fluka analytical grade. Daily standard solutions of Cd(II) and Pb(II) were prepared by appropriate dilution of stock solutions 10^{-2} mol L^{-1}, prepared from $Cd(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2 \cdot 4H_2O$ respectively and standardized complexometrically. Maleic acid–KOH buffer and acetic-acetate buffer solutions were used for pH control and KNO_3 0.1 mol L^{-1} was employed as supporting electrolyte. Ultrapure water (Milli-Q plus 185 system, Millipore) was used in all experiments.

2.2. Apparatus

Differential pulse anodic stripping voltammetric (DPASV) measurements were performed on Bismuth Screen Printed Carbon Electrodes (BiSPE) in 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).

The reference electrode (to which all potentials are referred) and the auxiliary electrode were Ag/AgCl/KCl (3 mol L^{-1}) and Pt wire, respectively.

The working electrode was in all cases a BiSPE. Ex-situ and In-situ BiSPCE were prepared from a commercial screen-printed carbon disk electrode of 4 mm diameter (ref. 110, DS SPCE) provided by DropSens (Spain). Bi_2O_3 bulk BiSPCE (Bi_{ox}SPCE) was obtained from the activation of a commercial bismuth oxide screen-printed carbon disk electrode of 4 mm diameter (ref. 110Bi, DS SPCE) provided by DropSens (Spain), and the Bi_{sp}SPE was a sputtered thick film bismuth of 4 mm of diameter (ref. Bi10, DS SPE) provided by DropSens (Spain).

All screen-printed electrodes were connected to the Autolab by means of a flexible cable (ref. CAC, DropSens).

All measurements were carried out in a glass cell at room temperature (20 °C) under a purified nitrogen atmosphere (Linde N50).

For In-situ BiSPCE and Bi_{ox}SPCE a deposition potential (E_d) of -1.25 V was applied with stirring during a deposition time (t_d) of 300 s and 45 s respectively; a E_d of -1.20 V during 120 s with stirring was applied for Ex-situ BiSPCE; and a E_d of -1.30 V during 360 s was applied for Bi_{sp}SPE also with stirring of the solution. A rest period (t_r) of 30 s for all electrodes was maintained between deposition and stripping step. Unless otherwise indicated, a pulse time of 40 ms, step potential of 2 mV, and pulse amplitude of 50 mV were applied in the stripping step.

2.3. Experimental procedure

2.3.1. In-situ preparation of BiSPCE

For the bismuth In-situ modification of SPCE, 0.4 ppm Bi(III) ions are directly added to the sample solution and electrochemically deposited with the target metal ion (lead and cadmium) on the electrode surface during the analysis.

2.3.2. Ex-situ preparation of BiSPCE

The SPCE, the reference, and the auxiliary electrodes were connected to the stand and immersed into 20 mL of a 0.2 mol L^{-1} acetate buffer solution (pH 4.5) containing 100 ppm Bi(III). After deaeration of the solution for 10 min, $E_d = -0.80$ V was applied for 300 s with solution stirring, followed by a rest period (without stirring) of 20 s. Once the bismuth film was deposited, all electrodes were rinsed carefully with water and the Bi(III) solution was replaced in the cell by the one to be measured. This methodology was previously tested showing a very high repetitivity and reproducibility [11].

2.3.3. Activation of the Bi_{ox}SPCE

Prior to be used the bismuth (III) oxide of the commercial screen-printed electrode has to be reduced to metallic bismuth following the reaction:

$$Bi_2O_3(s) + 3H_2O + 6e^- \rightarrow 2Bi(s) + 6OH^- \quad (1)$$

Therefore, the commercial device is connected to the Autolab by means of the flexible cable, and a drop of KOH 0.1 mol L^{-1} (50 μL) is put over the electrodic surface. The electrochemical reduction takes place by applying a potential of -1.2 V for 600 s.

2.3.4. Procedure

Before each set of measurements, the whole electrochemical cell including KNO_3 supporting electrolyte and maleic/maleate or acetic/acetate buffer solution was analyzed for traces of metals using DPASV on the corresponding BiSPE.

