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Nafion–mercury coated film electrode for the adsorptive stripping voltammetric determination of lead and cadmium in the presence of pyrogallol red

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ABSTRACT

An adsorptive stripping voltammetric (AdSV) method is presented for the simultaneous determination of Pb(II) and Cd(II) at trace levels in natural waters, based on metal complexation with pyrogallol red (PR) and subsequent adsorptive deposition on a Nafion–mercury coated glassy carbon electrode (NHgFE). Pyrogallol red forms complexes with a metal:ligand stoichiometry of 1:1 with Pb(II) and of 1:2 with Cd(II). Optimal analytical conditions were pH 4.0 (acetate buffer); $C_{PR}=2.8\ \mu mol\ L^{-1}$; $E_{ads}=-0.40$ V *vs.* Ag/AgCl; $t_{ads}=100$ s. The linear calibration curves ranged from 1.0 μg L^{-1} to 16.0 μg L^{-1} for Pb(II) and from 1.0 μg L^{-1} to 13.0 μg L^{-1} for Cd(II). The detection limits (S/N=3) were 0.05 μg L^{-1} for Pb(II) and 0.01 μg L^{-1} for Cd(II). The relative standard deviation was 1.0% and 2.0% ($n=7$), respectively, for a solution containing 5.0 μg L^{-1} Pb(II) and Cd(II). The method was validated by determining Pb(II) and Cd(II) in certified reference waste water (SPS–WW1). Finally, the method was applied to the determination of Pb(II) and Cd(II) in commercial mineral water samples after UV digestion.

1. Introduction

The monitoring of Pb(II) and Cd(II) in natural waters is of great importance for ecological assessments, due to the fact that these elements tend to concentrate in all aquatic environmental matrices and are taken up by marine species that form part of the human food chain. Anodic stripping voltammetry (ASV), the most popular stripping voltammetric technique, is effective for the determination of trace amounts of metal ions. Table 1 summarizes some of the published work on the application of Hg and Bi-modified electrodes for the simultaneous determination of Pb(II) and Cd(II) by ASV. For this determination modified electrodes have been used, such as Hg-coated glassy carbon [1–3], Hg-film supported on wax–impregnated carbon paste [4], Hg(II)-modified multiwalled carbon nanotubes [5], mercury film screen–printed carbon or graphite [6–8], and in the last years solid mercury amalgam [9], achieving detection limits of 0.94 ng L^{-1}, –5.0 μg L^{-1} for Pb(II) and 1.8 ng L^{-1}, –2.0 μg L^{-1} for Cd(II). Similarly to the mercury film electrode (HgFE), in the last 10 years the bismuth film electrode (BiFE) has been used by plating on glassy carbon [10] or modified with Nafion [11], Nafion graphene [12], 2,2'–bipyridyl [13], poly(p-aminobenzene sulfonic acid) [14] and other substrate materials such as carbon paste [15], graphite [16], and Nafion medical stone graphite [17]. Also, electrodes made with solid vibrating Bi [18], Bi nanopowder [19] and Bi bulk [20] have been introduced, and all of them exhibited excellent performance for anodic Pb(II) and Cd(II) determination.

Over the last years the popularity of adsorptive stripping voltammetry for trace metals has been increasing. However, the large majority of the published applications on the simultaneous determination of Pb(II) and Cd(II) using modified electrodes have utilized anodic stripping voltammetry (Table 1). These electrodes were shown to be extremely useful for adsorptive stripping measurements of trace nickel, cobalt, molybdenum, vanadium and chromium. However, to our best knowledge adsorptive determination of Pb(II) and Cd(II) has been unexplored.

The aim of this study was to optimize the adsorptive stripping voltammetric technique to determine Pb(II) and Cd(II) simultaneously, using pyrogallol red(PR) (3,4,5-trihydroxy-9-(2'-sulfophenyl)-6-isoxanthone; pyrogallolsulfonphthalein) as complexing and adsorbing ligand. This compound has been used in AdSV with HMDE as a chelating agent for molybdenum [21], germanium [22], copper [23], aluminum [24], antimony [25], and cobalt [26], but its use for the simultaneous determination of Pb(II) and Cd(II), using a glassy carbon electrode modified with Hg–Nafion has not been reported yet.

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Table 1
Selected published data for the application of Hg and Bi modified electrodes in the anodic stripping voltammetry of Pb(II) and Cd(II).

