

Short Communication

Determination of Lead (Pb^{2+}) by Anodic Stripping Voltammetry Based on $[\text{Ru}(\text{NH}_3)_6]^{3+}$ /Nafion Modified Electrodes

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Abstract: Chemically modified $[\text{Ru}(\text{NH}_3)_6]^{3+}$ doped Nafion[®] thin film was fabricated on indium tin oxide (ITO) coated glass electrodes by using the drop-coating method to detect heavy metal ions of Pb(II) in de-ionized water analyte solution via anodic stripping voltammetry (ASV). This study also determined the effect of varying the concentration of the mediator ($[\text{Ru}(\text{NH}_3)_6]^{3+}$) on the detection of the said heavy metals. The redox mediator $[\text{Ru}(\text{NH}_3)_6]^{3+}$ used in the study was effectively incorporated and immobilized within the Nafion modified electrodes. Lead concentration in the electrolyte solution and the concentration of the redox mediator was varied to control the properties of the fabricated electrodes which utilized for heavy metal detection through ASV. The conducting properties of ITO electrodes were enhanced with the deposition of Nafion[®] attaining minimal interference. The stripping current peaks increased with the concentration of the heavy metal present in the solution as well as with the mediator concentration.

Keywords: Nafion, Drop Coating, Anodic Stripping Voltammetry, Heavy Metal, Electrochemistry

1. INTRODUCTION

Trace elements of heavy metals (HMs) are beneficial important at very low concentrations, but are toxic at high concentrations [1,2]. Lead is among the most widely distributed, naturally occurring, and potentially toxic elements. It has a very long half-life and mostly accumulates in the bones and the kidneys[3]. It is listed in the United States Environmental Protection Agency as one of the primary contaminants of drinking water. With increasing industrial use, environmental pollution and associated toxic exposure, concern has increased about the huge disturbances it causes in the ecological balance in nature [4]. In recent years, various heavy metal pollution incidents, such as the pollution of lead, cadmium, chromium, and so on, result in serious ecological risk and human health. The major sources of heavy metal contamination include industry[5], traffic[6], domestic waste[7]. These sources of heavy metals pollute the soil, water and the atmosphere. Thus, it is imperative to detect heavy metals existing in complex substances in the environment [8].

In previous studies, mercury has been used as a working electrode precursor because of its high reproducibility and sensitivity to anodic stripping voltammetry[9,10]. However, it is toxic and

has limited anodic potential[11]. As an alternative to the mercury electrodes, this study aimed to use chemically modified electrodes, which are conducting that have their surfaces enhanced. This was to modify the electrochemical characteristics of the exposed surface. Coating the electrode surface with a thin film using a polymer such as Nafion[®] is one of the many common methods used in modifying electrodes [12].

2. MATERIALS AND METHODOLOGY

Materials and Setup

5% w/v Nafion solution was obtained from Fuel Cell Earth (Wakefield, Massachusetts, United States). Hexaammineruthenium(III) Chloride (98%) and ITO-coated rectangular glass slides with surface resistivity $15\text{-}25 \Omega \text{ sq.}^{-1}$, PbCl_2 powder was obtained from Aldrich (St Louis, Missouri, United States). All other chemicals and reagents used in the research were reagent grade quality. For the anodic stripping voltammetry, a standard three-electrode setup was used with platinum coil as counter electrode, Calomel as the reference electrode, and the fabricated electrodes as the working electrode.

2.1. Modification of Nafion[®] Electrodes

2.1.1. Preparation of substrates and coating solution

All glasswares and other equipment were placed in the BANDE-

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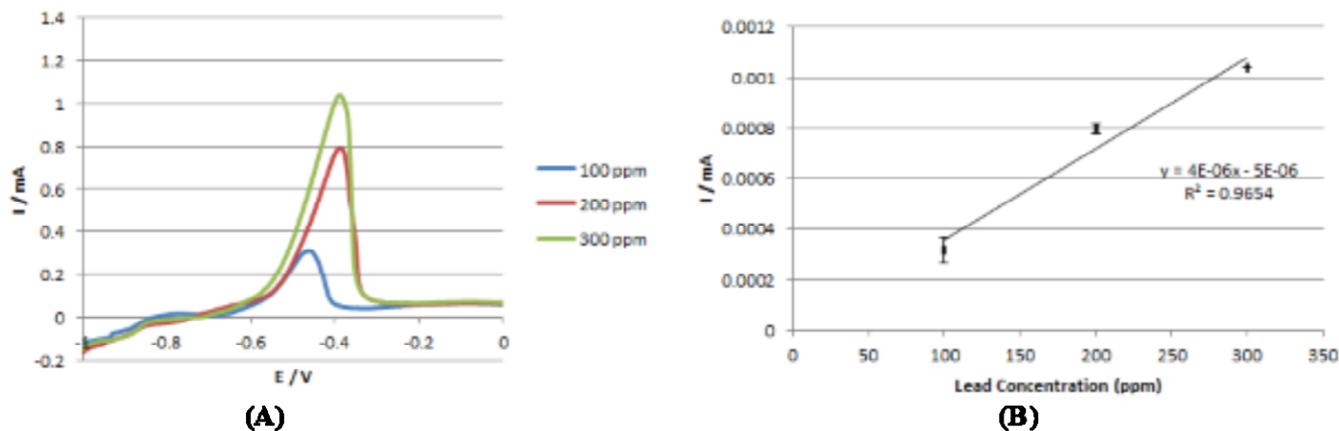


