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Determination of lead ion in the presence of pyridine-3-carboxylic acid using square wave voltammetry

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A B S T R A C T

A selective and sensitive electroanalytical method is developed for the determination of lead by square wave voltammetry (SWV) in the presence of pyridine-3-carboxylic acid (nicotinic acid, NA). The Pb-NA complex accumulates on the surface of controlled growth mercury electrode (GCME) and peak current is measured by square wave voltammetry (SWV). The complex is reduced and current increase by 1.5 folds when nicotinic acid is added to the sample solution. Assessment of the chemical and physical conditions that may favour optimum current enhancement was done by studying the effect of varying pH, scan rate, amplitude and also interference studies. Based on chronocoulometry and chronoamperometry technique the diffusion for Pb(II) were estimated by 8.01 x 10-5cm2/s and 0.46μc/cm2 respectively..

تحديد أيون الرصاص في وجود حمض بيريدين –3 كربوكسيليك باستخدام قياس التحليل الفولتميترى

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الملخص

تم تطوير طريقة التحليل الكهربائي الانتقائية والحساسة لتحديد الرصاص عن طريق قياس الجهد الفولتميترى (SWV) في وجود حمض البيريدين -3 الكربوكسيل (حمض النيكوتين ، NA). حيت يتراكم ويكون معقد Pb-NA على سطح قطب زئبقي (GCME) ويتم قياس تيار بواسطة قياس الجهد الفوليتمترى (SWV). حيت بتكوبن المعقد الدى يعمل على زيادة التيار بمقدار 1.5 مرة عند إضافة حمض النيكوتينيك فقط إلى محلول العينة. عند قباس الظروف الكيميائية والفيزيائية التي قد كان أفضل من خلال دراسة تأثير تغير الأس الهيدروجيني ومعدل المسح والسعة وكذلك دراسات التداخل. بناءً على مقياس الكرونوكولوميترى، تم تقدير انتشار الرصاص (II) بمقدار 8.01 × 10-5 سم 2 / ثانية و0.46 درجة مئوية / سم 2 على التوالي.

1. Introduction:

Nicotinic acid (NA) is an organic compound with the molecular formula $C_6H_5NO_2$. It is a derivative of pyridine, with a carboxyl group (COOH) at the 3-position. NA is an essential factor in the diet of mammals because of its importance in the production of the pyridine nucleotides NAD+ and NADP+ under physiological conditions. Pyridine and some of its derivatives have been the subject of numerous investigations on electrosorption at the metallic electrodes.. Transition metal complexes such as lead have been the subject of thorough investigation because of their extensive applications in wide ranging areas from material sciences to biological sciences [1-8] . Because of the increased industrial use of the lead and its serious hazardous effect to human health , the development of sensitive methods for the

determination of lead ions is required. Voltammetric techniques lend themselves as a powerful tool to study the interactions between metal ions and ligands, including simple monomeric or macromolecular ligands [9-11]. An electrochemical method such as square wave voltammetry for the determination of metal ions including lead is one of the most favorable techniques, because of its low cost, high sensitivity, easy operation and ability of analyzing element speciation[12-18].
Square wave voltammetry (SWV) is one of the electrochemical techniques more widely applied in quantitative analysis, due to its high sensitivity, which is mainly the consequence of the rejection of most the capacitive currents[19-21]. The aim of the present paper is to

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apply this method for the experimental response of solution containing Pb(II) in the presence of nicotinic acid onto the controlled growth mercury electrode (CGME). Due to its unique properties including a large potential window on both anode and the cathode region, the simplicity of its preparation, low cost, a simple modification of them, and low capacitive currents, leading to high signal to noise ratio, CPEs represent one of the most frequent types of working electrodes[22-24].This method provides a very low detection limit with good accuracy and precision and excellent selectivity against the other co-existing ionic species . The best set of SWV parameters from the analytical approach is also established.

