

Adsorptive Stripping Voltammetric Determination of Lead and Cadmium in Natural Waters in the Presence of Rutin Using a Nafion–Mercury Coated Film Electrode

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A sensitive method for the simultaneous determination of Pb(II) and Cd(II) based on the formation of their complexes with rutin (RUT) and subsequent adsorptive deposition on a Nafion–mercury coated glassy carbon electrode (GC-NHgFE) is presented. The effects of various operational parameters such as pH, ligand concentration, accumulation potential, and time were optimized. The best experimental conditions found were: pH 3.5; C_{RUT} : 0.10 mmol L⁻¹; t_{ads} : 100 s, and E_{ads} : 0.15 V. Under these conditions, the reductions signals of Pb–RUT and Cd–RUT complexes are found at –0.29 V and –0.46 V, respectively, while no signal of free RUT was seen. The relationship between peak current and Pb(II), Cd(II) concentrations are linear in the 1.0–62.0 µg L⁻¹ range. The detection limits (DLs) were found to be 0.16 and 0.06 µg L⁻¹ for Pb(II) and Cd(II), respectively. Finally, the method was applied to the determination of Pb(II) and Cd(II) in water from the Ambala river (Colombia) and in commercial mineral water with satisfactory results.

Keywords: Rutin; Lead and Cadmium; Adsorptive Stripping Voltammetry; Nafion–mercury coated glassy carbon electrode.

1. INTRODUCTION

The US Environmental Protection Agency (US–EPA) has classified lead and cadmium as priority pollutants due to their toxicity at very low concentrations. They have chronic and acute effects on human health and are considered to be potentially deleterious to the environment. The toxicity of these metals is in part due to the fact that they accumulate in tissues as a result of their exposure to

metals in food and in the environment [1,2]. In extreme cases lead poisoning leads to health problems such as anaemia, renal dysfunction, and reduced intelligence quotient levels in children [3,4], while cadmium produces nausea and vomit and as a result of its prolonged exposure, toxaemia in the liver, emphysema in the lungs, proteinuria, hypertension, and anaemia [5,6]. The International Agency for Research on Cancer classified lead and cadmium as chemicals that are probably carcinogenic to man. Since the concentrations of these metal ions are low in many natural waters, a highly sensitive and selective method is required for their simultaneous determination.

In trace analysis, mainly of heavy metal ions, anodic stripping voltammetry (ASV) and adsorptive stripping voltammetry (AdSV) have been the most popular electroanalytical techniques because of their speed, good selectivity and sensitivity, and low instrumentation cost compared to other methods. AdSV requires the presence of a ligand with adsorptive properties, the complexes must be formed quantitatively and quickly in solution, and they must be adsorbed on the electrode's surface and later the ligand or the metal are oxidized or reduced. The sensitivity of the method is directly related to the adsorption of the complex, and the adsorption of the complex is related to its net charge, size, and solubility [7–10]. Table 1 summarizes some of the published works on the simultaneous determination of lead and cadmium applying ASV or AdSV techniques with different electrodes.

The present paper describes an adsorptive stripping procedure for the simultaneous determination of lead and cadmium in tap water and river water using rutin (RUT) (3,3',4',5,7-pentahydroxyflavone-3-rutinoside. Vitamin P) as complexing and adsorbing agent. Rutin is a phenolic compound widely distributed in plants such as black tea and apple peels. It is an antioxidant with pharmacological benefits including antitumor, antiinflammatory, antidiarrheal, antimutagenic, and myocardial protection, and immune-modulation, and it has renal protective effects on ischemia/reperfusion induced renal injury [11,12]. Kang et al. reported the synthesis, characterization, and electrochemical properties of Cd(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with RUT using a glassy carbon electrode, and Giovani et al. reported the synthesis, spectral, and electrochemical properties of Al(III) and Zn(II) without analytical purposes [13,14]. On the other hand, AdSV of Cu(II) or using an in situ plated lead film electrode have been used for indirect determinations of RUT [15–17]. Qu reported (in Chinese language) the determination of trace lead by AdSV on a RUT-modified carbon paste electrode [19], but the use of RUT for the simultaneous determination of lead and cadmium and later application in analysis of natural waters using Nafion-mercury coated glassy carbon electrode has not been reported yet.

2. EXPERIMENTAL

2.1. Apparatus

Stripping voltammetry measurements were made with a DropSens μ Stat 400 with 3 mm glassy carbon electrode. The reference electrode was Ag/AgCl/KCl 3 mol L⁻¹ and the auxiliary electrode was platinum wire. pH was measured with an Ohaus model ST3100 pH meter.

