

A Mercury Free Dopamine Dithiocarbamate Modified Electrode For Pb (II) Determination by Anodic Stripping Voltammetry

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ABSTRACT

A mercury free dopamine dithiocarbamate (DDTC) modified electrode has been proposed for the anodic stripping voltammetric (ASV) determination of Pb (II). DDTC synthesized from dopamine and carbon disulfide. An ethanolic solution of this compound was drop casted on paraffin impregnated graphite electrode to prepare the modified electrode. This electrode was used for Pb (II) determination by ASV. Various parameters such as background electrolyte, pH and preconcentration time were optimized. Under optimized condition, the stripping method provided a linear range from 0.33 to 35 μM for the determination of Pb (II) by ASV. The proposed method is simple, sensitive and selective for the determination of Pb (II) by ASV.

Keywords: DDTC, ASV, pH, EDTA, MWCNT

I. INTRODUCTION

Heavy metals such as lead, arsenic, cadmium and mercury constitute global environmental hazards [1,2]. The environmental hazards of these heavy metals which pose a great threat to living organisms are due to their non- biodegradability and persistence [3, 4]. The concern about the toxic effects of heavy metals has led to an increasing demand to monitor trace metals in variety of matrices. This has resulted in the development of highly sensitive analytical methods for the determination of trace amounts of toxic heavy metals. Among the heavy metals, Pb (II) has been considered as a highly toxic metal as it has the tendency to accumulate in organism even in low concentrations [5, 6]. Pb (II) poisoning occurs due to the consumption of Pb (II) contaminated food or water, and in some cases accidental ingestion of contaminated soil, dust or air and Pb (II) based paints also led to lead poisoning [7]. Further Pb (II) is considered as the most toxic as it exhibits neurotoxicity and results in serious brain disorder [8]. Thus, the determination of Pb (II) at trace level has assumed greater significance.

Numerous analytical methods have been proposed for the determination of Pb (II). They include Uv-Visible spectroscopy [9], atomic absorption spectroscopy [10],

atomic fluorescence spectroscopy [11], flame atomic absorption spectroscopy [12], flow injection analysis [13], inductively coupled plasma – mass spectrometry [14], and solid phase extraction [15]. These methods were highly sensitive for trace level determination of Pb (II). Nevertheless, they are less attractive because of the requirement of expensive instruments, tedious sample preparation, lengthy operational procedures and unsuitability for online monitoring [16].

Electroanalytical techniques have been considered as powerful tools for the determination of metal ions in water samples and in wide variety of organic pollutants [17]. Anodic stripping voltammetry (ASV) is one of the versatile analytical technique which has been extensively used for the determination of metal ions [18]. ASV allows the quantification of metal ions in the concentration range from $\mu\text{g/L}$ to ng/L . The sensitivity in stripping method is achieved due to a preconcentration step in which the metal ions are deposited either as reduced metal (with mercury as amalgam) or accumulated as a complex on the working electrode surface [19].

The determination of metal ions by ASV has been mostly carried out using mercury based working electrodes, because they exhibited wide potential

window [20]. However, the toxicity associated with mercury and the difficulties related to the storage and handlings of mercury have discouraged the researchers to opt for non - mercury based electrodes for ASV [21, 22]. Researchers have attempted to develop mercury free electrodes for the determination of heavy metals. Among the various electrodes, bismuth film modified electrodes have been extensively used as mercury free electrodes for stripping analysis [23, 24, 25, 26].

Other electrodes in this category to be mentioned are antimony film based electrodes [27, 28, 29], copper electrode [30], tellurium based electrode [31], conducting polymer electrode [32], peptide modified electrode [33] and crown ether modified electrode [34]. Eventhough these electrodes have been used as mercury free electrodes for stripping analysis, they also have certain disadvantages and hence, even today electrodes that can potentially replace mercury based electrodes for stripping analysis are being sought. In our laboratory, we are working on the development of CMEs in lieu of mercury based electrodes for the determination of heavy metal ions by ASV. Recently we have reported a poly zincon film modified electrode as a mercury free electrode for anodic stripping voltammetric determination of Pb (II) ions [35].

CMEs have also been developed in our laboratory as amperometric sensors for the determination of substrates of pharmaceutically, biologically and environmentally important compounds. Recently we have reported the determination of hydrazine using MWCNT/dopamine dithiocarbamate (DDTC) modified electrode [36]. It is well known that dithiocarbamates are very good ligands for preparation of large number of metal complexes of dithiocarbamates [37]. Therefore an attempt has been made to use the DDTC modified electrode as a mercury free electrode for the determination of Pb by ASV. In this method, the DDTC ligand present on the electrode surface preconcentrates the metal ion through complexation which will be reduced subsequently for stripping analysis. It was found that this DDTC modified electrode exhibited good sensitivity and selectivity for the determination of Pb (II).