Electrode type	Mode	Linear range (μg L^{-1})	Detection limit (μg L^{-1})	Dep. time (s)	Ref.
Hg–glassy carbon	Sono–SWASV		Pb(II)=0.5* Cd(II)=1.0*	60	[1]
Hg–Nafion–glassy carbon	SWASV	Pb(II)=0–0.2 Cd(II)=0–1.1	Pb(II)=0.02 Cd(II)=0.11	60	[2]
Hg–wax carbon paste	ASV, CV,	Pb(II)=1.0–2072 Cd(II)=0.5–1124	Pb(II)=1.12 ng L^{-1}	120	[3]
Hg(II)–carbon nanotube	DPASV	Pb(II)=0.2–5.0 Cd(II)=0.2–5.0	Pb(II)=0.94 ng L^{-1} Cd(II)=1.8 ng L^{-1}	180	[4]
Hg–Nafion–screen printed carbon	SWASV	Pb(II)=10–200 Cd(II)=10–200	Pb(II)=1 Cd(II)=2	120	[5]
Hg–screen printed graphite	SWASV	Pb(II)=10–2000 Cd(II)=10–2000	Pb(II)=1.8 Cd(II)=2.9	120	[6]
Hg–methocel–screen printed graphite	SWASV	Pb(II)=1–1000 Cd(II)=1–1000	Pb(II)=0.3 Cd(II)=1	120	[7]
Ag–Hg–Nafion–glassy carbon	SWASV	Pb(II)=1–48 Cd(II)=1–28	Pb(II)=0.342 Cd(II)=0.551	120	[8]
Bi–glassy carbon	SWASV	Pb(II)=10–100 Cd(II)=10–100	Pb(II)=6.9 Cd(II)=1.4	90	[9]
Bi–Nafion–glassy carbon	SWASV SIA	Pb(II)=6–80 Cd(II)=2–60	Pb(II)=2 Cd(II)=2		[10]
Bi–Nafion–graphene–glassy carbon	DPASV	Pb(II)=0.5–50 Cd(II)=1.3–30	Pb(II)=0.02 Cd(II)=0.02	120	[11]
Bi–Nafion–2,2'-bipyridyl–glassy carbon	SWASV	Pb(II)=0.2–414 Cd(II)=0.1–225	Pb(II)=0.077 Cd(II)=0.12	120	[12]
Bi–poly(p-aminobenzene sulfonic acid)–glassy carbon	DPASV	Pb(II)=1.0–130.0 Cd(II)=1.0–110.0	Pb(II)=0.80 Cd(II)=0.63	240	[13]
Bi–carbon paste	SWASVDPASV		Pb(II)=0.8 Cd(II)=1.0	120	[14]
Bi–graphite	SWASV	Pb(II)=2–25 Cd(II)=1.2–13.5	Pb(II)=0.497 Cd(II)=0.326	120	[15]
Bi–Nafion–medical stone–Graphite	SWASV	Pb(II)=2.0–12.0 Cd(II)=2.0–12.0	Pb(II)=0.07 Cd(II)=0.47	300	[16]
Vibrating-Bi	SWASV	Pb(II) until 310.8	Pb(II)=0.03 Cd(II)=0.017	120	[17]
Bi nanopowder–screen printed carbon paste	SWASV		Pb(II)=0.07 Cd(II)=0.15	600	[18]
Bi bulk	SWASV	Pb(II)=10–100 Cd(II)=10–100	Pb(II)=0.093 Cd(II)=0.054	180	[19]

* Human saliva.

2. Experimental

2.1. Chemicals and reagents

Standard solutions of Pb(II) and Cd(II) were prepared by diluting commercial standards containing 1000 mg L^{-1}, Merck (Darmstadt, Germany). Water purified in a Milli-Q water purification system (Millipore) was used for all solution and sample preparations ($\Omega > 18$ MΩ cm^{-1}. Milford, USA). Nafion (5% w/v solution in a mixture of water and lower alcohols) and pyrogallol red were purchased from Aldrich (Milwaukee, WI). The stock solution of pyrogallol red in methanol (1×10^{-3} mol L^{-1}) was freshly prepared every three or four days. The method was validated by determining Pb(II) and Cd(II) in certified reference waste water (SPS–WW1). Finally, the method was applied to the determination of Pb(II) and Cd(II) in sea water and tap water samples after UV digestion.