2.2. Chemical and samples

Water used for dilution of the standard, reagents, and preparation of samples were obtained from Merck (Germany). Standard solutions of Cd(II), Pb(II) and Hg(II) were prepared by diluting commercial standards containing 1000 mg L⁻¹ (Merck). Standard stock solution of RUT (6.2 mmol L⁻¹) was prepared in methanol (Aldrich). Nafion was purchased from Aldrich (Milwaukee, USA). All other chemicals such as nitric acid, acetic acid, methanol, etc. were analytical grade from Merck. Phosphate buffer and acetate buffer (0.1 mol L⁻¹) were prepared from the corresponding acid, adjusting to the required pH with NaOH solution. Synthetic drinking water spiked with 100 µg L⁻¹ Co(II), Cu(II), Mo(VI), Zn(II), Ni(II) and 15.0 µg L⁻¹ (water A) and 20.0 µg L⁻¹ (water B) of Pb(II) and Cd(II) were used for validation of the method.

2.3. Procedure for the preparation of GC-NHgFE

Before the measurements, the glassy carbon electrode was polished using a polishing pad with 0.05 µm Al₂O₃ slurry, rinsed with 0.3 mol L⁻¹ HNO₃ and water for 5 min. The electrode was placed in 10 mL of Nafion with stirring (500 rpm) for 10 minutes. The solvents were left to evaporate at room temperature. The modified electrode GC-NE with mercury solution (GC-NHgFE) was prepared ex situ. The electrode was immersed in an electroanalytical cell containing the plating solution of Hg(II) (200 mg L⁻¹), and the mercury film was formed by holding the working electrode potential at -1.30 V for 150 s. The same electrode was used in a series of measurements.

2.4. Adsorptive stripping voltammograms

Deionized water 10.0 mL (or 5.0 mL of water samples), 200-µL of buffer solution (0.1 mol L⁻¹), 10-50 µL of Pb(II) and Cd(II) solutions (5.0 mg L⁻¹) and 150 µL of RUT solution (6.2 mmol L⁻¹) were added in the voltammetric cell. The pre-concentration step was then initiated for optimal t_{ads} and E_{ads} at a stirring speed of 500 rpm. After an equilibration time of 5 s, the voltammograms were recorded in the cathodic direction from 0.0 to -0.9 V using square wave modulation with 10 mV step amplitude, 100 mV pulse amplitude, and a frequency of 15 Hz. Each voltammogram was repeated three times. The calibration curves were obtained and linear regression and detection limits (DLs) were calculated. The DL was calculated from $y_{\text{DL}} = a + 3\sigma_{x/y}$ and $y_{\text{DL}} = a + bDL$, where a is the intercept, $\sigma_{x/y}$ is the random error in x and y , and b is the slope. In addition $DL = x_{\text{DL}} = 3\sigma_{x/y}/b$, assuming that errors occur mainly in the y -direction [20]. The standard addition method was used to eliminate matrix effects.

2.5. Water samples

Commercial mineral water was purchased in a supermarket. Five river water samples were collected on February 20, 2016, from three points of the Ambala river, which is close to Ibagué

University (Ibagué, Colombia). The samples were collected in high-density polyethylene bottles which had been acid-washed and rinsed with deionized water. The collected river water samples were filtered with a syringe filter (0.45 μm). Samples were frozen until analysis. All data were obtained at room temperature ($\approx 25\text{ }^\circ\text{C}$).

3. RESULTS AND DISCUSSION

3.1. Preliminary Experiments

It has been reported that the electrochemical oxidation of RUT ($\approx 0.5\text{ V}$) on the solid electrodes involves two electrons and two protons, producing 3,4-diquinone [21], however the reduction occurs at more negative potentials ($\approx -1.2\text{ V}$) and has not been studied. On the other hand, RUT forms neutral complexes with Pb(II) and Cd(II) with a 1:2 metal:ligand stoichiometry.

The electroanalytical performance of the mercury film electrode prepared ex situ for the adsorptive voltammetry measurements was examined using Cd(II) and Pb(II) with RUT as chelating agent. Fig. 1 shows the adsorptive voltammograms of Pb(II) and Cd(II) in the presence of RUT (0.09 mmol L^{-1}) in phosphate buffer solution at pH 3.5 (0.002 mol L^{-1}), using a glassy carbon electrode GCE (curve a); a Nafion-coated glassy carbon electrode GC-NE (curve b) and a Nafion-coated mercury film electrode, GC-NHgFE, (curve c).

