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Electrochemistry

ELECTROCHEMICAL CHARACTERIZATION OF AND STRIPPING VOLTAMMETRY AT SCREEN PRINTED ELECTRODES MODIFIED WITH DIFFERENT BRANDS OF MULTIWALL CARBON NANOTUBES AND BISMUTH FILMS

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A screen-printed electrode sensor has been fabricated by modifying the carbon ink surface with different brands of multiwall carbon nanotubes (MWCNTs) and bismuth film (BiF) for the determination of traces of lead, cadmium and zinc ions by square wave anodic stripping voltammetry. The MWCNTs, from three different sources, were functionalized and dispersed in Nafion (MWCNT-Nafion) solution and placed on screen printed electrodes (MWCNT-Nafion|SPE); bismuth films were then prepared by ex-situ plating of bismuth onto the MWCNT-Nafion|SPE electrodes. The electrochemical characteristics of BiF|MWCNT-Nafion|SPE| were examined by electrochemical impedance spectroscopy and showed differences; the charge transfer resistance tends to decrease with negative applied potentials. After optimizing the experimental conditions, the square-wave peak current signal is linear in the nmol L^{-1} range. The lowest limit of detection found for the separate determination of lead, cadmium and zinc were 0.7 nmol L^{-1}, 1.5 nmol L^{-1}, and 11.1 nmol L^{-1}, respectively, with a 120 s deposition time.

Keywords: Bismuth film; Electrochemical impedance spectroscopy; Heavy metals; Multiwall carbon nanotubes; Screen-printed electrodes; Square wave anodic stripping voltammetry

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INTRODUCTION

Contamination of the environment by trace metals is a major current problem and results in an ever-increasing demand for the determination of metal contaminants in environmental matrices. Electrochemical stripping analysis has long been recognized as a powerful technique for trace metals owing to its remarkable sensitivity, relatively inexpensive instrumentation, ability for multi-element determination, and capability of determining elements accurately at trace and ultratrace levels (Achterberg and Braungardt 1999). Anodic stripping voltammetry (ASV) is based on pre-concentration by reductive electrodeposition followed by anodic stripping of the reduced form of the analyte, nowadays usually in the sample solution. For many years, mercury film electrodes and the hanging mercury drop electrode were used for ASV owing to the advantageous analytical properties of mercury in the negative potential range. Since the year 2000, bismuth film electrodes (BFEs) have become attractive new alternative electrode materials as a potential replacement for mercury and mercury film electrodes (J. Wang et al. 2000; J. Wang 2005; Economou 2005). The behavior of bismuth electrodes has been shown to compare favorably with that of mercury electrodes, with attractive properties such as high sensitivity, well-defined stripping signals, good resolution of neighboring peaks, wide negative potential range, and insensitivity to dissolved oxygen. This latter characteristic is an essential property for on-site monitoring.

Bismuth films are usually deposited at constant potential. There are two main types of BiF: in situ, when Bi is deposited directly in sample solution in the presence of the analyzed ions; and ex-situ, when BiF is pre-plated in a separate plating solution and then transferred to the sample solution for analyte determination. In the first case the main aim is efficient film co-deposition using as low concentrations as possible and as short deposition time to get a continuous film. A thicker film is needed for ex-situ determination, and the thickness can be adjusted by changing Bi(III) concentration and deposition time, as well as the electrolyte solution and its pH. BiF stability mostly depends on the electrolyte solution and pH, so, from pH 1 to 5 it is stable in acetate, chloride and bromide solutions. At pH from 5 to 10, Bi(III) forms insoluble oxy salts, and from pH 10 to 12, it forms soluble hydroxy complexes (Švancara and Vytřas 2006; Švancara et al. 2010). Electrochemical Bi deposition processes from different media are described elsewhere (Švancara and Vytřas 2006).