The linear calibration plots for the simultaneous determination of Pb(II) and Cd(II) on different BiSPE were obtained from DPASV measurements at pH 4.5 acetic/acetate buffer and 0.1 mol L^{-1} ionic strength for In-situ BiSPCE and Bi_{ox}SPCE, and at pH 6.0 maleic/maleate buffer and 0.1 mol L^{-1} ionic strength for Ex-situ BiSPCE and Bi_{sp}SPE, increasing concentrations of Pb(II) and Cd(II).

In the analysis of the certified groundwater sample, voltammetric analysis started by placing in the cell a volume of the groundwater sample (BCR610) and 0.1 mol L^{-1} acetic/acetate buffer (pH 4.5) for In-situ BiSPCE and Bi_{ox}SPCE, and 0.01 mol L^{-1} maleic/maleate buffer (pH 6.0) for Ex-situ BiSPCE and Bi_{sp}SPE. Then, the sample was deaerated with pure nitrogen for 15 min to avoid the effect of oxygen in voltammetric measurements, and the groundwater sample scan was recorded. In the case of calibration by standard addition, five aliquots of Pb(II) and Cd(II) standard solution were further added and the respective curves were recorded. All solutions were deaerated and mechanically stirred for 1 min after each standard addition. In order to prevent changes in ionic strength and pH, the solutions to be added contained 0.1 mol L^{-1} KNO_3.

3. Results and discussion

3.1. Morphological surface characterization: SEM analysis

The surface morphology characterization was carried out by a Scanning Electron Microscope JSM 7100FE from JEOL (Japan). Fig. 1 compares the SEM images obtained at 10,000 × magnifications of a bare SPCE and the different BiSPEs. The scanning electron micrograph of a typical bare (commercial) SPCE (Fig. 1a) exhibits a uniform carbon surface in comparison with the BiSPE surfaces (Fig. 1b–f). Fig. 1b and c corresponds to SEM images of In-situ BiSPCE and Ex-situ BiSPCE respectively, in which the deposited Bi can be observed (especially in Ex-situ BiSPCE approach). Nevertheless, in both In-situ BiSPCE and Ex-situ BiSPCE the Bi-film formed by firmly fixed Bi does not cover the entire carbon surface.