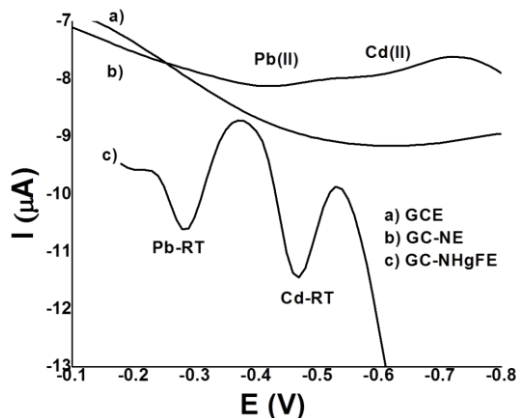


Figure 1. Adsorptive stripping voltammograms of Pb(II) and Cd(II) solutions using a glassy carbon electrode GCE (curve a), a Nafion coated glassy carbon electrode GC-NE (curve b) and a nafion coated mercury film electrode GC-NHgFE (curve c). Conditions: pH 3.5; $C_{\text{Pb(II)}}$, $C_{\text{Cd(II)}}$ 24.0 $\mu\text{g L}^{-1}$; C_{RUT} 0.09 mmol L^{-1} ; E_{ads} -0.10 V; t_{ads} 60 s. Step amplitude 10 mV; pulse amplitude 100 mV, and frequency 20 Hz.

With the GC and GC-NE the signals of Pb(II) and Cd(II) were not seen, and perhaps, due the electrochemical window at pH 3.5, the free signal of RUT was not seen with any of these electrodes. With the GC-NHgFE the two well-developed and separate stripping peaks at -0.29 and -0.46 V for Pb(II) and Cd(II), respectively, were observed. The signals of the free metal ion and the reduction of

the corresponding complex with RUT are only slightly displaced, indicating that the complexes are not very stable. On the other hand, anodic stripping voltammetry (ASV), the most popular stripping voltammetric technique, is very adequate for the determination of Pb(II) and Cd(II). In adsorptive voltammetry higher sensitivity could be achieved in the presence of adequate rutin concentration. In anodic stripping voltammograms (Fig. 2a), the oxidation peaks of lead and cadmium are seen at -0.09 and -0.29 V with peak currents of 3.28 and 5.34 μA , while in adsorptive stripping voltammograms (Fig.2b) the reduction peaks are seen at -0.26 and -0.46 V with peak currents of 12.80 and 7.35 μA for the same solution. The GC-NHgFE exhibit a well-developed adsorptive response and higher sensitivity for both metal ions.

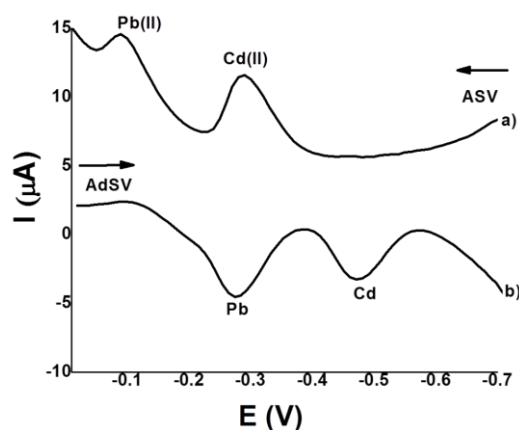


Figure 2. Anodic and adsorptive stripping voltammograms of Pb(II) and Cd(II) solution. Conditions: pH 3.5; $C_{\text{Pb(II)}}$, $C_{\text{Cd(II)}}$ $24.0 \mu\text{g L}^{-1}$; C_{RUT} 0.09 mmol L^{-1} ; E_{ads} -0.10 V; t_{ads} 60 s. Other conditions as in Fig. 1.

3.2. Influence of pH

The formation of the complexes, their stability, net charge, and adsorptive properties depend largely on the pH of the system. The influence of pH on the peak current of lead and cadmium were studied in the pH range of 2.0–3.5 using phosphate buffer (0.002 mol L^{-1}) and 4.0–5.0 using acetate buffer (0.002 mol L^{-1}) for solutions containing $24.0 \mu\text{g L}^{-1}$ of each metal ion and 0.09 mmol L^{-1} of RUT ($E_{\text{ads}} = -0.10$ V and $t_{\text{ads}} = 60$ s). The peak potentials of the Pb(II) and Cd(II) complexes shifted slightly toward more negative values with increasing pH, and as can be seen in Fig.3, maximum peak current was obtained at pH 3.5 for both metal ions and was used for further experiments.

3.3. Influence of ligand concentration

RUT concentration had a considerable effect on the method's linear range and sensitivity. The effect of C_{RUT} (range 0.01 to 0.12 mmol L^{-1}) was studied for Pb(II) and Cd(II) at concentration levels of $24.0 \mu\text{g L}^{-1}$ (pH 3.5, phosphate buffer, $E_{\text{ads}} -0.10$ V; t_{ads} 60 s) and it is illustrated in Fig.4. The results show that peak current increases with increasing ligand concentration up to 0.10 mmol L^{-1} and then tends slightly to level off. This behavior is due to competition of free RUT with lead and

cadmium complexes for adsorption on the GC-NH₂FE. An optimum ligand concentration of 0.10 mmol L⁻¹ was used for further experiments.

