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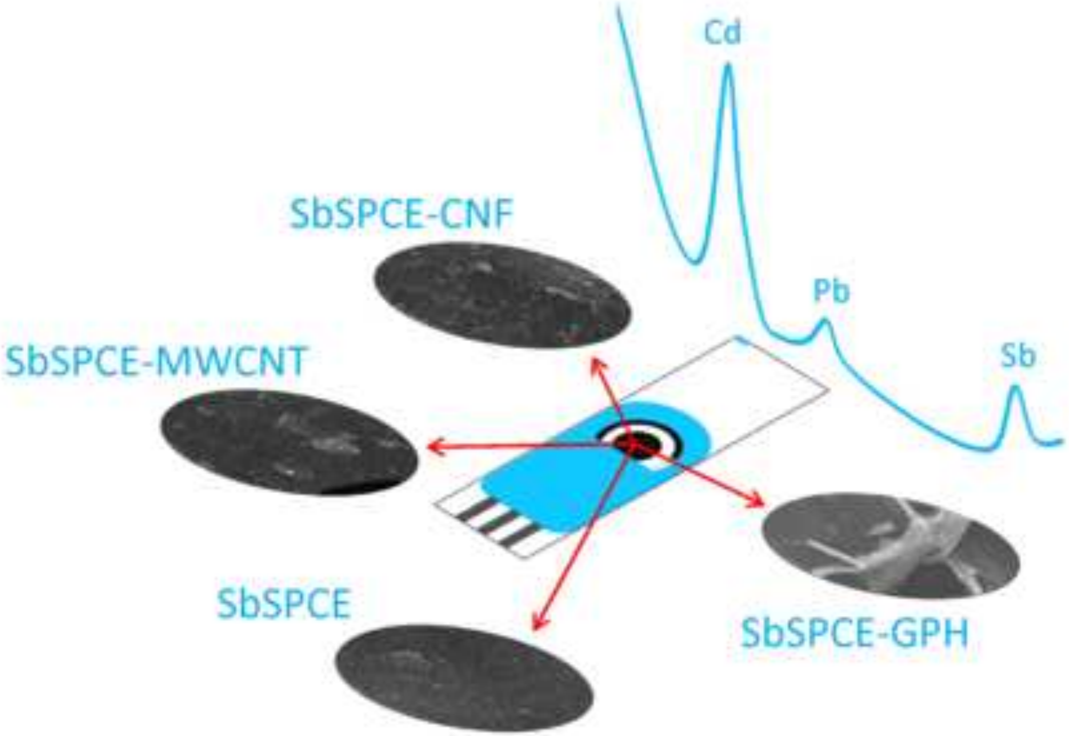
***Graphical Abstract**



New approaches to antimony film screen-printed electrodes using carbon- based nanomaterials substrates

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ABSTRACT

Three different commercial carbon nanomaterial-modified screen-printed electrodes based on graphene, carbon nanotubes and carbon nanofibers were pioneeringly tested as electrode platforms for the plating with Sb film. They were microscopically and analytically compared to each other and to the most conventional unmodified carbon screen-printed electrode (SPCE). The obtained detection and quantification limits suggest that the *in-situ* antimony film electrode prepared from carbon nanofibers modified screen-printed electrode (SbSPCE-CNF) produces a better analytical performance as compared to the classical SPCE modified with antimony for Pb(II) and Cd(II) determination, approving its appropriateness for measuring low μg L^{-1} levels of the considered metals. *In-situ* SbSPCE-CNF was successfully used for the simultaneous determination of Pb(II) and Cd(II) ions, by means of differential pulse anodic stripping voltammetry, in a certified reference estuarine water sample with a very high reproducibility and good trueness.

Keywords: antimony film electrodes, screen-printed electrodes, anodic stripping voltammetry, heavy metal ions

1. INTRODUCTION

Heavy metals are present in the environment from both natural and human sources. Their bioaccumulation and persistence constitutes a serious threat to human health, and this demands suitable methods for heavy metal monitoring [1]. The usual techniques for metal ion determination include atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS) and stripping techniques such as anodic stripping voltammetry (ASV), adsorptive stripping voltammetry (AdSV) and stripping chronopotentiometry (SCP). Particularly, ASV is accepted as one of the most suitable techniques for measuring trace metals in samples of biological and environmental interest, due to its sensitivity and reproducibility for metal ion determination, the low detection limits, its capability to multielement analysis, and its relatively low cost [2]. For many years, stripping methods were connected with the use of mercury- based electrodes as a working electrode, since they are very reproducible and have a wide cathodic window [3]. However, the potential risks of toxicity, contamination and disposal associated with the use of mercury have forced to search for other working electrode materials. In 2000, bismuth-based electrodes were introduced for voltammetric analysis of metal ions and, over the years, they were stablished as a successful alternative to mercury- based electrodes for analytical determinations [4, 5]. Nevertheless, in 2007, antimony was also proposed as a promising electrode material with a similar performance than that of mercury and bismuth-based electrodes. Subsequent studies revealed some remarkable features under chosen conditions of antimony film electrodes (SbFEs) such as wide operational potential window, favorably negative overvoltage of hydrogen evolution, suitable operation in solutions of more acidic pH than that reported for bismuth film electrodes (BiFEs) and a very small stripping signal for antimony itself. Moreover, antimony is much less toxic than mercury [6-8].

