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Preparation of Glassy Carbon Electrode Modified with Polymeric Meso–Tetrakistetrabromo Thienylporphyrin for Determination of Cadmium and Lead by Anodic Stripping Voltammetry

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The use of a glassy carbon electrode modified with polymeric meso–tetrakistetrabromothienyl porphyrin (TBrTP) to determine Pb(II) and Cd(II) is reported. TBrTP was prepared by electrochemical polymerization in acetonitrile. Using SWASV, variables like number of cycles on the electropolymerization, pH, time and accumulation potential (t_{acc}, E_{acc}) were optimized. Optimal analytical conditions were: pH 5.0 (acetate buffer); E_{acc} –1.00 V *vs.* Ag/AgCl and t_{acc} 60 s. The linear calibration curves ranged from 10.0 to 70.0 µg L^{-1} for Pb(II) and from 10.0 to 100.0 µg L^{-1} for Cd(II). The detection limits (3σ) were 0.03 and 0.02 µg L^{-1} for Pb(II) and Cd(II) respectively. The relative standard deviation was 4.8 % and 6.3 % (n=6), respectively, for a solution containing 10.0 µg L^{-1} of Pb(II) and Cd(II). The method was validated using TMDA 51.3 and SPS–WW1 certified reference materials and then applied to determination of Pb(II) and Cd(II) in spiked tap water.

Keywords: Porphyrin; Anodic Stripping Voltammetry; Lead; Cadmium; Chemically Modified Electrodes.

1. INTRODUCTION

The toxicity of metals has received considerable attention in recent years because heavy metals are widely distributed in the environment due to soil erosion and industrial and agricultural processes [1-5]. Contamination by heavy metals from various environmental sources, including natural waters are of great concern nowadays [6-8]. Lead and cadmium are two of the most hazardous elements to human health, because both metals can produce adverse effects on the metabolic processes of human beings [1]. Lead has been proved to be a carcinogenic agent and to cause disturbance in several organs. Cadmium is highly toxic even at low concentrations, causing damage to the kidneys, liver and lungs [9]. All these facts cause concern, demanding accurate analytical procedures for the quantification of these elements at trace levels [10].

Absorption spectroscopy (AAS) [11-14], inductively coupled plasma mass spectrometry (ICP–MS) [15-19] neutron activation analysis (NAA) [20] and electroanalytical techniques are sensitive, precise and accurate for the determination of trace metal. However, the last of them in addition are inexpensive and portable. Anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV) and adsorptive stripping voltammetry (AdSV) are the most used [21-24]. For many years mercury film or hanging drop electrodes have been irreplaceable in the analysis and characterization of trace metals and organic compounds using ASV, CSV or AdSV [25, 26], however, the toxicity of mercury restricts their use, and there have been many attempts to introduce mercury–free electrodes. As an alternative to use mercury electrodes, chemically modified electrodes (CMEs) have been proposed and reported in a number of review articles [23, 24, 27, 28]. They have the advantage they can preconcentrate an analyte on an electrode surface and being used to improve sensitivity and selectivity. Complexation prior to the electron–transfer step is particularly attractive, because the species may be trapped in a chemical environment that is conducive to a rapid electron transfer, and the analyte can be protected from interference by other species [2, 29, 30]. Research has been focused on the development of CMEs with various kinds of conducting polymers [31-36]. Electrode modification with polymeric materials can be performed in various ways (covalent bonding, adsorption, etc.), with electropolymerization as the most advantageous synthetic route *in situ,* simple, clean and efficient, and able to carefully control the rate and extent of the electropolymerization process by applying suitable conditions. This straightforward approach has however seldom been applied to the determination of trace metals and only few examples can be found in literature [33, 37-40].

This work establishes optimal conditions for the analysis of Cd^{2+} and Pb^{2+} by square wave anodic stripping voltammetry (SWASV), using a glassy carbon electrode modified with polymeric meso–tetrakistetrabromothienylporphyrin (TBrTP) generated by electropolymerization.