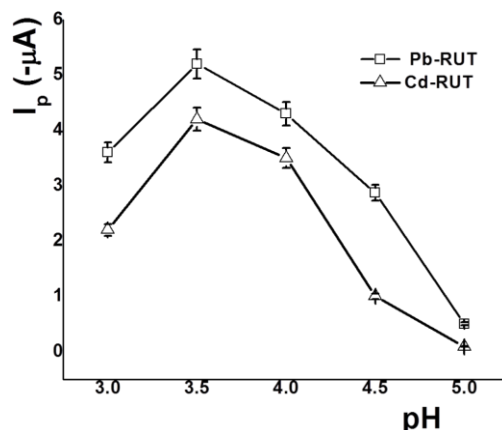


Figure 3. Influence of pH on the peak current of the Pb–RUT and Cd–RUT complexes. Conditions: $C_{\text{Pb(II)}}$, $C_{\text{Cd(II)}}$ 24.0 $\mu\text{g L}^{-1}$; C_{RUT} 0.09 mmol L⁻¹; E_{ads} -0.10 V; t_{ads} 60 s. Other conditions as in Fig. 1.

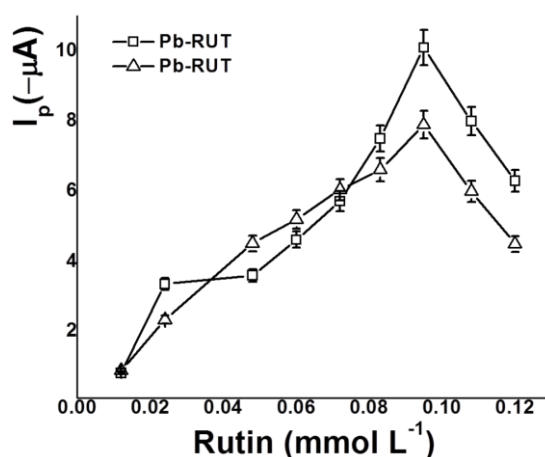


Figure 4. Influence of RUT concentration on the peak current of the Pb–RUT and Cd–RUT complexes. Conditions: pH 3.5; $C_{\text{Pb(II)}}$, $C_{\text{Cd(II)}}$ 24.0 $\mu\text{g L}^{-1}$; E_{ads} -0.10 V; t_{ads} 60 s. Other conditions as in Fig. 1

3.4. Influence of accumulation potential and time (E_{ads} , t_{ads})

The effect of the adsorption potential on the stripping peak current was studied in the 0.20 to -0.20 V range using 24.0 $\mu\text{g L}^{-1}$ of lead and cadmium concentrations (pH 3.5, C_{RUT} 0.10 mmol L⁻¹, t_{ads} 60 s). As shown in Fig. 5A, the peak current of the complexes increases when the potential is changed from 0.20 to 0.15 V, and at more negative values it decreased sharply. An adsorptive potential of 0.15 V gives the best sensitivity for lead and cadmium and was selected for further measurements.

On the other hand, the effect of accumulation time was examined in the 10–110 s range. Peak current increased with increasing accumulation time prior to the potential scan, indicating that the Pb–

RUT and Cd–RUT complexes are readily adsorbed on the GC–NHgFE. The peak current increased almost linearly with accumulation time until 90 s for the cadmium complex and 100 s for the lead complex, and then decreased slightly (Fig. 5B). On the basis of this study, we decided to use an adsorption time of 100 s for all further measurements.