For the preparation of the Sb electrodes, both the substrate on which the Sb will be plated and the Sb-coating method are two essential aspects that have to be taken into consideration. The available Sb-coating methods are analogous to those used for BiFEs, being the *in-situ*, *ex-situ* and bulk the most representative approaches [8-9]. Regarding the substrate, carbon- based substrates revealed better performance than metal electrode materials, being glassy carbon followed by carbon paste the most used supports for the preparation of the film [8, 10], although gold and platinum disk electrode [10] as well as boron doped diamond (BDD) were also used [11].

In the last years the screen-printing microfabrication technology has undergone a great progress allowing the mass production of numerous highly-reproducible single-use screen-printed electrodes (SPEs) with an accessible and low-cost character. These SPEs usually comprise a three-electrode configuration printed on the same strip. Some other important characteristics are related to its miniaturized size and the option of connecting it to portable instrumentation permitting the on-site determination of analytes. Furthermore, the design versatility and the possibility of using a great diversity of compositions of printing inks, as well as the easy modification of their surface are important advantages of these devices [5, 12].

Thus, the coupling of Sb film with disposable SPEs presents an attractive option for the determination of heavy metal ions. However, most of the studies devoted to the application of antimony screen-printed electrodes (SbSPE) for the determination of trace metals use the conventional bare carbon screen-printed electrode (SPCE) as a support for the preparation of the film [8], whereas the use of SPCEs with the working electrode surface modified with nanomaterials, which are of great interest for the development of electrochemical sensors, as a support for plating the Sb film are very scarce. To the best of our knowledge only a tentative study was carried out using an screen-printed antimony film electrode modified with multi-walled carbon nanotubes for the determination of Hg(II) and Pb(II) [13].

With the aim to improve the properties of SbSPCE using nanomaterials as electrode platform, this study discusses the effect of different substrate electrodes as multi-walled carbon nanotubes modified screen-printed electrode (SPCE-MWCNT), graphene modified screen-printed electrode (SPCE-GPH) and carbon nanofibers modified screen-printed electrodes (SPCE-CNF) on which the Sb film will be plated for the stripping performance of the simultaneous determination of Cd(II) and Pb(II) as model metal ions. Moreover, SbSPCE-MWCNT, SbSPCE-GPH and SbSPCE-CNF were microscopically and analytically compared with the conventional SbSPCE. Finally, SbSPCE-CNF as the optimal *in-situ* SbSPE was applied for the first time for the simultaneous monitorizacion of Pb(II) and Cd(II) ions in a certified estuarine water sample.

2. EXPERIMENTAL

2.1 Chemicals

Sb(III) 1.000 mg L^{-1} atomic absorption standard solution was purchased from Merck (Darmstadt, Germany). All other reagents used were Panreac (Barcelona, Spain) and Merck 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 $Pb(NO_3)_2{\cdot}4H_2O$ and $Cd(NO_3)_2{\cdot}4H_2O$ respectively and standardized complexometrically [14]. KNO_3 0.01 mol L^{-}

^{1} was used as supporting electrolyte and hydrochloric acid (pH 2) and acetate buffer (pH 4.5) solutions were employed for pH control. In all experiments, ultrapure water (Milli-Q plus 185 system, Millipore) was used.

Certified reference material, estuarine water LGC6016, was purchased from LGC Standards. As it is indicated in the certificate of measurement, estuarine water was collected from the Severn Estuary, UK, near Avonmouth (a heavily industrialized area). The water was filtered through a 0.45 μm membrane filter and then stabilized by the addition of concentrated nitric acid to achieve a pH of 2.

2.2 Apparatus

An Autolab System PGSTAT12 (EcoChemie, The Netherlands) attached to a Metrohm 663 VA Stand (Metrohm, Switzerland) was used to perform differential pulse anodic stripping voltammetric (DPASV) measurements. GPES version 4.9 software (EcoChemie) was used for data acquisition.

The auxiliary and the reference electrode (to which all potentials are referred) were Pt wire and Ag|AgCl|KCl (3 mol L^{-1}), respectively (Metrohm, Switzerland). The working electrode used was an *in-situ* antimony film electrode prepared from different carbon-based commercial screen-printed disk electrodes of 4 mm diameter provided by Dropsens (Spain): carbon screen-printed electrodes (ref. 110, DS SPCE), graphene modified screen-printed electrodes (ref. 110GPH, DS SPCE), multi-walled carbon nanotubes modified screen-printed electrodes (ref. 110CNT, DS SPCE) and carbon nanofibers modified screen-printed electrodes (ref. 110CNF, DS SPCE).

