

## Voltammetric method for the determination of Pb<sup>2+</sup> and Cd<sup>2+</sup> in water samples using a nafion–guanine-coated mercury film electrode

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A sensitive voltammetric method is reported for the simultaneous determination of Pb<sup>2+</sup> and Cd<sup>2+</sup> using a nafion–guanine-coated mercury film glassy carbon electrode. This modified electrode exhibited well-developed signals for the reduction of the adsorbed complexes Pb–Guanine and Cd–Guanine, at –0.59 and –0.76 V respectively. The effects of parameters such as pH, accumulation potential and time ( $E_{acc}$ ,  $t_{acc}$ ) were optimized. These studies were done using metallic ions on their own and also mixed together. The best pH for the individual analysis of Pb<sup>2+</sup> or Cd<sup>2+</sup> were 2.2 and 6.1 respectively, whereas a pH of 5.0 (acetate buffer 0.01 mol L<sup>-1</sup>) was chosen for simultaneous determination. Under the optimized conditions (pH = 5.0;  $t_{acc}$  = 60 s;  $E_{acc}$  = –1.0 V) reduction signal was found to be proportional to the concentration of Pb<sup>2+</sup> and Cd<sup>2+</sup> over the 6.6–35.0 µg L<sup>-1</sup> range, with 3σ detection limits (DL) of 2.2 and 4.6 µg L<sup>-1</sup>. However, for lower concentrations, a time of 120 s was applied, yielding a linear range from 0.5 to 12.0 µg L<sup>-1</sup> with DLs of 0.26 and 0.25 µg L<sup>-1</sup> for Pb<sup>2+</sup> and Cd<sup>2+</sup>, respectively. If the guanine (G) is in the solution, the signals are much lower than in the modified electrode. The method was validated by determining Pb<sup>2+</sup> and Cd<sup>2+</sup> in certified reference material (GBW08607) and synthetic sea water (ASTM D665), spiked with 22 metal ions, with satisfactory results. Subsequently, the method was applied in bottled mineral waters and sea water samples without previous treatment.

**Keywords:** Nafion–guanine coated mercury film electrode; Glassy carbon electrode; Adsorptive stripping voltammetry; Water analysis; Pb<sup>2+</sup> and Cd<sup>2+</sup> determination

## 1. INTRODUCTION

Lead and cadmium, even at trace levels, have been considered as some of the most dangerous pollutants. They can accumulate in the human's body, are non-biodegradable, have no known biological functions and have adverse effects on ecological areas as well as on human health. They can enter the body through the food chain and then accumulate, and cause severe damage to nerve connections, liver dysfunction, disturbance in endocrine and nervous systems, brain damage, gastrointestinal systems and various cancers [1–4]. Given rapid industrialization,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  may be generated by anthropogenic activities, like chemical, metallurgic, petrochemical and textile industries, and mineral processing, among others [5]. Finally, another significant route of exposure of cadmium is active and passive inhalation of tobacco smoke [6]. World Health Organization guidelines set an acceptable threshold concentration in drinking water of less than 10 and 3  $\mu\text{g L}^{-1}$  for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  respectively [7]. As a result, sensitive, selective and accurate methods are required for the determination of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in biological, foods and environmental matrices. Electroanalytical techniques have important advantages, including speed of analysis, high selectivity and sensitivity, low detection limit, relative simplicity and low equipment cost, over other techniques, in addition to portability [8]. Among these, stripping voltammetry is the most sensitive, due to the previous pre-concentration phase. This sensitivity depends on the electrode type and their modification. Electrodes modified with fine metal films or with organic compounds attached to an inert and hopefully conductive membrane have been reported. The Dupont company was the first to develop a chemically inert and electroinactive copolymer derived from tetrafluoroethylene and perfluoro-2-(fluorosulfonylethoxy) propyl vinyl ether, containing strongly acidic  $\text{CF}_2\text{CF}_2\text{SO}_3\text{H}$  terminal groups, which was given the trade name Nafion [9,10]. This membrane has excellent ionic conductivity and good properties for preparing modified electrodes, and was first introduced by Hoyer and Florence [11,12] in 1987 in ASV measurements of trace metals in untreated urine samples, blood, and sweat. Compared to conventional electrodes, mercury film electrodes coated with Nafion are robust to mechanical damage, antifouling properties, greater resistance to organic interference, and higher sensitivity [12]. Nowadays, Nafion is not only being used with mercury film electrodes, but it has also been widely used to create all kinds of chemically modified electrodes, with excellent results. Some examples of this are: Nafion/Ag–Hg(Hg–Bi)/glassy carbon electrode [13] for  $\text{Pb}^{2+}$  determination; Nafion/graphene and Nafion/BiFE electrodes [14,15] for  $\text{Cd}^{2+}$  determination and Nafion/HgFE, Nafion/graphene/glassy carbon, Nafion/pyrenetetrasulfonic acid/carbon nanotubes, Nafion/barium hydrogen phosphate/carbon paste, Bi/Nafion/reduced graphene/AuNPs/glassy carbon, Nafion/macrocyclic ester/HgFE/glassy carbon and Nafion/bismuth oxycarbide/glassy carbon electrodes [16–21] for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  determination and Nafion/ $\text{MnCo}_2\text{O}_4$ /glassy carbon electrodes [22] for  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  determination, among others.

