

Spin Coated Hexaammineruthenium(III)/Nafion/ITO electrodes for the Determination of Lead(II) and Cadmium(II) via Anodic Stripping Voltammetry

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Received: December 15, 2016, Accepted: May 03, 2017, Available online: May 30, 2017

Abstract: Hexaammineruthenium (III) $[Ru(NH_3)_6]^{3+}$ -Nafion®-isopropanol diluted films were spin coated on indium tin oxide (ITO)-coated glass substrates. The fabricated samples were used to determine the presence of lead and cadmium in solution using anodic stripping voltammetry (ASV). The calibration sensitivity of the electrodes for lead and cadmium were approximately equal. Detection limits of 5ppb and 4ppb were determined for lead and cadmium respectively. Real sampling tests with commercially available yellow water color yielded 0.7106 ppm of Pb with ASV. The result was verified with atomic absorption spectrometry (AAS) which yielded 0.6923ppm of Pb.

Keywords: Nafion, Stripping Voltammetry, Spin Coat, Modified Electrode, RuHex

1. INTRODUCTION

Environmental pollution has a detrimental effect on the quality of life and ecosystems of countries with established and rapidly growing industries [1-2]. Some of the pollutants are heavy metals, which though, low in concentration, are highly toxic, of high stability, and accumulate in living organisms through food chains [3-5]. In particular, lead and cadmium are well-known severely hazardous metals to humans [4, 6-8].

In calcium-dependent proteins, lead occupies the binding sites for calcium which results in the impairment of physiological functions [9]. Excessive exposure to lead can bring health problems such as nausea, renal failure, cancer, and negative effects on metabolism and intelligence [10]. Heavy metals have been used as pigments in paints [11-12]. Over time, these paints degrade and chip off and become health hazards as unsuspecting people may inhale or touch them [13]. The World Health Organization has set a guideline value of 10µg/L for lead and 3µg/L for cadmium [14-15].

The World Health Organization [16], set the limit of detection (LOD) for the determination of lead in blood for the following instruments: 10µg/L for AAS, 1µg/L for anodic stripping voltam-

metry (an electrochemical technique), and 0.01µg/L for ICP-MS. Research on electrochemical techniques have surged in recent years because of their promising high sensitivity, portability, low cost, ease of operation, selectivity, and lower limit of detection [6, 9]. Other methods on the other hand, are expensive, large, and complicated [4-5, 9].

Among the electrochemical techniques, stripping voltammetric analysis is a powerful method for metal ion detection as it owes its high sensitivity to the preconcentration step that is built in the process [1, 4, 7, 9, 17-18]. Electrodes are modified with Nafion® which is a perfluorosulfonated cation exchange polymer with anti-fouling capabilities, chemical inertness, and high permeability to cations [19]. Nafion, however, being an ionomer, does not conduct electrons. To abet this problem, mediators are introduced to facilitate electron transport between the solution and the electrode surface. Hexaammineruthenium(III) $[Ru(NH_3)_6]^{3+}$ or RuHex is a well-known cation model [20], which has uncomplicated chemistry [21], and displays fast electron transfer [22]. It is used for the determination of better sensors through the improvement of electrode kinetics of bare and modified carbon nanotube electrode biosensors [23, 24].

Traditional electrode materials such as gold, platinum, palladium, and glassy carbon are relatively expensive. They can be substituted with indium tin oxide (ITO) electrodes [25, 29, 31], the

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electrochemical abilities of which, when used as electrode substrates, are lower compared to other materials but can be compensated by electrode modification [32]. For this reason, ITO has been used as electrodes in many applications [25, 26-39].

