

Simultaneous Determination of Lead and Cadmium by Stripping Voltammetry Using in-situ Mercury Film Glassy Carbon Electrode Coated with Nafion-Macrocyclic Ester

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This work reports a sensitive and selective anodic stripping method for the simultaneous determination of Pb(II) and Cd(II) using (3,10,18,25-tetraoxapentacyclo [25.3.1.1^{12,16}.0^{4,9}.0^{19,24}] dotriacontal(31),4(9),5,7,12(32),13,15,19,21,23,27,29-dodecaene-2,11,17,26-tetrone) macrocyclic ester (**L**). Anodic peak currents were increased from 1.16 to 31.48 μA for Pb(II) and 0.22 to 6.68 μA for Cd(II) when the in-situ mercury film electrode was modified with nafion and (**L**). Moreover, potentials separation values for Cd-Pb shift from 150 to 190 mV. Optimal parameters such as: pH; **L** concentration (C_L), mercury concentration (C_{Hg}), accumulation potential (E_{ACC}) and accumulation time (t_{ACC}) were pH 4.0 for Pb(II) and 5.0 for Cd(II) using phosphate buffer solution (PBS), C_L 12.0 mmol L^{-1} , C_{Hg} 28.0 mg L^{-1} , E_{ACC} -1.0 V and t_{ACC} 60. Detection limits (DoL) were 0.085 and 0.80 $\mu\text{g L}^{-1}$ for Pb(II) and Cd(II) respectively. The relative standard deviation (RSD) for seven measurements of Pb(II) and Cd(II) 9.0 $\mu\text{g L}^{-1}$ were of 2.5 and 2.0% respectively. The method was validated by ICP multi-element standard solution IX (Merck) containing As, Be, Cd, Cr(VI), Hg, Ni, Pb, Se and Tl 100 mg L^{-1} . Finally, usefulness of the modified electrode was developed in the analysis of Pb(II) and Cd(II) using tap water samples.

Keywords: macrocyclic ester; stripping voltammetry; modified electrode; lead; cadmium.

1. INTRODUCTION

Lead and cadmium are classified as hazardous metals by the Agency for Toxic Substances and Disease Registry (ATSDR). The excessive presence of these metals in the environment is very harmful to humans, animals and plants [1]. In addition, are considered the oldest contaminants of natural

waters. It has been reported that their interactions with bio-elements in living organisms can cause irreparable damage to the DNA [2].

On the other hand, in extreme cases lead poisoning leads to health problems such as anemia, renal dysfunction, and reduced intelligence quotient levels in children [3,4], whereas cadmium produces nausea and vomit and as result its prolonged exposure toxaemia in the liver, emphysema in the lungs, proteinuria and hypertension [5,6]. Therefore, the need arises to develop new methodologies sensitive that allowing identification and quantification of lead and cadmium in natural waters. The electroanalytical techniques offer great advantage, related with the sensitivity and the low operational cost. Anodic stripping voltammetry (ASV) has proved to be very convenient for the determination of lead and cadmium, this is demonstrated in the amount of work published in the last decade using mercury film electrodes (HgFE) and hanging mercury drop electrode (HMDE). The use ligands as chelating-adsorbent agents to forming ions-complexes with metals ions can improve the sensibility and selectivity for ASV [7,8]. These chelating-adsorbent agents must forms complexes of fast kinetics. Some of the ligands used as chelating-adsorbent agents in the simultaneous determination of lead and cadmium are Clioquinol [9], 2-mercaptobenzothiazole [10], 8-hydroxyquinoline [8], 4-methylcatechol [11], uric acid [12] and pirogallol red [13]. Where have reported detection limits (DoL) between 0.05-17.0 $\mu\text{g L}^{-1}$ for lead and 0.01-10 $\mu\text{g L}^{-1}$ for cadmium. In this reports, complexes were formed in dissolution. Moreover, Pb(II) and Cd(II) were detected by adsorptive stripping voltammetry. Macrocyclic molecules, such as ether crown, has been used in the determination of Pb(II) and Cd(II) by anodic stripping voltammetry, where proven to be sensibility and selective [14-17]. Dichloromethane coated with macrocyclic ester (**L**) on glassy carbon electrode was used in the determination of Pb(II) with detection limit of 0.33 $\mu\text{g L}^{-1}$ [18]. In-situ mercury film nafion coated macrocyclic (**L**) on glassy carbon electrode for simultaneous detection of Pb(II) and Cd(II) not has been reported.