In the last two decades, carbon nanotubes (CNTs) have attracted increased attention, because of their unique electronic, chemical and mechanical properties. CNTs can be used as electrode materials with electrocatalytic properties and with enhanced current due to the larger surface area, for electrochemical and bioelectrochemical applications (Gooding 2005). Multiwalled carbon nanotubes (MWCNTs) consist of several concentric tubes of graphene inside one another. The reactivity of CNT has been shown to be due to the edge plane sites and to structural defects on the cylindrical surface of the nanotubes (Wildgoose et al. 2006). Owing to the good properties previously described, CNTs have been widely applied to modify electrodes in order to construct different chemical and biological sensors (Sun and Sun 2008; Agüí, Yeáñz-Sedeño, and Pingarrón 2008; Lahiff et al. 2010). Nevertheless, the insolubility of CNTs can be a major drawback to their use in electrochemical sensors and biosensors. Several strategies have been proposed to dissolve CNTs including oxidative treatment, polymer wrapping, and sidewall functionalization. Functionalization of CNTs improves solubility and processability, giving the opportunity to develop new types of nanotube-based materials (Agüí et al. 2008).

To achieve better performance, various polymers have been reported for the dispersion of CNTs, exploiting the surface wrapping effect. For example, amphiphilic polycations, polystyrene sulfonates, and hydrolysed poly(styrene-alt-maleic anhydride) were successfully employed to disperse CNTs (Agüí et al. 2008; Lahiff et al. 2010). Another possibility is Nafion, which has been widely used in recent years as an electrode chemical modifier because of its attractive permselective, ion-exchange, and antifouling properties (Wang 2005). The MWCNT can be dispersed in Nafion and cast on a glassy carbon (GC) electrode (Agüí et al. 2008) to construct an electrochemical sensor for the analytical determination of heavy metals in the presence of surfactants such as sodium dodecyl sulfate (SDS) and Triton X-100.

Surface functionalization aids in the carbon nanotube materials becoming biocompatible, improving their solubility in physiological solutions and their selective binding to biotargets. Functionalized MWCNTs are believed to be very promising in fields such as the preparation of functional and composite materials and in biological technologies. Also, nanotubes have large inner volumes, which, in principle, can be filled with any desired chemical or biochemical species ranging in size from proteins to small molecules. Thus, the development of simple and cost-effective chemical methods for the functionalization of carbon nanotube materials is becoming an area of growing fundamental and industrial importance (Agüí et al. 2008; Lahiff et al. 2010).

Although bismuth film electrodes have been extensively studied, BiF/CNT-modified electrodes are relatively rare and have only been employed for anodic stripping measurements of heavy metals (Hwang et al. 2008; Y. D. Wang et al. 2009; Gouveia-Caridade, Pauliukaite, and Brett 2006; N. Wang and Dong 2009; Xu et al. 2008). There is no information in the literature, to our knowledge, concerning interactions between bismuth and CNT.

In this work, a BiF/MWCNT modified screen printed electrode was fabricated for the determination of heavy metals by square wave anodic stripping voltammetry (SWASV). Different brands of MWCNT were dispersed in Nafion and tested. Bismuth film electrodes were prepared by ex situ plating of bismuth onto the MWCNTs-Nafion/SPE, and were characterized by electrochemical impedance spectroscopy (EIS). They were tested for trace analysis of Pb(II), Cd(II), and Zn(II) and simultaneous determination of trace heavy metals was performed by square wave anodic stripping voltammetry.

EXPERIMENTAL

Reagents

Nafion (5% w/v solution in a mixture of water and aliphatic alcohols) was purchased from Aldrich. Acetate buffer (0.1 mol L^{-1}) with pH adjusted to 4.5 was prepared with acetic acid and sodium acetate from Riedel-de Haen. Stock solutions for bismuth plating were prepared from bismuth nitrate (Merck, Germany), whereas lead nitrate, cadmium sulfate, and zinc sulfate (all from Merck, Germany) were employed in the preparation of 1000 mg L^{-1} metal-ion stock solutions. All chemicals were of analytical reagent grade and used as supplied and all solutions were prepared with ultrapure Millipore Milli-Q water (resistivity >18 MΩ cm).

Different brands of multiwalled carbon nanotubes were used: $MWCNT_{Sig}$ from Sigma, Germany with >90% purity, diameter 110–170 nm and length 5–9 µm, $MWCNT_{Nan}$ from Nanolab, USA with ~95% purity, diameter 30 ± 10 nm and length 1–5 µm, and $MWCNT_{She}$ from Shenzhen Nanotech, China with >90% purity, diameter 40–60 nm and length 5–15 µm.