2. EXPERIMENTAL PART

2.1. Apparatus

Square wave anodic stripping voltammograms (SWASV) were obtained with a CHI 660A electrochemical analyzer (CH Instruments) in a three−electrode configuration. A glassy carbon electrode (3 mm diameter, BAS, USA) was used as working electrode with an Ag/AgCl/KCl 3 mol L^{-1} reference electrode, and a platinum wire auxiliary electrode. pH measurements were performed with an Orion pH meter.

2.2. Chemicals

Water used for sample preparation, and also for dilution of the reagents and rinsing purposes, was obtained with a Milli–Q system (Millipore, USA). All the chemicals used in the synthesis and electrochemical measures were analytical grade: pyrrole and 5–bromo–2– thiophenecarboxaldehyde were from Sigma–Aldrich; propionic acid, hexane, chloroform, ethanol, methanol, acetonitrile, sodium hydroxide, acetone, acetic acid, boric acid, orthophosphoric acid and sodium sulfite were from Merck, whereas potassium chloride was purchased from Riedel–de–Haen and tetrabutylammonium perchlorate from J.T Baker.

Standard stock solutions of 1.0 mg L^{-1} of Pb(II) and Cd(II) were prepared from standard 1000 mg L^{-1} solutions (Merck). Britton Robinson (BR) and Acetic acid−acetate (HAc/Ac) buffers were used to investigate pH in the 3.5−5.5 range. BR buffers (0.1 mol L^{-1}) were prepared by mixing equal volumes of orthophosphoric acid, acetic acid, and boric acid, adjusting to the required pH with 2.0 mol L^{-1} NaOH solution and acetate buffers (0.1 mol L^{-1}) were prepared by mixing the corresponding amounts of acetic acid and sodium hydroxide solution.

TBrTP was synthesized as reported by Adler [21] and was characterized by combination of 1 and 2D NMR. The solutions were prepared in ethanol (≈ 2.5 mg mL^{-1}).

2.3 Preparation of GC/TBrTP electrode:

The surface of the glassy carbon electrode (GCE) was polished with alumina (0.3 μm) and then rinsed with deionized water and ethanol in an ultrasonic bath. The GCE was placed in a cell containing $1.0 \, x \, 10^{-3}$ mol L^{-1} TBrTP and 0.1 mol L^{-1} tetrabutyl ammonium hexafluorophosphate as supporting electrolyte (acetonitrile). The electropolymerization was carried out by cyclic voltammetry between 0.0 and 1.3 V *vs*. Ag/AgCl (scan rate 0.1 V $s^{-1).}$

2.4. General voltammetric procedure

All voltammetric measurements were carried out in 0.10 mol L^{-1} acetate buffer (pH 5.0) at room temperature (23 ± 2 ^{o} C). An accumulation potential of –1.0 V was applied to the working electrode. The solution was stirred during the deposition step (700 rpm), and after an equilibrium period of 5 s the stripping voltammogram was recorded, while the potential was scanned from –1.20 to -0.40 V using square wave modulation with 4 mV step amplitude, 25 mV pulse amplitude, and a frequency of 15 Hz.

3. RESULTS AND DISCUSSION

3.1 Synthesis of monomer meso–tetrakistetrabromothienylporphyrin (TBrTP).

Figure 1 shows the voltammograms obtained in the polymerization of TBrTP on the glassy carbon electrode. The oxidation current increased in successive sweeps due to doping, which occurs simultaneously with the growth of the film due to electropolymerization. In fact, thienyl groups are oxidized becoming radical cations that attack neutral monomers. A decrease in the oxidation potentials is also seen. This change has been attributed to lengthening of the oligomer chain, whose oxidation potential decreases due to an increase in the conjugation, and that also accounts for the formation of a deposit on the glassy carbon electrode [41, 42]. The selected anodic potential limit represents the overpotential that is needed to produce oxidation of the monomer and the subsequent polymerization without alter the voltammetric profile. The increasing current at 1.20 V represents the oxidation process of thienyl groups, and this indicates that a certain amount of pTBrTP has been deposited on the electrode. Polymerization occurs in the meso–thienyl groups.