2. EXPERIMENTAL

2.1. Reagents and instruments

Water required for the preparation of dissolutions was obtained from Purifier System Wasselab ASTM D1193. Standard solutions of Cd(II), Pb(II) and Hg(II) were prepared of standards solution Merck (Darmstadt, Germany). Nafion® (5% w/v solution in a mixture of water and lower alcohols) were purchased from Aldric. Macrocyclic ester (**L**) Fig. 1, was synthesized as was reported by Hurtado et al [18]. All other chemicals such as nitric acid, methanol, phosphoric acid etc. were analytical grade from Merck. Buffer phosphate solution (PBS) (0.1 mol L^{-1}) was prepared from $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$ adjusting to the required pH with NaOH solution. ICP multi-element standard solution IX (Merck) containing As, Be, Cd, Cr(VI), Hg, Ni, Pb, Se and Tl (100 mg L^{-1}) was used for interferences study. Square wave anodic stripping voltammograms (SWASV's) were obtained using a potentiostat DropSens μStat 400. Glassy carbon electrodes of diameter (3 mm) was used as working electrode.

Reference electrode was an Ag/AgCl/KCl 3 mol L⁻¹ and auxiliary electrode was a platinum wire. pH was measured with an Ohaus model ST 3100 pH meter.

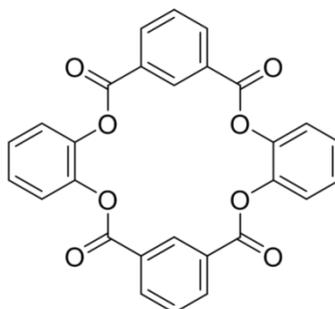


Figure 1. Structure of the macrocyclic ester (**L**)

2.2. General measure procedure

10.0 mL of ultra-pure water or 9.0 mL with 1.0 ml of sample; Hg (300 μ L, 28.0 mmol L⁻¹), PBS (300 μ L, 0.01 mol L⁻¹) and aliquots (10-100 μ L) of Pb(II) and Cd(II) (1.0 mg L⁻¹) were pipetted into the voltammetry cell. Then, pre-concentration step was initiated for an optimal potential and time at a stirring speed of 500 rpm. After an equilibration time of 3 s, SWASV's were recorded, while the potential was scanned from -1.0 to 0.0 V using square wave modulation with 10 mV step amplitude, 100 mV pulse amplitude, and a frequency of 25 Hz. Each voltammograms was repeated three times. The calibration curves were obtained and linear regression and detection limits (DoL) were calculated from $DL = 3S_{x/y}/b$, where $S_{x/y}$ is the random error in x and y , and b is the slope [19].

2.3. Sample preparation

Tap water was obtained from our laboratory. The samples were collected in high-density polyethylene bottles, which had been acid-washed and rinsed with water. Samples were stored frozen before analysis. The samples needed no treatment to remove organic matter. To eliminate matrix effects the standard addition method was used. All data were obtained at room temperature (≈ 25 °C).

2.4. Preparation of in-situ mercury film glassy carbon coated nafion and **L** electrode (in-situ HgF-N-L/GCE)

Before the measurements, the glassy carbon electrode was polished using a polishing pad with 0.05 and 0.3 μ m Al₂O₃ slurry, rinsed with water and submitted by 5 minutes in bath of ultra sound in a solution 1/1 of HNO₃ (0.3 mol L⁻¹) and ethanol. 3.0 mg of macrocyclic (**L**) was dispersed in 0.50 mL of Nafion[®]. 30 μ L of composite N-L was deposited on the electrode freshly polished. The solvents were left to evaporate at room temperature. The nafion coated with **L** glassy carbon electrode (N-L/GCE) and modified with mercury film was prepared in-situ. The electrode was immersed in an

electroanalytical cell containing the plating solution of Hg(II) (30 mg L^{-1}), and the mercury film was formed by holding the working electrode potential at -1.0 V for 60 s. It was not necessary to eliminate the excess of oxygen in the cell. The entire study was performed with 10 mL of dissolution of mercury.