II. EXPERIMENTAL METHOD

A. Reagent

Graphite rods of 3mm diameter and dopamine hydrochloride were purchased from Aldrich, Germany. Lead acetate, EDTA, KNO_3 , NaNO_3 , NH_4NO_3 were of AR grade and used as received. Phosphate and acetate buffers were prepared as reported [38]. Doubly distilled water was used for preparing aqueous solutions.

B. Instruments:

ASV was performed with 660B electrochemical work station (CH- Instruments CHI). The cell set up was a three electrode system in which Pt electrode was used as counter electrode SCE electrode as the reference electrode and DDTC modified electrode as the working electrode. The pHs of the solutions were checked with digital pH meter (DIGISUN electronic system). All experiments have been carried out a room temperature.

C. Preparation of DDTC modified electrode:

DDTC was synthesized by following the reported method with a slight modification [39]. The DDTC modified electrode was prepared using paraffin impregnated graphite electrode (PIGE) which was prepared as reported [40]. One end of the electrode was carefully polished first with emery paper then with $0.05\mu\text{m}$ alumina slurry, washed with distilled water and dried in air. DDTC in ethanol ($10\mu\text{L}$) was drop casted on the PIGE electrode and dried at room temperature.

D. Stripping procedure:

The DDTC modified electrode was kept in 0.1M acetate buffer (pH 6) containing Pb (II) ions for a period of 4 mins under stirring condition. This procedure helps in preconcentrating the metal ions on the electrode surface through complexation. The electrode was taken out washed thoroughly with distilled water and kept in a fresh acetate buffer solution of pH 6. Then a potential of -1.0V was applied to the electrode for 60 secs. This step reduces the Pb (II) present in the complex to metallic state. Finally the stripping was carried out anodically by scanning with differential pulse from -1.0V to -0.3V and the anodic current was measured. The modified

electrode was cleaned by immersing in 0.1M EDTA in hexamine buffer and washed thoroughly with distilled water for subsequent use.

III. RESULTS AND DISCUSSION

A. ASV study of Pb (II) using DDTC modified electrode:

The DPASV was employed for the determination of Pb (II) with both PIGE and DDTC modified electrode by following the stripping procedure described in the above section. Fig 1 shows the DPASV response of the PIGE (a) and DDTC modified electrode (b) in 0.1 M acetate buffer of pH 6 containing 2.9 μM of Pb (II). The DDTC modified electrode showed a higher anodic current than the PIGE electrode as Pb (II) was preconcentrated on the modified electrode through complexation. The PIGE electrode showed an anodic peak at -0.55 V and the modified electrode showed the anodic peak at -0.57 V for Pb (II). The stripping current for Pb (II) with DDTC modified electrode was higher than the PIGE electrode. Thus the DDTC modified electrode showed nearly 10 fold higher stripping current than the PIGE electrode for Pb (II) ions. The enhancement in the stripping current was due to the preconcentration of Pb (II) ions through complexation with DDTC present on the electrode surface. Only a smaller current was observed for the PIGE electrode as only absorbed Pb (II) was present on the electrode surface for stripping analysis. The higher peak current observed with the DDTC modified electrode indicated that this electrode could be used for trace level determination of Pb (II) ions.