2.2. Instrumentation

The voltammograms were obtained on a BASi CV50W with 3 mm and 2 mm ∅ glassy carbon electrodes. The 3 mm ∅ and the 2 mm ∅ glassy carbons were obtained from BASi and Metrohm, respectively, but all measurements were made with a BASi instrument. The reference electrode was Ag/AgCl/KCl 3 mol L^{-1} and the auxiliary electrode was a platinum wire. The solutions were deaerated using high-purity nitrogen. pH was measured with an Orion model 430 pH meter. UV-irradiation of water samples was carried out in quartz tubes using a 705 UV-digester (Metrohm).

2.3. Procedure for the preparation of NHgFE

Before measurement, the glassy carbon electrodes were thoroughly polished using a polishing pad with a 0.3 μm Al_2O_3 slurry, rinsed with ethanol and water in an ultrasonic bath and dried with N_2. A drop of the Nafion solution (10 μL) was placed on the electrode surface and the solvents were left to evaporate at room temperature for 10 min. The electrode was then transferred into the plating solution containing 200 mg L^{-1} Hg(II) and the Hg film was formed by holding the working electrode potential at −1.30 V for 150 s. The same electrode was used for a series of measurements.

2.4. Mineral water samples

Commercial mineral waters (Jahuel and Puyehue) were purchased in a supermarket. Before the analysis all the samples were digested with UV irradiation for 90 min at 90 °C (10.0 mL of sample with 100 μL of 30% H_2O_2).

2.5. Procedure for obtaining adsorptive voltammograms

Water (10.0 mL), 1.0 mL of acetate buffer (0.4 mol L^{-1}), 20–40 μL of pyrogallol red solution (1×10^{-3} mol L^{-1}), and aliquots of Pb(II) or Cd(II) solution (0.5 or 1.0 mg L^{-1}) were pipetted into the voltammetric cell. The solution was purged with nitrogen (saturated with water vapor) for 5 min for a given t_{ads} and E_{ads} at a stirring speed of 1800 rpm. After a 10 s quiescent period, the potential was scanned between −0.20 and −1.20 V using square wave modulation with 10 mV step amplitude, 45 mV pulse amplitude, and a frequency of 15 Hz. The calibration curves were obtained and linear range and detection limits were calculated. The proposed method was applied to the determination of Pb(II) and Cd(II) in mineral water. In order to eliminate matrix effects the standard addition method was used.

3. Results and discussion

Pyrogallol red (PR) contains four donor oxygen atoms forming two functional analytical groups: 3,4-dihydroxy and 5-hydroxy-6-oxy. These groups are separated but can form complexes of two types depending on the nature of the metal and the state of the reagents. Complexation at 3,4-dihydroxy groups occurs only at pH < 6 unless the 3-hydroxy group is dissociated [26]. PR forms complexes with a metal:ligand stoichiometry of 1:1 with Pb(II) and of 1:2 with Cd(II).

Fig. 1A shows adsorptive voltammograms for 4.1 μmol L^{-1} of PR (curve a) and in the presence of 11.5 μg L^{-1} of Pb(II) and Cd(II) (curve b) in acetate buffer solution at pH 4.5 using a mercury film electrode (HgFE). The stripping peak of PR was observed at −0.73 V; in the presence of Pb(II) and Cd(II) the peak current of this signal decreased and a small peak was observed at −0.52 V, which corresponds to the reduction of the Pb–PR complex, while the reduction of the Cd–PR complex is overlapped with the signal