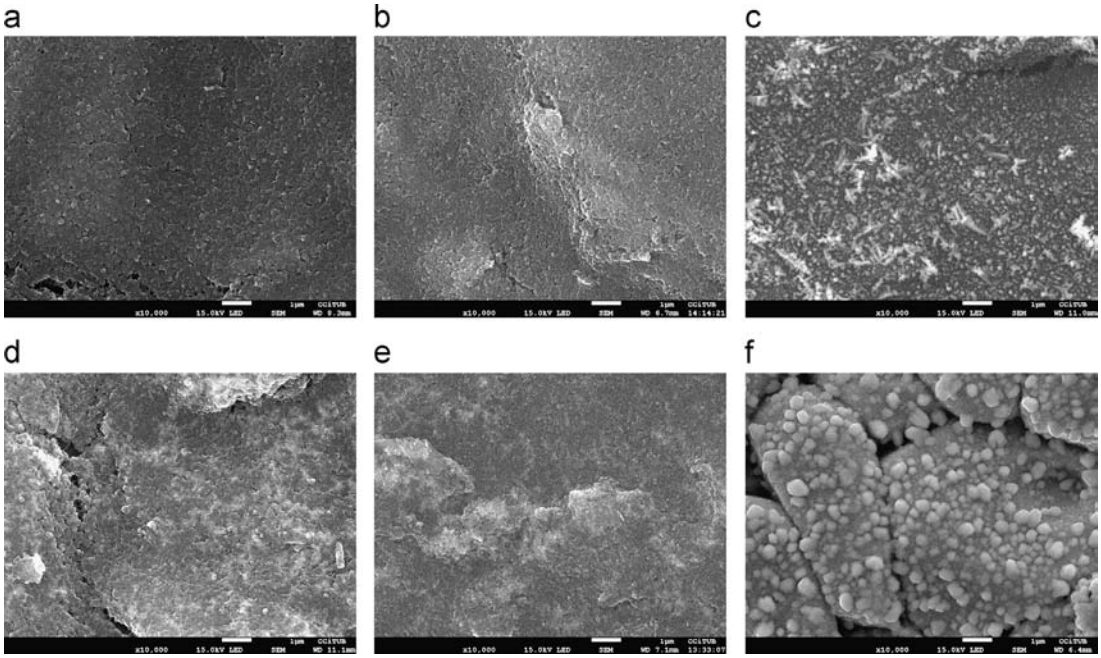

Fig. 1. Scanning electron micrographs: (a) commercial screen-printed carbon electrode (SPCE); (b) bismuth film coated In-situ on a commercial SPCE; (c) bismuth film coated Ex-situ on a commercial SPCE; (d) commercial bismuth oxide screen-printed carbon electrode before and (e) after electrochemical reduction at −1.2 V for 600 s in a 0.1 mol L^{-1} KOH solution; and (f) commercial bismuth sputtered screen-printed electrode. Resolution of 1 μm, magnification of 10,000× and accelerating potential of 15.0 kV were used.

Surface morphologies of Bi$_{Ox}$SPCE before and after the electrochemical reduction of the precursor are illustrated in Fig. 1d and e respectively. Before the electrochemical reduction Bi_2O_3 particles were uniformly distributed throughout the electrode surface, and were successfully changed to Bi after electrochemical reduction following reaction (1), resulting in a reasonably uniform Bi film slightly different to that observed for In-situ BiSPCE and Ex-situ BiSPCE. The surface morphology of Bi$_{sp}$SPE was the most different from the rest of BiSPE as it can be seen in its scanning electron micrograph (Fig. 1f). The main differences are that the substrate of this electrode is ceramic instead of carbon and that Bi was sputtered directly on it, showing a rough surface with a granular structure due to the Bi deposited on the electrode surface.

The comparison of the scanning electron micrographs makes evident the different surface morphologies of the different BiSPEs, which could certainly affect their electroanalytical performance.

3.2. Calibration data

Calibration data for the simultaneous determination of Cd(II) and Pb(II) ions on In-situ BiSPCE, Ex-situ BiSPCE, Bi$_{Ox}$SPCE, and Bi$_{sp}$SPE by stripping voltammetry (DPASV) are summarized in Table 1. The lowest value of the linear concentration range was established from the corresponding limit of quantification (LOQ). The LOQ was calculated as 10 times the standard deviation of the intercept over the slope of the calibration curve of the target ions. LOD was evaluated by considering three times the previous relation. For LOD and LOQ determinations, ten standard concentrations of Cd(II) and Pb(II) were used as calibration samples. Well defined peaks for Pb(II) and Cd(II) were obtained for In-situ BiSPCE, Ex-situ BiSPCE, and Bi$_{sp}$SPE approaches, whereas for Bi$_{Ox}$SPCE approach a stripping peak for Pb(II) and Cd(II) was observed at low concentrations, but after increasing the Pb(II) and Cd(II) concentrations the Cd(II) signal splits in two overlapping peaks. This Cd(II) behavior was previously observed with a conventional Ex-situ Bi film electrode (BiFE) [15]. A possible explanation of this behavior could be related with the accumulation step in which two different association mechanisms could be implied, one with the formed bismuth and another with the base electrode surface. In agreement with this preceding work [15], the total area of the voltammograms can be considered. Then an excellent linear response of the peak area versus both Cd(II) and Pb(II) concentrations is obtained for all BiSPE types. As shown in Table 1, the obtained LOQ are in all cases around or slightly lower than the LOQ reported for Ex-situ BiSPCE, In-situ BiSPCE, and Bi$_{Ox}$SPCE in a recent review [7]. For Bi$_{sp}$SPE no previous LOQ data for Cd(II) and Pb(II) are available in the literature. Regarding LOD values, the BiSPE obtained using the In-situ approach was the one with the highest LOD for both Cd(II) and Pb(II) determination; while the lowest LODs were provided by Bi$_{Ox}$SPCE and Bi$_{sp}$SPE for Cd(II), and Ex-situ BiSPCE for Pb(II), although it was not significantly different from that obtained with Bi$_{Ox}$SPCE and Bi$_{sp}$SPE. In comparison with previous studies (and Tables 1 and 2 in [7]), the Cd(II) and Pb(II) LODs obtained in this work for In-situ and Ex-situ approaches are relatively lower than those previously reported [10,16–25]. Regarding Bi$_{Ox}$SPCE, the LOD values are significantly lower than those shown in literature (Table 3 in [7]) for both Cd(II) [12,20,26,27] and Pb(II) [12,19,20,26,27]. Despite there are no studies reported in the literature about the use of Bi$_{sp}$SPE for Cd (II) and Pb(II) determination, the obtained calibration data suggest that Bi$_{sp}$SPE could be a good alternative for the determination of trace level concentrations of Pb(II) and Cd(II) in natural samples, with the additional advantage that is commercially available and does not need any previous treatment.