Nafion also provides a convenient way to immobilize other species, such as chelating reagents, onto the electrode surface to improve the selectivity of the modified electrodes. Appropriate amounts of coumarin, L-cysteine, the complex  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  [23–25] have been used for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  determination, while 8-quinolinol [26] has been used for Te(IV) determination; other authors have incorporated dipyrindine-containing macrocyclic polyamine [27] for lead determination and

diethyldithiocarbamic acid or 1,4,7,10,13,16-hexaoxacyclooctadecane(18-crown-6) [28] for Pb(II), Cu(II), and Hg(II) determination among others.

Guanine (2-amino-6-oxypurine) is one of the four main nucleobases found in the nucleic acids DNA and RNA and consists of a fused pyrimidine-imidazole ring system with conjugated double bonds. The interaction between these nucleobases and heavy metal ions has been used previously for the detection of to detect toxic heavy metals in waters. Removing of Pb<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> from aqueous solution has been studied using guanine-functionalized iron oxide nanoparticles or guanine functionalized Santa Barbara Amorphous-16 (SBA-16). Pb<sup>2+</sup>, Cd<sup>2+</sup> or Hg<sup>2+</sup> binds to the carbonyl oxygen O(6) and/or the imidazolyl nitrogen N(7) of guanine [29-33]. ~~On the other hand,~~ In addition, guanine has been reported to be strongly adsorbed on mercury electrodes [34], obtaining a different capacity with pH: 4 (primary adsorption with acetic acid) or pH:6.0 (primary adsorption with acetate ions). It would be expected that guanine adsorbed on mercury can then interact with metal ions such as Pb<sup>2+</sup> and Cd<sup>2+</sup> and a sensitive methodology could be obtained.

The main objective of this study was to optimize the adsorption stripping voltamperometry for determining lead and cadmium in bottled mineral water and seawater obtained in areas close to industries and/or high population density and tourism, using a nafion-guanine-coated mercury film glassy carbon electrode. Guanine adsorbed on mercury interacts with metals ions and Nafion also immobilizes it onto the electrode surface to improve the selectivity and sensitivity of the modified electrode. To the best of our knowledge, the voltammetric determination of Pb<sup>2+</sup> and Cd<sup>2+</sup> using this modified electrode has not been reported yet.

## 2. EXPERIMENTAL PART

### 2.1. Apparatus

SWV experiments were performed using a CHI 852E Electrochemical Analyzer (CHI Instruments, Austin, TX) with a two-electrode arrangement, consisting of modified glassy carbon electrode as a working electrode, with a combined ORP (HANNA) reference/auxiliary electrode. Some measures were carried out with a VA 797 Computrace voltammeter, controlled by 797 PC Software (Metrohm) using a hanging mercury drop electrode (HMDE) as a working electrode. The reference electrode was Ag/AgCl/KCl 3 mol L<sup>-1</sup>, and the auxiliary electrode was a platinum wire. Dissolved oxygen was removed with argon. pH measurements were performed with an Orion-430 pH meter.