2. Material and methods
2.1 Instrument and apparatus
The electrochemical studies were performed at a Voltammetric Analyzer (BAS 100W) using a conventional three-electrode electrochemical cell to perform square wave voltammetry(OSWV) and cyclic voltammetry (CV). It was used together with the Controlled Growth Mercury Electrode (CGME, BAS) system. All potential were measured against the Ag/AgCl (3M NaCl) as a reference electrode. A platinum wire was used as a counter electrode. Unless otherwise stated, the voltammetric experiments were carried out at 25 ±2°C using 0.1 M KCl as supporting electrolyte. Solution was degassed with nitrogen gas for 10 – 15 minutes prior to recording the voltammogram.

2.2Reagentsand materials
All reagents and materials of analytical reagent grade purity were used without further purification. All chemical operations and preparations of the electrolyte solutions were carried out using deionised reversed osmosis (RO) watermodel Elken (BIO PURE).A lead ion was prepared as a stock solution from lead (II) nitrate salts by diluting it with 0.1M potassium chloride (KCl) as supporting electrolyte. A stock solution of nicotinic acid was prepared fresh in deionised RO water. 0.5M acetate buffer was used, with adjustment to pH 4-6 by either an addition of acetic acid or NaOH. Unbuffered solution of pH < 4 was used with the addition of sulphuric acid.

3. Results and discussion
### 3.1 Electrochemical characterization

Figure 1 show that the presence of suitable ligand such as nicotinic acid which is able to cause a significant increase in the reduction peak current of Pb(II) during square wave voltammetry at the CGME. From the result it shows that the presence of 0.5mM of nicotinic acid caused a 1.5 fold increase in the peak height in the position of the reduction peak of 1×10^{-4}M Pb(II) in KCl.
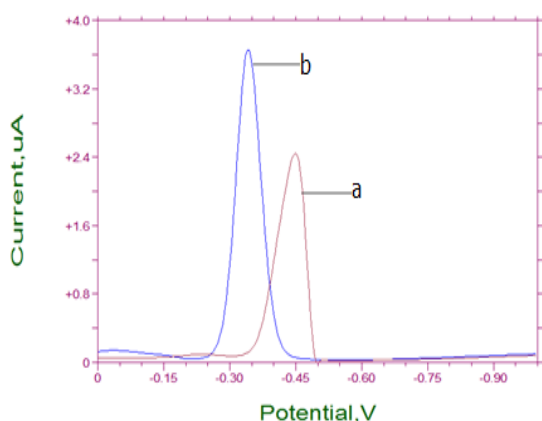
Figure 1: Square-wave voltammogram of 1.0×10^{-4}mMPb(II), 0.1M KCl, 0.5M sodium acetate buffer pH 4.0   (a) without nicotinic acid (b) with 0.5mM nicotinic acid; 4mV step potential, 15Hz frequency, using CGME as working electrode during SWV.

While, Figure 2 demonstrates the individual current component (forward and backward current) as well as differential normalised current obtained for 1.0×10^{-4}mMPb(II) with 0.5mM nicotinic acid. This current measurement is made during the forward-going pulse, and second measurement is made during the reverse pulse. The differential current is the forward current minus the reverse current [21]. The

forward current is that for reduction of Pb(II) to the amalgam, and the reverse current is that for the reoxidation of the product of amalgam to Pb(II). The difference current appears to as similar to that obtained in the SW mode.
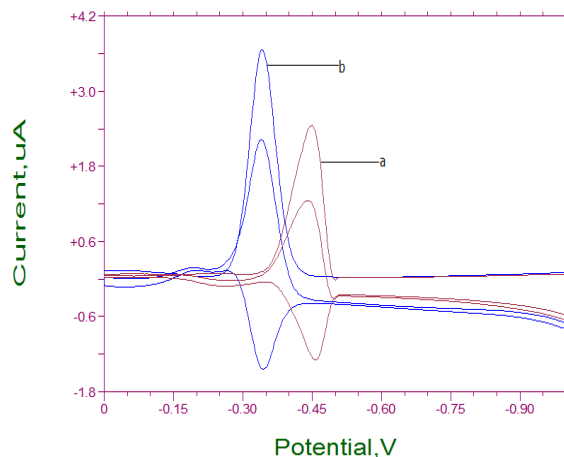
Figure 2 : Individual current component of figure 1; (a) without NA (b) with 0.5mM NA4mV step potential, 15Hz frequency, using CGME as working electrode during SWV.