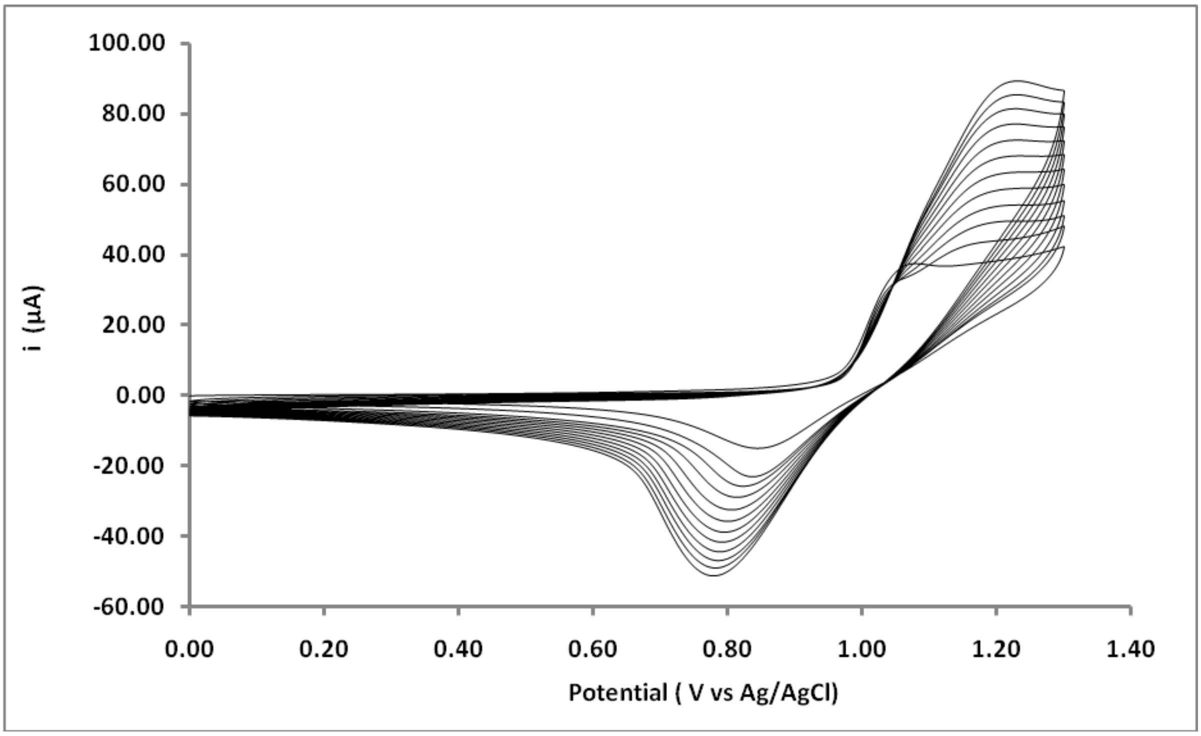


Figure 1. Cyclic voltammograms obtained in the electropolymerization of TBrTP recorded on a glassy carbon electrode. in 0.1 M CH_3CN, 3 *x* 10^{-3} mol L^{-1} TBrTP, scan rate 0.1 V s^{-1}.

3.2. Effect of the number of cycles on the electropolymerization.

In order to obtain a stable and conductive electrode it is necessary to determine the effect of the polymer layer thickness on the peak current of Cd^{2+} and Pb^{2+}, which in this case was controlled by the number of voltammetric cycles (Figure 2). It is seen that although there is a direct relation between the number of cycles of the modified electrode and peak current, the modified electrodes from less than 10 cycles were not stable in their responses, a behavior attributed to the smaller number of cycles, with the layer deposited on the surface of the glassy carbon electrode not uniform and therefore does not cover it is entire surface, with little response reproducibility and sensitivity. After about 40 cycles of the deposited polymer film, a reproducible response is obtained, and it may be possible that an excess of deposited polymer can readily show cracks after some use.