Apparatus

The SPEs were a kind gift from the University of Rome "Tor Vergata" and were produced with a 245 DEK (Weymouth, England) screen-printing machine. Graphite-based ink (Elettrodag 421) from Acheson (Milan, Italy) was used to print the working and counter electrode. The substrate was a flexible polyester film (Autostat HT5) obtained from Autotype Italia (Milan, Italy). Finally, an insulating ink was used to define the area of the working electrode surface. A curing period of 10 min at 70°C was used. The working and counter electrodes were printed from carbon ink and the pseudo reference electrode was printed from silver ink. The diameter of the working electrode was 0.3 cm, corresponding to a geometric area of 0.070 cm^2.

All voltammetric experiments were carried out using a PalmSens portable electrochemical analyzer (Palmsens BV, Houten, Netherlands) with PS-Lite software.

EIS measurements were carried out in the same cell with a PC-controlled Solartron 1250 frequency Response Analyser coupled to a Solartron 1286 Electrochemical Interface (Solartron Analytical, UK). A sinusoidal voltage perturbation of 10 mV amplitude was applied over the frequency range 65 kHz to 0.1 Hz with 10 measurement points per frequency decade; integration time was 60 s using short integration mode. Fitting to electrical equivalent circuits was performed with ZView 2.4 software (Solartron Analytical, UK).

All experiments were performed in an air-conditioned laboratory at room temperature (25 ± 1°C).

Procedures

Electrode pre-treatment. The electrode surface was conditioned at +1.6 V for 120 s and at +1.8 V for 60 s; in 50 mM acetate buffer solution (pH = 4.6) before the voltammetric measurement. The application of high positive potentials in acidic media seems to increase the hydrophilic properties of the electrode surface through the introduction of oxygenated functionalities by oxidative cleaning (Rice, Galus, and Adams 1983; Palchetti and Mascini 2006).

Functionalization of the multiwall carbon nanotubes. The MWCNTs were purified and functionalized by stirring in 3 M nitric acid solution for 24 h. The solid product was collected on a filter paper and washed several times with nanopure water until the filtrate pH became nearly neutral. The functionalized MWCNTs obtained were then dried in an oven at ≈80°C for 24 h. This procedure was performed to ensure complete removal of transition metal ion catalyst, used in the production of nanotubes, as well as of amorphous carbon. Nitric acid also causes significant destruction of carbon nanotubes and introduces –COOH groups at the ends of, or at the sidewall defects in the nanotube structure (Agüí et al. 2008; Lahiff et al. 2010).

Preparation of the bismuth Film/MWCNT modified SPE. A MWCNT-Nafion suspension was made by adding 0.5 mg of functionalized MWCNT to 1.0 ml, 0.1% Nafion solution (in ethanol) and then sonicating in an ultrasonic bath for 30 min. A volume of 5 μL of MWCNT-Nafion suspension was dropped onto the carbon working electrode surface and dried for 30 min in air. To preplate the substrate with a bismuth film, the MWCNT-Nafion/SPE was immersed in the bismuth plating solution, containing 2.39 μmol L^{-1} of Bi(III), and the bismuth film was formed by holding the working electrode potential at -1.1 V under constant stirring conditions. Then, the electrode was removed from the solution, rinsed with water, and transferred to sample solution.

Determination of lead, cadmium, and zinc by stripping voltammetry using BiF/MWCNT-Nafion/SPE. The BiF/MWCNT-Nafion/SPE was immersed in the sample solution, and SWASV was carried out using experimental conditions optimized in a previous paper (Mandil and Amine 2009). Deposition of the heavy metals was carried out at -1.0 V under stirring for a defined period of time, followed by a 15 s rest period. The square wave stripping voltammograms were recorded between -1.0 and -0.2 V, and the electrode was then cleaned of residual metal at $+0.3$ V for 30 s without stirring. All measurements were carried out in 0.1 mol L^{-1} acetate buffer (pH = 4.6) plus 50 mmol L^{-1} KCl solution. Zinc was determined using a pre-concentration potential of -1.3 V under stirring conditions for 120 s. The stirring was then stopped and, after a 15 s equilibration time, the SW stripping voltammogram was recorded between -1.3 V and -0.7 V (frequency: 15 Hz, pulse height: 20 mV, step increment: 5 mV). For the determination of lead and cadmium the deposition potential was -1.0 V and all the other conditions, in the stripping potential range from -1.0 to $+0.2$ V, were as for Zn(II).