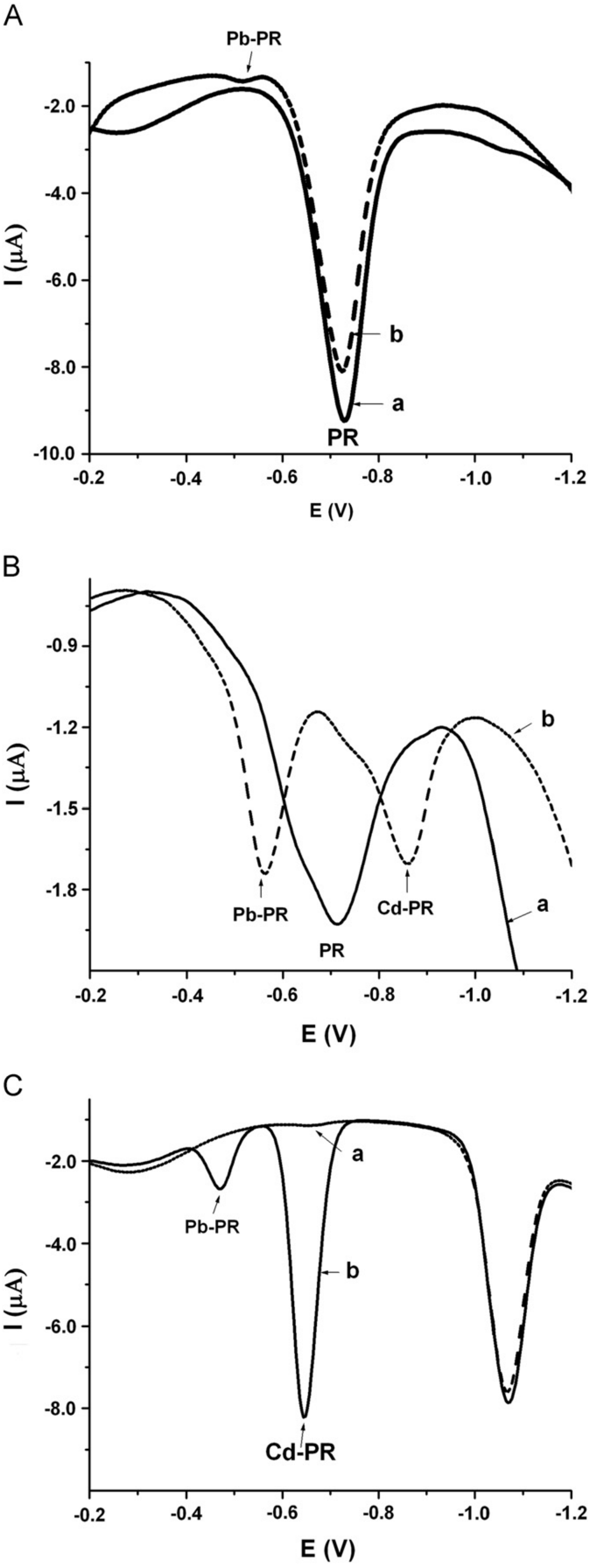


Fig. 1. AdSV with HgFE (A), NE (B) and NHgFE (C) electrodes. Conditions: pH 4.5 (acetate buffer); C_{RP} 4.1 μmol L^{-1} (curve a); $C_{Pb(II)}$; $C_{Cd(II)}$ 11.5 μg L^{-1} (curve b); E_{ads} −0.40 V; t_{ads} 60 s; square-wave frequency 15 Hz; amplitude 45 mV; potential step 10 mV.

of the free ligand. With the Nafion-coated glassy carbon electrode (NE) (Fig. 1B) the stripping peak of free PR was observed at −0.73 V (curve a), but the current is only −1.9 μA instead of −9.2 μA in the absence of Nafion. In the presence of Pb(II) and Cd(II) two broad peaks were observed at −0.56 and −0.86 V (curve b) for the reduction of the corresponding complexes, but the small signal at −0.73 V (reduction of free PR) prevented good resolution of the Pb–PR and Cd–PR signals. Finally, with the Nafion–mercury coated glassy carbon electrode (NHgFE) (Fig. 1C) the free ligand peak (curve a) was not observed due to the fact that this negative membrane prevents the adsorption of organic compounds, whereas the electrochemical reduction of the Pb–PR and Cd–PR complexes occurs at −0.47 and −0.65 V with currents of −2.6 and −8.2 μA, respectively (curve b). The NHgFE was selected as the optimum for this study (scheme 1). Inclusion of the PR in the electrode was not possible.