Spin coating is a technique widely utilized to fabricate uniform thin solid films on flat surfaces (40-41). The advantages of spin coating over other methods like dip coating and Langmuir-Blodgett are better uniformity, better reproducibility, shorter fabrication time, simplicity, higher packing density, and higher surface coverage for the possibility of using larger samples [41-44]. In a previous study, RuHex incorporated Nafion films on ITO were fabricated via spin coating and characterized using scanning electron microscopy and cyclic voltammetry [45]. Still, in other previous studies, RuHex-Nafion modified electrodes were fabricated via drop coating and used to determine the presence of lead, cadmium and zinc in solution [46-48]. In this study, spin coated RuHex incorporated Nafion films on ITO substrates were used as modified working electrodes for the determination of lead and cadmium in solution and in commercially available water color paint using anodic stripping voltammetry.

2. METHODOLOGY

2.1. Preparation of Substrates

Indium tin oxide (ITO)-coated glass substrates of surface resistivity of 15-25 Ω/sq were obtained by cutting ITO-coated glass slides (Sigma-Aldrich Pte. Ltd., Singapore) into 2.5cm x 1.0cm segments using a diamond tip glass cutter. The cut was performed on the non-conducting side of the ITO-coated glass slide.

The substrates were then rinsed under running tap water to remove glass fragments and placed in a petri-dish. The petri-dish was filled with enough deionized water, acetone, and isopropyl alcohol of GR grade (Duksan Pure Chemicals Co., Ltd., Seonggok-dong, Ansan-si, Gyeonggi-do, South Korea) to immerse the substrates. The dish was then set afloat on a Bandelin Sonorex RK-100 ultrasonic bath (Bandelin Electronic GmbH & Co. KG, Heinrichstraße, Berlin, Germany) and sonicated for 5 minutes each to remove surface contaminants. They were air dried before spin coating.

2.3. Preparation of Casting Solution

The casting solutions to be used for spin coating were prepared by first adding 24mL of 5wt% Nafion solution (Fuel Cell Earth, Woburn, MA, USA) with 6mL of isopropyl alcohol to obtain a 4wt% Nafion-Isopropanol solution. Fifty milligrams (50mg) of Hexaammineruthenium (III) chloride, $(\text{Ru}(\text{NH}_3)_6)\text{Cl}_3$, or RuHex (Duksan Pure Chemicals Co., Ltd., Seonggok-dong, Ansan-si, Gyeonggi-do, South Korea) was added to the mixture. The mixture was then partially immersed in an ultrasonic bath and sonicated for 5 min, 6 times with swirling and cooling intervals in between to aid dissolution and to prevent evaporation, respectively.

2.4. Fabrication of Modified Electrodes

A Spin Coat G3P-8 (Specialty Coating Systems, Indianapolis, USA) was used to spin coat the mixture on the surface of the substrates. The mixture was placed in the spin coater canister, sealed, and pressurized to 10psi with compressed air. The substrates were then loaded onto the spin coater chuck. A vacuum pump was used to hold the substrate in place during spin coating.

A dynamic dispense spin-coating process was used. It is com-

posed of two stages: a deposition stage where substrate is initially spun at a low rate and where the casting solution is deposited on the substrate and a thinning stage where the substrate is spun at a higher rate to obtain films of different thicknesses. Dynamic dispense was preferred over a static dispense because it requires less casting solution as centrifugal force from the initial rotation of the deposition stage assists the solution to spread throughout the surface [45].

The substrates were initially spun to 750rpm for 10s where the casting solution was sprayed onto the substrate. The substrates were then spun to 2000rpm for 30s to thin the solution and produce films [45].

After spin coating, the substrates were placed in a Thermolyne 4800 furnace (Barnstead Thermolyne Corporation, Iowa, USA) and the temperature was monitored using a Fluke 53 II B thermometer (Fluke Corporation, Washington, USA). The temperature was increased at a rate of 2.2°C and held at 70°C for 30 min and annealed to room temperature [49].

2.5. Voltammetric Setup

A BST8-stat potentiostat/galvanostat (MTI Corporation, Richmond, California, USA) was used for anodic stripping voltammetry (ASV) tests. The potentiostat was interfaced with a computer with BST8-stat software (V.5.2.12.730).

The voltammetric cell setup involves a 3-electrode setup, a sparging inlet, and a magnetic stirrer. The 3-electrode setup consisted of the fabricated modified electrode as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and platinum coil as the counter electrode. The electrodes were attached to the potentiostat with alligator clips.