After each stripping experiment, the electrode was conditioned at $+0.55$ V for 30 s to remove any residual metal.

RESULTS AND DISCUSSION

Influence of Bismuth Film

The SWASV of Zn(II), Cd(II), and Pb(II) was carried out at SPE, MWCNT-Nafion/SPE, and at BiF/MWCNT-Nafion/SPE and the signal responses were compared in order to observe the influence of the bismuth film. Functionalized MWCNTs were used, because preliminary results with non-functionalized carbon nanotubes gave small current responses.

Figure 1 illustrates the results obtained with a solution containing 0.19 μmol L^{-1} of Pb(II) in 0.1 mol L^{-1} acetate buffer pH 4.6. illustrated using $MWCNT_{Nan}$. The peak current was 2 times greater at the $MWCNT_{Nan}$-Nafion/SPE modified with a bismuth film (Fig. 1c) than without Bi (Fig. 1b), in turn more than twice that without CNT

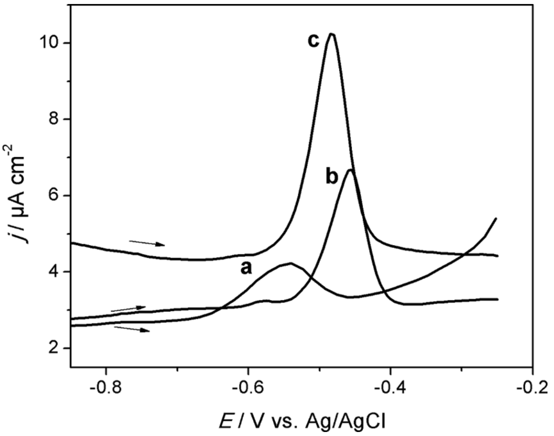

Figure 1. Square wave anodic stripping voltammograms at (a) SPE modified with bismuth film, (b) $MWCNT_{Nan}$-Nafion/SPE without BiF, and (c) $MWCNT_{Nan}$-Nafion/SPE modified with bismuth in a solution containing 0.19 μmol L^{-1} of Pb(II) in 0.1 mol L^{-1} acetate buffer (pH 4.5). See text for SWASV experimental conditions.

(Fig. 1a). These results can be explained by the fact that: 1) bismuth can form an "alloy" with Pb and cause Pb^{2+} to be reduced more easily (Li et al. 2002); 2) the strong adsorptive ability and large electroactive area of MWCNTs attracts Pb(II) and Bi(III) from bulk solution to the electrode surface (Y. D. Wang et al. 2009; Xie et al. 2010).

Similar increases in current response were obtained for Zn(II) and Cd(II) as for Pb(II) on addition of MWCNT. In view of these results, the MWCNT-Nafion/SPE modified with bismuth (BiF/MWCNT-Nafion/SPE) was chosen for the following experiments.

Sensitivity of Different Brands of Carbon Nanotubes

The three different brands of carbon nanotubes used to construct BiF/MWCNT-Nafion/SPE were compared with respect to their sensitivity for Zn (II), Cd(II), and Pb(II) in 0.1 mol L^{-1} acetate buffer +50 mmol L^{-1} KCl solution. Figure 2 shows the response of these different electrodes to 19.2 nmol L^{-1} of lead. The BiF/$MWCNT_{Nan}$-Nafion/SPE exhibited the sharpest peak and the highest peak current for lead and the response was two times higher than that of BiF/$MWCNT_{Sig}$-Nafion/SPE; the Shenzhen nanotubes gave a lower response. The sensitivity of the electrodes increased in the order of $MWCNT_{She} < MWCNT_{Sig} < MWCNT_{Nan}$ for lead and cadmium. The sensitivity dependence on the nature of CNT may be caused either by the different quality of CNTs (size, number of defects and purity) obtained by different producers. There are reports in the literature that the purification procedure or chemical treatment of CNTs has a big effect on their electrochemical properties (Carvalho, Gouveia-Caridade, and Brett 2010). Thus, the performance of CNTs depends on the purification and treatment procedures used by different producers. The order of the electroanalytical performance of these three brands of MWCNTs towards oxidation of ascorbic acid (Carvalho et al. 2010) was similar to that obtained here for heavy metal determination.