3.1. *Effect of operational parameters*

3.1.1. *Influence of pH*

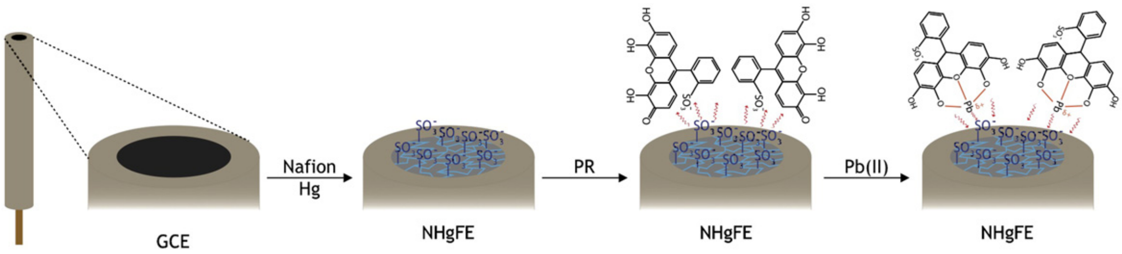
The effect of pH on the peak current of the Pb–PR and Cd–PR complexes was investigated in 3.5–5.5 range using acetate buffer (0.4 mol L^{-1}). The results obtained using C_{PR} 4.1 μmol L^{-1} and C_{Pb} and C_{Cd} of 11.5 μg L^{-1} (E_{ads}=−0.40 V and t_{ads}=60 s) are shown in Fig. 2. The peak potentials of Pb(II), Cd(II) and the free PR peak shifted towards more negative values with increasing pH, and maximum peak current was obtained at pH 4.0 for Pb–PR and pH 4.5 for Cd–PR. Because the peak current of the Pb–PR complex is lower than that of the Cd–PR complex, pH 4.0 was chosen for the whole study. PR contains one sulfonic acid group and three hydroxyl groups. In acidic solution (pH <1) the SO_3H group is deprotonated, while the hydroxyl groups at positions 3, 4 and 5 have dissociation constants of 2.89, 6.43 and 10.22, respectively [26]. At pH 4.0 the charge of the Pb–PR complex is 0 and that of Cd–PR is −2.

3.1.2. *Influence of ligand concentration*

The effect of C_{PR} (concentration range from 0.0 to 4.0 μmol L^{-1}) was studied for Pb(II) and Cd(II) at a concentration of 11.5 μg L^{-1} (pH 4.0, acetate buffer, E_{ads} −0.40 V; t_{ads} 60 s) and is illustrated in Fig. 3. The results show that peak current increases with increasing ligand concentration up to 2.8 μmol L^{-1}, and this was chosen for further optimization studies.

3.1.3. *Influence of t_{ads} and E_{ads} and scan rate on the stripping step*

The effect of t_{ads} was examined in the 0–110 s range. Peak current increases with increasing t_{ads} prior to the potential scan, indicating that the PR ligand and the Pb–PR, Cd–PR complexes are readily adsorbed on the modified electrode. Peak current of the Pb–PR and Cd–PR complexes increased almost linearly with accumulation time until 100 s, and then tended to a constant value (Fig. 4A), which was used for further studies. The influence of E_{ads} was also evaluated (Fig. 4B). The effect of the adsorption potential on the stripping peak current was studied over the 0.00–1.50 V range. The peak current is maximum until −1.10 V. However, the signals of the Pb–PR and Cd–PR complexes are very broad, losing selectivity, and the stability of the modified electrode is low. On this basis, an E_{ads} of −0.40 V was chosen for further studies, losing sensitivity. Another parameter studied was scan rate in the accumulation step. Fig. 4C shows plots of the cathodic peak current *vs.* scan rate for the Pb–PR and Cd–PR complexes. Peak current of the complexes increased linearly with scanning rate until 0.16 V s^{-1}, and this value was chosen for further measurements.



Scheme 1. Preparation of the modified electrode.

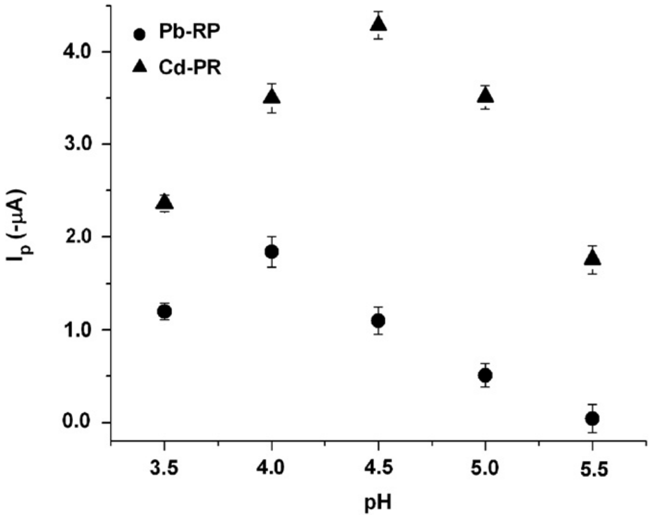


Fig. 2. Influence of pH on the peak current of the Pb–PR and Cd–PR complexes. Conditions: C_{RP} 4.1 μmol L^{-1}; $C_{Pb(II)}$;$C_{Cd(II)}$ 11.5 μg L^{-1};E_{ads} –0.40 V; t_{ads} 60 s. Other conditions as in Fig. 1.

