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Ex-situ antimony screen-printed carbon electrode for voltammetric determination of Ni(II) - ions in wastewater

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Abstract

An *Ex-situ* antimony film screen-printed carbon electrode (*Ex-situ* SbSPCE) was successfully applied for the determination of Ni(II), by means of adsorptive stripping voltammetry using dimethylglyoxime as complexing agent, in a certified reference wastewater sample. This electrode is proposed as an alternative to more conventional antimony film electrodes. *Ex-situ* SbSPCE was analytically characterized and the obtained parameters suggest that *Ex-situ* SbSPCE behaves much better than both *Ex-situ* BiSPCE and Bi_{sputtered}SPE for Ni(II) determination. The results confirm the applicability of *Ex-situ* SbSPCE for the determination of low concentration levels of Ni(II) in natural samples with a very high reproducibility and good trueness.

Keywords: antimony film electrodes, screen-printed electrodes, adsorptive stripping voltammetry, nickel

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1. Introduction

Heavy metals such as cadmium, lead, mercury, arsenic, chromium, copper, manganese and nickel have been associated with contamination and potential toxicity or ecotoxicity [1]. Heavy metals may enter the body in food, water, air, or by absorption through the skin, and they are especially dangerous because they tend to bioaccumulate [2]. Particularly, nickel is a common industrial pollutant with concentrations in wastewater around industrial parks sometimes reaching the low millimolar range [3]. Nickel is commonly used to make coins, magnets, jewellery, stainless steel, electronics, and components of industrial machines. Therefore, common sources of Ni(II) are from industry, primarily refining, electroplating, and welding. This metal is typically found in the Ni(0) or Ni(II) state due to the stability of these species in water [4]. Nickel toxicity in humans has received intensive attention due to the link of nickel to cancer [5-8]. Similarly, nickel toxicity to plants is well documented [9].

Stripping techniques are particularly suitable for the determination of trace metals in samples of environmental and biological origin, due to their excellent detection limits, their sensitivity to the presence of different metal species, their capacity to multielement

determination and their simple but complete instrumentation and scarce maintenance. In particular, adsorptive stripping voltammetry (AdSV) was used in the stripping determination of those metal ions that cannot form intermetallic compounds or amalgams with the working electrode [10]. For several decades, electrochemical stripping methods were linked with the use of working mercury electrodes due to their wide cathodic potential range [11]. However, the introduction of bismuth and antimony film electrodes (BiFE and SbFE, respectively), which demonstrated their applicability for electroanalytical purposes, makes mercury electrodes progressively fell into disuse [12-14]. Thus, the determination of Ni(II) was also carried out using different BiFE and SbFE devices modified via *in situ* or *ex situ* electrochemical plating [15-17], as well as with sputtered BiFE [18] and sputtered SbFE [19].

Nowadays the screen-printing technology is a recognized method for the fabrication of sensors and biosensors for the determination of metal ions in several applications [20]. Screen-printed electrodes (SPEs) usually include a three electrode configuration (working, counter and reference electrodes) printed on the same strip. Moreover, SPEs are known for their accessible, low-cost character, miniaturized size, and the possibility

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of connecting them to portable instrumentation. Despite bismuth screen-printed electrodes (BiSPEs) [21] were successfully used for the determination of Ni(II) by AdSV, from the best of our knowledge studies devoted to the application of antimony screen-printed electrodes (SbSPE) for analysis of nickel are not yet attempted.

Thus, in the present work, an *Ex-situ* antimony electrode obtained from the modification of a commercial screen-printed carbon electrode (*Ex-situ* SbSPCE) was applied for the first time to the determination of Ni(II) - ions by AdSV and using dimethylglyoxime (DMG) as complexing agent for Ni(II) in a certified wastewater sample, as an example of its applicability for the analysis in environmental samples. Moreover, *Ex-situ* SbSPCE was analytically compared with *Ex-situ* BiSPCE and sputtered BiSPEs (Bi_{sputtered}SPEs) as working electrodes.