3.2 Effect of varying pH

Figure 3 represents the effect of varying pH on the square wave voltammetric behaviors of 1×10^{-4}Pb(II) ion were studied at (DME) dropping mercury electrode in the presence of 0.5mM of nicotinic acid. There was no obvious increase in peak current of Pb(II)-NA complex below pH 3.5. However, as pH increased from 3.5 onwards, a rapid increase in peak current was observed until pH 4.0. From pH 4.0 onwards, the peak current decreased. The optimum pH range appears to be between pH 3.5 – 4.0. This indicates the enhancement effect which is pH dependent was greatly felt only under weakly acidic condition strongly shows that the presence of nicotinic anion is a precondition for the specific adsorption of Pb(II)-NA complex to take place. However, when pH is high (> pH 7.0), the solid compound become less soluble due to the precipitation process. Hence lesser amount of electroactive soluble species would form and this led a lower current response.
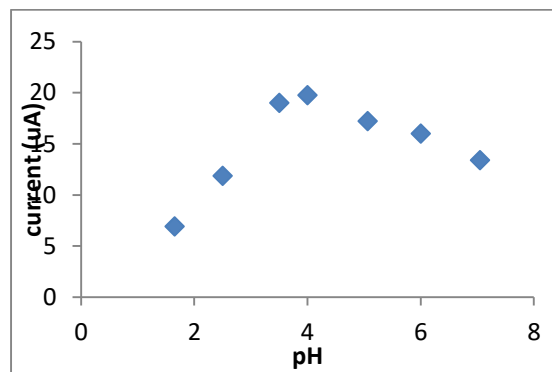

Figure 3 :Graph of current against pH for Pb(II) peak with 0.1M KCl, 0.05M sodium acetate buffer,1.0×10^{-4}M Pb(II), 0.5mM nicotinic acid, 4mV step potential, 15Hz frequency, using CGME as working electrode during SWV.

3.3 Scan rate study
In this study, scan rate was varied by varying frequency while maintaining potential step constant at 4 mV. Figure 4 shows, a plot of ln (i_p) vs ln (scan rate, υ) at constant experimental parameters except scan rate (varied by varying frequency at constant potential). According to Randles-Servic equation, where $I = k\ n^{2/3}\ FACD^{1/2}\ \upsilon^{1/2}$, the plot of ln i_p vs υ should be linear with a slope of 0.5 for a simple and reversible diffusion controlled process in solution, and 1.0 for adsorption controlled process, other thanthat it is probably a complicated surface process. Corresponding to this theory, the dependence of i_p on scan rate of Pb(II)-NA, simple system of Pb(II), i.e. the one without ligand were investigates by SWV. For a simple

system of pb(II) the power dependence of scan rate on i_p is 0.2 indicating surface process. While the experimental value of i_p for pb(II)-NA system depicting scan rate dependence by a power of 0.8 which is closer to one indicating complex surface process.
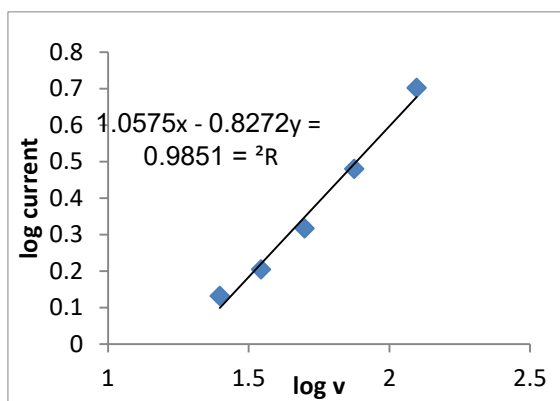

Figure 4:Graph of log I against log v of 1.0×10^{-4}M Pb(II) with 0.5mM nicotinic acid in 0.1M KCl using CGME as working electrode at pH 4.0 during SWV with scan rate (varied by varying frequency, 15 – 125Hz at constant potential, 4mV)