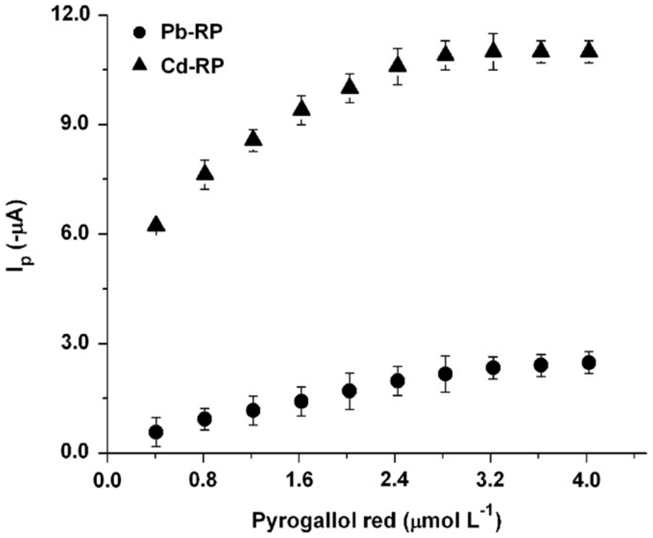


Fig. 3. Influence of C_{PR} on the peak current of the Pb–PR and Cd–PR complexes. Conditions: pH 4.0; $C_{Pb(II)}$; $C_{Cd(II)}$ 11.5 μg L^{-1}; E_{ads} –0.40 V; t_{ads} 60 s. Other conditions as in Fig. 1.

3.1.4. *Effect of instrumental variables (frequency, step potential and amplitude)*

The instrumental parameters studied were frequency, step amplitude and pulse amplitude. Peak current increased as all the parameters increased. However, when the frequency was higher than 15 Hz the signal of the Pb–PR and Cd–PR complexes was very broad, losing resolution. A step amplitude of 10 mV and a pulse amplitude of 45 mV at a frequency of 15 Hz were selected for further experiments.

3.2. *Linear range, detection limit, and reproducibility of the method*

Optimal analytical conditions were found to be: PR concentration of 2.8 μmol L^{-1}, pH 4.0 (acetate buffer ~0.04 mol L^{-1}); an E_{ads} of –0.40 V with an t_{ads} of 100 s (stirring rate 1800 rpm; step amplitude 10 mV; pulse amplitude 45 mV, and frequency 15 Hz). Under these conditions the peak current was proportional to the concentration of Pb(II) over the 1.0–16.0 μg L^{-1} range (Fig. 5), with a 3σ detection limit of 0.05 μg L^{-1}, and to that of Cd(II) over the 1.0–13.0 μg L^{-1} range, with a 3σ detection limit of 0.01 μg L^{-1}. The relative standard deviations were 1.0% and 2.0%, respectively, (n=7) for solutions containing Pb(II) and Cd(II) 5.0 μg L^{-1}. The results obtained with adsorptive stripping voltammetry were better than those obtained by anodic stripping voltammetry (Table 1).

3.3. *Validation of the method*

The usefulness of the present method was evaluated by determining Pb(II) and Cd(II) in certified reference waste water (SPS–WW1) containing Al 2000; As 100.0; Cd 20.0; Co 60.0; Cu 400; Fe 1000; Mn 400; Ni 1000; Pb 100.0; V 100.0 and Zn 600 μg L^{-1}. Voltammograms and the calibration curve are shown in Fig. 6. The value obtained was 103.0 ± 1.9 μg L^{-1} (RE 3.0%) for Pb(II) and 19.6 ± 1.1 μg L^{-1} for Cd(II) (RE 2.0%). These values are satisfactory because the tested waste water contains many metal ions (Al, As, Cu, Fe, Mn, Ni and Zn) at higher concentrations than those of Pb and Cd.

3.4. *Real samples analysis*

The proposed method was applied to the determination of Pb(II) and Cd(II) in commercial mineral waters previously digested under UV radiation in the presence of H_2O_2 solution. Pb(II) concentration was 0.24 ± 0.7 μg L^{-1} in Jahuel water and 0.11 ± 0.3 μg L^{-1} in Puyehue water (three samples). Cd(II) was not detected in any of these samples. To check the reliability of the method the samples were analyzed by ICP–AES, but the results obtained with this technique were below 5.0 μg L^{-1}, which is the detection limit of this methodology.