The solutions being tested were sparged with high purity nitrogen gas to remove dissolved oxygen that interferes with the redox reactions of the analytes. High purity nitrogen gas from its gas tank was first ran through a deionized water bubble filter, then to the sparging inlet, and finally to the solution. The magnetic stirrer was used to ensure that the solution being tested is homogenized. For the supporting electrolyte, 100mL of 0.1M NaCl was used.

The results of voltammetry tests were strongly dependent on the area of the working electrode. To ensure a constant exposure area, the fabricated modified electrode was wrapped with Teflon tape to expose 1cm² on end.

2.6. Anodic Stripping Voltammetry

2.6.1. Recipe optimization

The initial recipe or parameters for the anodic stripping voltammetry (ASV) tests were the following: deposition or accumulation at -1.0V for 60s, rest period at -1.0V for 15s, and a potential ramp from -1.0V to +1.0V at a scan rate of 0.1V/s and a potential step of 0.01V. The deposition potential was optimized by having -0.5V increments of the initial deposition potential. The deposition time was optimized by having 1min increments of the initial deposition time. Sparging was done in all steps whereas stirring was done on the deposition stage and turned off 4s before the end of the aforementioned stage. The heavy metal stock solution was used for the optimization tests.

2.6.2. Calibration Curve

The heavy metal stock solution was prepared by dissolving 1mg

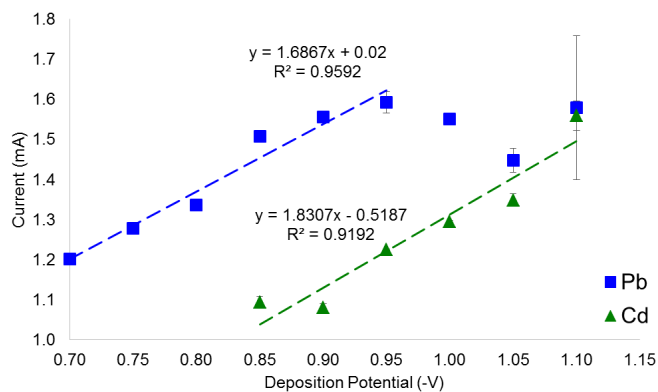


Figure 1. Deposition potential Optimization

of Lead (II) chloride, $PbCl_2$ of 99% purity (Techno Pharmchem, Bahadurgarh, Haryana, India) and 1mg of $CdCl_2$, of 99.99% purity (Duksan Pure Chemicals Co., Ltd., Seonggok-dong, Ansan-si, Gyeonggi-do, South Korea) in a 100mL 0.1M NaCl solution. The resulting solutions were calculated to be 7.45ppm for Pb and 6.13ppm for Cd. The calibration points were chosen to be succeeding halves of the preceding solution i.e. 3.725ppm, 1.863ppm, 0.931ppm, 0.0466ppm, 0.015ppm for Pb; and 3.066ppm, 1.533ppm, 0.767ppm, 0.038ppm, and 0.012ppm for Cd. The solutions for the calibration points were prepared by diluting succeeding halves of the preceding solution. To summarize, 50mL, 75mL, 87.5mL, 93.75mL, and 98mL of 0.1M NaCl was added to 50mL, 25mL, 12.5mL, and 6.25mL, and 2mL of the heavy metal stock solution, respectively.