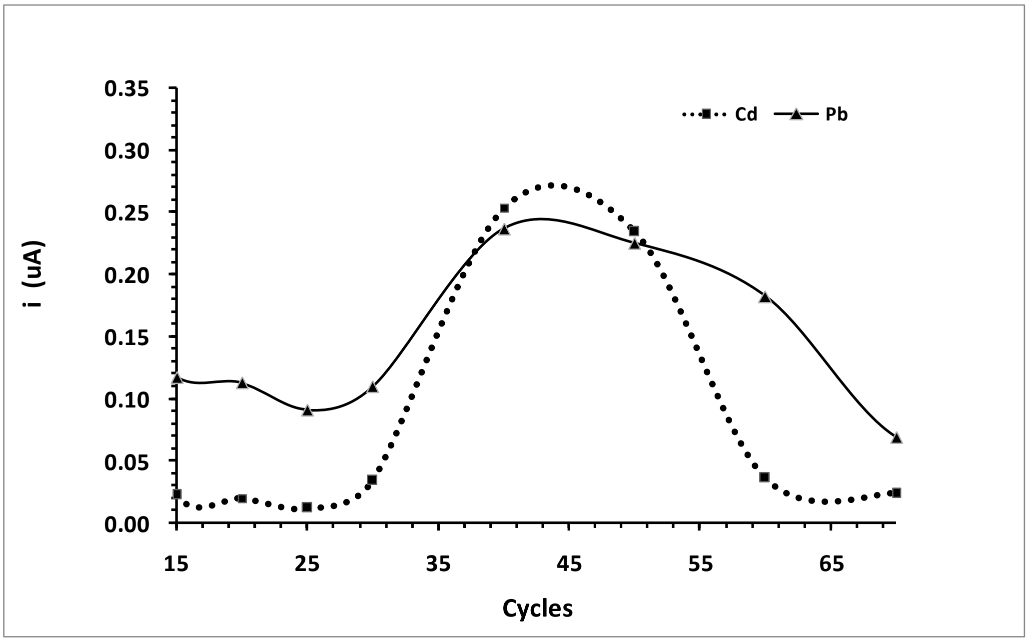


Figure 2. Effect of the cycles in the electropolymerization on the peak current of Pb and Cd: Conditions: Pb(II) and Cd(II) 10.0 µg L^{-1} ; pH 5.0 (acetate buffer 0.1 mol L^{-1}); E_{acc} –1.00 V; t_{acc} 60 s; amplitude 25 mV; frequency 15 Hz; step potential 4 mV, and stirring speed in the accumulation step 700 rpm.