2. Experimental

2.1. Chemicals

A Sb(III) 1.000 g L⁻¹ atomic absorption standard solution and a Bi(III) 1.000 g L⁻¹ atomic absorption standard solution were purchased from Merck. Certified reference material, wastewater (SPS-WW2) was purchased from Spectrapure Standards. All other reagents used were Fluka and Panreac analytical grade. Working Ni(II) metal ion solution was prepared from 1.000 g L⁻¹ atomic absorption standard after appropriate dilution. Other reagents used were: 0.1 mol L⁻¹ solution of dimethylglyoxime (DMG) in 95% methanol, 0.01 mol L⁻¹ hydrochloric acid, 0.2 mol L⁻¹ acetate buffer solution (pH 4.5) and 0.1 mol L⁻¹ ammonia buffer (pH 9.2) solution. Ultrapure water (Milli-Q plus 185 system, Millipore) was used in all experiments.

2.2. Apparatus

Adsorptive stripping voltammetric (AdSV) measurements were performed 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 an antimony or bismuth screen-printed electrode. *Ex-situ* SbSPCE and *Ex-situ* BiSPCE were prepared from a commercial screen-printed carbon disk electrode of 4 mm of diameter (ref. DRP-110, DS SPE) provided by DropSens (Spain). Bi_{sp}SPE

was a sputtered thick film bismuth of 4 mm of diameter (ref. Bi10, DS SPE) provided by DropSens (Spain).

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

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

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

Unless otherwise indicated, a pulse time of 40 ms, step potential of 5 mV, and pulse amplitude of 50 mV were applied in the stripping step. A deposition potential (E_d) of -0.7 V was applied with stirring during the optimized deposition time (t_d) of 120 s, and a rest period (t_r) of 20 s was maintained between deposition and stripping steps.

2.3. Experimental procedure

2.3.1. *Ex-situ* preparation of SbSPCE

For the antimony *Ex-situ* modification of SPCE, the SPCE, the reference, and the auxiliary electrodes were connected to the stand and immersed into 20 mL plating solution containing 0.01 mol L⁻¹ HCl and 50 ppm of Sb(III). After deaeration of the solution for 10 min, an E_d of -0.50 V was applied during 300 s with solution stirring, followed by a rest period (without stirring) of 20 s. Once the antimony film was deposited, all electrodes were rinsed carefully with water and the Sb(III) solution was replaced in the cell by the one to be measured. This methodology, which partially modifies a previous one [16], showed a very high repeatability and reproducibility. The surface morphology characterization of the *Ex-situ* SbSPCE was previously carried out by Scanning Electron Microscopy (SEM) [22].

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, an E_d of -0.80 V was applied during 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 repeatability and reproducibility [23]. The scanning electron micrographs of the *Ex-situ* BiSPCE and the Bi_{sp}SPE were compared in previous work (Figure 1 in [24]).

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2.3.3. Procedure

The linear calibration plots for the determination of Ni(II) on an *Ex-situ* SbSPCE, *Ex-situ* BiSPCE and Bi_{sp}SPE by AdSV were obtained increasing metal concentration in 0.1 mol L⁻¹ ammonia buffer (pH 9.2) and 5 × 10⁻⁵ mol L⁻¹ DMG [16].

In the analysis of the certified wastewater sample using an *Ex-situ* SbSPCE, voltammetric analysis started by placing in the cell a volume of the sample (SPS-WW2) in 0.1 mol L⁻¹ ammonia buffer (pH 9.2) and 5 × 10⁻⁵ mol L⁻¹ DMG. Then, the sample was deaerated with pure nitrogen for 15 min, to avoid the effect of oxygen in voltammetric measurements, and the AdSV scan was recorded. In the case of calibration by standard addition, six aliquots of Ni(II) standard solution were further added and the respective voltammograms were recorded. All solutions were deaerated and mechanically stirred for 30 s after each standard addition.

In both, linear calibration plots and analysis of the certified wastewater sample, before each measurement on an *Ex-situ* SbSPCE a cleaning step was performed by keeping the working electrode at -1.25 V for 30 s.

3. Results and discussion

3.1. Linearity, limit of detection (LOD) and limit of quantification (LOQ)

The selected E_d , t_d and t_r were firstly optimized to ensure the detection of Ni(II) at *Ex-situ* SbSPCE, *Ex-situ* BiSPCE and Bi_{sp}SPE in the selected concentration range; the compromise conditions were in all cases a E_d of -0.7 V applied with stirring during a t_d of 120 s and followed for a t_r of 20 s.