A flexible cable ref. (CAC, DropSens) was used to connect the screen-printed electrodes to the Autolab System.

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

Scanning electron microscope JSM 7100FE from JEOL (Japan) was used for the surface morphology characterization.

2.3 Experimental procedure

2.3.1 In-situ preparation of SbSPE

In-situ modification of the screen-printed electrodes was carried out by directly adding a 0.5 mg L^{-1} Sb(III) solution to the sample solution usually containing 0.01 mol L^{-1} hydrochloric acid and the target metals. Then, Sb(III) is codeposited onto the bare based-carbon electrode together with Cd(II) and Pb(II) ions at the deposition potential (E_d) and deposition time (t_d) defined by the own analytical determination.

2.3.2 Procedure

DPASV determinations of Cd(II) and Pb(II) using an *in-situ* SbSPE were performed at an E_d of -1.5 V (vs. Ag/AgCl), applied with stirring, during a t_d of 120 s and followed by a rest period (t_r) of 5 s. Determinations were done by scanning the potential from -1.5 to -0.1 V (vs. Ag/AgCl) using pulse times of 50 ms, step potentials of 5 mV and pulse amplitudes of 50 mV.

In order to obtain the linear calibration plots for the simultaneous determination of Pb(II) and Cd(II) by DPASV using an *in-situ* SbSPE, metal concentrations were increased in a solution of 0.01 mol L^{-1} HCl and 0.01 mol L^{-1} KNO_3.

In the analysis of the certified estuarine water sample, a volume of the sample (LGC6016) in 0.1 mol L^{-1} acetate buffer (pH 4.5) was placed in the cell and deaerated with pure nitrogen for 15 min in order to avoid the effect of oxygen in voltammetric measurements. Then, the estuarine water sample scan was recorded. In the case of calibration the standard addition method was applied, five aliquots of Pb(II) and Cd(II) standard solutions were further added and the respective curves were recorded.

In both linear calibration plots and analysis of the certified estuarine water sample, the solution was deaerated and mechanically stirred for 120 s after each addition and a cleaning step was performed before each measurement by applying a conditioning potential (E_{cond}) of 0.5 V (vs. Ag/AgCl) for 15 s.

3. RESULTS AND DISCUSSION

3.1 Morphological surface characterization: SEM analysis

Figure 1 compares the SEM images obtained at 10.000 x magnification of the different commercial bare carbon- based SPE substrates (Figure 1a-d) and the different Sb film coated SPEs (Figure 1e-h). The scanning electron micrograph of a typical unmodified SPCE (Figure 1a) exhibits a uniform rough surface with grains in contrast with the ribbon-like tube appearance in the form of small bundles of SPCE-CNF (Figure 1b), the twisted spaghetti-like character of SPCE-CNT (Figure 1c), and the characteristic hexagonal arrangement of the SPCE-GPH (Figure 1d). The special surface morphologies shown by modified SPCE offer a much larger real surface area than the unmodified SPCE.

The surface morphologies of bare carbon- based SPEs look different from those of the respective SbSPEs, in which the deposited Sb can be observed (Figure 1e-h). In all SbSPEs the Sb film was formed by firmly fixed Sb of different sizes randomly dispersed on the carbon- based SPE surface, without covering the entire surface, but resulting in a reasonably uniform Sb film as it is seen in the corresponding insets of Figures 1e-h. However, the comparison of the scanning electron micrographs makes obvious the diverse surface morphologies of the different SbSPEs, which could certainly affect their electroanalytical performance.

3.2. Optimization of electrochemical parameters and condition media for the *in-situ* SbSPCE

Several key electrochemical parameters, such as t_d, E_d and Sb(III) concentration, in connection with the simultaneous detection of Pb(II) and Cd(II) by DPASV using an *in-situ* plated SbSPE were optimized. This optimization was performed using the conventional SbSPCE as a SbSPE model. 0.01 mol L^{-1} HCl solution was selected as medium since it is the most used in the literature for the simultaneous determination of Pb(II) and Cd(II) on *in-situ* antimony film electrodes coated on carbon substrates [6, 8, 15-17].