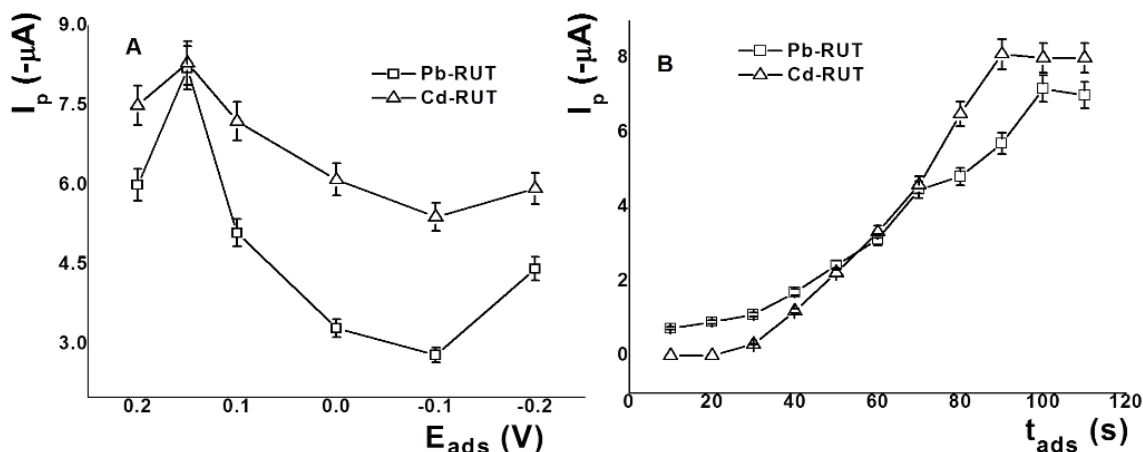


Figure 5. (A) Influence of E_{ads} on the peak current of the Pb–RUT and Cd–RUT complexes. Conditions: pH 3.5; $C_{\text{Pb(II)}}$, $C_{\text{Cd(II)}}$ $24.0 \mu\text{g L}^{-1}$; C_{RUT} 0.10 mmol L^{-1} ; t_{ads} 60 s. (B) Influence of t_{ads} on the peak current of the Pb–RUT and Cd–RUT complexes. Conditions: pH 3.5; $C_{\text{Pb(II)}}$, $C_{\text{Cd(II)}}$ $24.0 \mu\text{g L}^{-1}$; C_{RUT} 0.10 mmol L^{-1} ; E_{ads} 0.15. Other conditions as in Fig. 1.

3.5. Influence of instrumental variables.

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–RUT and Cd–RUT complexes was very broad, losing resolution. A step amplitude of 10 mV, a pulse amplitude of 100 mV, and a frequency of 15 Hz were selected for further experiments.

3.6. Linear range, detection limit, and repeatability of the method

Fig. 6 shows adsorptive stripping voltammograms obtained for 0.10 mmol L^{-1} RUT in 10.0 mL of phosphate buffer pH 3.5 (0.002 mol L^{-1}) with different Pb(II) and Cd(II) concentrations (E_{ads} : 0.15 V, t_{ads} : 100 s). Under these conditions the peak current was proportional to the concentration of lead and cadmium in the 1.0 – $62.0 \mu\text{g L}^{-1}$ range, with $3\sigma/b$ DLs of 0.16 and $0.06 \mu\text{g L}^{-1}$ for Pb(II) and Cd(II), respectively. Reproducibility for a $4.7 \mu\text{g L}^{-1}$ lead and cadmium solution was 2.0 and 1.5% respectively ($n = 7$). Table 2 summarizes all the statistical and instrumental parameters.

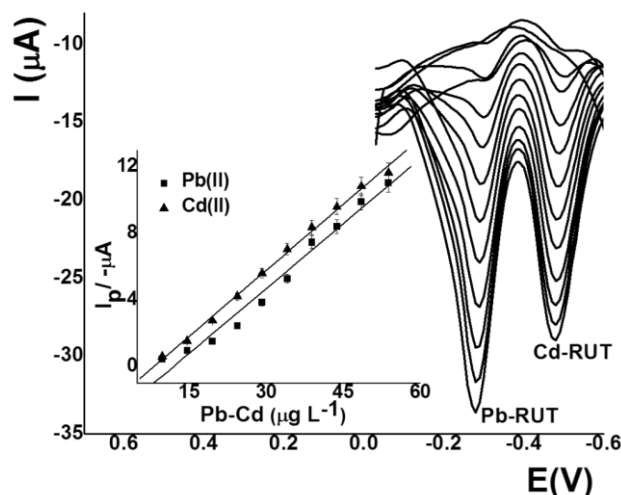


Figure 6. Adsorptive voltammograms and calibration curve for increasing concentration of Pb(II) and Cd(II). Conditions: pH 3.5; C_{RUT} 0.10 mmol L⁻¹; E_{ads} 0.15, t_{ads} 100 s. Other conditions as in Fig. 1.

Table 1. Determination of lead and cadmium using different electrodes and techniques.

