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Abstract: The use of an antimony film coated on a screen-printed carbon electrode (ex-situ SbSPCE) is proposed for the determination of Pd(II) at ppb levels in natural samples by adsorptive stripping voltammetry using dimethylglyoxime as chelating agent. Ex-situ SbSPCE produces a better analytical performance as compared to a commercially sputtered bismuth screen-printed electrode (BispSPE). The detection and quantification limits were 2.7 and 9.0 μg L-1 respectively with a good linear behaviour in the wide examined concentration range (from 1 μg L-1 up to 100.0 μg L-1, R2= 0.998). The proposed ex-situ SbSPCE showed an excellent repeatability with a relative standard deviation of 0.5 % for ten successive measurements and a very good reproducibility (1.6 % for three different ex-situ SbSPCE units within series of ten repetitive assays). Moreover, the ex-situ SbSPCE was successfully applied for the determination of low concentration levels of Pd(II) in spiked tap water with a very high reproducibility (0.2 %) and providing equivalent results to those achieved by ICP-MS measurements.

Graphical abstract
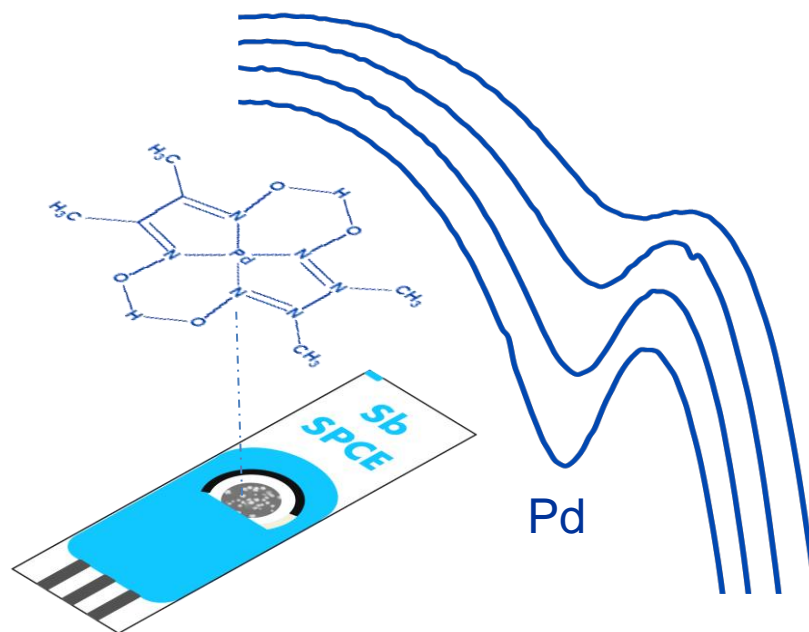
Determination of Pd(II) using an antimony film coated on a screen−printed electrode by adsorptive stripping voltammetry

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ABSTRACT

The use of an antimony film coated on a screen-printed carbon electrode (*ex-situ* SbSPCE) is proposed for the determination of Pd(II) at ppb levels in natural samples by adsorptive stripping voltammetry using dimethylglyoxime as chelating agent. *Ex-situ* SbSPCE produces a better analytical performance as compared to a commercially sputtered bismuth screen-printed electrode ($Bi_{sp}SPE$). The detection and quantification limits were 2.7 and 9.0 µg L^{-1} respectively with a good linear behaviour in the wide examined concentration range (from 1 µg L^{-1} up to 100.0 µg L^{-1}, R^2= 0.998). The proposed *ex-situ* SbSPCE showed an excellent repeatability with a relative standard deviation of 0.5 % for ten successive measurements and a very good reproducibility (1.6 % for three different *ex-situ* SbSPCE units within series of ten repetitive assays). Moreover, the *ex-situ* SbSPCE was successfully applied for the determination of low concentration levels of Pd(II) in spiked tap water with a very high reproducibility (0.2 %) and providing equivalent results to those achieved by ICP-MS measurements.

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1. INTRODUCTION

Palladium is a metal that possesses strong catalytic activity, the demand of which has been more than doubled in the past ten years. It is used in electrical equipment, dental appliances, chemical catalysts and jewellery, being the maximum increase in demand for palladium in automotive emission control catalysts. In contrast to other metals, there is little information concerning concentrations of palladium in the environment. However, in the last decades it has been detected that the concentration of palladium is increasing in the overall environment mainly due to its greater use in automobile catalysts and jewellery industry [1-3]. Concentrations of palladium reported in soil samples collected from areas near major roads range from <0.7 to 47 μg/Kg and, concentrations reported in sewage sludge range from 18 to 260 μg/Kg, although a concentration of 4700 μg/Kg has been reported in a sludge contaminated by discharges from the local jewellery industry [3]. Thus, because both its increasing use and the toxicity of compounds of Pd(II) to mammals, fishes and higher plants, the Pd(II) determination is increasingly important [4,5].