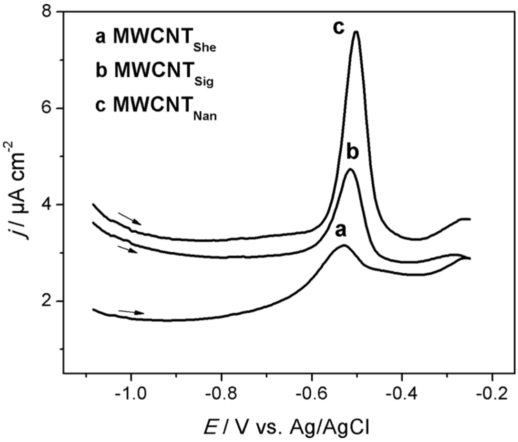

Figure 2. SWASV of 0.0192 nmol L^{-1} Pb(II) in 0.1 M acetate buffer +50 mM KCl containing 2.39 μmol L^{-1} of Bi(III) using different brands of carbon nanotubes. See text for SWASV experimental conditions.

Electrochemical Impedance Spectroscopy at BiF/MWCNT-Nafion/SPE

The impedance characteristics of the different BiF/MWCNT-Nafion/SPE constructed with the various carbon nanotubes were investigated after BiF deposition. Lead, cadmium, and zinc ions (193 nmol L^{-1}) were then added from solutions containing similar concentrations as those used in SWASV, and electrochemical impedance spectra were again recorded. The applied potentials for recording spectra were chosen considering the deposition potential of the bismuth film ex situ (−1.1 V) and the stripping potentials of lead (−0.5 V) and bismuth (−0.2 V), and where no faradaic process occurs (0.0 V). The open circuit potentials were: −0.0112, −0.0187, −0.0184 mV, at MWCNT$_{She}$, MWCNT$_{Sig}$, and MWCNT$_{Nan}$, respectively.

Figure 3 shows impedance spectra obtained in acetate buffer solution for the BiF/MWCNT-Nafion/SPE at −0.5 and −1.1 V vs. Ag/AgCl. Of particular note is the fact that there is a significant difference between the bismuth film alone and bismuth with lead ions alone, with lead plus cadmium and lead, cadmium and zinc, the last of these showing higher impedance values at low frequency at −1.1 V.

Fitting of spectra was done using an equivalent electrical circuit, Figure 4, which comprises the cell resistance, R_Ω, (around 15 Ω cm^2 in all cases) in series with two parallel *R*CPE combinations, representing the metal solution interface and the effects of the Nafion film. The constant phase element, CPE, was necessary due to the non-homogeneous surface and is modeled as a non-ideal capacitor of capacitance C and roughness/non-uniformity factor α, where an α value of 1 represents a perfectly smooth surface, as in previous studies (Gouveia-Caridade et al. 2008). In some cases a circuit with only one parallel *R*CPE combination was used at less negative potentials and for the MWCNT from Shenzhen and Sigma, this by itself showing differences between the Nanolab MWCNT and the other brands. Values obtained for BiF in buffer solution and for BiF with the three metal cations are given in Table 1.