3.3. Effect of operational parameters in the Pb and Cd determination

3.3.1. Effect of pH

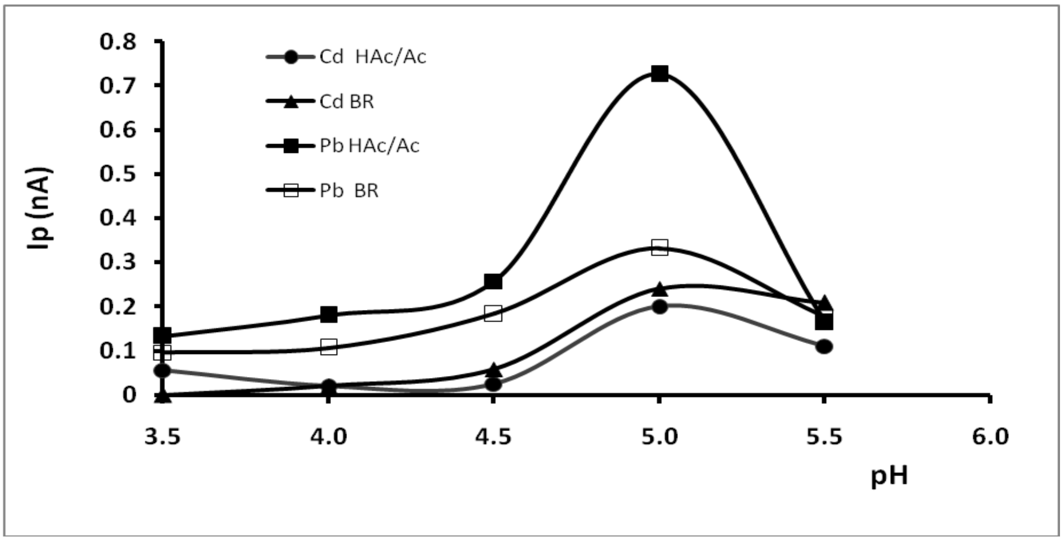


Figure 3. Effect of pH on the anodic peak current of Pb and Cd. Conditions: Pb(II) and Cd(II) 10.0 µg L^{-1} ; pH 5.0 (acetate buffer 0.1 mol L^{-1}); E_{acc} –1.00 V and t_{acc} 60 s. Other conditions as in Fig. 2.

The influence of pH on the peak current of Pb(II) and Cd(II) was studied in the pH 3.5–5.5 range in Britton Robinson (BR) and acetate buffers (HAc/Ac). As can be seen from Figure 3, at the peaks current sharp signals with good reproducibility were obtained with a pH 5.0 acetate buffer whereas in BR buffer the peak current is lower for both ions. The decreasing of the stripping current at pH lower then 5.0 may be attributed to electrostatic repulsion between the protonated polymer and metallic cations. At pH values higher than 5.0; $Pb(OH)_2$ and $Cd(OH)_2$ precipitate, consequently the amount of Cd(II) and Pb(II) decreasing in solution.

This profile indicates that the most favorable performance occurs around pH 5.0, and this value was used in all succeeding measurements.

3.3.2. Effect of accumulation potential (E_{acc})

The effect of the accumulation potential on the stripping peak current of the Pb and Cd was studied in the 1.10 to −1.20 V range. The experimental conditions were: Pb(II), Cd(II) 10.0 μg L^{-1}, pH 5.0 (acetate buffer) and t_{acc} = 60 s. As shown in Figure 4, the peak current of the complexes increases when the potential is changed from −1.20 to −1.00 V, and at more positive values it decreased sharply due to proton reduction occurs. An accumulation potential of −1.00 V gives the best sensitivity and was selected for further measurements.