There are different techniques such as atomic absorption spectrometry [5-7], high-performance liquid chromatography with photodiode array detector [8], inductively coupled plasma [9], spectrophotometry [4, 10, 11], etc, available for the sensitive analysis of palladium in samples. However, these techniques have some disadvantages such as expertise required, need of sample pre-treatments, time-consuming procedures,

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high initial investment (equipment) and high cost of consumables. In this sense, electroanalytical methods are stated as a very good alternative. In particular, voltammetric stripping techniques provide excellent properties for the determination of metal ions with excellent detection and quantification limits. Moreover, they are highly reproducible, relative low cost, sensitive and selective, and they present capability to multielement analysis [12]. When stripping techniques are coupled with screen-printed electrodes (SPEs), they become especially suitable for *on-site* analysis, since SPE devices usually incorporate the whole electrode system (working, reference and auxiliary). In addition, the use of SPEs instead of classical working electrodes avoids the continuous and tedious cleaning processes. In fact, SPEs have in recent years undergone great improvements, allowing the mass production of reproducible and low-cost miniaturized size devices [13-15].

Traditionally Pd(II) determination based on voltammetric methods was carried out using the hanging mercury drop electrode (HMDE) as working electrode with an excellent analytical performance [16]. Nevertheless, the potential high toxicity of mercury-based electrodes, if they are not conveniently used, has led to their replacement by other electrodes more environmentally friendly but with a similar analytical performance. In this respect, some attempts were undertaken using some substitute voltammetric sensors. Bobrowski *et al.* reported on the applicability of a cylindrical silver-based amalgam film electrode (Hg(Ag)-FE) for the Pd(II) determination by adsorptive stripping voltammetric (AdSV) in the presence of dimethylglyoxime (DMG) [17]. Bismuth and antimony-based electrodes have been postulated over the years as an important alternative to mercury electrodes with great results for analytical purposes [18-21]. Particularly, Van der Horst *et al.* [22, 24] and Silwana *et al.* [23] described good results for the determination of Pd(II) by the AdSV approach using a bismuth film

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coated on a glassy carbon electrode [22] or on a screen-printed carbon electrode [23] and, using a bismuth-silver bimetallic nanoparticles coated on a glassy carbon electrode [24]. Nevertheless, studies devoted to the application of antimony-based electrodes for analysis of Pd(II) are really scarce. In fact, from the best of our knowledge, only a glassy carbon electrode modified with a composite of reduced graphene oxide impregnated with antimony nanoparticles was proposed for this purpose [25]; but the application of antimony coated on screen-printed electrodes (SbSPE) for the Pd(II) determination are not yet attempted. It is worth noting that SbSPE, unlike antimony coated on glassy carbon electrodes (SbGCE), do not require any pre-polishing and in particular Sb film coated on screen-printed carbon electrodes (SbSPCE) can be used for a large set of measurements using the same electrode unit [26].

Thus, in the present study, antimony film coated via *ex-situ* on a commercial screen-printed carbon electrode (*ex-situ* SbSPCE) was successfully applied for the determination of Pd(II) in water samples by means of the AdSV approach using DMG as chelating agent. Furthermore, the *ex-situ* SbSPCE analytical performance was compared with that of a commercial sputtered bismuth screen-printed electrode ($Bi_{sp}SPE$).

2. EXPERIMENTAL SECTION

2.1. Chemicals and Solutions.

Sb(III) 1.000 mg L^{-1} atomic absorption standard solution was obtained from Merck (Darmstadt, Germany). Working Pd(II) solutions were prepared by appropriate dilution of 1.000 g L^{-1} standard solution with HCl 0.01 mol L^{-1}. Other solutions used were: 0.1 mol L^{-1} solution of dimethylglyoxime (DMG) in 95% methanol and 0.1 mol L^{-1} acetate buffer solution (pH 4.5). All other reagents used were Sigma-Aldrich (St. Louis, MO,

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USA) and Panreac (Barcelona, Spain) analytical grade. Ultrapure water was obtained from a Milli-Q plus 185 system, Millipore.

Tap water samples were collected in our laboratory from the local water distribution network, managed by Agbar Company (Barcelona; http://www.agbar.es/eng/home.asp) and mostly using water coming from Llobregat River.

2.2. Instrumentation.

Adsorptive stripping voltammetric (AdSV) measurements were performed using a μAutolab Type III (EcoChemie, The Netherlands) coupled to a Metrohm 663 VA Stand (Metrohm, Switzerland) and a personal computer with GPES version 4.9 data acquisition software (EcoChemie).