3. RESULTS AND DISCUSSION

3.1. Anodic stripping property of Pb(II) and Cd(II) on *in-situ* HgF-N-L/GCE .

Preliminary, experiments were conducted to identify the properties and anodic behavior of Pb(II) and Cd(II) on the modified electrode (*in-situ* HgF-N-L/GCE) by square wave anodic stripping voltammetry (SWASV). Fig. 2A shows the SWAdSV's responses of Pb(II) and Cd(II) $9.0 \text{ } \mu\text{g L}^{-1}$ using GCE (black curve) and mercury film (red curve). Using *in-situ* mercury film were seen two well defined anodic peak currents for Pb(II) and Cd(II) at -0.50 V and -0.65 V with separation potential for Pb-Cd of 150 mV. When Gassy carbon was coated with nafion (*in-situ* HgF-N/GCE) Fig 2B (black curve), anodic peak current shift at -0.61 and -0.78 V for Pb(II) and Cd(II) respectively. The signal to Cd(II) was much smaller. Moreover, when *in-situ* HgF-N/GCE was modified with L Fig 2B (red curve), anodic peak currents for Pb(II) and Cd(II) were increased more than 50%.

On the other hand, anodic peak potentials of Pb(II) and Cd(II) change to less positive potential values, requiring less energy to oxidation compared with the electrodes without nafion and L. These changes in the anodic signals can confirm that the complexes have been formed on the surface of the electrode between Pb(II), Cd(II) and L. Using other macrocyclic substances; such as crown ethers, were observed similar potential values for Pb(II) and Cd(II) [14, 20].

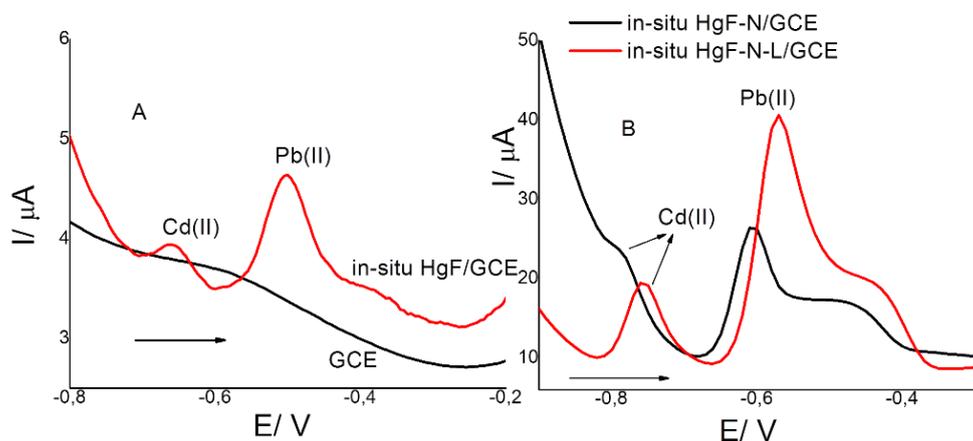


Figure. 2. (A) Anodic stripping voltammograms of Pb(II) and Cd(II) solution using GCE (black curve) and *in-situ* HgF/GCE (red curve). (B) *in-situ* HgF-N/GCE (black curve) and *in-situ* HgF-N-L/GCE (red curve). Conditions: pH 4.0; $C_{\text{Pb(II)}}$, $C_{\text{Cd(II)}}$ $9.0.0 \text{ } \mu\text{g L}^{-1}$; C_{L} $10.0; \text{ mmol L}^{-1}$; C_{Hg} 30.0 mg L^{-1} ; E_{ACC} -1.0 V ; t_{ACC} 60 s. Step amplitude 10 mV; pulse amplitude 100 mV and frequency 25 Hz.