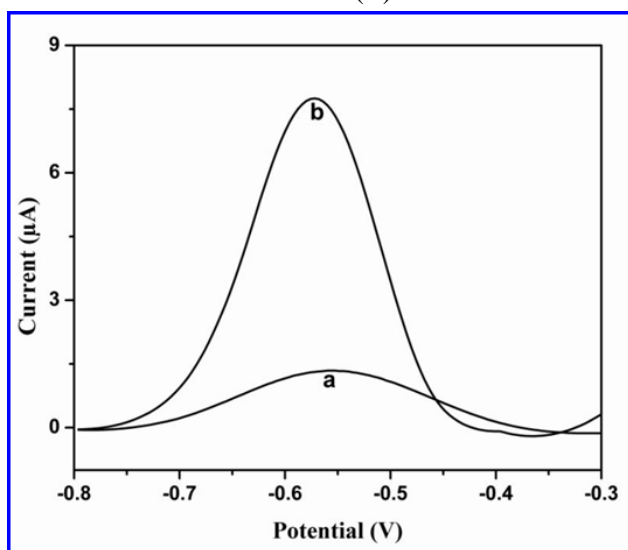
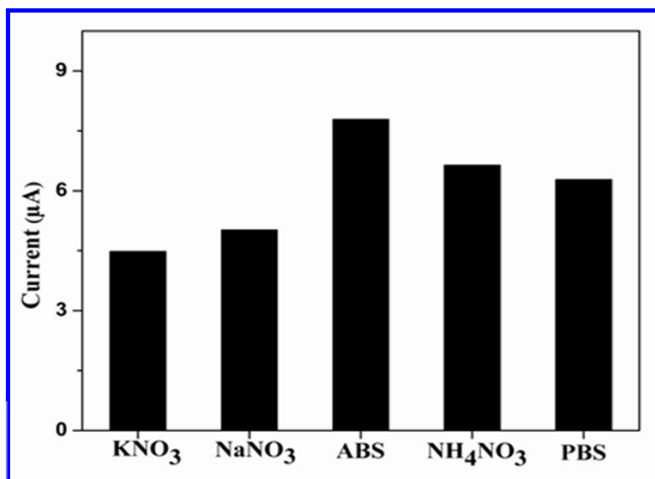


Figure 1. DPASV of (a) PIGE electrode and (b) DDTC modified electrode for 2.9 μM of Pb (II) at a scan rate of 50 mVs^{-1} in Acetate buffer (pH 6) as background electrolyte, Pulse amplitude: 0.1 V; Pulse width: 0.5s.

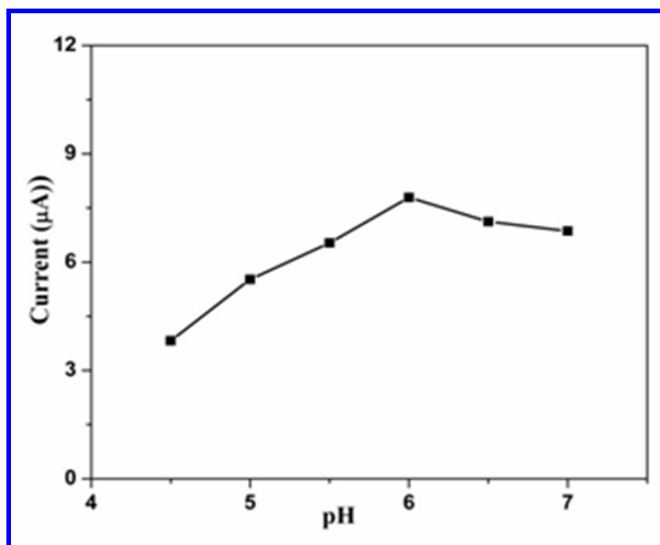
B. Optimization of Parameters

The experimental conditions such as nature of electrolytes, pH of the medium, preconcentration time were optimized to obtain maximum sensitivity for the determination of Pb (II) by ASV. The results obtained in the above study are presented below. The nature of electrolyte may alter the complexation of Pb (II) with DDTC. Hence the preconcentration of Pb (II) with the modified electrode was carried out with different electrolyte of same concentration such as KNO_3 , NaNO_3 , NH_4NO_3 , acetate buffer and phosphate buffer (PBS). The anodic stripping currents obtained in the above study for the different electrolyte are shown in fig 2 (i) as bar diagram. It is clear from the figure that the acetate buffer solution (ABS) was the most suitable medium for preconcentration of Pb (II) on the modified electrode. Therefore ABS was chosen for the preconcentration of Pb (II) on the modified electrode. In addition to the nature of electrolyte, the pH of the medium plays an important role in complex formation and hence the effect of pH on the preconcentration was also studied. The pH of the acetate buffer was varied from pH 4.5 to 7 for preconcentration of Pb (II) and the stripping currents in the above are shown in figure 2 (ii). It is clearly seen from the figure that the maximum stripping current was observed at pH 6 and hence acetate buffer (0.1 M) of pH 6 was chosen for the stripping analysis of Pb (II). The effect of preconcentration time was also studied by varying the time from 1-5 min for preconcentration and stripping of Pb (II) was carried out. The results obtained are shown in fig 2 (iii). It is seen from the figure that the stripping current increased with increase in time upto 3 min beyond which it remained constant. This indicated that 3 min stirring was sufficient for maximum complex formation. A time of 4 min was chosen as the optimum time for the preconcentration of Pb (II) on the DDTC modified electrode. A reduction time of 60 sec was chosen for the reduction of Pb (II) ions present on the modified electrode for carrying out stripping analysis. The DDTC modified electrode was regenerated after each stripping experiment by immersing the modified electrode in a stirred solution of 0.1M EDTA in