### 2.2. Chemicals and materials

All solutions were prepared with Milli-Q water (18.2 MΩ). Standard solutions of Pb<sup>2+</sup> and Cd<sup>2+</sup> were prepared by diluting commercial solutions containing 1000 mg L<sup>-1</sup>, Merck (Darmstadt, Germany). Nafion 5% and guanine (G) were purchased from Aldrich (Milwaukee, USA). The stock solution of G in sodium hydroxide (0.01 mol L<sup>-1</sup>) was freshly prepared every three days. Britton-Robinson buffers (BRB) were prepared from orthophosphoric acid, acetic acid and boric, and adjusted to the required pH using 2 mol L<sup>-1</sup> NaOH solution (suprapur grade from Merck). Acetate buffer was prepared from acetic

acid and adjusted to the required pH with NaOH solution. Synthetic sea water (ASTM D665, Aldrich), was spiked with ICP multi-element standard solution IV (1000 mg L<sup>-1</sup>, CertiPUR, Merck) containing Al, Be, Bi, Ca, Cd, Co, Fe, K, Ni, Li, Mg, Mn, Mo, Pb, Sb, Se, Tl and Zn. Certified reference water (GBW08607), with Cd 0.100; Cr 0.500; Cu 1.00; Ni 0.500; Pb 1.00 and Zn 5.00 µg g<sup>-1</sup> was used for validation measurements.

### 2.3. Preparation of nafion-guanine-coated mercury film electrode (NG-HgFE)

The glassy carbon electrode surface was polished with alumina (0.3 and 0.05 µm) and was washed with ethanol-water in an ultrasonic bath. The electrode was then transferred in a solution containing 2.0 mg L<sup>-1</sup> Hg(II) and a constant film of mercury was obtained by plating at -1.40 V under rotation of the electrode for 900 s (1400 rpm). After mercury film had formed, the electrode was rinsed with deionized water and left to air dry. Subsequently, the electrode was placed in a 5 % Nafion solution for 300 s and the solvents were left to evaporate in a hot air stream from a heat-gun for 5 min. On another opportunity, the nafion was added first and then the mercury film was created, with the same results being obtained. Afterwards, the electrode was submerged in a 2.6 m mol L<sup>-1</sup> guanine solution and a potential of -0.80 V was applied for 600 s for it to accumulate on the electrode. Finally the electrode was washed with deionized water and submerged in a dissolution containing Pb<sup>2+</sup> and Cd<sup>2+</sup>.

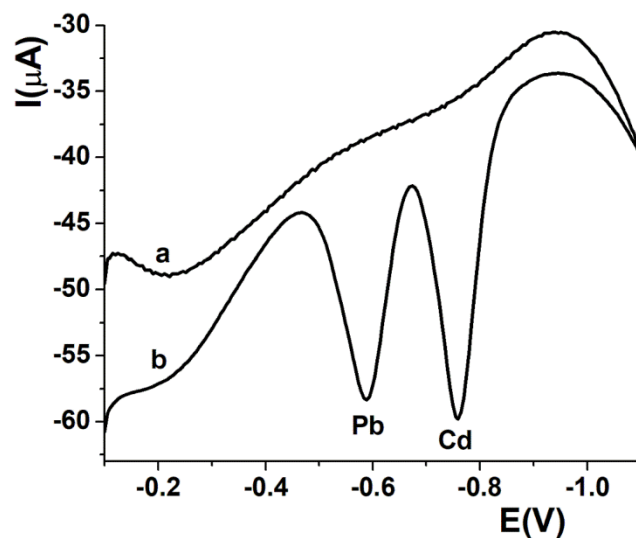
### 2.4. Electrochemical measurements

10.0 mL of BR 0.01 mol L<sup>-1</sup> buffer was added in the electroanalytic cell and Pb<sup>2+</sup> and Cd<sup>2+</sup> aliquots were added from a 1.0 mg L<sup>-1</sup> solution. Subsequently, square wave voltammograms were recorded from -0.1 to -1.2 V with 50 mV amplitude and 5 (50) Hz frequency. The proposed method was applied to the determination of Pb<sup>2+</sup> and Cd<sup>2+</sup> in bottled mineral water and sea water samples. The standard action method was used to eliminate or minimize the matrix effects. All data were obtained at room temperature (~25 °C).