Calibration of Ni(II) - ions by adsorptive stripping voltammetry (AdSV) was carried out on an *Ex-situ* SbSPCE, *Ex-situ* BiSPCE and Bi_{sp}SPE. The LOD was calculated as 3 times the standard deviation of the intercept over the slope of the calibration curve of the target ions. LOQ was evaluated by considering 10 times the previous ratio. The lowest value of the linear concentration range was established from the corresponding limit of quantification (LOQ). For LOD and LOQ determinations, twelve standard concentrations of Ni(II) were used as calibration samples. A well-defined stripping peak without any evidence of signal splitting was observed over the selected concentration range for all the considered modified screen-printed electrodes. It is worth noting that, while no stripping signals for Ni(II) were obtained in a previous work [19] by AdSV using also DMG as complexing agent on an *Ex-*

situ electroplated antimony film electrode (*Ex-situ* SbFE), regular-shaped Ni(II) stripping peaks were obtained in this work with the *Ex-situ* SbSPCE adsorptive approach. Excellent linear responses of the peak area *versus* concentration were also obtained for Ni(II) until a concentration level of 197 µg L⁻¹ for *Ex-situ* SbSPCE, and 226 µg L⁻¹ for an *Ex-situ* BiSPCE and Bi_{sp}SPE.

The corresponding regression equations and the correlation coefficient for the three considered screen-printed electrodes are shown in Table 1. It must be pointed out that similar voltammetric responses for Ni(II) were observed using *Ex-situ* SbSPCE, *Ex-situ* BiSPCE and Bi_{sp}SPE at the same experimental conditions. Nevertheless, regarding the sensitivities considered as the value obtained from the slope of the calibration curves, it can be mentioned that Ni(II) shows the best sensitivity with an *Ex-situ* SbSPCE followed by an *Ex-situ* BiSPCE; on the contrary, Bi_{sp}SPE offers the lowest sensitivity. Figure 1 compares AdSV measurements of 45 µg L⁻¹ of Ni(II). Consequently, *Ex-situ* SbSPCE (thick solid line) exhibited a higher signal for Ni(II) than *Ex-situ* BiSPCE (dotted line) and, the *Ex-situ* BiSPCE (dotted line) revealed a higher contribution for Ni(II) determination than Bi_{sp}SPE (thin solid line).

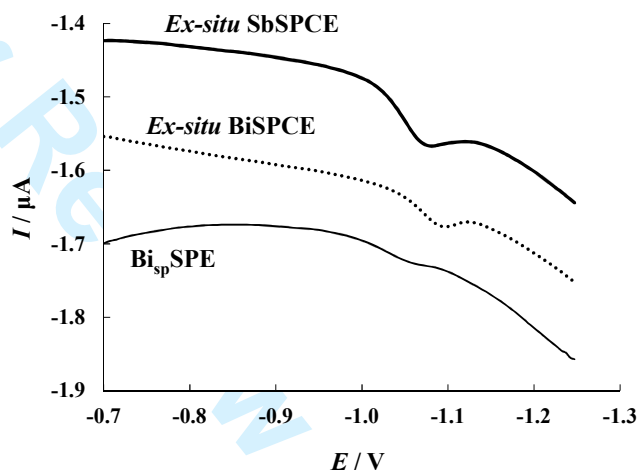


Fig. 1. AdS voltammograms of 45 µg L⁻¹ Ni(II) on *Ex-situ* SbSPCE (thick solid line), *Ex-situ* BiSPCE (dotted line) and Bi_{sp}SPE (thin solid line) in 0.1 mol L⁻¹ ammonia buffer (pH 9.2) and 5 × 10⁻⁵ mol L⁻¹ DMG using a E_d of -0.70 V during a t_d of 120 s and t_r of 20 s.

As shown in Table 1, both LOD and LOQ were at the level of µg L⁻¹ for all considered modified screen-printed electrodes. Regarding LOD values, it must be pointed out that the SbSPCE units obtained using the *Ex-situ* approach produced the lowest LOD; while the highest

Table 1. Calibration data for the determination of Ni(II) on *Ex-situ* SbSPCE, *Ex-situ* BiSPCE and Bi_{sp}SPE at pH 9.2.