Figure 1. Voltammogram and (B) calibration curve for Lead concentration with 5mg $\text{Ru}(\text{NH}_3)_6]^{3+}$ electrodes

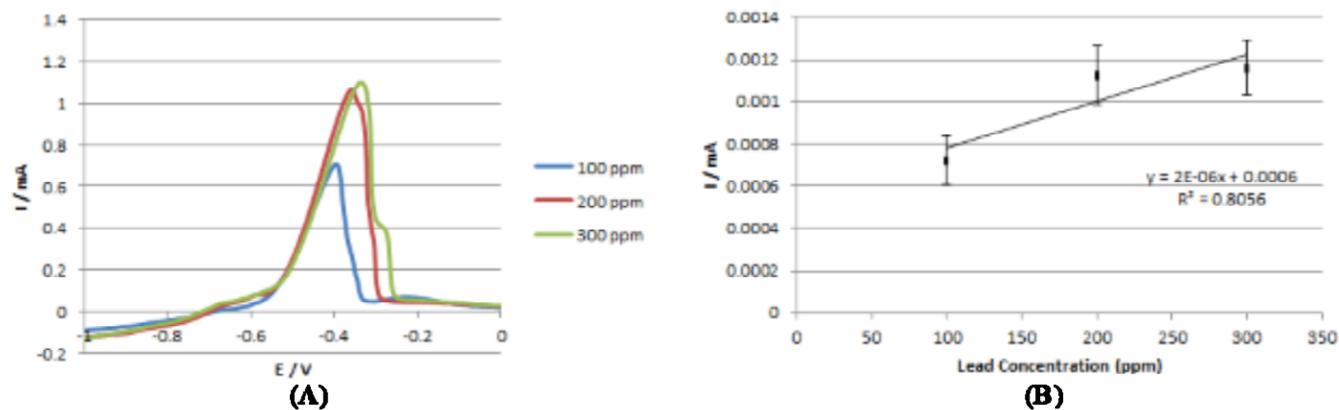


Figure 2. (A) Voltammogram and (B) calibration curve for Lead concentration with 10mg $\text{Ru}(\text{NH}_3)_6]^{3+}$ electrodes

LIN SONOREX ultrasonic bath for about 5 minutes to clean the materials from all unnecessary particulates that may affect the data. Using a diamond tip glass cutter, ITO coated glass substrates were cut with dimensions 2.5 cm x 1.0 cm.

The amounts of mediator to be dissolved were varied at 5mg, 10mg, and 15mg and were measured using the BOSCH SAE200 electronic balance. Solutions of 5% Nafion[®] with the said respective concentrations of hexammineruthenium chloride $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ were then prepared. 6 mL of deionized water was then used to dilute the Ruthenium compound. 20 μL of each were mixed with 20 μL of 5 wt% Nafion[®]. All these were measured through a Transferpette[®]S micropipette. Each of the prepared solutions were diluted with 1.0 mL methanol.

2.1.2. Fabrication

In this step, a Transferpette[®]S micropipette was used to drop coat the ITO coated substrates with the respective concentrations of the prepared casting solution for the fabrication of Nafion[®] electrodes. The coated substrates were air dried at and ambient temperature $26^\circ\text{C} \pm 1^\circ\text{C}$ for 24 hours.

2.2. Anodic Stripping Voltammetry (ASV)

The heavy metal concentration varied at 100ppm, 200ppm, and 300ppm to obtain the calibration curves. A fresh electrode was used for every set of runs. During the stripping voltammetry procedure, the solution was stirred continuously by a metal stirrer applying a potential of -1.40 V for 2 minutes. After the pre-concentration set-up, voltammograms were acquired through a potential range of -1.4 and $+0.2\text{V}$. These showed the presence of metal ions through the characteristic stripping current peak responding to the heavy metal's redox potential. After every measurement, the modified electrodes were stripped of impurities by sustaining the potential at $+0.30\text{V}$ for 30 seconds.

3. RESULTS AND DISCUSSION

As shown in Fig 1 to 3, the peak stripping current of Pb^{2+} increased linearly as the heavy metal concentration was increased from 100 ppm to 300 ppm. The linearity of the calibration curves obtained yielded correlation values(r) close to 1. Results were obtained from getting the averages of three trials on each electrodes. The electrode utilized was fabricated using the 5mg $\text{Ru}(\text{NH}_3)_6]^{3+}$ mediator casting solution. Stripping peaks were obtained at the potentials -0.45 V to -0.34 V signifying that the heavy metal detect-