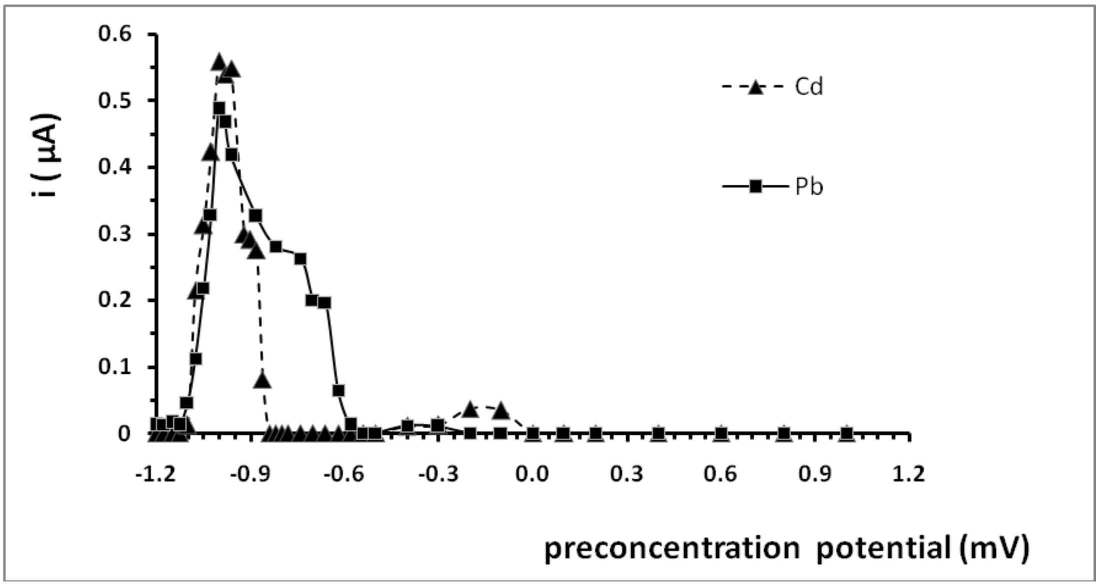


Figure 4. Effect of E_{acc} on the peak current of Pb and Cd. Conditions: Pb(II), Cd(II): 10.0 μg L^{-1}; pH 5.0 (acetate buffer); t_{acc}: 60 s. Others conditions as in Fig. 2.

3.3.3. Effect of accumulation time (t_{acc})

The effect of accumulation time (t_{acc}) was examined in the 0–1,100 s range. The experimental conditions were: Pb(II), Cd(II) 10.0 μg L^{-1}; pH 5.0 (acetate buffer) and E_{acc} = −1.00 V. As seen in