3.2. Anodic stripping property for Pb(II) and Cd(II) using *in-situ* HgF-N-L/GCE in function of C_L and C_{Hg} .

With the aim of using minimal amounts of (**L**) and dissolution of Hg(II) without affecting the sensitivity, were studied the concentration of **L** and Hg(II) in the preparation of the electrode in relation to the height of the oxidation currents with Pb(II) and Cd(II) $9.0 \mu\text{g L}^{-1}$ using *in-situ* HgF-N-L/GCE. Fig. 3A shows the anodic peak currents vs C_L . Result showed that anodic peak currents for Pb(II) and Cd(II) were increased to 12 mmol L^{-1} of (**L**). At higher concentrations, anodic peak currents for Pb(II) and Cd(II) decreases. Possibly, electrode surface is saturated affecting the oxidation of Pb(II) and Cd(II) in the complex. Moreover, with 28.0 mg L^{-1} de Hg(II) solution was observed highest anodic peak currents for Pb(II) and Cd(II). At higher concentrations, the anodic peak currents were constant. Based on these results, 12.0 mmol L^{-1} of (**L**) and 28.0 mg L^{-1} were used for further experiments.

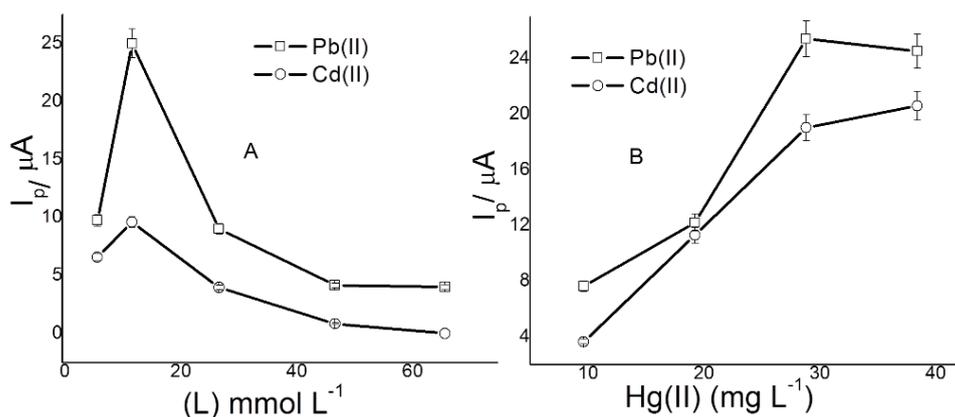


Figure 3. (A) Influence of C_L on the peak current of Pb(II) and Cd(II). (B) Influence of C_{Hg} on the peak current of the Pb(II) and Cd(II). Conditions: pH 4.0; $C_{Pb(II)}$, $C_{Cd(II)}$ $9.0 \mu\text{g L}^{-1}$; E_{ACC} -1.0 V; t_{ads} 60 s. Others conditions as in Fig. 2.

3.3. Study in function of pH

The variation of the anodic peak currents for Pb(II) and Cd(II) as a function of pH was studied in pH range 3.0-7.0 (Fig. 4) using *in-situ* HgF-N-L/GCE with BPS. The experimental conditions were: Pb(II) and Cd(II); $9.0 \mu\text{g L}^{-1}$, C_L ; 12.0 mmol L^{-1} ; C_{Hg} ; 28.0 mg L^{-1} , E_{ACC} -1.0 V and t_{ACC} 60 s. Anodic peak currents were highest at pH 4.0 for Pb(II) and pH 5.0 for Cd(II) (Fig 4). At higher pH values, an anodic peak current decreases. Possibly, Pb(II) and Cd(II) form complexes with OH^- to pH values greater. pH 4.0 and 5.0 for both metal were used for further experiments.

3.4. Influence of E_{ACC} and t_{ACC} .

The effect of accumulation potential (E_{ACC}) on the anodic peak currents for Pb(II) and Cd(II) using *in-situ* HgF-N-L/GCE were studied over the -1.2 to -0.7 V range with Pb(II) and Cd(II) $9.0 \mu\text{g L}^{-1}$.