The electrochemical cell used consisted in the conventional three-electrode system: an Ag|AgCl|KCl (3 mol L^{-1}) as reference electrode, Pt wire as an auxiliary electrode, and antimony or bismuth screen-printed electrode as working electrode. *Ex-situ* SbSPCE was prepared using a commercial screen-printed carbon disk electrode of 4 mm of diameter (ref. DRP-110, DS SPE) supplied by DropSens (Oviedo, Spain), and Bi$_{sp}$SPE was a sputtered thick film bismuth of 4 mm of diameter (ref. Bi10, DS SPE) obtained also from DropSens.

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

A Crison micro pH 2000 pH-meter was used for pH measurements,

All electrochemical measurements were carried out at room temperature (20 °C) and the antimony film preparation was performed under a purified nitrogen atmosphere (Linde N50).

Inductively coupled plasma mass spectrometry Perkin-Elmer model Elan 6000 (USA) was used for ICP-MS measurements.

2.3. Preparation of *ex-situ* SbSPCE.

Before measurements, the SPCE, the auxiliary, and the reference electrodes were connected to the stand and immersed into a 0.01 mol L^{-1} HCl solution containing 50 mg L^{-1} of Sb(III). After purging the solution for 600 s, a deposition potential of -0.5 V was applied for 300 s with constant stirring, followed by a rest period of 20 s, without stirring. Then, the *ex-situ* SbSPCE was rinsed with water and ready to use. This procedure was tested earlier [26], yielding a very high reproducibility and repeatability.

2.4. Voltammetric measurements.

Linear calibration curves for the determination of Pd(II) using *ex-situ* SbSPCE and $Bi_{sp}SPE$ by AdSV were constructed by adding small volumes of the Pd(II) concentrated standard solution into the electrochemical cell containing 20 mL of 0.1 mol L^{-1} acetate buffer (pH 4.5) and 2 x 10^{-4} mol L^{-1} DMG [17]. Unless otherwise indicated, AdSV measurements were performed applying an accumulation potential (E_{acc}) of -0.6 V during an accumulation time (t_{acc}) of 180 s with constant stirring. After a rest period (t_r) of 20 s without stirring, voltammograms were recorded by scanning the potential from -0.45 to -1.0 V (on *ex-situ* SbSPCE) and from -0.5 V to -1.2 V (on $Bi_{sp}SPE$), using pulse times of 50 ms, pulse amplitudes of 100 mV and a step potential of 5 mV.

Analysis of Pd(II) in the tap water sample by the proposed voltammetric method using an *ex-situ* SbSPCE were carried out measuring 3 replicates of a spiked tap water sample with Pd(II) concentration distributed in the range of the calibration curves. The standard addition method was used to eliminate matrix effects.

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In both cases, linear calibration curves and analysis of tap water samples, in order to eliminate the remaining bound Pd(II)-DMG complex from the working electrode surface a conditioning potential (E_{cond}) of -1.0 V (on *ex-situ* SbSPCE) or of -1.2 V (on $Bi_{sp}SPE$) for 30 s was applied before each measurement.

2.5. Sample preparation.

Water samples collected from the local water distribution network were spiked with 180 µg L^{-1} of Pd(II). This concentration value was further determined by ICP-MS. For voltammetric determinations, a volume of the spiked tap water sample was added into the voltammetric cell containing 0.1 mol L^{-1} acetate buffer (pH 4.5) and 2 x 10^{-4} mol L^{-1} DMG resulting in solution concentrations of 45 µg L^{-1} of Pd(II). The AdSV scan was recorded under the aforementioned electrochemical conditions.

3. RESULTS AND DISCUSSION

3.1. Condition media and optimization of electrochemical parameters.

First it is worth noting that all experiments in this work were performed using 0.1 mol L^{-1} acetate buffer (pH 4.5) and 2 x 10^{-4} mol L^{-1} DMG [17], because even though the best sensitivity in some previous studies for Pd(II) determination [22, 23] was obtained in 0.01 mol L^{-1} ammonia buffer (pH= 9.0 [22] and pH= 9.2 [23]), an analytical misbehavior of stripping signals for Pd(II) (no reproducible signals could be obtained) was observed in this study using the adsorptive approach in ammonium buffer.

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Looking for the highest analytical response the effect of the accumulation potential (E_{acc}), initial potential (E_i) and accumulation time (t_{acc}) on Pd(II) determination were firstly evaluated using *ex-situ* SbSPCE by AdSV.

Then, the effect of E_{acc} over the peak area of Pd(II)-DMG complex reduction signal was tested in the range from -0.2 to -0.9 V with a t_{acc} of 120 s in a solution containing 50 µg L^{-1} Pd(II) at acetate buffer pH 4.5 and 2 x 10^{-4} mol L^{-1} DMG (Figure 1a). As E_{acc} was shifted from -0.2 V to more negative potentials, peak area increased significantly up to -0.6 V. For more negative E_{acc} a diminution of peak area was progressively observed. Therefore, an E_{acc} of -0.6 V was chosen for further experiments.