## 3. RESULTS AND DISCUSSION

### 3.1. Electrochemical behavior of Pb-G and Cd-G complexes at the modified electrode (NG-HgFE)

Pb(II) and Cd(II) have been reported to form complexes with guanine, with a metal:ligand stoichiometric ratio of 1:1 with lead and 1:2 with cadmium [35,36]. Figure 1 shows adsorptive voltammograms for a solution containing 9.9 µg L<sup>-1</sup> Pb<sup>2+</sup> and Cd<sup>2+</sup> on a Hg-Nafion-guanine modified glassy carbon electrode. Two cathodic peaks, due to reduction of the corresponding Pb-G and Cd-G complexes, were observed at -0.58 V and -0.76 V, with peak currents of ≈ 1.5 and 2.0 µA respectively (E<sub>acc</sub> = -0.35 V t<sub>acc</sub> = 60 s). If guanine was in the solution, instead of on the modified electrode, these signals were not observed.

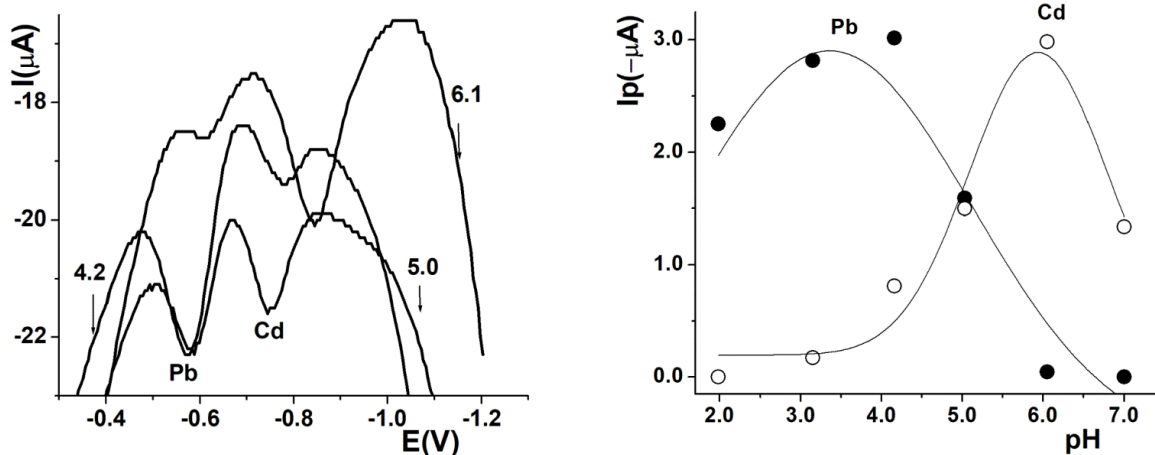


**Figure 1.** Adsorptive voltammograms for: a) Water and Britton–Robinson buffer pH 6.0. b) In the presence of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$   $9.9 \mu\text{g L}^{-1}$ . Conditions:  $t_{\text{acc}} 60 \text{ s}$ ;  $E_{\text{acc}} = -0.35 \text{ V}$ ;  $5 \text{ mV}$  step amplitude;  $50 \text{ mV}$  pulse amplitude; and  $50 \text{ Hz}$  frequency.

### 3.2. Effect of pH

The formation of the complexes with G, their stability and their reduction potentials are dependent on the solution pH. The effect of Pb–G peak current and Cd–G peak signal was investigated in the 2.0 to 7.0 pH range using Britton–Robinson buffer (BRB). Figure 2a illustrates some voltammograms obtained at pH = 4.2; 5.0 and 6.1, while Fig. 2b shows the  $i_{\text{peak}}$  vs. pH graph. Conditions:  $C_{\text{Pb}}$  and  $C_{\text{Cd}}$  were  $9.9 \mu\text{g L}^{-1}$  ( $E_{\text{acc}} = -0.35 \text{ V}$  and  $t_{\text{acc}} = 60 \text{ s}$ ).