Fig.5 the peak current of Pb increases with increasing accumulation time up to 1,100 s whereas the peak current of Cd increases until 100 s and then is almost constant, attributed to the saturation of the sites actives. The accumulation time of 60 s was selected for subsequent measurements as a compromise between sensitivity and a relatively short experiment time.

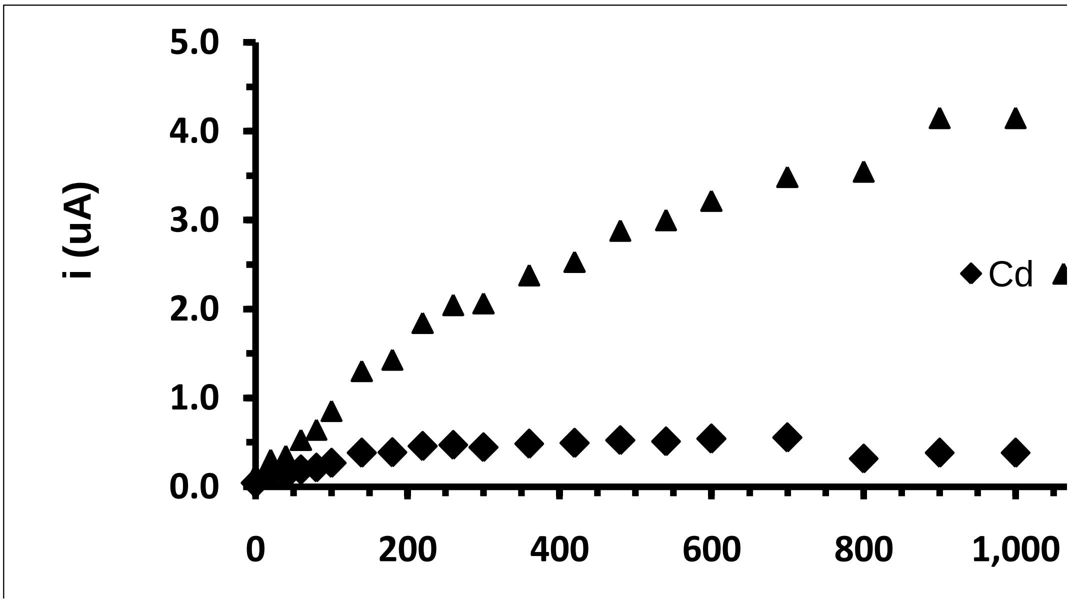
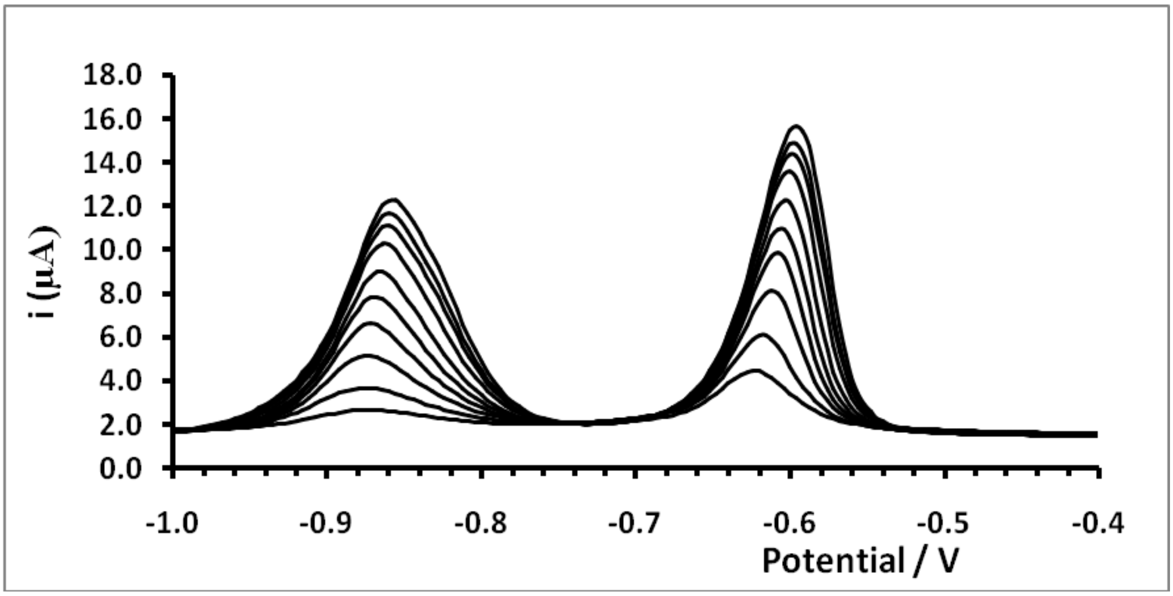