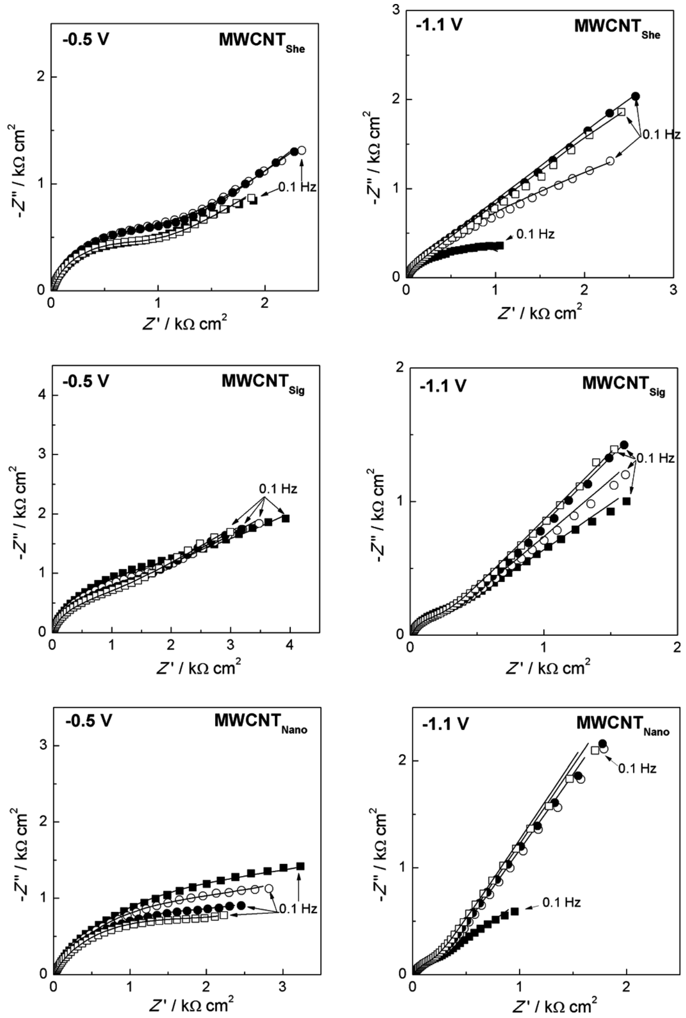

Figure 3. Complex plane impedance plots at −0.5 and −1.1 V in acetate buffer solution for ■ BiF/MWCNT-Nafion/SPE, ○ BiF/MWCNT-Nafion/SPE + Pb(II), ● BiF/MWCNT-Nafion/SPE + Pb(II) + Cd(II), □ BiF/MWCNT-Nafion/SPE + Pb(II) + Cd(II) + Zn(II). Lines show equivalent circuit fitting.

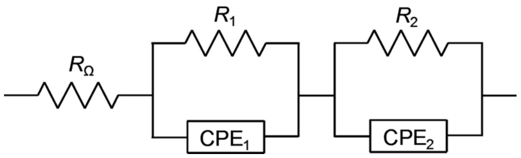

Figure 4. Equivalent circuit for fitting impedance spectra at BiF/MWCNT-Nafion/SPE.

Table 1. Data obtained from analysis of the impedance spectra obtained in 0.1 M acetate buffer pH 4.5 using the equivalent electrical circuit in Figure 4

		R_1/kΩ cm^2		C_1/μF cm^{-2} s$^{\alpha-1}$			R_2/kΩ cm^2		C_2/μF cm^{-2} s$^{\alpha-1}$		
CNT brand	E/V	+Bi	+Pb, Cd, Zn	+Bi	+Pb, Cd, Zn	α_1	+Bi	+Pb, Cd, Zn	+Bi	+Pb, Cd, Zn	α_2
MWCNT$_{\text{She}}$	0.0	0.7	0.8	88	78	0.86	–	–	263	267	0.76
	−0.2	0.9	1.1	76	56	0.87	–	–	229	256	0.80
	−0.5	0.7	0.8	59	54	0.86	2.3	2.5	556	624	0.79
	−1.1	0.3	0.4	73	91	0.85	1.2	5.2	332	301	0.80
MWCNT$_{\text{Sig}}$	0.0	1.3	0.6	65	74	0.83	–	–	137	205	0.81
	−0.2	1.9	1.1	50	53	0.84	–	–	122	151	0.82
	−0.5	1.6	1.0	41	44	0.84	5.0	4.7	258	319	0.80
	−1.1	0.3	0.2	52	57	0.83	3.4	7.3	506	555	0.70
MWCNT$_{\text{Nan}}$	0.0	0.9	0.9	252	224	0.81	32.0	14.0	169	215	0.80
	−0.2	1.3	0.5	190	269	0.77	39.0	66.4	169	175	0.72
	−0.5	1.9	1.1	113	129	0.73	3.8	2.0	413	536	0.73
	−1.1	0.2	0.2	125	164	0.71	12.2	15.6	574	490	0.71