DPASV measurements of a 50 μg L^{-1} Pb(II) and Cd(II) in 0.5 mg L^{-1} Sb(III), 0.01 mol L^{-1} KNO_3 and 0.01 mol L^{-1} HCl, were performed at different E_d ranging from -1.2 to -1.6 V (vs. Ag/AgCl) and applying a t_d of 120 s. Pb(II) peak increased when using more negative E_d while Cd(II) increased until -1.5 V (vs. Ag/AgCl) and significantly decreased at -1.6 V (vs. Ag/AgCl). According to this study an optimal E_d of -1.5 V (vs. Ag/AgCl) was selected. Once the E_d was selected, different t_d ranging from 30 to 300 s were studied. Well-defined stripping peaks for Pb(II) and Cd(II) that increase proportionally with t_d were observed (Figure not shown). In agreement with these results, a t_d of 120 s was selected as a good compromise between the peak current and the time of the analysis. Finally, the effect of Sb(III) concentration was also studied. DPASV measurements of a 50 µg L^{-1} Pb(II) and Cd(II) solution, in 0.01 mol L^{-1} HCl, 0.01 mol L^{-1} KNO_3 and different Sb(III) concentrations ranging from 0.25 to 1.25 mg L^{-1}, were carried out applying a E_d of -1.5 V (vs. Ag/AgCl) during 120 s (Figure 2). From 0.5 to 0.75 mg L^{-1} Sb(III) similar Cd(II) peaks, at *ca.* -0.96 V (vs. Ag/AgCl), where obtained while a decrease in the signal could be observed for higher or lower Sb(III) concentrations, obtaining the lowest signal at 0.25 followed by 1 mg L^{-1} Sb(III). On the other hand, Pb(II) peak, at *ca.* -0.69 V (vs. Ag/AgCl), started to decrease already at 0.75 mg L^{-1} Sb(III). As expected, Sb(III) peak, at *ca.* -0.23 V (vs. Ag/AgCl), increased proportionally to its concentration. After analyzing these results, an optimal Sb(III) concentration of 0.5 mg L^{-1} was selected.

3.3 Repeatability and reproducibility

Once the electrochemical parameters and the media were optimized, four different carbon substrates (bare carbon, graphene, carbon nanotubes and carbon nanofibers) were tested. Figure 3 shows a comparison of the electroanalytical performance of the *in-situ* SbSPEs prepared on the different carbon substrates for the simultaneous determination of a solution containing 100 µg L^{-1} Pb(II) and Cd(II) in the previous optimized conditions. In all cases a well-defined peak is observed for Cd(II), obtaining the lowest signal with the *in-situ* SbSPCE-GPH (thin solid line) and the highest signal with SbSPCE-CNF (thick solid line). Related to Pb(II), a well-defined peak is also obtained with SbSPCE-CNF, SbSPCE (dashed thin line) and SbSPCE-GPH, while a double peak can be observed in the case of SbSPCE-MWCNT (dashed thick line). This fact could be attributed to the lack of uniformity of these surfaces, which allows antimony ions to deposit in different ways when the film is formed. The highest signal for Pb(II) is also obtained with the *in-situ* SbSPCE-CNF. Finally, a Sb(III) stripping peak was also detected on all *in-situ* SbSPEs, being more prominent in the case of SbSPCE-MWCNT (dashed thick line) and very small with the *in-situ* SbSPCE-GPH (thin solid line).

In order to test the repeatability and reproducibility of the *in-situ* SbSPE coated on the different carbon substrates, stripping measurements of a solution containing 50 μg L^{-1} Pb(II) and Cd(II) in 0.01 mol L^{-1} HCl, 0.01 mol L^{-1} KNO_3 and 0.5 mg L^{-1} Sb(III) were carried out. Table 1 shows the repeatability and reproducibility values calculated for Pb(II) and Cd(II) with each electrode. Repeatability was estimated using the same *in-situ* SbSPE unit for five repetitive measurements whereas reproducibility was calculated from three different *in-situ* SbSPE units within a series of five repetitive measurements. In all cases, the repetitive measurements yielded excellent repeatability, with RSDs ranging from 1.1 to 3.5% for Pb(II) and from 1.0 to 2.8 for Cd(II), obtaining the best results for the *in-situ* SbSPCE-CNF. These values are similar or even better to those reported for *in-situ* antimony films coated on glassy carbon [6], carbon paste [17] or carbon fiber microelectrodes [15]. Regarding the reproducibility, good values were also obtained with SbSPCE and SbSPCE-CNF whereas SbSPCE-GPH and SbSPCE-MWCNT presented higher RSD%. These high reproducibility values observed in SbSPCE-GPH and SbSPCE-MWCNT could be attributed to the low homogeneity between the different units commercially purchased.

3.4 Linearity, limit of detection (LOD) and limit of quantification (LOQ)

Calibration data for the simultaneous determination of Cd(II) and Pb(II) ions on the *in-situ* SbSPEs prepared on the different carbon substrates by stripping voltammetry (DPASV) are summarized in Table 2. Linear calibration curves were obtained at the optimized conditions by measuring eight increasing concentrations of Cd(II) and Pb(II) ranging from 1.1 to 100.3 and from 1.0 to 100.9 µg L^{-1} respectively. The limit of detection (LOD) was calculated as 3 times the standard deviation of the intercept over the slope of the calibration curve of the target ions. The limit of quantification (LOQ), which was considered as the lowest value of the linear concentration range, was evaluated by considering 10 times the previous ratio.