3.4 Chronocoulometry

Chronocoulometry (CC) is the integral analogs of the corresponding chronoamperometry approaches. The integral of the Cottrell equation gives the cumulative charge passed in reducing or oxidizing the diffused component .

$$Q=2nFAD1/2Co2\pi1/2t1/2 \qquad (1)$$

where Q = Charge and the other parameters have its usual meanings
The diffusion coefficient, D of Pb-NA complex species is estimated to be equal to 8.01×10^{-5} cm²/s, as compared with D of Pb(II) in KCl = 5.92×10^{-5}cm²/s. The slightly value of D of Pb(II)-NA can be explained by its bigger size of the compound which reduces mobility of the species and hence lower D value.
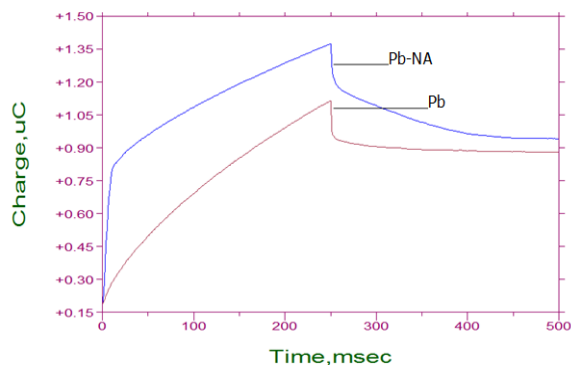
Figure 5: Chronocoulograms of 1.0×10^{-4}M Pb(II), 0.1M KCl, 0.5M sodium acetate buffer pH 4.0 (a) without nicotinic acid (b) with 0.5mM nicotinic acid.

3.5 Chronoamperometry

In Chronoamperometry (CA) the potential is stepped from an individual value Ei to Et and the accompany current is recorded as a function of time for an electrode in unstirred solution. The current decays as the electrolysis proceeds to deplete the solution near the electrode of electroinactive species. The current response is described by the Cottrell equation:

$$I = nFAC(D/\pi t)1/2 \qquad (2)$$

where   I = Current
n = Number of electron per molecule
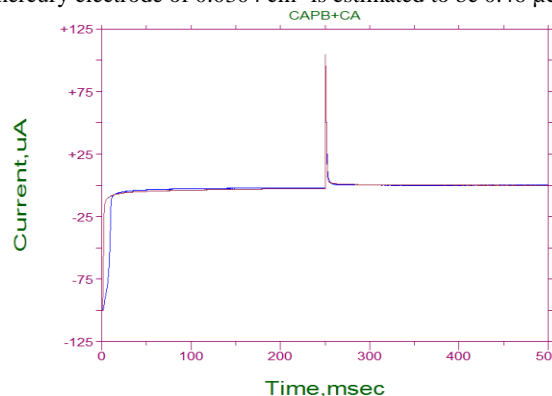F = Faraday constant
A = Electrode area
D = Diffusion coefficient of electroactive species
C = Concentration of electroactive species
T = Time

Surface charge coverage of 1.0×10^{-4}M Pb(II) – 0.5mM nicotinic acid at a mercury electrode of 0.0304 cm² is estimated to be 0.46 μc/cm².

Figure 6: Chronoamperograms of 1.0×10^{-4}M Pb(II), 0.1M KCl, 0.5M sodium acetate buffer pH 4.0 (a) without nicotinic acid (b) with 0.5mM nicotinic acid.

3.6 Varying of pulse amplitude

The optimum pulse amplitude, ΔE range for well defined and enhanced peak current for Pb(II) of SWV in the presence of nicotinic acid was between 10 – 150 mV (Table 1) . According to Barker and Gardner [23] the half-width ($W_{1/2}$) for 1, 2 and 3 electron transfer are 90.4, 45.2 and 30.1 mV respectively at 25°C for small amplitudes of the order of 5 or 10mV. Based on the it shows that the pb(II)-NA system produced differential waveforms having a $W_{1/2}$ of 45 – 54mV at ΔE between 10 – 25mV. Therefore, an electron transfer of 2 is indicated as this agreeing reasonably well with the theory for small ΔE ≤ 50mV, n=2. Furthermore, peak broadening became obvious at ΔE > 50mV, as $W_{1/2}$ increased with an increase in ΔE.