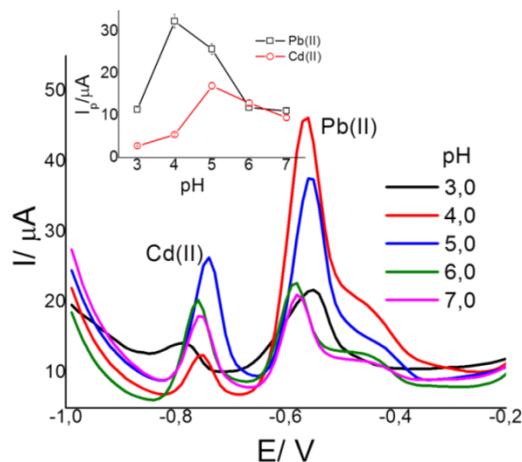


Figure 4. Influence of pH on the peak current of Pb(II) and Cd(II). Conditions: $C_{\text{Pb(II)}}$, $C_{\text{Cd(II)}} 9.0 \mu\text{g L}^{-1}$; $C_{\text{L}} 12.0 \text{ mmol L}^{-1}$; $C_{\text{Hg}} 28.0 \text{ mg L}^{-1}$; $E_{\text{ACC}} -1.0 \text{ V}$; $t_{\text{ACC}} 60 \text{ s}$. Others conditions as in Fig. 2.

The anodic peak currents of Pb(II) and Cd(II) were maximum to -1.0 V . However, the stability of the modified electrode was high. On this basis, an E_{ACC} of -1.0 V was chosen for further studies. Another parameter studied was the accumulation time (t_{ACC}), examined between 10–100 s. Anodic peak currents for Pb(II) and Cd(II) increased almost linearly with accumulation time until 60 s, and then tended to a constant. 60 s was used for further studies.

3.5. Effect of instrumental variables; frequency (Hz), step potential (mV) and amplitude pulse (mV).

These instrumental parameters are related to the step of stripping where Pb(II) and Cd(II) are oxidized. The instrumental parameters studied were frequency, step amplitude and pulse amplitude. Anodic peak currents increased as all the parameters increased. However, when the frequency was higher than 25 Hz the signal of Pb(II) and Cd(II) were very broad, losing resolution. Step amplitude of 10 mV and pulse amplitude of 100 mV at a frequency of 25 Hz were selected for further experiments.

3.6. Detection limit (DoL) and reproducibility (% RSD) of the method

Analytical parameters (LoD and %RSD) using *in-situ HgF-N-L/GCE* with optimal conditions ($C_{\text{L}} 12.0 \text{ mmol L}^{-1}$; $C_{\text{Hg}} 28.0 \text{ mg L}^{-1}$ $E_{\text{ACC}} -1.0 \text{ V}$; t_{ACC} of 60 s and pH 4.0 for Pb(II) and pH 5.0 for Cd(II) (PBS 0.01 mol L^{-1}), stirring rate 500 rpm; step amplitude 10 mV; 100 mV, and frequency 15 Hz were studied. Under these conditions the anodic peak currents were proportional between $0.40\text{--}30.0 \mu\text{g L}^{-1}$ for Pb(II) Fig 5A and $1.8\text{--}25.0 \mu\text{g L}^{-1}$ for Cd(II) Fig. 5B. Detection limit ($3S_{x/y}/b$) were of 0.085 and $0.80 \mu\text{g L}^{-1}$ for Pb(II) and Cd(II) respectively. The relative standard deviations were 2.5% and 2.0% for Pb(II) and Cd(II) respectively, ($n=7$) for solutions containing Pb(II) and Cd(II) $9.0 \mu\text{g L}^{-1}$. The results obtained were equally acceptable to the shown in Table 1. Where used other ligands and different electrodes such as, bismuth and antimony film. Compare the results according to the sensitivity with other substances, such as; 4-carboxybenzo-18-crown-6 and 4-carboxybenzo-15-crown-

5 [14, 17], the modified electrode reached a greater sensitivity and potential separation Cd-Pb was higher. Moreover, the modification was more simple.