2.6.3. Sensitivity

Calibration sensitivity, indicated by the slope of the calibration curve, is the change of the response signal per unit of concentration. A steeper slope indicated a more sensitive calibration curve. Analytical sensitivity on the other hand is the calibration sensitivity with the standard deviation taken into account. (50) The analytical sensitivity is determined using Eq.1 where γ is the analytical sensitivity, m is the slope, and S_S is the standard deviation [50].

$$\gamma = \frac{m}{S_S} \quad (1)$$

2.6.4. Limit of Detection

The theoretical limit of detection (LOD) was determined using Eq.2 where C_m is the theoretical LOD, S_m is the minimum detectable analytical signal, S_{bl} is the blank signal, and m is the slope. The minimum detectable analytical signal was determined using eq.2 where S_m is the minimum detectable analytical signal, k is the confidence factor, and std_{bl} is the standard deviation of the blank signal. Equation 2 can be simplified into eq. 4 using Eq.3 [50]. The experimental LOD, on the other hand, was determined by the successive addition of microliter (μL) aliquots of the stock solution into a blank solution. The experimental LOD was identified once a peak could be seen in its corresponding voltammogram.

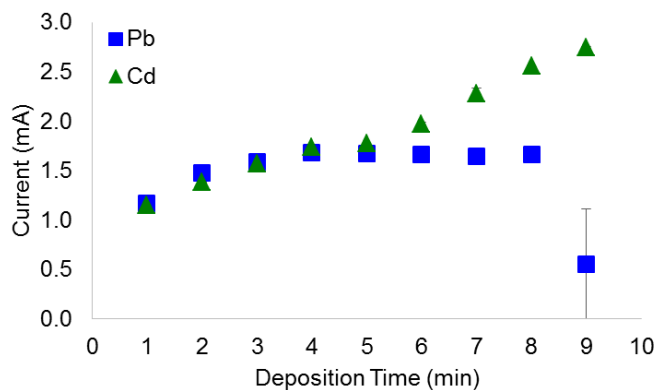


Figure 2. Deposition time optimization

$$C_m = \frac{S_m - S_{bl}}{m} \quad (2)$$

$$S_m = S_{bl} + k(std_{bl}) \quad (3)$$

$$C_m = \frac{k(std_{bl})}{m} \quad (4)$$

2.6.5. Real sampling

Yellow water color paint, from a commercially available water color set, was tested for its lead and cadmium content. Yellow water color of mass 0.3588g was placed in 50mL of concentrated nitric acid (HNO_3). The resulting mixture was heated on a hotplate until boiling for 1hour. To prevent total evaporation and to flush ions that may have stuck on the walls of the beaker, deionized water was occasionally sprayed around the walls of the beaker. A 10 μL aliquot was added to 100mL of 0.1M NaCl solution and tested for the presence of lead and cadmium. The results were verified using atomic absorption spectrometry (AAS).

3. RESULTS AND DISCUSSION

3.1. Recipe Optimization

Results from the deposition potential optimization are presented in Fig. 1. Lead was detected at deposition potentials of less than -0.7V and cadmium was detected at deposition potentials of less than -0.85V. Lead peaked at -0.95V whereas cadmium continued to increase. The deposition time optimization results are presented in Fig. 2. Lead began to plateau at 3min deposition time whereas cadmium continued to increase.

From Fig. 1, the best deposition parameters were at -0.95V for 3min. However, a closer examination of the electrodes used reveal that there was an irreversible increase of discoloration of the electrodes (Fig. 3). The discoloration could be attributed to the oxidation of the ITO layer of the electrode. The electrodes were rendered useless when the discoloration was noticeably dark. The optimum deposition parameters were therefore set at -0.9V for 60s as discolorations were not observed at these conditions.