As shown in Table 2 excellent linear responses of peak area *versus* metal ion concentration were observed for both Pb(II) and Cd(II) for all the SbSPEs. LOD and LOQ were at the level of µg L^{-1} in all cases, being those obtained for Cd(II) slightly better than those obtained for Pb(II). The LODs obtained for the *in-situ* SbSPCE, which are similar to those previously reported with screen-printed supports [9], are of the same order, although slightly higher, than those reported using glassy carbon [6] or carbon paste [17] as supports for the preparation of the film, also with the *in-situ* approach and a t_d of 120 s (Table 3). The obtained LODs were even higher when using the SbSPCE-GPH (Table 2), which proves that the use of these commercial screen-printed carbon electrodes modified with graphene as a platform for the Sb(III) deposition does not seem to provide a more suitable Sb electrode for the simultaneous determination of Cd(II) and Pb(II). In contrast, with SbSPCE-MWCNT, a slight improvement of the LODs can be observed. However, this minimum improvement, coupled with their low reproducibility previously observed, does not justify the use of multi-walled carbon nanotubes modified screen-printed electrodes as a support for plating the Sb film, as they are much more expensive than the conventional

SPCE. SbSPCE-CNF, on the other hand, provides LODs significantly lower which, coupled with its excellent repeatability and reproducibility, make it a more suitable support for the Sb film deposition even considering its higher cost. Furthermore, as it can be seen in Table 3, SbSPCE-CNF provides LODs much similar to those obtained using glassy carbon or carbon paste as support, with the advantages associated to the screen-printed electrodes (commercially available, no pretreatment required…), and similar or even better than LODs reported for screen-printed electrodes using other coating methods such as bulk modifications [18-19]. It should be pointed out that for SbSPCE-GPH, SbSPCE-MWCNT and SbSPCE-CNF no previous LOD and LOQ data for Cd(II) and Pb(II) are available in the literature.

The improvement observed for SbSPCE-MWCNT and SbSPCE-CNF could be attributed to the much larger effective surface area that present these modified carbon- based SPEs in comparison to the conventional unmodified SPCE as can be seen in the scanning electron micrographs. Regarding SbSPCE-GPH, although its surface area should be also enhanced and lower LODs should be expected, the achieved results do not agree with the above-mentioned supposition indicating maybe a problem with the commercial purchased device.

Therefore the reported calibration data suggests that SbSPCE-CNF could be fully suitable and a valuable alternative to more conventional SbSPCE for the simultaneous determination of Cd(II) and Pb(II) at trace levels in natural samples as well as in drinking water [20], being able to quantify lower concentrations than SbSPCE.

3.5 Application to the analysis of an estuarine water reference material

At the view of the above results, SbSPCE-CNF was selected to study its applicability for the determination of Cd(II) and Pb(II) in a certified estuarine water reference material (LGC6016). Considered metal ions were determined by means of the standard addition method. Then, voltammetric stripping measurements following the optimized conditions were carried out including the additions of Pb(II) and Cd(II). Figure 4a shows representative stripping voltammograms obtained in the analysis of the estuarine water samples using SbSPCE-CNF. Cd(II) and Pb(II) peaks behave in the same way as in the calibration data: well-defined peaks for both metal ions were obtained.

Standard addition plot for both Cd(II) and Pb(II) (Figure 4b) shows the good correlation of the representative stripping voltammetric measurements carried out using SbSPCE-CNF. It should be mentioned that the presence of other constituents of the reference material such as Cu, Mn, Ni and Zn at similar concentrations as the considered metals does not seem to interfere in the simultaneous determination of Cd(II) and Pb(II).

The metal concentration data obtained from the voltammetric determination of three replicates of the certified estuarine water sample performed using SbSPCE-CNF are reported in Table 4. A good concordance between Cd(II) and Pb(II) concentrations were obtained, as well as with the certified metal ion values. Therefore, these good results confirm the applicability of the *in-situ* antimony film electrode prepared from carbon nanofibers modified screen-printed electrodes for the simultaneous determination of Cd(II) and Pb(II) in natural samples, being an interesting and valuable alternative for the determination of these metal ions not only to the most traditional devices such as mercury and bismuth electrodes but also to the most conventional *in-situ* SbSPCE.