Table 1: Effect of pulse amplitude on half-peak width ($W_{1/2}$)

| Amplitude (mV)	ip (µA)	$W_{1/2}$ (mV)
10	1.029	45.9
15	1.477	50.4
25	2.388	54.4
50	4.515	72.8
100	8.407	114.1
150	11.89	150.8

3.7 Interference Studies

In order to evaluate possible interference of other species in the square wave voltammetry, determination of lead was studied by addition of the interfering ion to a solution containing 1.0mM of Pb(II) using the optimized conditions. Interferences may be caused by the competitive adsorption of ions on the mercury electrode forming a complex with nicotinic acid or producing a reduction current at potentials near that of Pb(II)-NA complex. The results of this study are summarized in Table 2 (Figure 7).

Table 2: Effect of interfering metal ion on the peak current and potential of Pb(II) during SWV. Conditions: 0.1 M KCl, 1mM Pb(II), using mercury as working electrode; freq. = 25^{s-1}, E$_{step}$= 4 mV

Interfering Metal(II) ion	SWV Parameters of Pb(II)				Percentage of current increment (%)
	Ip/µA (a)	Ip/µA (b)	Ep/mV (a)	Ep/mV (b)	
Cd	13.96	14.87	-360	-304	6.1
Zn	15.55	14.81	-336	-336	-5.0

(a) Absence and (b) of interfering metal ion (M(II))(1:10=[Pb(II) : [M(II)]).
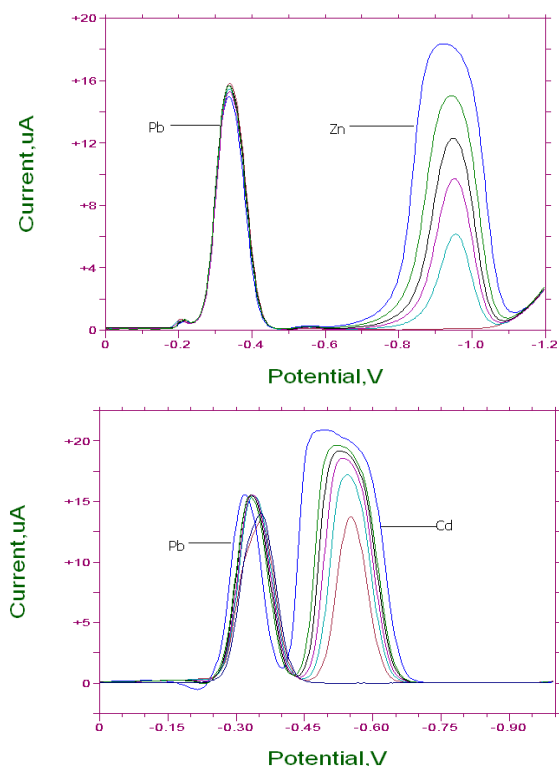
Figure 7 : Effect of varying amount of (a) Zn (b) Cd ion in the OSWV voltammograms of 1.0mM of Pb(II) ion with 0.01M nicotinic acid, 0.1M KCl at pH 4.0; scan rate:100mV/s

4. Conclusions

Various evidence obtained in these studies have pointed towards the enhancement of the reduction peak current of Pb(II) observed in the presence of excess amount of nicotinic acid at a mercury electrode during square wave voltammetry, CC and CA techniques. From the result presented it is clear that the feasibility of current enhancement of Pb(II) ion in the presence of selected ligand depends on a series of factors. Under proper conditions, an addition of ligand such as nicotinic current enhancement in the reduction current of Pb(II) by SWV was successfully investigated. Based on the scan rate and pH studies, the redox reaction of   Pb(II) ion in the presence of nicotinic acid observed is a complex surface process with optimum response at pH 4.

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