Technique	Electrode	DL ($\mu\text{g L}^{-1}$) Pb(II),Cd(II)	LR($\mu\text{g L}^{-1}$) Pb(II),Cd(II)	tacc (s)	Sample	Ref.
ASV	HMDE	0.25 0.12	0.5-200 0.3-220	20	Milk	[22]
ASV	Bi -SPCNTes	0.2 0.8	2-100 2-100	120	Herbs	[23]
ASV	Cu -DPABA-NGCE	0.37 0.13	1.0-10360 0.56-5620	180	River water	[24]
ASV	NCB iFE	0.17 0.17		180	vegetables	[25]
ASV (SI)	Bi -SPCE	0.89 0.69	0-0.70 0-0.70	180	Water	[26]
ASV	SPE	1.8 2.9	10-2000	120	Sea water	[27]
ASV	HAP -CILE	0.04 0.056	0.2-20.7 0.1-11.2	180	Wastewater	[28]
ASV	BispSPE	0.16 0.10	0.53-19.8 0.33-12.3	300	Groundwater	[29]
ASV	SbSPCE	5.0 3.4	16.8-66.2 11.5-72.4	120	Groundwater	[30]
AdSV	GCN -NNBiFE	0.08 0.07	10-70 10-70	120	Tap water	[31]
AdSV	Diacetyldioxime -CPE	2.1 4.5	21-2072 28-2810	300	Water	[32]
AdSV	HMDE in presence of Clioquinol	0.10 0.06	0.10-40.0 0.06-31.0	30	Natural water	[33]
AdSV	HMDE in presence of 2-mercaptobenzothiazole	0.017 0.01	0.5-70 0.2-30	160	Rice, soya, sugar	[34]
AdSV	NSbFE in presence of Pyrogallol red	0.4 0.5	0.9-12 0.9-12	100	Tap water, mineral water	[35]
AdSV	NHgFE in the presence of Pyrogallol red	0.05 0.01	1.0-16.0 1.0-13.0	100	Mineral water	[36]
AdSV	GC-NHgFE in the presence of Rutin	0.16 0.06	1-62 1.62	100	River water, mineral water	This work

Table 2. Optimum and quantity parameters

Parameter	optimum and quantity
technique	AdSV
Electrode	Glassy carbon (3 mm)
stirring rate	500 rpm
E_{ads}	0.15 V
Tads	90-100 s
step amplitude	10.0 mV
pulse amplitude	100.0 mV
Frequency	15 Hz
DLs	Pb= 0.16 $\mu\text{g L}^{-1}$
	Cd= 0.06 $\mu\text{g L}^{-1}$
QLs	62.0 $\mu\text{g L}^{-1}$
Reproducibility (RSD)	Pb= 2.0 %
	Cd= 1.5 %

Bi-SPCNTe: Bi-screen-printed carbon nanotubes electrode. **Cu-DPABA-NGCE**: Nafion-modified glassy carbon electrode and **Cu-DPABA** complex. **DPABA**: methyl 3,5-bis{bis-[(pyridin-2-yl)methyl]amino}methyl-benzoate). **NCBiFE**: Nafion-coated bismuth film electrode. **Bi-SPCE**: bismuth film screen-printed carbon electrode. **HAP-CILE**: hydroxyapatite-modified carbon ionic liquid electrode. **GCN-NNBiFE**: glassy carbon electrode modified with Nafion, 1-nitroso-2-naphthol and bismuth film. **BispSPE**: sputtered bismuth screen-printed electrode. **SbSPCE**: Antimony film screen-printed carbon electrode. **NSbFE**: nafion-coated antimony film electrode. **GC-NHgFE**: Nafion-mercury coated glassy carbon electrode.

Similar DLs values were obtained by Abbasi et al. [34] using a HMDE in the presence of 2-mercaptobenzothiazole (Pb^{II} : 0.017; Cd^{II} : 0.01 $\mu\text{g L}^{-1}$); by Li et al. [28] using hydroxyapatite-modified carbon ionic liquid electrode (HAP-CILE) (Pb^{II} : 0.040; Cd^{II} : 0.056 $\mu\text{g L}^{-1}$), Nagles et al. [36] using Nafion-mercury coated glassy carbon electrode (GC-NHgFE) (Pb^{II} : 0.05; Cd^{II} : 0.01 $\mu\text{g L}^{-1}$) and by Segura et al. [31] using a glassy carbon electrode modified with Nafion, 1-nitroso-2-naphthol and bismuth film (GCN-NNBiFE) (Pb^{II} : 0.08; Cd^{II} : 0.07 $\mu\text{g L}^{-1}$). On the other hand, DL is in the same order of magnitude of those obtained by Sosa et al. [29] using a sputtered bismuth screen-printed electrode (BispSPE) (Pb^{II} : 0.16; Cd^{II} : 0.10 $\mu\text{g L}^{-1}$) and by Herrero et al. [33] using a HMDE in the presence of clioquinol (Pb^{II} : 0.010; Cd^{II} : 0.06 $\mu\text{g L}^{-1}$). Moreover, DL is between 5 to 30 times lower than those obtained by Chuanuwatanakul et al. [26], Abbasi et al. [27], Hu et al. [32] and Sosa et al. [30] using bismuth film screen-printed carbon electrode (Bi-SPCE), screen-printed carbon electrode (SPCE), Diacetyldioxime-CPE and antimony film screen-printed carbon electrode (SbSPCE) (Table 1).