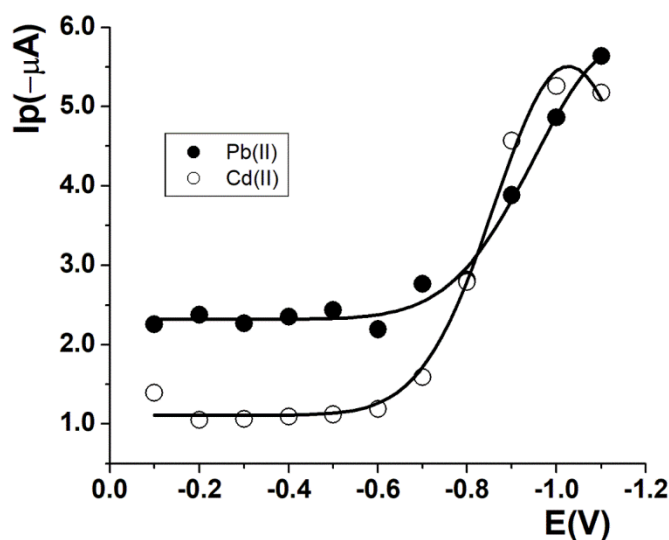
It is clear that the peak current of the Pb–G complex is at its maximum at pH: 4.2 (Pb–G  $i_{\text{peak}}$ :  $3.1 \mu\text{A}$ ; Cd–G  $i_{\text{peak}}$ :  $0.9 \mu\text{A}$ ), whereas the peak current of Cd–G complex is maximized at pH: 6.1 (Cd–G  $i_{\text{peak}}$ :  $2.9 \mu\text{A}$ ; Pb–G  $i_{\text{peak}}$ :  $0.8 \mu\text{A}$ ). On the other hand, lower signals are obtained at pH 5.0, but they are more symmetrical and the both metal ions could be determined simultaneously (Pb–G  $i_{\text{peak}}$ :  $1.8 \mu\text{A}$ ; Cd–G  $i_{\text{peak}}$ :  $1.6 \mu\text{A}$ ). A pH of 5.0 was chosen for the whole study. Acetate buffer solution  $0.01 \text{ mol L}^{-1}$  was used as an electrolyte for all experiments except for pH optimization studies, where the Britton–Robinson buffer  $0.01 \text{ M}$  was used. Comparatively, the study was also carried out as a function of pH using a hanging drop mercury electrode (HMDE), adding guanine in solution. At pH:8.8 the peak current of Cd–G complex was at its maximum with this electrode. The pKa of guanine has been reported to be in the range of pH 7–8 [37].



**Figure 2.** (A) AdV of Pb–G and Cd–G complexes at pH: 4.2; 5.0 and 6.1. (B). Influence of pH on peak current of the Pb–G and Cd–G complexes. Conditions:  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$   $9.9 \mu\text{g L}^{-1}$ ;  $t_{\text{acc}}$  60 s;  $E_{\text{acc}} = -0.35 \text{ V}$ .

### 3.3. Effect of accumulation potential and time ( $E_{\text{acc}}$ , $t_{\text{acc}}$ ).

The influence of accumulation potential variation on peak current, examined over the  $-0.10$  to  $-1.10 \text{ V}$  range, is shown in Fig. 3.  $C_{\text{Pb}}$  and  $C_{\text{Cd}}$  were  $9.9 \mu\text{g L}^{-1}$  (pH = 5.0 ( $0.01 \text{ mol L}^{-1}$  acetate buffer;  $t_{\text{acc}} = 60 \text{ s}$ )). The largest peak currents were obtained for accumulation potentials up to  $-1.00 \text{ V}$  for the two complexes, so an accumulation potential of  $-1.00 \text{ V}$  was chosen for this study.