3.5. *Effect of the type of electrode*

Using the optimal analytical conditions, measurements were made replacing the working 3 mm diameter glassy carbon electrode by one of 2 mm diameter from different origin. As observed in Fig. 5, with the 3 mm electrode the Cd–PR complex signal is higher than that of the Pb–PR complex, whereas with the 2 mm

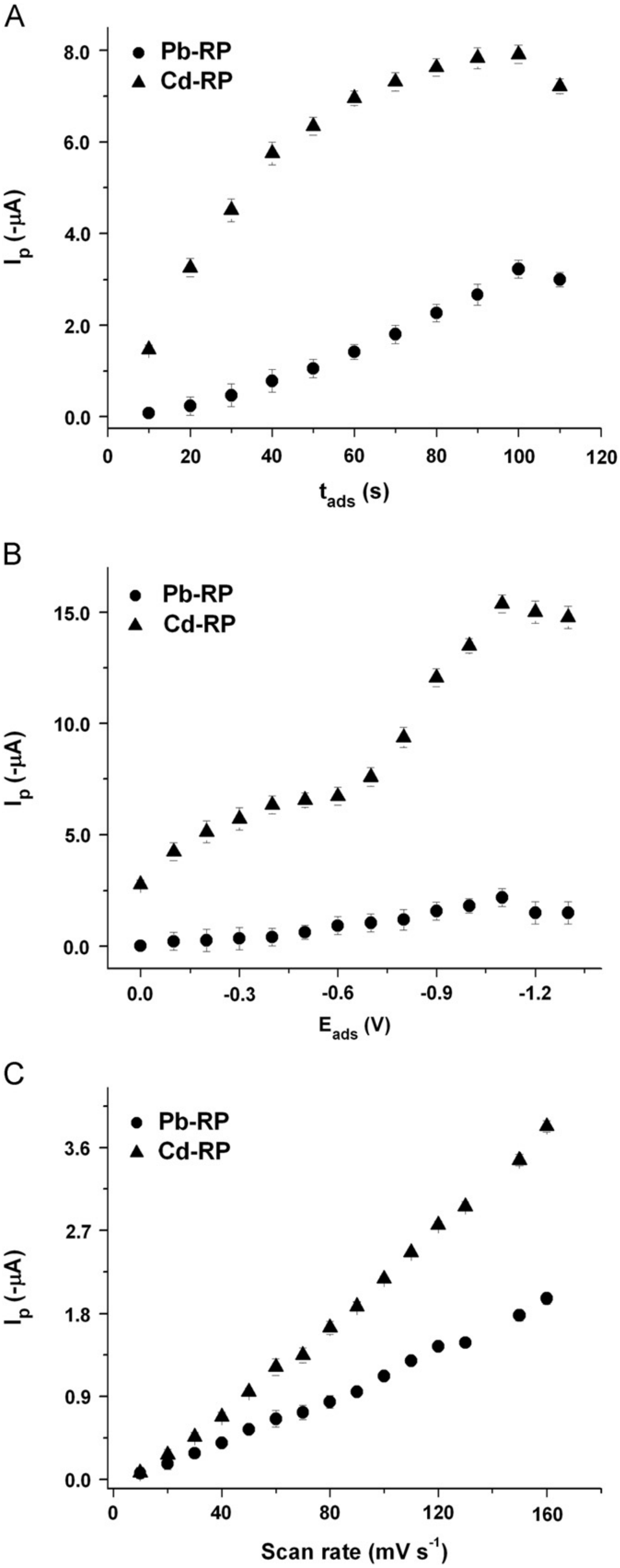


Fig. 4. Influence of t_{ads}(A); E_{ads} (B) and scan rate (*C*) on the peak current of the Pb–PR and Cd–PR complexes. Conditions: pH 4.0; $C_{Pb(II)}$; $C_{Cd(II)}$ 11.5 μg L^{-1}; C_{PR}: 2.8 μmol L^{-1}; (A) E_{ads} −0.40 V. (B) t_{ads} 100 s. (C) E_{ads} −0.40 V; t_{ads} 100 s. Other conditions as in Fig. 1.