3.7. Validation of the method

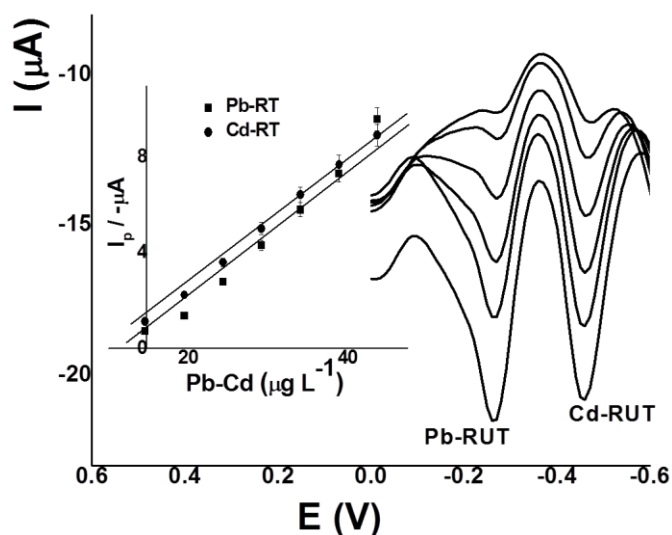


Figure 7. Adsorptive voltammograms and calibration curve for synthetic drinking water spiked with 100 mg L^{-1} of Co(II), Cu(II), Mo(VI), Zn(II) and Ni(II) ($C_{\text{Pb(II)}}$, $C_{\text{Cd(II)}}$ $15.0 \text{ } \mu\text{g L}^{-1}$). Conditions: pH 3.5; C_{RUT} 0.10 mmol L^{-1} ; E_{ads} 0.15 , t_{ads} 100 s . Other conditions as in Fig. 1

The usefulness of the present method was evaluated by determining lead and cadmium in two synthetic drinking water samples spiked with 100 mg L^{-1} of Co(II), Cu(II), Mo(VI), Zn(II) and Ni(II) in the presence of 15.0 (water A) and $20.0 \text{ } \mu\text{g L}^{-1}$ (water B) of Pb(II) and Cd(II). The values obtained were $16.06 \text{ } \mu\text{g L}^{-1}$ (RE 7.0%) for Pb (II) and $13.5 \text{ } \mu\text{g L}^{-1}$ for Cd(II) (RE -10.0%) for water A and $18.75 \text{ } \mu\text{g L}^{-1}$ (RE -6.2%) for Pb (II) and $19.1 \text{ } \mu\text{g L}^{-1}$ for Cd(II) (RE -4.5%) for water B. These values are satisfactory because this synthetic drinking water contains other metal ions. Fig. 7 shows square wave stripping voltammograms and the calibration plot obtained with water A.

3.8. Water samples analysis

The proposed method was applied to the determination of lead and cadmium in water from the Ambala river (Colombia), getting Pb(II) concentrations of $3.0 \pm 0.2 \text{ } \mu\text{g L}^{-1}$ (five samples). The method was also applied to the analysis of three bottled mineral water samples, getting a Pb(II) concentration of $1.0 \pm 0.1 \text{ } \mu\text{g L}^{-1}$. Cd(II) was not detected in any of these samples.

4. CONCLUSIONS

The determination of trace amounts of lead and cadmium were carried out by forming Pb–RUT and Cd–RUT complexes which are adsorbed on a glassy carbon electrode coated with a Nafion–mercury film (GC–NHgFE). In the analyzed water samples the concentration of cadmium was too low. Normally, the reported Pb(II) and Cd(II) determinations were carried out by ASV. However, with our system the peak currents obtained by AdSV are higher than those obtained by ASV. On the other hand,

with an accumulation time of 100 s the sensitivity is better than that for AAS and ICP–AES for the determination of lead and cadmium.