4. Conclusions

In this work, analytical and microscopic features of antimony film coated on different commercial carbon modified screen-printed electrodes were compared to each other and to the most conventional *in-situ* SbSPCE. Firstly, the electrochemical parameters for the simultaneous determination of Cd(II) and Pb(II) were optimized, obtaining the best voltammetric response using a E_d of -1.5 V (vs. Ag/AgCl), a t_d of 120 s and a Sb(III) concentration of 0.5 mg L^{-1}. At the above optimized conditions, all the SbSPEs provided LODs and LOQs at levels of μg L^{-1} for both metals. SbSPCE-GPH did not achieve the results obtained with the most conventional SbSPCE and only a slight improvement could be observed when using the SbSPCE-MWCNT. The best results in terms of sensitivity, repeatability, reproducibility and detection limits were obtained with the SbSPCE-CNF. Moreover, the achieved LODs and linear ranges were similar or even much better than values reported in previous studies for Sb modified electrodes using other supports or coating methods. Therefore, the *in-situ* antimony film electrode prepared from carbon nanofibers modified screen-printed electrodes could be a valuable alternative to the most conventional SbSPCE for environmental applications. Although they are somewhat more expensive, they can be also used for a large set of measurements without signs of degradation or loss of sensitivity.

Furthermore, SbSPCE-CNF was successfully applied for the determination of Cd(II) and Pb(II) in an estuarine water sample, as an example of its applicability for the analysis of natural samples, being able to quantify both Cd(II) and Pb(II) concentrations with very high reproducibility and good trueness inferred by the relative standard deviation (0.5 % for Pb(II) and 1.2 % for Cd(II)) and the relative error (0.4 % for Pb(II) and 2.2 % for Cd(II)), respectively.

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Caption to figures

Figure 1. Scanning electron micrographs of carbon (a), carbon nanofibers (b), carbon nanotubes (c) and graphene (d) commercial screen-printed electrodes and antimony films coated *in-situ* on these electrodes (e-h). Resolution of 1 µm, accelerating potential of 20.0 kV and magnification of 10,000×, 20,000× (inset c), 5,000× (inset d) and 500× (insets e-h) were used.

Figure 2. a) DPASV measurements of 50 µg L^{-1} Pb(II) and Cd(II) on *in-situ* SbSPCE at 0.01 mol L^{-1} HCl and 0.25 (dotted-dashed line), 0.5 (thick line), 0.75 (thin line), 1 (dashed thick line) and 1.25 (dashed thin line) mg L^{-1} Sb(III) applying a E_d of -1.5 V (vs. Ag/AgCl) during 120 s at 0.01 mol L^{-1} KNO_3. b) Plot of peak area *vs* Sb(III) concentration.

Figure 3. DPASV voltammograms of 100 µg L^{-1} Pb(II) and Cd(II) on *in-situ* SbSPCE-GPH (thin line), SbSPCE (dashed thin line), SbSPCE-MWCNT (dashed thick line) and SbSPCE-CNF (thick line) applying a E_d of -1,5 V (vs. Ag/AgCl) during 120 s at 0.01 mol L^{-1} HCl, 0.01 mol L^{-1} KNO_3 and 0.5 mg L^{-1} Sb(III).

Figure 4. a) DPASV measurements in an estuarine water sample by using an *in-situ* SbSPCE-CNF at pH 4.5 with E_d of -1.5 V (vs. Ag/AgCl) during a t_d of 120 s and t_r of 5 s; and, b) Cd(II) and Pb(II) standard addition plot.