3.3. Application to the analysis of groundwater samples

A groundwater certified reference material (BCR-610) was selected to study the applicability of Bi$_{sp}$SPE for the determination of Cd(II) and Pb(II), and to compare its analytical performance with In-situ, Ex-situ and Bi$_{Ox}$SPCE. Pb(II) and Cd(II) ions were determined by means of the standard addition method. Then, voltammetric stripping measurements following the aforementioned conditions were carried out including the additions of Pb(II) and

Table 1
Calibration data for the simultaneous determination of Pb(II) and Cd(II) on different bismuth screen-printed electrodes at pH 4.5 and 0.1 mol L^{-1} ionic strength for In-situ BiSPCE and Bi$_{Ox}$SPCE, and at pH 6.0 and 0.1 mol L^{-1} ionic strength for Ex-situ BiSPCE and Bi$_{sp}$SPE.

Electrode	Pb(II)				Cd(II)			
	Regression	R^2	Linear range (μg L^{-1}) [a]	LOD (μg L^{-1})	Regression	R^2	Linear range (μg L^{-1}) [a]	LOD (μg L^{-1})
In-situ BiSPCE	$y=7.17x+11.27$	0.9998	0.83–23.3	0.25	$y=6.62x+2.14$	0.9991	1.35–14.5	0.40
Ex-situ BiSPCE	$y=3.53x+4.33$	0.9999	0.48–19.6	0.14	$y=2.78x-3.30$	0.9998	0.80–17.2	0.24
Bi$_{Ox}$SPCE	$y=5.41x+29.59$	0.9998	0.52–12.0	0.16	$y=31.52x-7.12$	0.9999	0.33–9.0	0.10
Bi$_{sp}$SPE	$y=3.03x+0.47$	0.9998	0.53–19.8	0.16	$y=0.78x+0.18$	0.9999	0.33–12.3	0.10

[a] The lowest value of the linear range was considered from the LOQ.

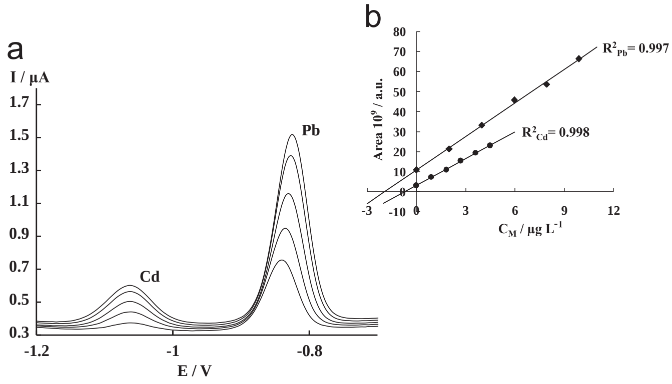

Fig. 2. (a) DPASV measurements in groundwater samples on In-situ BiSPCE at pH 4.5 acetic/acetate buffer and 0.1 mol L^{-1} ionic strength using a E_d of −1.25 V during a t_d of 300 s and t_r of 30 s; and (b) standard addition plot for the determination of Cd(II) and Pb(II).

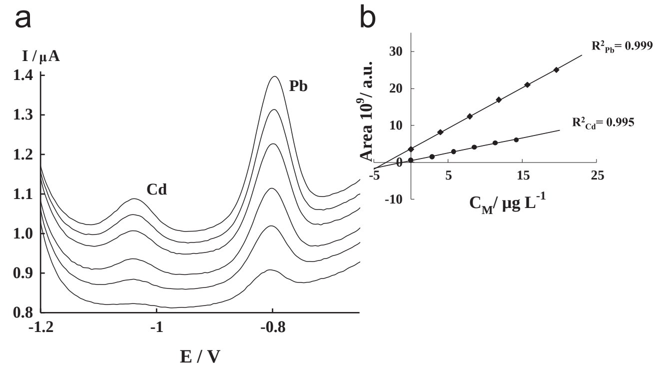

Fig. 3. (a) DPASV measurements in groundwater samples on Ex-situ BiSPCE at pH 6.0 maleic/maleate buffer and 0.1 mol L^{-1} ionic strength using a E_d of −1.20 V during a t_d of 120 s and t_r of 30 s; and (b) standard addition plot for the determination of Cd(II) and Pb(II).