The value of E_i is another critical point in the determination of Pd(II) by AdSV. Thus, the influence of the E_i over the peak area of Pd(II)-DMG complex was also evaluated in the range from -0.3 to -0.5 V (Results not shown). Maximal peak area was obtained at E_i of -0.45 V and this E_i value was chosen as optimal.

The effect of the t_{acc} over the peak area of Pd(II)-DMG complex was studied in the range of 30-300 s applying an E_{acc} of -0.6 V in the aforementioned solution (Figure 1b). Peak area linearly increases with t_{acc} until 180 s, where the area stabilizes. Therefore, a t_{acc} of 180 s was chosen as ideal looking for a compromise between the time of the analysis and the peak area.

The selected E_{acc}, E_i and t_{acc} to ensure the determination of Pd(II) at Bi_{sp}SPE were also firstly optimized in a solution containing 50 µg L^{-1} Pd(II) at acetate buffer pH 4.5 and 2 x 10^{-4} mol L^{-1} DMG (Results not shown); the compromise conditions were an E_{acc} of -0.6 V applied during a t_{acc} of 180 s and an E_i of -0.5 V. It must be pointed out that using Bi_{sp}SPE more positive potentials cannot be applied to prevent the oxidation of the bismuth [27].

3.2. Analytical characterization

With the purpose of comparing the repeatability and reproducibility of the *ex-situ* SbSPCE and the Bi$_{sp}$SPE, AdSV measurements in a solution containing 50 µg L^{-1} Pd(II) at acetate buffer pH 4.5 and 2 x 10^{-4} mol L^{-1} DMG following the above-mentioned conditions were carried out. Bi$_{sp}$SPE was selected given its commercial character and good analytical performance [28, 29] as the representative bismuth screen-printed electrode. The repeatability was calculated as the relative standard deviation (RSD) of ten repetitive measurements using the same *ex-situ* SbSPCE or Bi$_{sp}$SPE unit yielding a RSD of 0.5 % and 1.3 % for *ex-situ* SbSPCE and Bi$_{sp}$SPE, respectively. The reproducibility estimated from three different *ex-situ* SbSPCE and Bi$_{sp}$SPE units within a series of ten repetitive measurements produced RSD of 1.6 % and 5.0 %, respectively. Calibration plots of Pd(II)-ions ranging from 1.0 to 100.0 µg L^{-1} by AdSV on both *ex-situ* SbSPCE and Bi$_{sp}$SPE were constructed using a concentration of DMG as complexing agent of 2 x 10^{-4} mol L^{-1} and following the above optimized experimental conditions (Figure 2A and 2B, respectively). When an *ex-situ* SbSPCE was used, a well-shaped and defined stripping peak close to -0.7 V was detected over the selected concentration range, whereas the use of a Bi$_{sp}$SPE leaded to a less symmetrical and regular signal close to -0.9 V.

Limit of detection (LOD) and limit of quantification (LOQ) were calculated as 3 and 10 times the standard deviation of the intercept over the slope of the calibration curve respectively. For their determination twelve standard concentrations of Pd(II) were used as calibration samples. The corresponding LOQ was established as the lowest value of the linear concentration range. As shown in Table 1, good linear responses of peak area *vs* Pd(II) concentration was achieved using both *ex-situ* SbSPCE and Bi$_{sp}$SPE and similar sensitivities (a.u. / µg L^{-1}), obtained as the slope value of the calibration curves

of Pd(II), were attained. However, although LODs reached for Pd(II) were at µg L^{-1} level for both *ex-situ* SbSPCE and Bi$_{sp}$SPE, the LOD value obtained using the *ex-situ* SbSPCE was better than that provided by the Bi$_{sp}$SPE.

As it is shown in Table 1, although sensitivities are similar, a lower LOQ was achieved using *ex-situ* SbSPCE, resulting consequently in a wider linear range. Therefore, the described calibration data, together with the much better signal resolution, shape and symmetry and, the notably repeatability and reproducibility, suggest that *ex-situ* SbSPCE could be a better sensor than Bi$_{sp}$SPE for Pd(II) determination.

Regarding previous results, the LOD obtained for the determination of Pd(II) with an *ex-situ* SbSPCE are slightly higher in comparison to those achieved by AdSV using DMG as chelating agent with a cylindrical silver-based amalgam film electrode (Hg(Ag)-FE), 0.15 µg L^{-1}[17]. Nevertheless, it should be pointed out that in contrast: i) the Hg(Ag)-FE repeatability is significantly worse (3.0 %); ii) Hg(Ag)-FE presents a shorter linear range (1-50 µg L^{-1}); and iii) unlike Hg(Ag)-FE, SPCEs which are the basis of *ex-situ* SbSPCE, do not require any polishing prior Sb deposition, whit the plus of the environmental friendly character related to antimony electrodes [21]. Regarding the determination of Pd(II) using other bismuth film electrodes (BiFE), somewhat lower LODs were achieved using a glassy carbon bismuth film electrode (0.12 µg L^{-1}) [22], a SPCE coated with a bismuth film (0.008 µg L^{-1}) [23], or a glassy carbon electrode coated with bismuth-silver bimetallic nanoparticles (0.19 ng L^{-1}) [24]. However, it should be mentioned that in the present work the obtained linear range is much wider and less restricted to lower concentrations (until 100.0 µg L^{-1}) than values obtained in [22] (until 2.5 µg L^{-1}), in [23] (until 0.1 µg L^{-1}) and especially in [24] (until 1 ng L^{-1}). Moreover, the reproducibility reported using Bi film modified SPCE (BiSPCE), the unique reported electrode based on SPEs for Pd(II) determination, is really poor (8.95