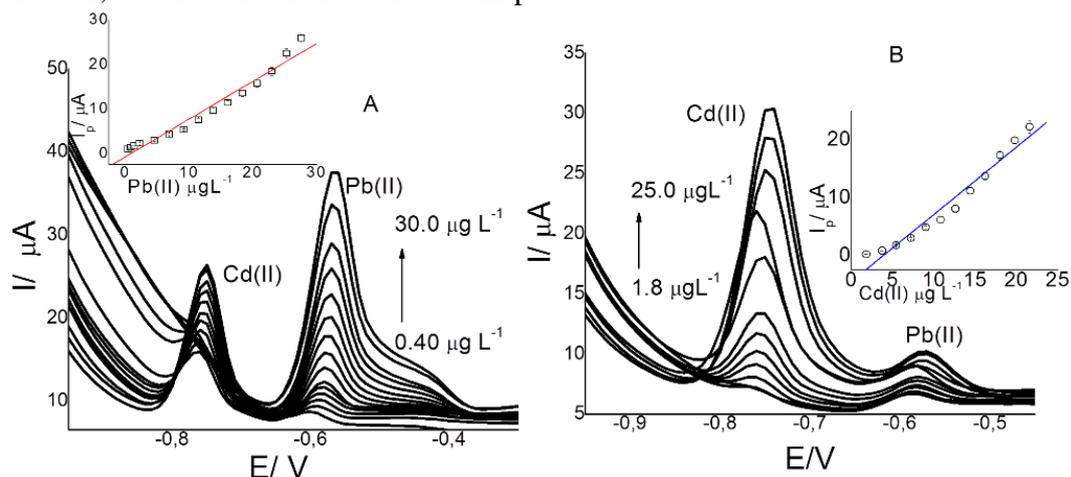


Figure 5. (A) Influence of C_{Pb} on the peak currents in the presence of $Cd(II)$ $5.0 \mu g L^{-1}$ (insert calibration curve). (B) Influence of C_{Cd} on the peak current in the presence of $Pb(II)$ $5.0 \mu g L^{-1}$ (insert calibration curve). Conditions: pH 4.0 for $Pb(II)$ and pH 5.0 for $Cd(II)$; E_{ACC} -1.0 V; t_{ads} 60 s. Others conditions as in Fig. 2.

3.7 Validation of the method and interference study.

The accuracy and interferences of the present method was evaluated in the determination of $Pb(II)$ and $Cd(II)$ using ICP multi-element standard solution IX (Merck) containing As, Be, Cd, Cr(VI), Hg, Ni, Pb, Se and Tl $100 mg L^{-1}$. The standard solution of $100 mg L^{-1}$ were prepared two dilutions of $1.0 mg L^{-1}$ to be analyzed. In the electrochemical cell (10.6 mL) were added 60 and 120 μL of the standard dissolution $1.0 mg L^{-1}$. Concentrations in the dissolution were 5.62 and $11.51 \mu g L^{-1}$.

Table 1. Detection limits for lead and cadmium with others ligands and electrodes.

Technique	Electrode	Ligand	DoL ($\mu g L^{-1}$)		References
			Pb (II)	Cd(II)	
AdSV	Carbon paste	diacetyldioxine	2.07	4.48	[21]
AdSV	HMDE	2-mercaptobenzothiazole	0.017	0.01	[10]
AdSV	HMDE	3-aminophthalhydrazine	-	0.02	[22]
ASV	OHp/IL	-	0.041	0.056	[23]
AdSV	N-HgF	Clioquinol	0.10	0.06	[9]
AdSV	HMDE	Morin	0.08	-	[24]
AdSV	N-BiF	1-nitroso-2-naphthol	0.08	0.07	[25]
ASV	BiF-SPC	-	0,14	0,24	[26]
ASV	SbF-SPC	-	5.0	3.0	[27]
ASV	N-L-HgF/GCE	-	0.08	0.1	This work

AdSV: Adsorptive stripping voltammetry; ASV: Anodic stripping voltammetry; HMDE: Hanging mercury drop electrode; OHp: Hydroxypatite; IL: Ionic liquids; N-HgF; nafion mercury film; N-BiF: nafion bismuth film; SbF: antimony film; SPC: screen printed carbon.