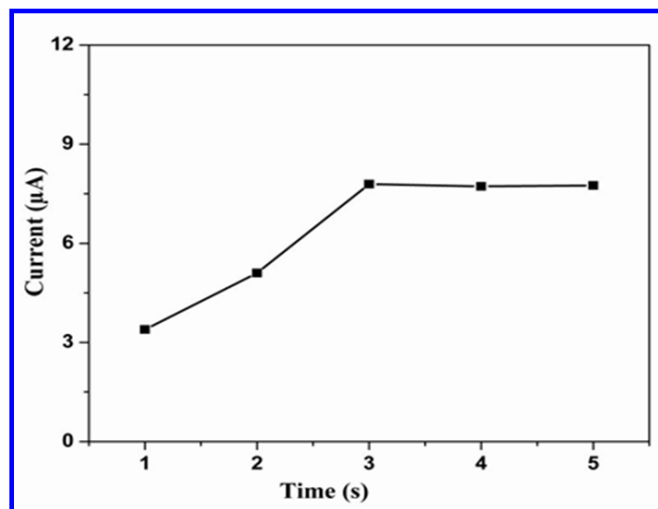
hexamine medium which removed all the Pb (II) from the electrode surface through water soluble Pb (II)-EDTA complex formation. The modified electrode was then washed with distilled water to remove all the absorbed Pb-EDTA complex to regenerate the electrode and this method did not affect the stability of the DDTC present on the electrode surface. Using the optimized parameters differential pulse anodic stripping voltammetry of Pb (II) was carried out as detailed below.



(i)



(ii)



(iii)

Figure 2. DPASV of Pb (II) with DDTC modified electrode

(i). In different electrolytes (0.1 M).

(ii). Effect of pH for pre-concentration of Pb (II) .

(iii). Effect of pre-concentration time for Pb (II) determination.

Concentration: $2.9 \mu\text{gL}^{-1}$ Pb (II) ions, Scan rate of 50mVs^{-1} , Pulse amplitude: 0.1V ; Pulse width: 0.5 s.

C. Determination of Pb (II) by ASV using DDTC modified electrode.

Different aliquots of Pb (II) were pre-concentrated on the DDTC modified electrode for 4 mins. Then the electrode was washed thoroughly to remove the absorbed / uncomplexed Pb (II) from the electrode surface. The electrode was then placed in a fresh 0.1 M acetate buffer of pH 6 and a potential of -1.0 V was applied for 60 sec. The step has converted all the Pb (II) present on the electrode surface as Pb (0). Stripping of the reduced metal was carried out by DPASV in the potential range from -1.0 to -0.3 V. The anodic stripping peak currents for different concentration of Pb (II) ions were measured around -0.57 V where the anodic peaks appeared for Pb oxidation. The DPASV of different concentrations (lower side) of Pb (II) are shown in Fig 5. From the figure it is seen that the stripping current increased with increase in the concentration of Pb (II). A calibration plot was drawn for the concentrations of Pb (II) taken against the anodic stripping peak currents and the plot is shown in figure.6. It is seen from the plot that there was a linear increase in the stripping current as the concentration of Pb (II) was increased. A linear range from $0.33 \mu\text{M}$ to $35 \mu\text{M}$ for Pb (II) determination was observed with a correlation coefficient of 0.998. A

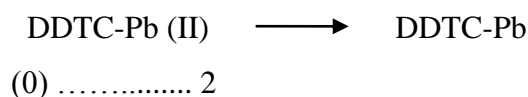
negative deviation at higher concentration of Pb (II) was observed which may be due to the saturation of the electrode with the metal ion. The proposed electrode showed good linear range, higher sensitivity, good reproducibility and a reasonable LOD for Pb (II) determination by ASV.

The mechanism of the Pb (II) determination involves the following steps.