Figure 5. Effect of t_{acc} on the peak current of Pb and Cd. Conditions: Pb(II), Cd(II): 10.0 μg L^{-1}; pH 5.0 (acetate buffer); E_{acc}: −1.00 V. Others conditions as in Fig. 2.

3.4. Linear range, detection limit, and reproducibility of the method



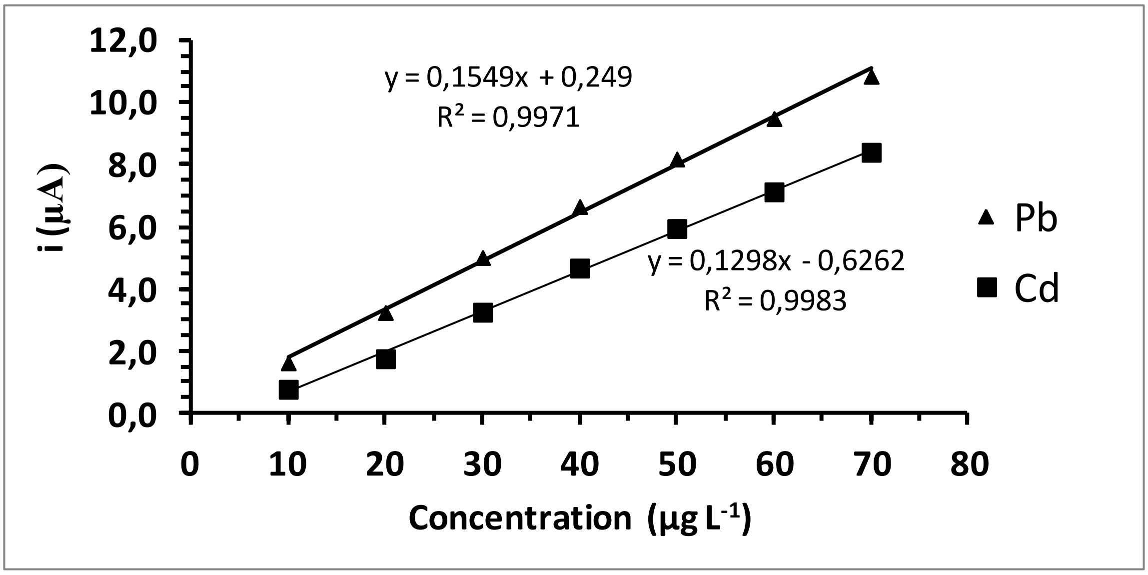


Figure 6. Stripping voltammograms (A) and calibration curve of Pb(II) and Cd(II) solution (B). Conditions: pH 5.0 (0.1 mol L^{-1} acetate buffer); E_{acc} –1.00 V; t_{acc}: 60 s. Other conditions as in Fig. 2.

Optimal analytical conditions were found to be: pH 5.0 (acetate buffer 0.1 mol L^{-1}); an E_{acc} of –1.10 V with an t_{acc} of 60 s (stirring rate 700 rpm; step amplitude 4 mV; pulse amplitude 25 mV, and frequency 15 Hz). Stripping voltammograms and calibration curve are shown in Figure 6A and 6B respectively. Under these conditions the peak current was proportional to the concentration of Pb(II) over the 10.0–70.0 µg L^{-1} range with a 3σ detection limit of 0.03 µg L^{-1}, and to that of Cd(II) over the 10.0–100.0 µg L^{-1} range (showed only up to 70.0 µg L^{-1} in Figure 6B) with a 3σ detection limit of 0.02 µg L^{-1}. The relative standard deviations for solutions containing Pb(II) and Cd(II) 10.0 µg L^{-1} were 4.8 % and 6.3 %, respectively (n=6).

3.5. Validation of the method

The usefulness of the present method was evaluated by determining Pb(II) and Cd(II) in certified references SPS–WW1 (waste water) and TMDA 51.3 (water with trace metals). The results obtained are presented in Table 1.

Table 1. Determination of Cd^{2+} and Pb^{2+} in certified references.

	Cd^{2+}		Pb^{2+}	
Sample	Found (µg L^{-1})	Certified (µg L^{-1})	Found (µg L^{-1})	Certified (µg L^{-1})
SPS–WW1	18.9 (5.5%)	20.0	74.6 (1.7%)	73.3
TMDA 51.3	26.4 (2.3%)	25.8	112.0 (12%)	100.0

Relative percentage standard deviations are given in parentheses (n= 8)

3.6. Real Samples

The proposed method was applied to the determination of Pb(II) and Cd(II) in spiked tap water from laboratory. These samples were spiked with 10.0 (S1), 40.0 (S2) and 60.0 (S3) µg L^{-1} of Cd^{2+} and Pb^{2+}. The results are presented in Table 2.

Table 2. Analysis of drinking water samples spiked with Cd^{2+} and Pb^{2+}

Sample	Cd^{2+} (µg L^{-1})	Pb^{2+} (µg L^{-1})
S1 (10.0 µg L^{-1})	11.0 (1.0 %)	10.8 (8.0 %)
S2 (40.0 µg L^{-1})	37.0 (7.5%)	36.1 (9.8 %)
S2 (60.0 µg L^{-1})	59.0 (1.7 %)	58.4 (2.7 %)

Relative percentage standard deviations are given in parentheses (n= 4)

3.7 Interference studies

In the validation studies with reference waters and spiked tap water Pb(II) and Cd(II) was successfully quantified without interference problems. The influence of 7 foreign metal ions (Al(III), As(III), Bi(III), Cu(II), Cr(III), Mo(VI), and Zn(II)) at 100.0 µg L^{-1} concentrations on the determination of 20.0 µg L^{-1} of Pb(II) and Cd(II) were investigated by ASV under the above optimized conditions and the peak current was affected under ± 5% relative error.

4. CONCLUSIONS

The present study shows the Pb and Cd can be effectively analyzed by square wave anodic stripping voltammetry using a glassy carbon electrode modified with polymeric meso–tetrakistetrabromo thienylporphyrin as working electrode. Acceptable agreement between the results obtained and those of certified reference material and spiked tap water were found.

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