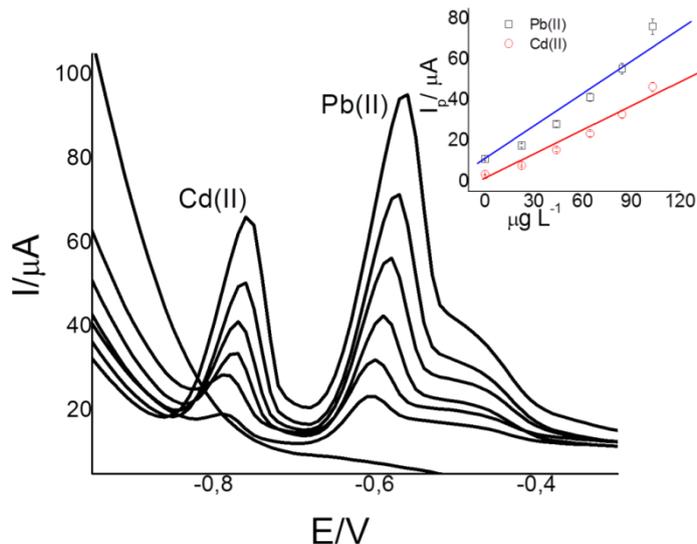


Figure 6. SWASV's and calibration curve (insert) of standard solution $11.51 \mu\text{g L}^{-1}$ using in-situ HgF-N-L/GCE. Conditions: pH 5.0; C_L 12.0 mmol L^{-1} ; C_{Hg} 28.0 mg L^{-1} ; E_{ACC} -1.0 V ; t_{ACC} 60 s . Others conditions as in Fig. 2.

Anodic Voltammograms and the calibration curve for standard solution 1 are shown in Fig. 6. The value obtained for standard 1 were $6.8 \mu\text{g L}^{-1}$ (RE 21.0%) for Pb (II) and $4.5 \mu\text{g L}^{-1}$ for Cd(II) (RE -19.0%) and the values obtained for standard 2 were $12.58 \mu\text{g L}^{-1}$ (RE 9.0 %) for Pb(II) and $9.7 \mu\text{g L}^{-1}$ for Cd(II) (RE -15.7%). These values are satisfactory because the tested water contains others metal ions (Co, Cu, Mo, Zn and Ni). Moreover, Co, Cu, Mo, Zn and Ni, do not cause interference with the signals of Pb(II) and Cd(II) up to 100 times higher concentrations.

3.8. Real samples analysis

The proposed in-situ HgF-N-L/GCE was applied for the determination of Pb(II) and Cd(II) in tap waters without previously treatment. The results are summarized in Table 2.

Table 2. Detection of Pb(II) and Cd(II) in tap water

Tap water samples	Added ($\mu\text{g L}^{-1}$)		Found ($\mu\text{g L}^{-1}$)		% Relative error	
	Pb(II)	Cd(II)	Pb(II)	Cd(II)	Pb(II)	Cd(II)
1	-	4.6	2.1	4.0	-	13.0
2	-	9.0	1.7	6.5	-	27.0
3	-	4.6	3.0	3.4	-	26.0

Cd(II) was not detected in any of these samples. Possibly, the concentration of Cd(II) was below the detection limit. The amounts detected of Pb(II) were below $5.0 \mu\text{g L}^{-1}$, which is the allowed range for human consumption.

4. CONCLUSIONS

This work reports the simultaneous trace determination of Pb(II) and Cd(II) in the presence of macrocyclic ester (**L**). The presence of **L** allowed the increases of the anodic peak currents for Pb(II) and Cd(II) more than 50%. Therefore, proposed method was more sensibility. The analysis time was significantly reduced by that is not necessary to the pretreatment of the samples and the time of each measurement was of 60 s.

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