Figure 1

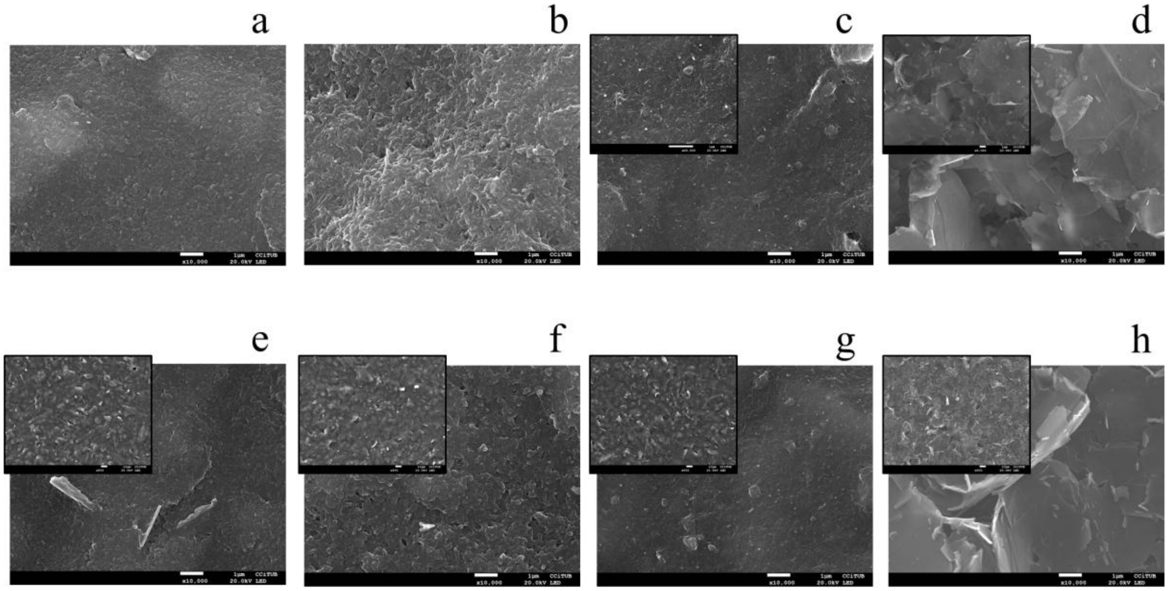

Figure 2

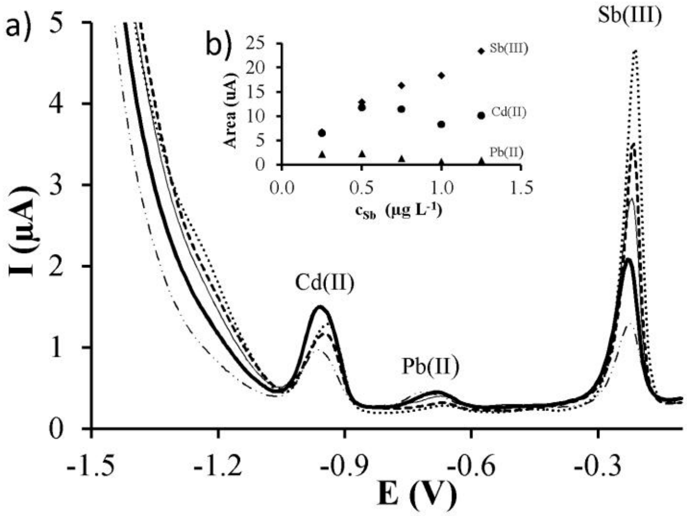
a)
b)
Sb(III)
Cd(II)
Pb(II)
I (µA)
E (V)
0
1
2
3
4
5
-1.5
-1.2
-0.9
-0.6
-0.3
Area (uA)
0
5
10
15
20
25
0.0
0.5
1.0
1.5
c_{Sb} (µg L⁻¹)
Sb(III)
Cd(II)
Pb(II)

Figure 3

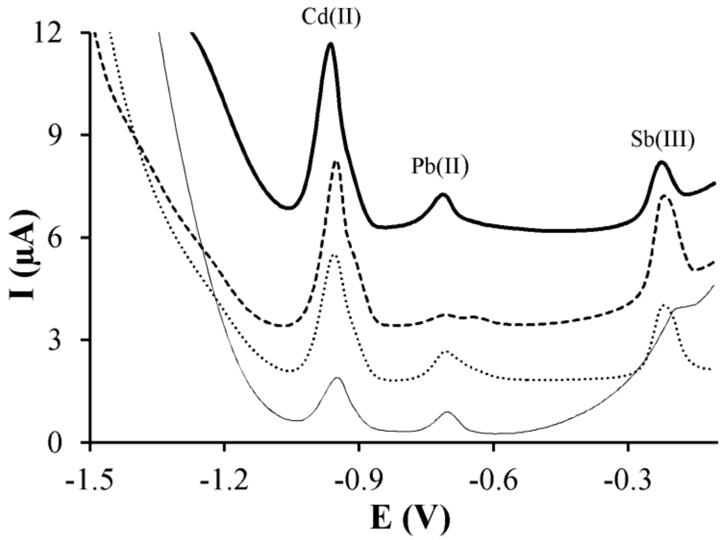

Figure 4

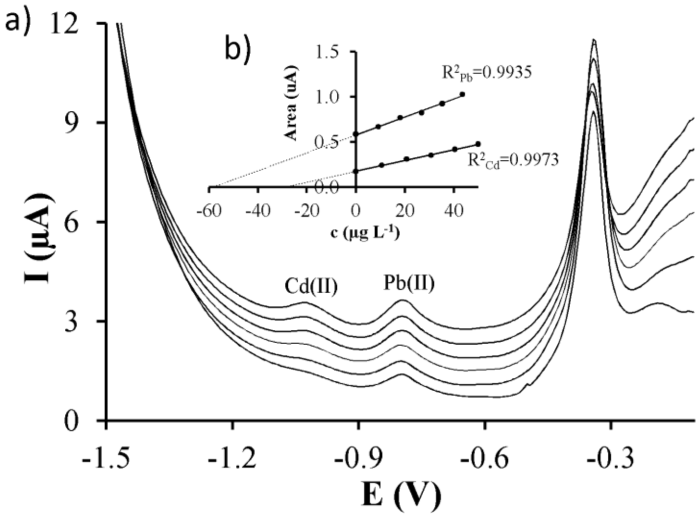
a)
b)
I (µA)
12
9
6
3
0
-1.5
-1.2
-0.9
-0.6
-0.3
E (V)
Cd(II)
Pb(II)
Area (uA)
1.5
1.0
0.5
0.0
-60
-40
-20
0
20
40
c (µg L-1)
R2Pb=0.9935
R2Cd=0.9973

Table 1. Repeatability and repreducibility data for the simultaneous determination of Pb(II) and Cd(II) on *in-situ* SbSPCE, SbSPCE-GPH, SbSPCE-MWCNT and SbSPCE-CNF at pH 2 HCl, 0.01 mol L^{-1} KNO_3 and 0.5 mg L^{-1} Sb(III).