Electrode	Ni(II)			
	Regression ^(a)	R ²	Linear range (µg L ⁻¹) ^(b)	LOD (µg L ⁻¹)
<i>Ex-situ</i> SbSPCE	$y = 8.50x - 0.57$	0.9999	3.1 – 197	0.9
<i>Ex-situ</i> BiSPCE	$y = 3.67x + 16.1$	0.9992	9.8 – 226	2.9
Bi _{sp} SPE	$y = 0.99x - 15.0$	0.9985	15.6 – 226	4.7

^(a) y is the peak area (a.u.) and x the concentration (µg L⁻¹).

^(b) The lowest value of the linear range was considered from the LOQ.

LOD was provided by Bi_{sp}SPE. In comparison with previous works using other antimony modified electrodes, the LOD provided by *Ex-situ* SbSPCE was similar than the LOD obtained using *In-situ* antimony film electrodes (*In-situ* SbFE) [17] and sputtered antimony film electrodes (Sb_{sp}FE) [19]. In this work a t_d of 120 s was selected instead of the value of 60 s used in previous studies, although the glassy carbon substrate electrode used in these works for the preparation of the SbFE [17, 19] had a lower diameter (2 mm) than the screen-printed disk electrodes (4 mm) modified in the present study.

In order to compare the repeatability and reproducibility of the screen-printed carbon electrodes modified via *ex-situ* with both antimony and bismuth, adsorptive stripping measurements following the above-mentioned conditions were carried out. The reproducibility, from three different units modified with the same electrode material, was calculated as the relative standard deviation (RSD) of 10 consecutive determinations in independent solutions containing 45 µg L⁻¹ of Ni(II) and appeared to be 4.4 % and 6.1 % for *Ex-situ* SbSPCE and *Ex-situ* BiSPCE, respectively. The repeatability estimated using the same *Ex-situ* SbSPCE or *Ex-situ* BiSPCE units for ten repetitive measurements produced RSD of 1.9 % and 2.6 %, respectively.

In agreement with the better analytical performance of SbSPCE versus BiSPE, the *Ex-situ* SbSPCE could be considered as a valuable alternative to more widespread bismuth modified electrodes for the determination of traces of Ni(II) - ions in real samples. In addition, it is demonstrated that *Ex-situ* SbSPCE is also an interesting alternative to other SbFEs, since the low-cost commercial availability of the screen-printed carbon electrodes which are the basis of SbSPCE ensures a cheap and user-friendly methodology (unlike glassy carbon electrode, SPCE units do not require any polishing prior to

antimony deposition), with the plus that the Sb(III) hydrolysis, which occurs at relatively high pH, is avoided via the acidic *ex-situ* protocol.

3.2. Interference study

Some metal ions could interfere with the determination of Ni(II) by complexing competitively with DMG or giving peaks that overlap with the Ni(II) peak. In this work, the possible interference of Co(II) and Fe(III) using an *Ex-situ* SbSPCE were examined: Co(II) - ions were considered as potential interferences since they appear at similar potential range as Ni(II), and Fe(III) - ions were considered because of their ubiquity. AdSV measurements obtained until a 100:1 Fe(III)-to-Ni(II) ratio show that Fe(III) does not interfere with the Ni(II) peak. However, in the case of Co(II) - ions, the presence of similar concentrations of Ni(II) and Co(II) produces AdSV signals that are overlapping with each other as in some bismuth based electrodes [18]. Therefore, the simultaneous determination of both metal ions demands the use of multivariate calibration methods. In this sense, further detailed studies based on the application of multivariate calibration methods to the AdSV determination of Ni(II) and Co(II) with DMG at bismuth and antimony electrodes are in progress in our laboratory.

3.3. Application to the analysis of wastewater samples

After comparing the analytical performance of the different considered screen-printed electrodes, an *Ex-situ* SbSPCE was selected to study its applicability for the determination of Ni(II) in a wastewater certified reference material (SPS-WW2). Ni(II) - ions was determined by means of the standard addition method.

Table 2. Total concentrations of Ni(II) determined in certified wastewater (SPS-WW2) by adsorptive stripping voltammetry on *Ex-situ* SbSPCE by standard addition calibration method applying an E_d of -0.7 V and t_d of 120 s at pH 9.2.