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%) [23] compared to that obtained in this study with *ex-situ* SbSPCE (1.6 %). Regarding the determination of Pd(II) with other antimony-based electrode contributions, a glassy carbon electrode modified with a composite of reduced graphene oxide impregnated with antimony nanoparticles (GCE/rGO-SbNPs) [25] provides a detection limit of 0.45 pg L^{-1}, which are considerable lower that the LOD obtained in this study. However, the examined concentration range using GCE/rGO-SbNPs is severely restricted to extremely low concentrations (40-400 pg L^{-1}) and the repeatability is again significantly worse (4.2 %). Finally, it is worth noting that no studies are reported in the literatures about the use of Sb film based- electrodes for Pd(II) determination.

In the last decades a marked increase of palladium in the environment due to the increased use of catalytic converters in automobiles has been shown in air and dust samples, i.e. the concentration of palladium in a roadside dust sample of South East England was 70 ng g^{-1} (mean) or a tunnel dust sample of Munich (Germany) was 100 ng g^{-1} (mean) [1, 2]. Thus, the reported analytical performance suggest that the use of an *ex-situ* SbSPCE at the aforementioned conditions can be fully appropriate for the determination of Pd(II) at ppb levels in natural samples. In addition, the modification of a SPCE support via a film deposition is easier, less time consuming and cheaper than the preparation of a GCE modified with a nanocomposite [21]. Moreover, the *ex-situ* plating or preplated method in comparison with the *in-situ* deposition modality is also a good option if the metal speciation in the sample can be disturbed by the presence of Sb(III)-ions, with the plus that the screen-printed electrode configuration allows an easy connection to portable instrumentation making possible on-site analysis.

3.3. Interference study

The study of the effect of interferences is important because some metal ions can interfere with the determination of Pd(II) by complexing competitively with DMG or producing reduction peaks that overlap with or even totally suppress the Pd(II) peak. In this paper, the potential interference of Co(II), Fe(III) and Ni(II) as commonly occurring interfering ions was studied using *ex-situ* SbSPCE under the optimum conditions detailed above. From the obtained AdSV measurements until a 100:1 Co(II)-to-Pd(II) ratio it seems that Co(II) does not interfere with Pd(II) peak. It is also shown from the obtained results that in the case of Fe(III) and Ni(II) − ions the presence of similar concentrations of Pd(II) and the interfering metal ion generates a decrease on the peak area of Pd(II) close to 20 %. Higher Fe(III) or Ni(II) concentration ratios produce a progressive reduction of Pd(II) peak area. This loss is about 50 % for a concentration ratio of 100:1 Fe(III)-to-Pd(II), whereas for the same Ni(II)-to-Pd(II) ratio the Pd(II) peak is practically suppressed.

Compared with previous reported results using a BiSPCE, as an example of other based-SPE, the presence of Ni(II) and Fe(III) as interfering ions delivered similar effect in the Pd(II) determination [23]. In contrast, in the proposed method for Pd(II)-DMG determination using an *ex-situ* SbSPCE Co(II) does not interfere.

3.4. Tap water analysis

At the view of the preceding results, the *ex-situ* SbSPCE was considered for the determination of Pd(II) in natural waters and its applicability was tested on a spiked tap water. The determination of Pd(II) - ions was carried out by means of the standard addition method. AdSV measurements using the aforementioned conditions were performed, including four metal additions. Figure 3 shows representative adsorptive voltammograms acquired in the analysis of the spiked tap water using *ex-situ* SbSPCE.

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Well- shaped peaks for the Pd(II) - ions were obtained and, as it is shown in inset of Figure 3, good correlation of the representative AdSV measurements was also observed for Pd(II).

Three AdSV replicates of the tap water were analysed using *ex-situ* SbSPCE. The obtained results are summarised in Table 2. A good concordance, inferred by the obtained RSD%, was attained between the different replicates. In order to test the accuracy of the proposed AdSV method the sample was also analysed by ICP-MS, a well-established technique for the determination of metals, and the results obtained from both techniques were statistically compared. In this sense, a two-tailed t-test (equal variances) was carried out and it was concluded that the *ex-situ* SbSPCE and ICP-MS for a confidence level of 95% provide statistically similar results.