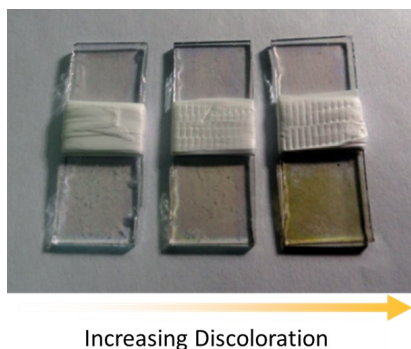


Figure 3. Dicoloration of ITO electrodes

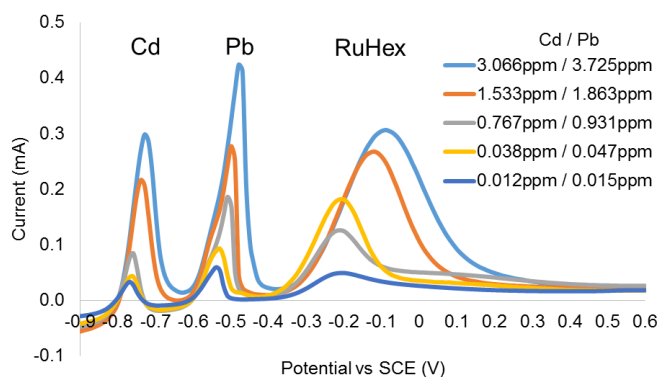


Figure 4. Anodic stripping voltammograms of different concentrations of lead and cadmium

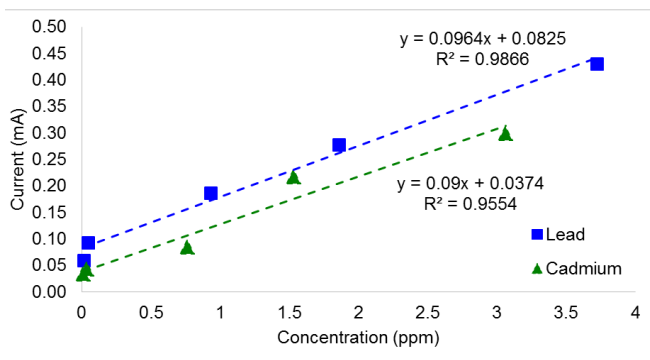


Figure 5. Calibration curves for the determination of lead and cadmium

3.2. Calibration Curve

The ASV voltammograms for the calibration curves are presented in Fig. 4. Higher peak currents correspond to higher concentrations. The linear correlation plots of the calibration curves are presented in Fig. 5. From Fig. 5, Pb and Cd had high Pearson coefficients indicating a highly linear relationship. Moreover, their slopes were roughly similar indicating a similar calibration sensitivity. The linear correlations of Fig. 5 were used to derive eq. 5 and eq. 6 to determine the unknown concentrations of Pb and Cd, respective-

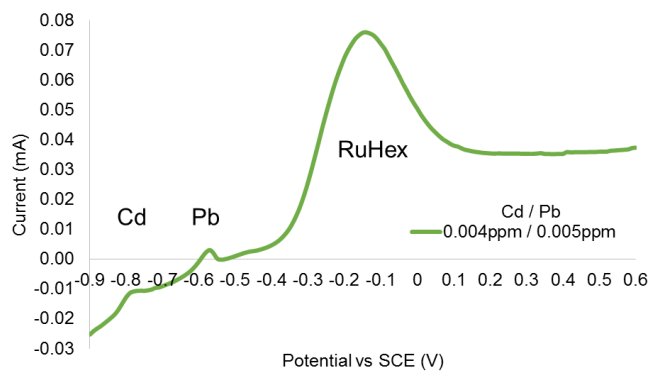


Figure 6. Experimental LOD for lead and cadmium

ly.

$$C_{Pb} = \frac{P - 0.0825}{0.0964} \quad (5)$$

$$C_{Cd} = \frac{P - 0.0374}{0.09} \quad (6)$$

3.3. Sensitivity

From eq. 1 and Fig. 3, the analytical sensitivity for Pb and Cd were determined in Table 1. The calibration sensitivities of the modified electrode for the two analytes were approximately equal. Analytical sensitivities, being inversely proportional of the standard deviation, were significantly higher as the standard deviation and concentration of the analyte decreased.