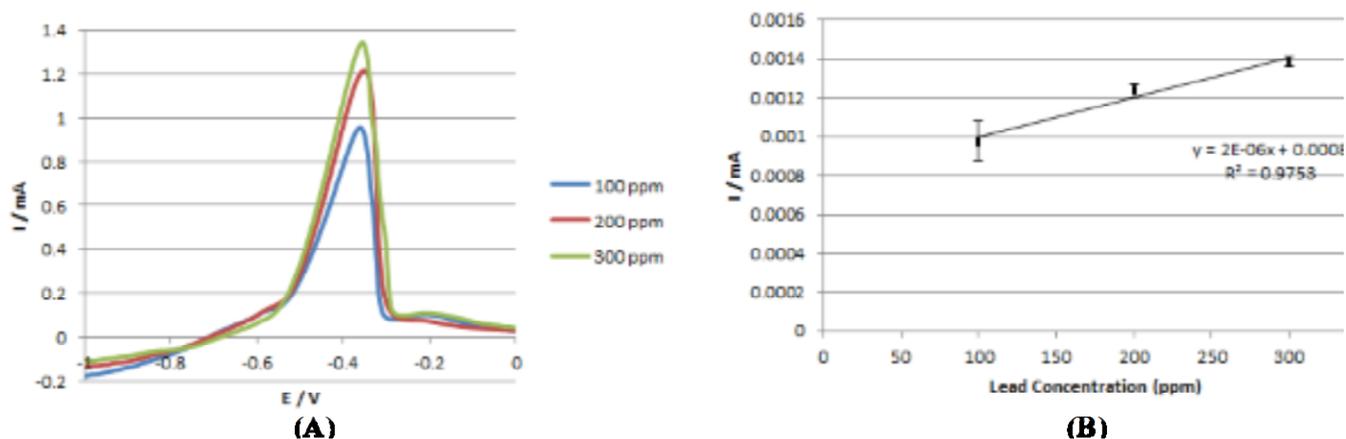


Figure 3. (A) Voltammogram and (B) calibration curve for Lead concentration with 15mg $Ru(NH_3)_6^{3+}$ electrodes

ed was lead (Pb^{2+}).

From the calibration curves, the lead (Pb^{2+}) concentrations ($[Pb^{2+}]$) at which the resulting peak currents are zero are 1.25ppm, -300ppm, and -400ppm, for the three electrodes respectively. This means that the given values are the minimum concentrations at which the electrode will not have any peak current. However, these concentrations can be accounted for by the noise from the empirical data. This implies that the signal from samples containing no Pb^{2+} ions would not be zero (attributed to noise in the order of 10^{-9} to 10^{-7} Ampere) as given in the calibration curve. Thus, when $[Pb^{2+}] = 0$, the resulting peak currents are $I_1 = -5 \times 10^{-6}$, $I_2 = 6 \times 10^{-4}$, and $I_3 = 8 \times 10^{-4}$.

From these graphs, pertinent information can be derived such as the sensitivity of the sensor which is defined as the instrument's ability to distinguish minute variances in concentration and respond to small changes in analyte concentration. Calibration sensitivity is defined to be equal to the slope of the calibration curve and among the three sets of electrodes, the 5mg $Ru[(NH_6)]^{3+}$ electrodes' yielded the steepest calibration curve. The larger slope for the calibration curve implies a larger change in signal per unit change in analyte concentration, thus higher sensitivity.

Analytical sensitivity (γ), on the other hand can be computed for each concentration to incorporate precision in the sensitivity definition and compare the sensors with equal calibration curve slopes. That is,

$$\gamma = m / \text{stdev}(I)$$

where m is the slope of the calibration curve and $\text{stdev}(I)$ is the corresponding standard deviation of the current measurement for each concentration.[13] Summarized in the table below are the analytical sensitivity of each measurement from each set of electrode.

4. CONCLUSION

This study was able to fabricate chemically modified electrodes and detect Lead ions in deionized water solution using anodic stripping voltammetry. The drop coating method was used to successfully produce redox-active thin films of Nafion. The redox mediator $Ru(NH_3)_6^{3+}$ used in the study was effectively incorporated within the Nafion modified electrodes. As seen from the results, parameters such as the Lead concentration in the analyte solution and the concentration of the redox mediator was varied to control the properties of the fabricated electrodes to undergo heavy metal detection through ASV. The stripping current peaks increased with the concentration of the lead ions present in the solution as well as with the concentration of the mediator, $[Ru(NH_3)_6]^{3+}$. The calibration curves provided can be used as basis for determining Lead concentration in contaminated water with unknown contamination levels. It was seen that the 5mg $Ru[(NH_6)]^{3+}$ electrode yielded the highest calibration sensitivity and analytical sensitivity suggesting that the first electrode is the most sensitive among the three that were fabricated.

5. ACKNOWLEDGEMENT

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Table 1. Analytical Sensitivity values for each concentration of Pb^{2+} computed for the three electrodes

Electrode	Analytical Sensitivity (γ)		
	100ppm	200ppm	300ppm
5mg $Ru[(NH_6)]^{3+}$	0.04330	0.12372	*
10mg $Ru[(NH_6)]^{3+}$	0.00996	0.00840	0.00888
15mg $Ru[(NH_6)]^{3+}$	0.01138	0.03381	0.04142

*peak current values that were averaged were equal

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