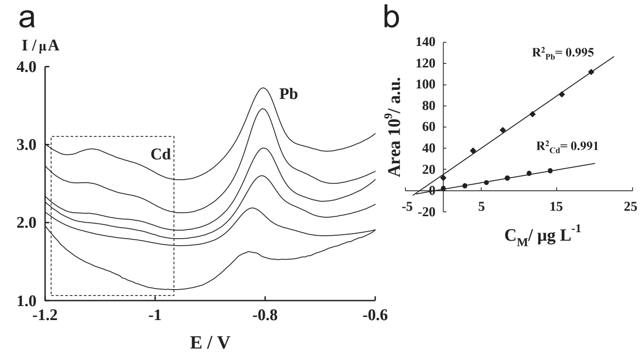

Fig. 4. (a) DPASV measurements in groundwater samples on Bi$_{ox}$SPCE at pH 4.5 acetic/acetate buffer and 0.1 mol L^{-1} ionic strength using a E_d of −1.25 V during a t_d of 45 s and t_r of 30 s; and (b) standard addition plot for the determination of Cd(II) and Pb(II).

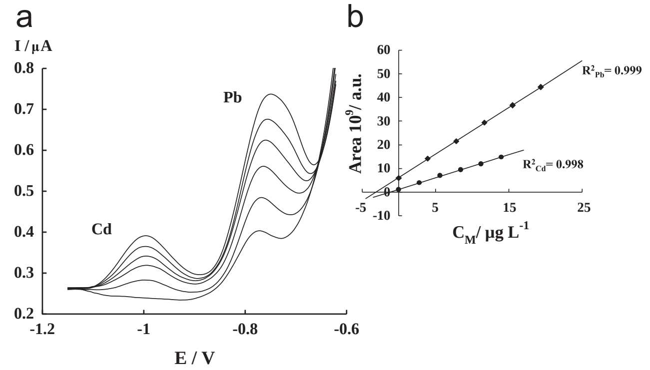

Fig. 5. (a) DPASV measurements in groundwater samples on Bi$_{sp}$SPE at pH 6.0 maleic/maleate buffer and 0.1 mol L^{-1} ionic strength using a E_d of −1.30 V during a t_d of 360 s and t_r of 30 s; and (b) standard addition plot for the determination of Cd(II) and Pb(II).

Cd(II). It should be considered that for In-situ SPCE, Ex-situ SPCE and Bi$_{sp}$SPE approaches, the same BiSPE device was used for the DPASV measurements of a complete replicate, whereas for Bi$_{Ox}$SPCE a new device was required for each DPASV measurement. Figs. 2a, 3a, 4a and 5a, show representative DP voltammograms obtained in the analysis of the groundwater samples using In-situ BiSPCE, Ex-situ BiSPCE, Bi$_{Ox}$SPCE, and Bi$_{sp}$SPE, respectively. The selected deposition potential and deposition time were optimized for each BiSPE (data not shown), being for In-situ BiSPCE −1.25 V and 300 s, Ex-situ BiSPCE −1.20 V and 120 s, Bi$_{Ox}$SPCE −1.25 V and 45 s and Bi$_{sp}$SPE −1.30 V and 360 s. Pb(II) and Cd(II) peaks behave in the same way as in the case of the calibration data: well defined peaks for Pb(II) and Cd(II) were observed for In-situ BiSPCE, Ex-situ BiSPCE, and Bi$_{sp}$SPE approaches, whereas for Bi$_{Ox}$SPCE approach a stripping peak for Pb(II) and Cd(II) was observed in the groundwater sample, but after Pb(II) and Cd(II) standard additions the Cd(II) signal splits again in two overlapping peaks. Therefore, the total area of the voltammograms were once again considered [15], being linear with Pb(II) and Cd(II) concentrations. The standard addition plots and the good correlation coefficients resulting from the representative DPASV measurements carried out using In-situ BiSPCE, Ex-situ BiSPCE, Bi$_{Ox}$SPCE, and Bi$_{sp}$SPE are shown in Figs. 2b, 3b, 4b and 5b, respectively. The Cd(II) and Pb(II) concentration data obtained from the DPASV determination of three replicates of the certified groundwater sample performed using the different BiSPEs are reported in Table 2. A good concordance between each metal concentration obtained from the different BiSPEs approaches, as well as with the certified Cd(II) and Pb(II) value in groundwater, was observed. The relative standard deviation (RSD%) was at most 4.6% for Cd(II) determination using an In-situ BiSPE, and 3.5% for Pb(II) determination using an Ex-situ BiSPE. The RSD obtained using Bi$_{Ox}$SPCE and Bi$_{sp}$SPE for Cd(II) and Pb(II) determination was not higher than 2.5%. Regarding the relative error, the Bi$_{Ox}$SPCE approach was the