3.4. Limit of Detection

From eq. 4, the theoretical LOD values were determined to be 14.59ppb and 34.23ppb for Pb and Cd, respectively (Table 2). As for the experimental LOD, a noticeable peak emerged after the addition of 720 μ L of the heavy metal stock solution (Fig. 6). The

Table 1. Analytical Sensitivity for Lead and Cadmium

	Conc. (ppm)	Slope	Standard Deviation	Analytical Sensitivity (ppm ⁻¹)
Pb	0.0149	0.0964	2.6379 $\times 10^{-3}$	36.5443
	0.0466		2.0366 $\times 10^{-3}$	47.3337
	0.9313		3.2711 $\times 10^{-3}$	29.4703
	1.8626		7.2111 $\times 10^{-3}$	13.3683
	3.7253		2.2510 $\times 10^{-2}$	4.2825
Cd	0.0123	0.09	1.1505 $\times 10^{-3}$	78.2244
	0.0383		2.5242 $\times 10^{-3}$	35.6550
	0.7665		4.0423 $\times 10^{-3}$	22.2644
	1.5331		5.4129 $\times 10^{-3}$	16.6268
	3.0661		1.2280 $\times 10^{-2}$	7.3290

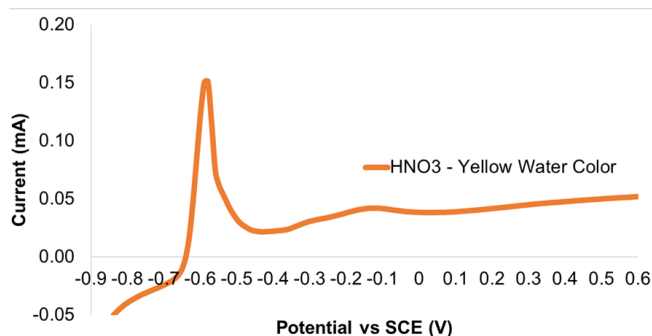


Figure 7. ASV voltammogram of the HNO₃ digested yellow water color

solution was calculated to contain 5ppb of Pb and 4ppb of Cd. The theoretical LODs were considerably higher than the experimental values which could be explained by the possibility that the solution was not homogeneous.

3.5. Real sampling

The HNO₃ digested yellow water color sample was tested with ASV and lead was detected (Fig. 7). The concentration, using eq. 5, was determined to be 0.7106ppm Pb. Performing an AAS analysis of the same solution reveal that the results were not significantly different from each other (Table 3).

4. CONCLUSIONS

RuHex-incorporated Nafion-isopropanol films were fabricated on indium tin oxide coated glass substrates via spin coating. The fabricated modified electrodes were used as the working electrodes for the detection of lead and cadmium in standard solutions and in commercially available yellow water color. At deposition potentials of less than -0.9V and at extended deposition periods, the electrodes have a high tendency of turning orange. The electrodes were rendered useless when it transitioned into a dark orange color.

Calibration curves obtained from ASV scans of 3.725ppm, 1.863ppm, 0.931ppm, 0.0466ppm, 0.015ppm for Pb; and 3.066ppm, 1.533ppm, 0.767ppm, 0.038ppm, and 0.012ppm for Cd were very linear and had similar slopes. It is worth noting that the calibration range obtained in this study were significantly lower

Table 2. Theoretical Limit of Detection

	Confidence level (<i>k</i>)	Standard Deviation of Blank Signal (<i>std_{bl}</i>)	Slope (<i>m</i>)	Limit of Detection (ppb)
Pb	1	1.4067×10^{-3}	0.0964	14.5923
Cd		3.0811×10^{-3}	0.09	34.2344

Table 3. Real sampling comparison between ASV and AAS

HNO ₃ – Yellow Water Color	Pb conc. (ppm)	Cd conc. (ppm)
ASV	0.7106	-
AAS	0.6923	-0.1805

compared to previous studies that modified ITO electrodes with drop coating (46-48). The detection limit was determined to be 5ppb for Pb and 4ppb for Cd.

Commercially available yellow water color was digested with concentrated HNO₃ for the determination of their Pb and Cd content. The results were verified with AAS. ASV determined 0.7106ppm Pb and AAS determined 0.6923ppm Pb. Cadmium was not detected in both solutions.

5. ACKNOWLEDGMENT

This work was supported in part by the Department of Science and Technology – Science Education Institute (DOST-SEI) of the Republic of the Philippines and the University Research Coordination Office (URCO) of De La Salle University, Manila, Philippines.

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