Thus, these results confirm the suitability of *ex-situ* SbSPCE for the determination of Pd(II) in natural samples, being a valuable alternative to other electrodes such as mercury or bismuth based- electrodes for the determination of Pd(II) at ppb levels in samples of environmental interest. Moreover, adsorptive stripping voltammetric measurements using an *ex-situ* SbSPCE are proposed as a cheaper and interesting alternative to more conventional techniques such as ICP-MS.

4. CONCLUSIONS

The proposed AdSV method for the determination of Pd(II) is the first approach on Sb film-based electrodes with the additional advantage of using a low-cost commercially available SPCE as a support. In this study the analytical performance of the *ex-situ* SbSPCE was compared with a commercial $Bi_{sp}SPE$, concluding that the *ex-situ* SbSPCE behaves much better for the determination of Pd(II) at $\mu g\ L^{-1}$ levels. Regarding the unique SPE-based approach for Pd(II) determination previously reported, although the

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detection limit achieved using the *ex-situ* SbSPCE is somewhat higher it is essential to note that the reproducibility estimated from different *ex-situ* SbSPCE unit is so much better (it presents also an excellent repeatability) and, the examined linear concentration range is much wider. Moreover, *ex-situ* SbSPCE signifies a notable improvement in comparison with the other reported antimony-based electrode contributions, since the deposition of the Sb film on a SPCE does not require a pre-polishing of the carbon screen-printed surface, which is imperative when a glassy carbon electrode is used as a support. Moreover, *ex-situ* SbSPCE has also the characteristic features of SPEs such as commercial availability, low-cost, disposable character and the easy portability that makes feasible the on-site analysis.

The viability of the AdSV method using the *ex-situ* SbSPCE for Pd(II) determination using DMG was demonstrated using a spiked tap water sample with a very good reproducibility inferred by the RSD (%), providing also comparable results to those obtained by ICP-MS measurements.

Therefore, the above described results suggest that *ex-situ* SbSPCE can be fully suitable for the determination of Pd(II) at ppb levels in environmental samples, particularly considering the reports concerning the increased palladium concentrations in autobahns in the last decades [1-3].

5. AKNOWLEDGMENTS

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Table 1

Table 1. Calibration data for the determination of Pd(II) by DPAdSV on *ex-situ* SbSPCE and Bi_{sp}SPE at 0.1 mol L^{-1} acetate buffer (pH 4.5) and using DMG as complexing agent.

Electrode	Pd(II)			
	Sensitivity (a.u. μg^{-1} L)[a]	R^2	Linear range ($\mu g\ L^{-1}$)[b]	LOD ($\mu g\ L^{-1}$)
Ex-situ SbSPCE	2.25 (0.03)	0.998	9.0 – 100.2	2.7
Bi_{sp}SPE	1.84 (0.05)	0.993	17.9 – 100.2	5.4

(a) The standard deviations are denoted by parenthesis.
(b) The lowest value of the linear range was considered from the LOQ.

Table 2

Table 2. Total concentration of Pd(II) determined in tap water samples by DPAdSV on *ex-situ* SbSPCE by standard addition calibration method applying an E_{acc} of -0.6 V and t_{acc} of 180 s at 0.1 mol L^{-1} acetate buffer (pH 4.5) and by ICP-MS.

	Pd(II)	
	$c_{Pd(II)}$ (µg L^{-1})	RSD (%)
DPAdSV	178.6	0.2
ICP-MS	178.4	0.3

n=3 for RSD (%).

Caption to figures

Figure 1. Effect of accumulation potential (a) and accumulation time (b) on the peak area of Pd(II)-DMG complex signal using an *ex-situ* SbSPCE in 0.1 mol L^{-1} acetate buffer (pH 4.5) and 2 x 10^{-4} mol L^{-1} DMG. An E_{acc} of -0.6 V was used for t_{acc} optimization.

Figure 2. Adsorptive voltammograms and calibration plots (inset) of Pd(II)-DMG system in 0.1 mol L^{-1} acetate buffer (pH 4.5) and 2 x 10^{-4} mol L^{-1} DMG: (a) *Ex-situ* SbSPCE; and (b) Bi_{sp}SPE.