Table 2
Total concentrations of Pb(II) and Cd(II) determined in certified groundwater (BCR610) by DPASV on different bismuth screen-printed electrodes by standard addition calibration method at pH 4.5 and 0.1 mol L^{-1} ionic strength for In-situ BiSPCE and Bi$_{Ox}$SPCE, and at pH 6.0 and 0.1 mol L^{-1} ionic strength for Ex-situ BiSPCE and Bi$_{sp}$SPE.

Electrode	Lead (μg L^{-1})	RSD (%)	Relative error (%)	Cadmium (μg L^{-1})	RSD (%)	Relative error (%)
In-situ BiSPCE	7.76	0.8	0.3	2.89	4.6	1.7
Ex-situ BiSPCE	7.95	3.5	2.2	2.99	2.9	1.7
Bi$_{Ox}$SPCE	7.65	1.4	1.7	2.66	0.8	9.5
Bi$_{sp}$SPE	7.80	0.7	0.3	3.01	2.5	2.4
Certified value	7.78	1.7	–	2.94	2.7	–

$n=3$ for RSD (%).

one with the highest value (9.5%) for Cd(II) determination; while for Pb(II) determination was at most 2.2% using an Ex-situ BiSPE. These good results confirm the applicability of the more conventional BiSPCEs obtained from In-situ and Ex-situ plating, and "bulk" methods for the determination of low level concentrations of Cd(II) and Pb(II). In addition, it is demonstrated that BiSPE obtained from Bi sputtered method can be also an interesting and valuable alternative for the determination of these metal ions in natural samples.

4. Conclusions

In this study, analytical and microscopic features of different commercial BiSPEs approaches were compared. At the view of the results, it can be concluded that Bi$_{sp}$SPE constitutes a good improvement for the simultaneous determination of Cd(II) and Pb(II) ions at low μg L^{-1} level. As in the case of the more conventional BiSPCEs, the low toxicity, the disposable character, the good reproducibility, the homogeneous surface morphology and the low-cost commercial availability of the Bi$_{sp}$SPEs make them attractive for environmental applications. In addition, Bi$_{sp}$SPE could be an alternative to BiSPCE if the presence of Bi(III) ion can affect the metal speciation in the sample. In comparison with more conventional BiSPCEs, the Bi$_{sp}$SPEs are somewhat more expensive, but in contrast can be used as they are commercially acquired without any previous treatment before measurements. Moreover, the disposable device can be used for a large set of measurements without signs of degradation or loss of sensitivity. Related to their analytical performances, Bi$_{sp}$SPEs produce normal-shaped stripping signals for both Cd(II) and Pb(II) ions. The provided LOD and LOQ were at levels of μg L^{-1} and slightly lower than the ones obtained using In-situ BiSPCE for Pb(II) and Cd(II) determination, and Ex-situ BiSPCE for Cd(II) determination. Furthermore, the above reported results show that Bi$_{sp}$SPE can be successfully applied for the determination of Pb(II) and Cd(II) in a natural sample with very high reproducibility and good trueness inferred by the relative standard deviation (0.7% for Pb(II) and 2.5% for Cd(II)) and the relative error (0.3% for Pb(II) and 2.4% for Cd(II)), respectively.

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