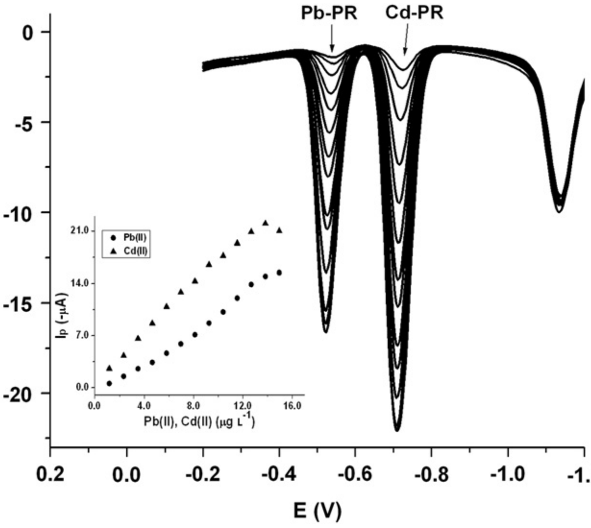


Fig. 5. AdSV and calibration curve for increasing concentration of Pb(II) and Cd(II) with NHgFE (3 mm ∅). Conditions: pH 4.0; C_{RP} 2.8 μmol L^{-1}; E_{ads} −0.40 V; t_{ads} 100 s. Other conditions as in Fig. 1.

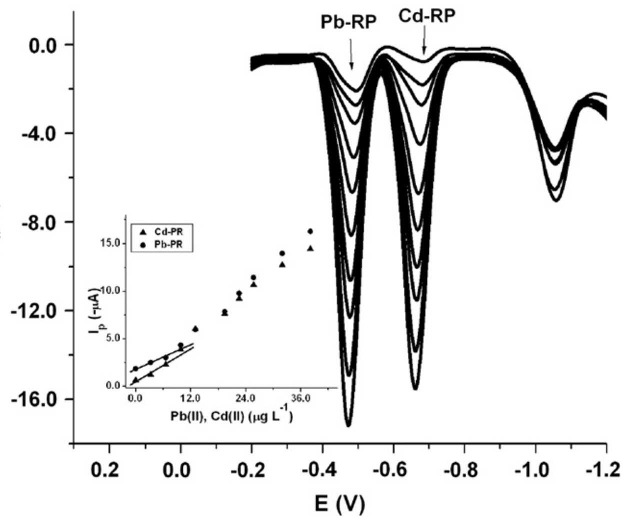


Fig.6. AdSV and calibration curve of certified reference water (SPS–WW1) with NHgFE. Conditions: pH 4.0; C_{PR}: 2.8 μmol L^{-1}; E_{ads}=−0.40 V; t_{ads}: 100 s. Other conditions as in Fig. 1.

electrode the Pb–Cd complex signal is higher than that of the Cd–PR complex (Fig. 7). These modified electrodes were prepared by exactly the same treatment, but since the area, thickness and morphology are different the selectivity for the Pb(II) or Cd(II) complex change.

4. Conclusions

The determination of Pb(II) and Cd(II) was carried out by forming Pb–PR and Cd–PR complexes which are adsorbed on Nafion–mercury glassy carbon electrodes (NHgFE). The Nafion membrane, which is negative, prevented a higher signal of free PR between the signals of the Pb(II) and Cd(II) complexes and the resolution was optimum. When the modified electrode is prepared, the origin and size of the glassy carbon electrode is an important parameter because the electrodes can be obtained with different adsorptive properties, even applying the same procedure of cleaning, nafion coating and mercury deposition. To our knowledge, similar results have not yet been reported.

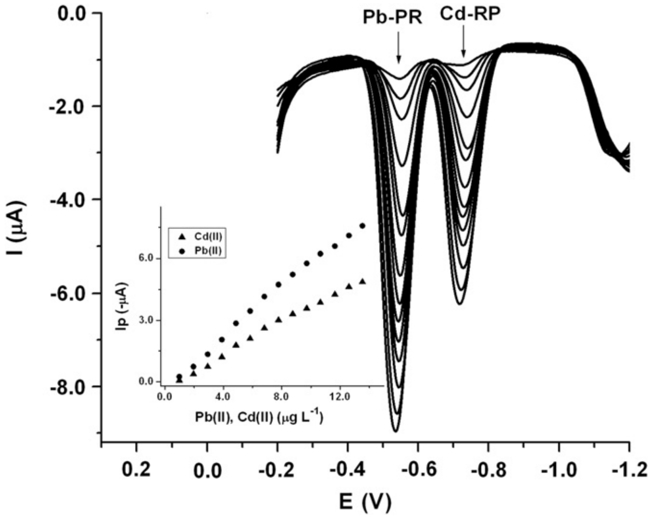


Fig.7. AdSV and calibration curve for increasing concentration of Pb(II) and Cd(II) with NHgFE (2 mm ∅). Conditions: pH 4.0; C_{PR}: 2.8 μmol L^{-1}; E_{ads}=−0.40 V; t_{ads}: 100 s. Other conditions as in Fig. 1.

Acknowledgments

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