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References

- 1 B.E. Reed, S. Arunachalam, B. Thomas, *Environ. Prog.*, 13 (1994) 60.
- 2 M.C. Yebra–Biurrun, A. Bermejo–Barrera, M.P. Bermejo–Barrera, *Analyst*, 116 (1991) 1033.
- 3 E. Evans, M. Ma, L. Kingston, S. Leharne, *Environ. Int.*, 18 (1992) 153.
- 4 H.L. Needle, C. Gunnoe, A. Levitson, R. Reed, H. Peresie, C. Maherand, P. Barrett, *N. Engl. J. Med.*, 300 (1979) 689.
- 5 A.M. Massadeh, R.D. Snook, *J. Environ. Monit.*, (2002) 567
- 6 J. Staessen, P. Bruaux, F. Thoreau, P. de Plaen, G. Ducoffre, R.R. Lauwerys, H. Roels, D. Rodia, F. Sartor, A. Amery, *Environ. Health Perspect.*, 78 (1988) 127.
- 7 O. Abollino, M. Aceto, C. Zarzanini, E. Mentasti, *Electroanalysis*, 11 (1999) 870.
- 8 A. Economou, P.R. Fielden. *TRAC–Trend. Anal. Chem.*, 16 (1997) 286.
- 9 M.G. Paneli, A. Voulgaropoulos, *Electroanalysis*, 5 (1993) 355.
- 10 C. Rojas–Romo, V. Arancibia, D. Moreno–da Costa, R.A. Tapia, *Sensor Actuat. B–Chem.*, 224 (2016) 772.
- 11 S.S. Chen, J. Gong, F.T. Liu, U. Mohammed, *Immunology*, 100 (2000) 471.
- 12 K.H. Janbaz, S.A. Saeed, A.H. Gilani, *Fitoterapia*. 73 (2002) 557.
- 13 J. Kang, B. Su, X. Lu, *Indian J. Chem.*, 44 (2005) 2010.
- 14 R.F.V. de Souza, W.F. de Giovani, *Spectrochim. Acta Part A*, 61 (2005) 1985.
- 15 J. Gomes, M. Rodrigues, A. Carlos de Oliveira, J. Rodrigues, C. Vaz, C. Silva, *J. Food Compos Anal.*, 25 (2012) 1.
- 16 K. H. García, O. Fatibello–Filho, I. de Mattos, *Brazilian J. Pharm. Sci.*, 48 (2012) 639.
- 17 A.A. Ensafi, R. Hajian, *Electroanalysis*, 18 (2006) 579.
- 18 K. Tyszcuk, *J. Pharm. Biomed. Anal.*, 49 (2009) 558.
- 19 W. Qu, *Huagong Keji*, 11 (2003) 47.
- 20 J.C. Miller, J.N. Miller, *Statistics and Chemometrics for Analytical Chemistry*, fourth ed., Pearson Education, Londres, 2002.
- 21 J.W. Kang, X.Q. Lu, H.J. Zeng, H.D. Liu, B.Q. Lu, *Anal. Lett.*, 35 (2002) 677.
- 22 Y. Shabhazi, F. Ahmadi, F. Fakhari, *Food Chem.*, 192 (2016) 1060.
- 23 U. Injang, P. Noyrod, W. Siangproh, W. Dungchai, S. Motomizu, O. Chailapakul, *Anal. Chim. Acta*, 668 (2010) 54.
- 24 D. Stankovic, D. Manojlovic, G. Roglic, S. Kostic–Rajacic, I. Andjelkovic, B. Dojcinovic, J. Mutic, *Electroanalysis*, 23 (2011) 1928.
- 25 H. Xu, L. Zeng, D. Huang, Y. Xian, L. Jin, *Food Chem.*, 109 (2008) 834.
- 26 S. Chuanwatanakul, W. Dungchai, O. Chailapakul, S. Motomizu, *Anal. Sci.*, 24 (2008) 589.
- 27 S. Abbasi, A. Bahiraei, F. Abbasai, *Food Chem.*, 129 (2011) 1274.
- 28 Y. Li, X. Liu, X. Zeng, Y. Liu, X. Liu, W. Wei, S. Luo, *Sensor Actuat. B–Chem.*, 139 (2009) 604.
- 29 V. Sosa, N. Serrano, C. Ariño, J. M. Díaz–Cruz, M. Esteban, *Talanta*, 119 (2014) 348.
- 30 V. Sosa, C. Barceló, N. Serrano, C. Ariño, J. M. Díaz–Cruz, M. Esteban, *Anal. Chim. Acta*, 855 (2015) 34.

- 31 R. A. Segura, J. A. Pizarro, M. P. Oyarzun, A. D. Castillo, K. J. Díaz, A. B. Placencio, *Int. J. Electrochem. Sci.*, 11 (2016) 1707.
- 32 C. Hu, K. Wu, X. Dai, S. Hu, *Talanta*, 60 (2003) 17.
- 33 E. Herrero, V. Arancibia, C. Rojas–Romo, *J. Electroanal. Chem.*, 729 (1993) 9.
- 34 S. Abbasi, K. Khodarahmiyan, F. Abbasi, *Food Chem.*, 128 (2011) 254.
- 35 V. Arancibia, E. Nagles, C. Rojas, M. Gómez, *Sensor Actuat. B–Chem.*, 182 (2013) 368.
- 36 E. Nagles, V. Arancibia, C. Rojas, R. Segura, *Talanta*, 99 (2012) 119.

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