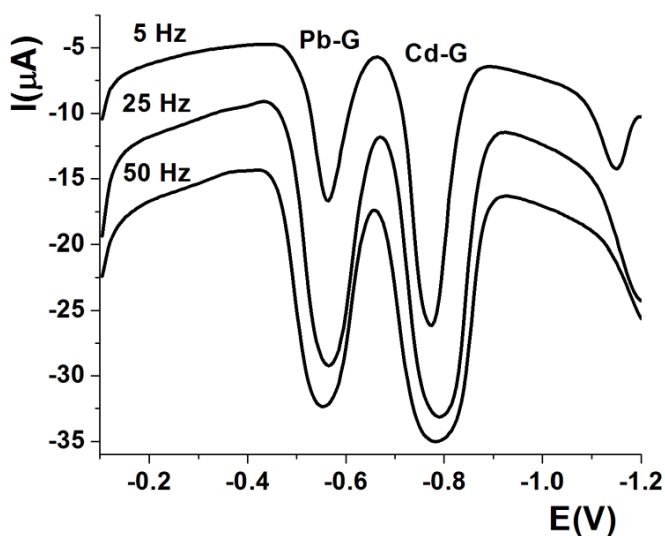


**Figure 3.** Influence of  $E_{\text{acc}}$  on peak current of the Pb–G and Cd–G complexes. Conditions:  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$   $9.9 \mu\text{g L}^{-1}$ ; pH = 5.0 (acetate buffer);  $t_{\text{acc}} = 60 \text{ s}$ .

Accumulation time is another important parameter that has a pronounced effect on sensitivity in stripping procedures. Accumulation times were examined in the range of 0 – 300 s for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , while other standard measuring conditions remained constant ( $\text{pH} = 5.0$ ,  $E_{\text{acc}} = -1.00$  V). The peak current of both complexes increased as accumulation time grew, which is characteristic for an adsorption process. The increase in current was observed up to 240 s; however, as to not unnecessarily increase the analysis time, a value of 60 s was chosen, raising it to 120 or 240 s in low  $\text{Pb}^{2+}$  or  $\text{Cd}^{2+}$  content samples.

#### 3.4. Effect of frequency of square wave.

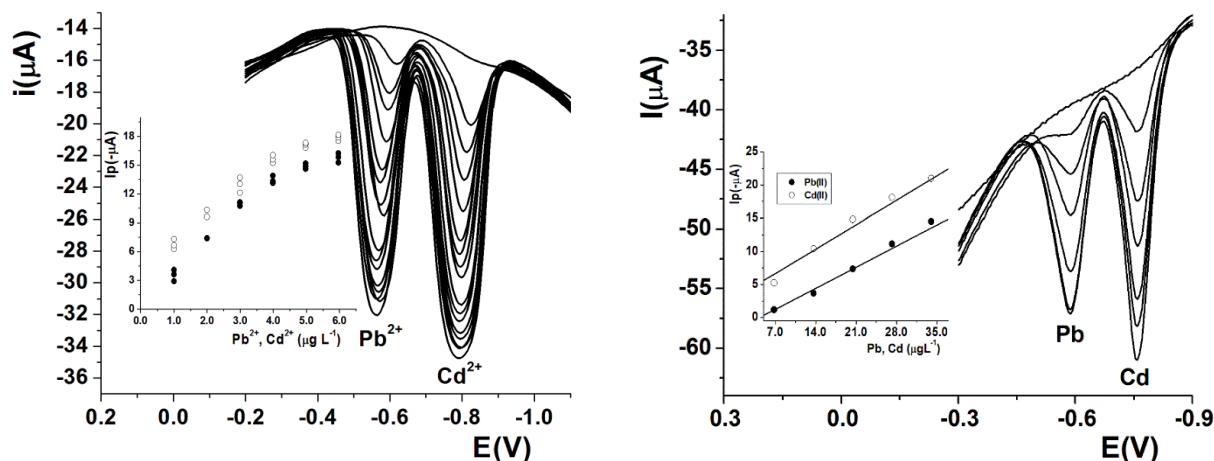
The SW parameters studied were potential increment, amplitude and frequency. Peak current of Pb-G and Cd-G increased as all the parameters increased. The influence of the frequency variation on peak currents, examined at 5, 25 and 50 Hz, is shown in Fig.4. The results show that peak current increases when frequency is higher; however, when the frequency was 25 or 50 Hz, the Pb-G and Cd-G current peaks were higher, but very broad.



**Figure 4:** Adsorptive voltammograms of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  standard solution to different frequencies. Conditions:  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$   $6.0 \mu\text{g L}^{-1}$ ;  $\text{pH} = 5.0$  (acetate buffer);  $t_{\text{acc}} = 60$  s.

#### 3.5. Linear range, detection limit and repeatability of the method

Optimal analytical conditions were found to be:  $\text{pH} 5.0$  (acetate buffer  $0.01 \text{ mol L}^{-1}$ );  $E_{\text{acc}} = -1.00$  V;  $t_{\text{acc}} = 60$  s. A frequency of 50 Hz was applied first and then one of 25 Hz. Adsorptive voltammograms and calibration curves are presented in Fig.5A and 5B respectively.