The complex plane spectra for all types of carbon nanotubes are similar at 0.0 V and −0.2 V: the spectra show a semicircle at high frequencies, due to interfacial processes on the metal/carbon surface; at low frequencies the beginning of a second semicircle, which appears almost as a straight line, can be attributed to processes though the Nafion film. At more negative potentials (−1.1 V), see Figure 3, the real and imaginary impedance values are slightly larger after the addition of metal ions (except when MWCNT$_{\text{Sig}}$ were used), reflected by the higher capacitance values.

A detailed discussion of the impedance spectra and the values of the parameters is beyond the scope of this paper. However, concentrating on a few important points aids in elucidating the main characteristics of the interfacial processes. The value of the α_1 exponent varies between MWCNT$_{\text{She}}$ and MWCNT$_{\text{Sig}}$ on the one hand (~0.84) and MWCNT$_{\text{Nan}}$ (from 0.81 at 0.0 V to 0.71 at −1.1 V); lower values of α_2 for MWCNT$_{\text{Nan}}$ at around 0.70 rather than 0.80 are also seen. Such differences are indicative of different concentrations of active sites for metal deposition on the MWCNT, as noted elsewhere (Carvalho et al. 2010). This, together with the fact that MWCNT$_{\text{Nan}}$ give different spectral profiles and, as mentioned above, show effects of the existence of the MWCNT-Nafion film at less negative potentials (the necessity of including the R_2CPE$_2$) suggest that the behavior in anodic stripping voltammetry will be different.

Analytical Parameters for the Determination of Pb(II), Cd (II) and Zn (II) at BiF/MWCNT-Nafion/SPE

Analytical parameters characterizing the BiF/MWCNT-Nafion/SPE electrode performances for Pb(II), Cd(II) and Zn(II) in acetate buffer 0.1 M and 50 mM KCl solution containing 2.39 μmol L^{-1} of bismuth ions are reported in Table 2. These data refer to separate analysis of each metal on different brands of carbon

Table 2. Analytical parameters obtained for Pb(II), Cd(II), and Zn(II) with different brands of carbon nanotubes

	Linear range nmol L^{-1}	Sensitivity $\mu A\ cm^{-2}\ \mu mol^{-1}\ L$	Detection limit nmol L^{-1}	R^2	RSD% ($n=4$)
Pb(II)					
$MWCNT_{She}$	2.4–19.2	34.20	1.0	0.998	9.3
$MWCNT_{Sig}$	4.8–38.4	58.70	0.7	0.999	4.8
$MWCNT_{Nan}$	2.4–19.2	94.70	0.8	0.994	4.5
Cd (II)					
$MWCNT_{She}$	8.8–70.4	1.50	3.4	0.997	4.9
$MWCNT_{Sig}$	8.8–70.4	2.60	2.3	0.998	6.7
$MWCNT_{Nan}$	8.8–70.4	3.31	1.5	0.999	5.7
Zn (II)					
$MWCNT_{She}$	90.0–760	1.48	47.0	0.995	5.6
$MWCNT_{Sig}$	75.0–600	0.30	11.0	0.999	6.8
$MWCNT_{Nan}$	75.0–600	0.18	16.0	0.999	3.9

nanotubes. The linear calibration curve equations of stripping peak current (I_p) vs. concentration (c), illustrated for Pb(II), over the linear range at different electrodes were: $I_p(MWCNT_{Shen}) = 0.028 + 34.3c$, $I_p(MWCNT_{Sig}) = 0.02 + 58.8c$, and $I_p(MWCNT_{Nano}) = 0.04 + 94.8c$, where I_p is in nA and c in nmol L^{-1}, demonstrate the close-to-zero intercepts.