Electrode	**Pb(II)**		**Cd(II)**	
	Repeatability (RSD%)	**Reproducibility (RSD%)**	**Repeatability (RSD%)**	**Reproducibility (RSD%)**
SbSPCE	3.5	4.5	2.6	2.8
SbSPCE-GPH	2.9	17.2	2.8	18.0
SbSPCE-MWCNT	1.3	11.3	1.5	11.4
SbSPCE-CNF	1.1	4.4	1.0	1.2

Table 2. Calibration data for the simultaneous determination of Pb(II) and Cd(II) on *in-situ* SbSPCE, SbSPCE-GPH, SbSPCE-MWCNT and SbSPCE-CNF at pH 2 HCl, 0.01 mol L^{-1} KNO_3 and 0.5 mg L^{-1} Sb(III). The standard deviations are denoted by parenthesis.

Electrode	Pb(II)					Cd(II)				
	Sensitivity (a.u. μg^{-1} L)[a]	**Intercept (a.u.)**	**R^2**	**Linear range[b] (μg L^{-1})**	**LOD (μg L^{-1})**	**Sensitivity (a.u. μg^{-1} L)[a]**	**Intercept (a.u.)**	**R^2**	**Linear range[b] (μg L^{-1})**	**LOD (μg L^{-1})**
SbSPCE	0.87 (0.03)	-9 (2)	0.997	17.5-100.9	5.3	3.24 (0.05)	-37 (3)	0.999	9.5-100.3	2.8
SbSPCE-GPH	0.48 (0.02)	-10 (1)	0.994	28.8-100.9	8.6	1.37 (0.03)	-15 (2)	0.995	13.2-100.3	4.0
SbSPCE-MWCNT	0.49 (0.01)	-3.1 (0.7)	0.998	14.7-100.9	4.4	4.33 (0.06)	-48 (4)	0.999	8.6-100.3	2.6
SbSPCE-CNF	1.36 (0.01)	-14.2 (0.9)	1.000	6.9-100.9	2.1	4.74 (0.03)	-66 (2)	1.000	3.7-100.3	1.1

[a] Sensitivity was considered from the slope of the calibration curve.

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

Table 3. Comparative of LODs and linear ranges obtained for Cd(II) and Pb(II) using different electrode supports and coating methods for the formation of the Sb film

Electrode support	**Coating method**	**t_d (s)**	**Linear range (µg L^{-1})**		**LOD (µg L^{-1})**		**Ref.**
			Cd(II)	**Pb(II)**	**Cd(II)**	**Pb(II)**	
Glassy carbon	*In-situ*	120	20-140	20-140	0.7	0.9	[6]
Carbon paste	*In-situ*	120	5-50	5-50	0.8	0.2	[17]
SPCE	*In-situ*	120	11.5-72.4	16.8-62.6	3.4	5.0	[9]
SPCE	*In-situ*	120	9.5-100.3	17.5-100.9	2.8	5.3	This work
SPCE-GPH	*In-situ*	120	13.2-100.3	28.8-100.9	4.0	8.6	This work
SPCE-CNF	*In-situ*	120	3.7-100.3	6.9-100.9	1.1	2.1	This work
SPCE-MWCNT	*In-situ*	120	8.6-100.3	14.7-100.9	2.6	4.4	This work
SPCE	Bulk-modified with Sb_2O_3	600	20-100	---	20	---	[18]
SPCE	Bulk-modified with Sb_2O_3	240	10-90	5-45	2.5	0.9	[19]
SPCE	Bulk-modified with SnO_2/Sb_2O_5	240	10-90	5-45	1.8	1.1	[19]
SPCE	Bulk-modified with $Sb^{III}(C_2O_4)OH$	240	10-90	5-45	3.5	1.1	[19]

Table 4. Total concentrations of Pb(II) and Cd(II) determined in certified estuarine water (LGC6016) by DPASV on *in-situ* SbSPCE-CNF by standard addition calibration method applying an E_d of -1.5 V and t_d of 120 s.

	Pb(II)			**Cd(II)**		
	c (µg L^{-1})	**RSD (%)**	**Relative error (%)**	**c (µg L^{-1})**	**RSD (%)**	**Relative error (%)**
	195.2	0.5	0.4	98.8	1.2	2.2
Certified metal value	196	1.5	—	101	2.0	—

n=3 for RSD (%)