**Figure 5:** Adsorptive voltammograms and corresponding calibration plot of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  standard solutions. (A) low concentration. (B) high concentration. Conditions: pH = 5.0 (acetate buffer);  $E_{\text{acc}} = -1.0$  V;  $t_{\text{acc}} = 60$  s; 5 mV step amplitude; 50 mV pulse amplitude; 50 Hz (A) and 25 Hz (B) Hof frequency.

**Table 1.** Electroanalytical methods for simultaneous determination of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$

Electrode	Technique	DL of $\text{Pb}^{2+}$ ( $\mu\text{g L}^{-1}$ )	DL of $\text{Cd}^{2+}$ ( $\mu\text{g L}^{-1}$ )	$t_{\text{acc}}$ (s)	Ref
$\text{Bi}_2\text{O}_3@\text{NPBi}$	SWASV	0.02	0.03	180	38
polyPCA/GE	SWASV	13.6	15.4	125	39
Graphene Paper-Nafion-BiN	SWASV	0.1	0.1	1200	40
Mont-IPGE	SWV	1.14 nM	0.42 nM	300	41
Si@C/GCE	DPASV	0.105	0.068	240	42
MWCNT/CPE	SWASV	0.099	0.157	240	43
SPE/SWCNHs/BiF	SWASV	0.4	0.2	150	44
PyTS-CNTs	DPASV	0.02	0.8	270	45
BiF-LEGCN/GCE	SWASV	0.41	0.47	300	46
NCQDs-GO	ASV	1.17	7.45	300	47
Cu/Hg-WE	DPV	50	80	60	48
Nafion/PA-PANI/GCE	DPASV	0.05	0.02	180	49
GCE-MWCNT/poly(PCV)	DPASV	0.40	0.20	420	50
GCE/DMSO	SWASV	1.9	3.2	250	51
SPE-BiFE	SWASV	0.10	0.60	180	52
NG-HgFE	SWASV	0.26	0.25	120	This work

Under a frequency of 50 Hz, the reduction peaks were found to be proportional to the  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  concentration over the 1.0–4.0  $\mu\text{g L}^{-1}$  range (Pb:  $Y=0.4588 + 3.3557X$ ;  $R=0.9925$ ; Cd:  $Y=3.9015 + 2.9767X$ ;  $R=0.9902$ ) with  $3\sigma$  detection limits (DL) of 0.5  $\mu\text{g L}^{-1}$  for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ( $t_{\text{acc}}=60$  s). Under a 25 Hz frequency, reduction peaks were found to be proportional to the  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  concentration over the 6.6–35.0  $\mu\text{g L}^{-1}$  range (Pb:  $Y=-2.6585 + 0.5013X$ ;  $R=0.9979$ ; Cd:  $Y=2,1516 + 0.5768X$ ;  $R=0.9924$ ) with  $3\sigma$  detection limits (DL) of 2.2 and 4.6  $\mu\text{g L}^{-1}$  for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , respectively. For lower



concentrations, a time of 120 s was applied, yielding a linear range from 0.5 to 12.0  $\mu\text{g L}^{-1}$  with DLs of 0.26 and 0.25  $\mu\text{g L}^{-1}$  for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , respectively.

Many studies into the simultaneous determination of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  have been reported, using a great variety of modified electrodes, which obtained similar detection limits by applying accumulation times from 60 to 1200 s. Table 1 illustrates some of these studies.

### 3.6. Interference studies, validation and repeatability of the method

A 6.8-mL aliquot of synthetic sea water, contaminated with a standard solution containing Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl and Zn ions in equal concentrations (5.0  $\mu\text{g L}^{-1}$ ), was added to the electrochemical cell that contained 0.2 mL of acetate buffer (pH 5.0), and the analysis of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  were carried out in three replicates, using the standard addition method. The results obtained for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  were  $5.1 \pm 0.4 \mu\text{g L}^{-1}$  and  $4.7 \pm 0.5 \mu\text{g L}^{-1}$  respectively. Conditions: pH = 5.0;  $t_{\text{acc}} = 120 \text{ s}$ ;  $E_{\text{acc}} = -1.00 \text{ V}$ .