Figure 3. AdSV measurements in tap water samples on *ex-situ* SbSPCE at pH 4.5 and 2 x 10^{-4} mol L^{-1} DMG using an E_{acc} of -0.6 V during a t_{acc} of 180 s and an E_i of -0.45 V. Inset: Pd(II) standard addition plot.
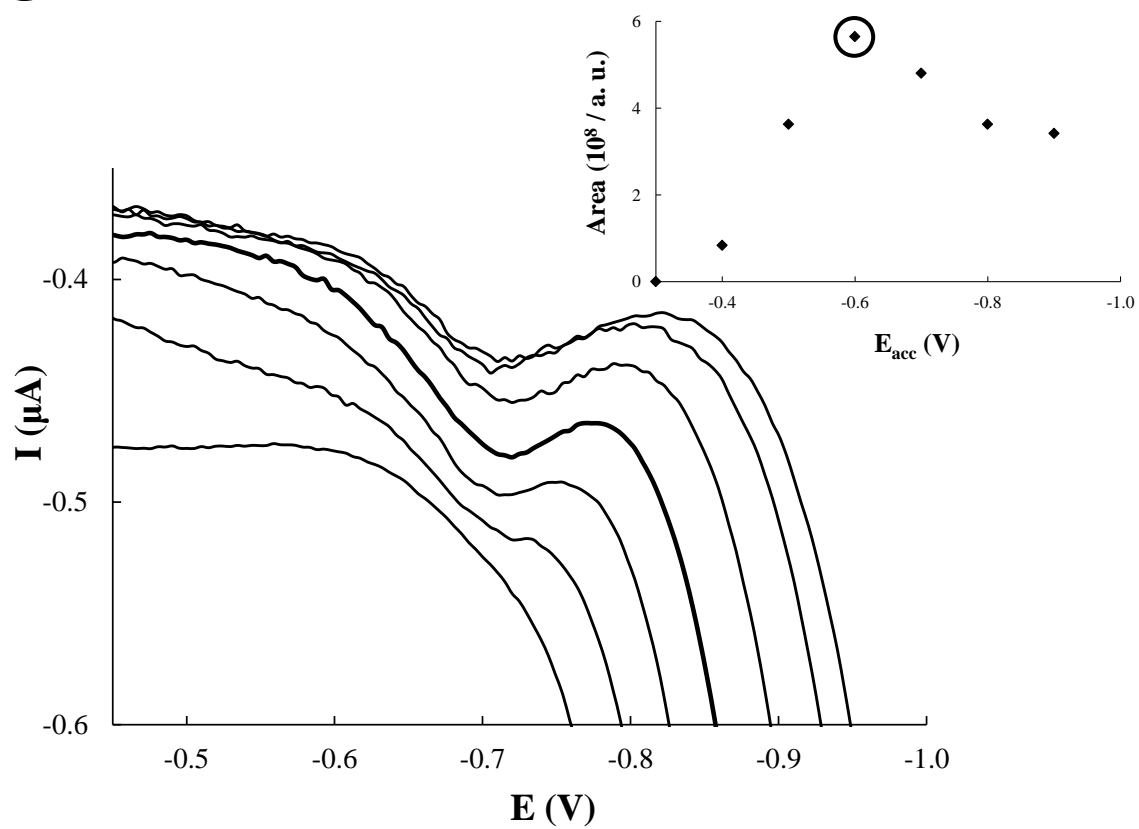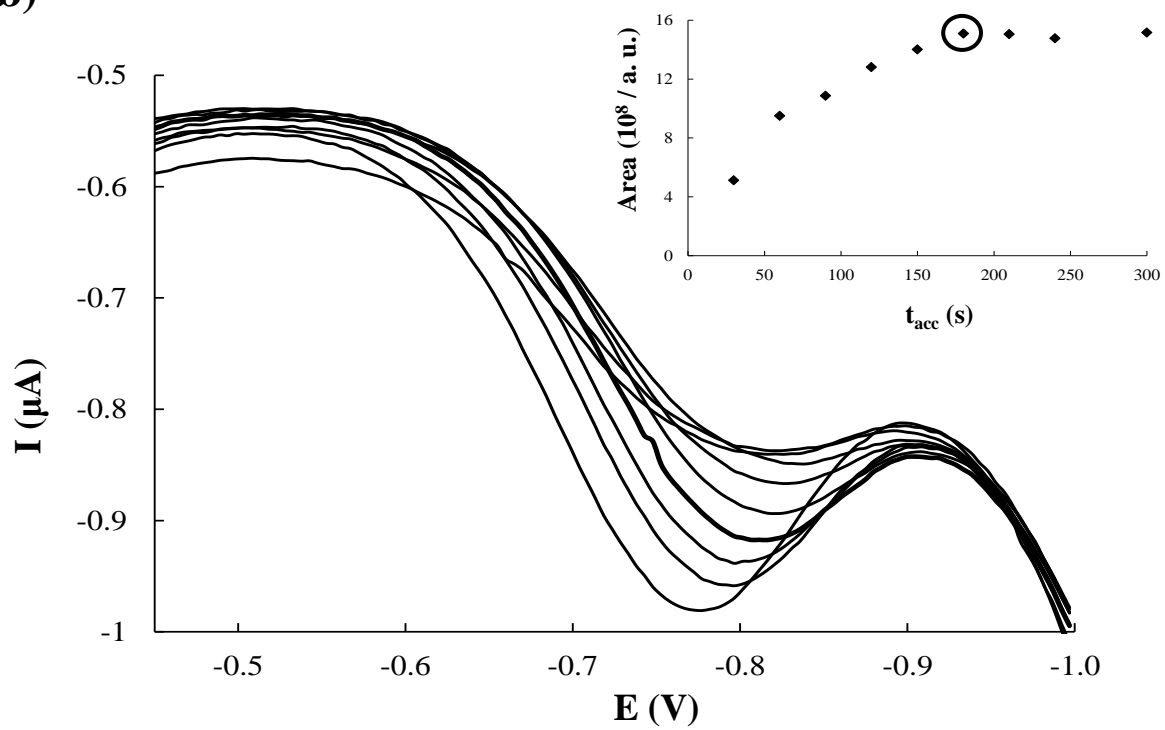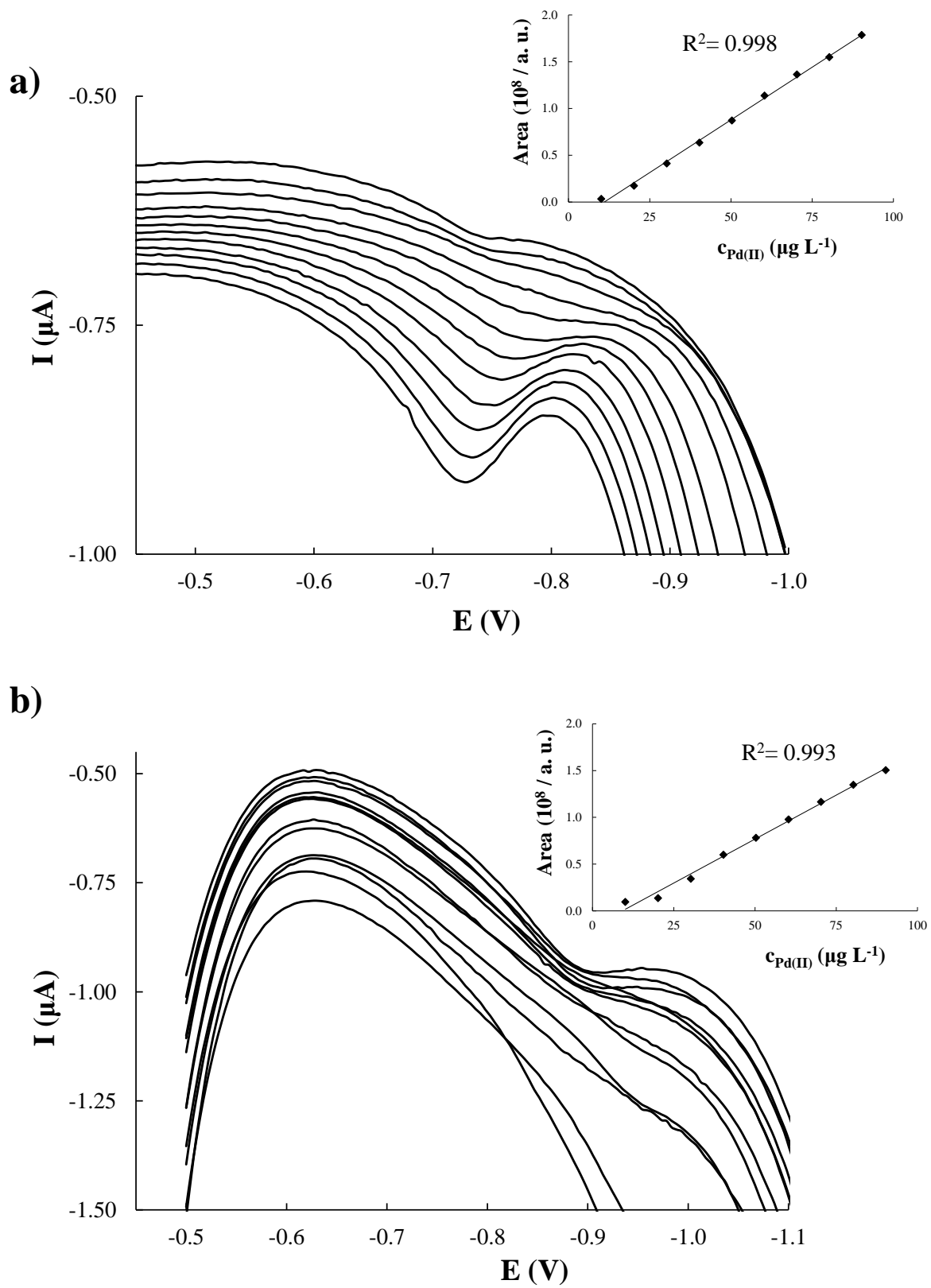
Figure 1

Figure 1

Figure 2

Figure 2

Figure 3

Figure 3