	Ni(II)		
	c ($\mu\text{g L}^{-1}$)	RSD (%)	Relative error (%)
	4992.5	0.1	0.2
Certified metal value	5000.0	0.5	—

n=3 for RSD (%)

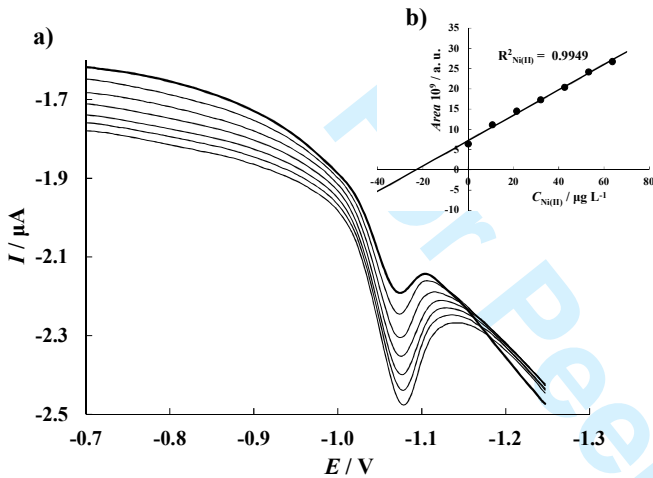


Fig. 2. a) AdSV measurements in wastewater samples on *Ex-situ* SbSPCE at pH 9.2 and $5 \times 10^{-5} \text{ mol L}^{-1}$ DMG using a E_d of -0.70 V during a t_d of 120 s and t_r of 20 s; and, b) Ni(II) standard addition plot.

Then, adsorptive stripping voltammetric measurements following the aforementioned conditions were carried out including the additions of Ni(II). It should be considered that the same *Ex-situ* SbSPCE device was used for the AdSV measurements of a complete replicate. Figure 2a shows representative AdS voltammograms obtained in the analysis of the wastewater samples using *Ex-situ* SbSPCE. Ni(II) behaves in the same way as in the calibration data: a well-defined peak for the metal ion was obtained.

Standard addition plot for Ni(II) (Figure 2b) shows the good correlation of the representative adsorptive stripping voltammetric measurements carried out using *Ex-situ* SbSPCE. The Ni(II) concentration data obtained from the AdSV determination of three replicates of the certified wastewater sample performed using the *Ex-situ* SbSPCE are reported in Table 2. An excellent concordance between Ni(II) concentration, as well as with the certified Ni(II) value in wastewater, was obtained.

Thus, *Ex-situ* SbSPCE is postulated as a good and less toxic substitute for mercury electrodes for the determination of low level concentrations of Ni(II) in samples of environmental interest.

4. Conclusions

In this study, the analytical performance of *Ex-situ* SbSPCE was compared with these of *Ex-situ* BiSPCE and Bi_{sp}SPE. At the view of the results, it can be concluded that *Ex-situ* SbSPCE behaves much better than both *Ex-situ* BiSPCE and Bi_{sp}SPE for the determination of Ni(II) - ions below $\mu\text{g L}^{-1}$ level. Regarding to other SbFE approaches, although *Ex-situ* SbSPCE requires a pre-plating it is important to note that this protocol avoids the Sb(III) hydrolysis occurring at relatively high pH. Moreover, the main advantage of the *Ex-situ* SbSPCE is that in contrast to the GCE, which are the basis of the *In-situ* and *Ex-situ* SbFE, SPCEs do not require any polishing prior to antimony deposition. On the other hand, the low-cost commercial availability of the SPCEs in comparison with the sputtered devices (somewhat more expensive), and the good reproducibility exhibited positioned them as a suitable choice for the determination of Ni(II). Moreover, the *Ex-situ* SbSPCE can be used for a large set of measurements without signs of degradation or loss of sensitivity. Related to its analytical behavior, *Ex-situ* SbSPCE generates a well-defined peak for Ni(II) without signal splitting in all the concentration range. The provided LOD and LOQ were at levels of $\mu\text{g L}^{-1}$ and similar as those obtained using other SbFE electrodes. Furthermore, the above reported results show that *Ex-situ* SbSPCE can be successfully applied for the determination of Ni(II) in a wastewater sample with very high reproducibility and good trueness inferred by the relative standard deviation (0.1 %) and the relative error (0.2 %), respectively.

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