The usefulness of the present method was also evaluated by examining the analysis of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in certified reference water (6.8 mL of water; 0.2 mL of acetate buffer (0.4 mol  $\text{L}^{-1}$ ), and 200  $\mu\text{L}$  of reference water). The values obtained were  $\text{Pb}^{2+} 1.10 \pm 0.04 \mu\text{g g}^{-1}$  and  $\text{Cd}^{2+} 0.11 \pm 0.03 \mu\text{g g}^{-1}$  (GBW08607, certified values: Pb 1.00 and Cd 0.100  $\mu\text{g g}^{-1}$ ). Conditions: pH = 5.0;  $t_{\text{acc}} = 60 \text{ s}$ ;  $E_{\text{acc}} = -1.00 \text{ V}$ .

A solution containing 5.0  $\mu\text{g L}^{-1}$  of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  was measured 10 times to check the repeatability of the modified electrode, achieving relative standard deviations of 2.3 and 3.1 % for lead and cadmium respectively. Conditions: pH = 5.0;  $t_{\text{acc}} = 60 \text{ s}$ ;  $E_{\text{acc}} = -1.00 \text{ V}$ .

### 3.7. Analysis of $\text{Pb}^{2+}$ and $\text{Cd}^{2+}$ in mineral water and seawater

**Table 2.** Concentration of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in water samples. Standard deviation for 3 replicate measurements.

Sample	Added or Certified value		Founded		ICP-MS	
	$\text{Pb}^{2+}$ ( $\mu\text{g L}^{-1}$ )	$\text{Cd}^{2+}$ ( $\mu\text{g L}^{-1}$ )	$\text{Pb}^{2+}$ ( $\mu\text{g L}^{-1}$ )	$\text{Cd}^{2+}$ ( $\mu\text{g L}^{-1}$ )	$\text{Pb}^{2+}$ ( $\mu\text{g L}^{-1}$ )	$\text{Cd}^{2+}$ ( $\mu\text{g L}^{-1}$ )
Synthetic seawater	5.0	5.0	$5.1 \pm 0.4$	$4.7 \pm 0.5$		
GBW08607 ( $\mu\text{g g}^{-1}$ )	1.00	0.100	$1.10 \pm 0.04$	$0.11 \pm 0.03$		
Seawater Las Salinas			$1.7 \pm 0.1$	< 0.25	$2.0 \pm 0.1$	< 1.0
Seawater Con Con			$2.9 \pm 0.3$	< 0.25	$2.3 \pm 0.1$	< 1.0
Seawater Las Ventanas			$3.1 \pm 0.2$	< 0.25	$2.8 \pm 0.1$	< 1.0
Bottled mineral 1			$1.3 \pm 0.3$	< 0.25		
Bottled mineral 2			$1.6 \pm 0.2$	< 0.25		

The optimized method was successfully applied to the determination of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in 3 seawater samples (Fifth Region, Chile) from a beach near a heavily populated area, popular with tourists, (Las Salinas), near an oil refinery (Con Con) and near a copper smelting industry (Las Ventanas), adding 6.8 mL of sea water and 0.2 mL of Britton–Robinson buffer to the electrochemical cell (Conditions: pH = 5.0;  $t_{\text{acc}} = 60 \text{ s}$ ;  $E_{\text{acc}} = -1.00 \text{ V}$ ). So as to compare the obtained results, these samples were analyzed in

a service laboratory using the ICP-MS technique. In the same conditions, two bottled mineral waters were bought from our University store. All the results are presented in Table 2.

#### 4. CONCLUSIONS

The present work reports on a simple methodology for the simultaneous determination of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  by modifying a glassy carbon with Hg-nafion-guanine ~~is report~~. Mercury has very good adsorbent properties that can be used to adsorb guanine. Nafion also enhances adsorption properties and can neutralize positive charge of the complexes and Guanine interacts with  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , obtaining a sensitive and selective methodology for these highly toxic trace metals. Detection limits of 2.2 and 4.6  $\mu\text{g L}^{-1}$  were obtained with just 60 s, and the detection limit is 0.26 and 0.25  $\mu\text{g L}^{-1}$  when accumulation is increased to 120 s. The procedure has been optimized, validated and applied to analysis of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in seawater and commercial mineral water.

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