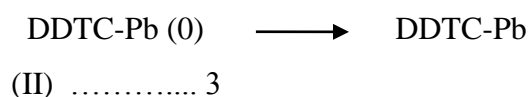
1. Preconcentration through complexation in 0.1M acetate buffer (pH 6) - 5minutes



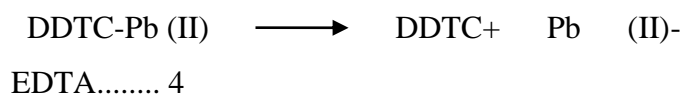
2. Reduction in 0.1M Acetate buffer (pH 6) at -1.0 V for 60seconds



3. Stripping in the potential range -1.0 to -0.3 V in 0.1 M Acetate buffer (pH 6).



4. Regeneration of electrode surface by dipping in 0.1 M EDTA in Hexamine medium



Experiments with 5 aliquots of the same concentration of Pb (II) ions showed an RSD of 2.4 % indicating good repeatability of the proposed method.

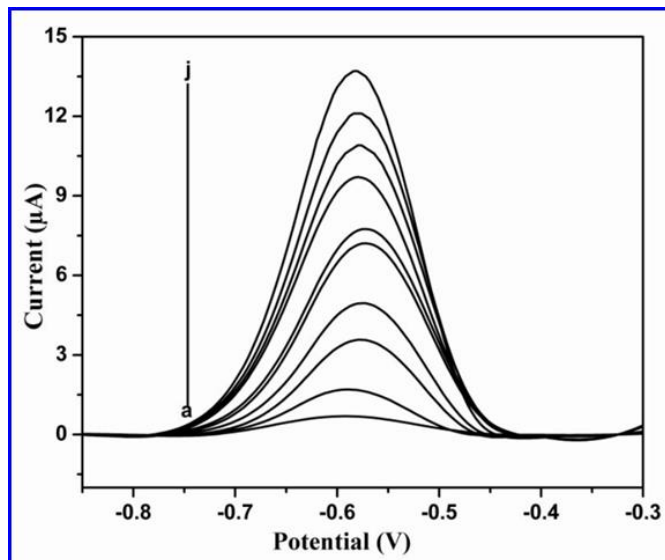


Figure 3. DPASV responses of different concentration of Pb (II) from 0.33- 35µM with DDTC modified electrode.

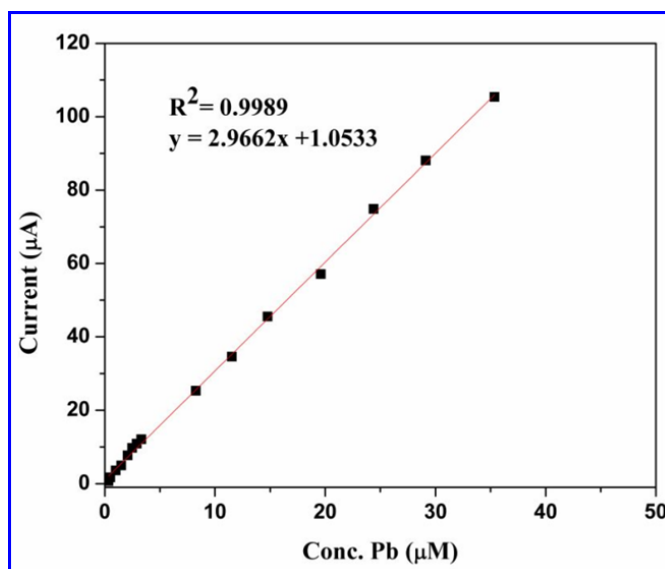


Figure 4. Calibration graph for the determination of Pb (II) in the concentrations range from 0.33- 35µM with DDTC modified electrode

D. Interference studies

The DDTC modified electrode was examined for the possible interference from other ions in the determination of Pb (II) ions. Studies with Cd (II), Zn (II), Hg (II) showed no interference as the stripping potentials of these metal ions were different from that of Pb (II). Some common cations such as Ca (II), Mg (II), Na (I) and K (I) did not interfere in the determination. Cu (II) ion reduced the current of Pb (II) by 50 % when

present up to 10 folds and higher concentration of Cu caused complete decrease in anodic current of Pb indicating that Cu will interfere in the determination of Pb if present more than 10 folds. This may be due to the competition between Cu and Pb for complex formation with DDTC and also may be due to bimetallic complex formation.

IV. CONCLUSION

A mercury free DDTC modified electrode was fabricated and used for the anodic stripping voltammetric determination of Pb (II). Various parameters such as background electrolyte, pH and preconcentration time were optimized for the sensitive determination of Pb (II) ions. The linear range of determination was from 0.33 to 35 μM with a correlation coefficient of 0.998. The modified electrode can be easily regenerated for subsequent use. The modified electrode showed good stability, high sensitivity and good repeatability.

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