The limit of detection (estimated as the concentration corresponding to three times the standard deviation (SD) of the blank divided by slope of the calibration curve) for $MWCNT_{Nan}$ and $MWCNT_{Sig}$ for lead, cadmium and zinc were 0.7 nmol L^{-1}, 1.5 nmol L^{-1} and 11.1 nmol L^{-1}, respectively, with a deposition time of 120 s. The limits of detection obtained were lower than those obtained at SPE where CNTs were mixed with carbon ink and printed on an electrode substrate and the electrode was afterwards modified with BiF. The LODs obtained in that case were 9.7, 71.4, and 169.2 nmol L^{-1} for Pb, Cd and Zn, respectively, even after metal pre-concentration for 180 s (Injang et al. 2010). Also higher detection limits were obtained when CNTs were cast on a glassy carbon electrode using 2,2′-azinobis(3--ethylbenzothiazoline-6-sulfonate) as compound for homogenisation: BiF was plated on the top of this electrode and gave LODs for Pb and Cd of 4.8 and 17.9 nmol L^{-1}, respectively (Deng et al. 2010). However, much lower detection limits are reported at CNT/BiF electrode, where CNT was attached to a glassy carbon electrode using poly(sodium 4-styrenesulfonate). The LODs after 120 s of metal pre-concentration were 0.19 nmol L^{-1} for lead and 0.17 nmol L^{-1} for cadmium (Jia, Li, and Wang 2010).

Investigation of Interferences

Mutual interferences between the metal ions were tested. Under the optimised experimental conditions discussed above (i.e., accumulation time 120 s, accumulation potential −1.1 V, in 0.1 mol L^{-1} acetate buffer + 50 mmol L^{-1} KCl), a concentration of 0.09 µmol L^{-1} of Cd(II) interfered with the measurement of 0.045 µmol L^{-1} of Pb(II), since the anodic stripping peak current increased in the presence of Cd

Table 3. The effect of addition of Pb(II) or Cd(II) on the stripping response of Pb, Cd, and Zn (concentrations 0.045, 0.090, and 0.30 μmol L^{-1}, respectively) at BiF/$MWCNT_{Nan}$-Nafion/SPE

	Relative Response (%) on Addition of	
	Pb(II)	Cd(II)
Cd(II) peak	133	100
Pb(II) peak	100	50
Zn(II) peak	102	111

(II). Conversely, interference was found in the determination of 0.09 μmol L^{-1} of Cd (II) after the addition of 0.045 μmol L^{-1} of Pb(II) at BiF/MWCNT-Nafion/SPE, since the sensitivity decreased 50%. Although this appears to represent an important limitation to the use of these modified SPEs, if the standard addition method for a specific metal ion is used, then the correct concentrations expected are obtained.

Interestingly, no interference was found for the determination of 0.045 μmol L^{-1} of lead and 0.09 μmol L^{-1} Cd(II) after the addition of 0.3 μmol L^{-1} of Zn(II) (Table 3). This suggests that the reason for the interference is due to the formation of intermetallic compounds and that zinc prevents this happening between lead and cadmium (note that when there is interference the peak becomes broader as the peak current diminishes).

CONCLUSIONS

An electrochemical sensor based on MWCNT-Nafion and bismuth film was developed for the determination of trace of lead, cadmium and zinc by square wave anodic stripping voltammetry, comparing three different brands of MWCNT (Shenzhen, Sigma and Nanolab). The bismuth film was prepared by ex-situ plating of bismuth on the surface of the MWCNT-Nafion/SPE.

The experimental results show that the proposed electrode BiF/MWCNT-Nafion/SPE enhanced the sensitivity of the determination of Pb(II), Cd(II), and Zn(II). The lowest limits of detection were 0.7 nmol L^{-1}, 1.5 nmol L^{-1}, and 11 nmol L^{-1} for Pb(II), Cd (II), and Zn(II), respectively, and the sensitivity of the electrodes increased in the order $MWCNT_{She}, < MWCNT_{Sig}, < MWCNT_{Nan}$ for Pb and Cd and in the opposite order for Zn. Finally, the SPE/MWCNT-Nafion/BiF were characterized by electrochemical impedance spectroscopy. The results obtained showed the higher impedance values were obtained with carbon nanotubes from Nanolab and Sigma than from Shenzhen, and the charge transfer resistance R_{ct} tends to decrease with negative applied potentials due to metal re-oxidation or deposition at the potentials studied.

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