

# Detection of Cadmium, Lead and Mercury Ions by a Chemically Modified Carbon Paste Electrode with Schiff Base Using Square-wave Anodic Stripping Voltammetry

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## Abstract

**Purpose:** A modified carbon paste electrode (CPE) was developed to determine the content of cadmium ( $\text{Cd}^{2+}$ ), lead ( $\text{Pb}^{2+}$ ) and mercury ( $\text{Hg}^{2+}$ ) ions in aqueous solutions.

**Methods:** The CPE was modified using the Schiff base of 2-hydroxy-5-nitrobenzaldehyde with S-benzyl-dithiocarbamate. The performance of modified and unmodified electrodes were compared. Several important parameters controlling the performance of the modified electrode were optimized using square-wave anodic stripping voltammetry (SWASV). The electrochemical behavior of the modified electrode was characterized by cyclic voltammetry.

**Results:** The modified electrode exhibited good selectivity, stability and reproducibility. Under optimized conditions, calibration curves demonstrated linearity over a concentration range of 25 – 1000  $\text{ng mL}^{-1}$  for  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ; and 25 – 2500  $\text{ng mL}^{-1}$  for  $\text{Pb}^{2+}$  using a deposition time of 70 s. The limits of detection for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  were 9.50, 17.09 and 13.16  $\text{ng mL}^{-1}$ , respectively. Simultaneous determination of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  was performed and no interference was observed.

**Conclusion:** The modified electrode was successfully used to determine the content of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  in river water samples, giving results that agreed well with those obtained by atomic absorption spectrometry (AAS).

**Keywords:** Anodic stripping voltammetry, Chemically modified electrodes, Heavy metals, Schiff base ligand

## 1 Introduction

Heavy metals like lead (Pb), cadmium (Cd) and mercury (Hg) are hazardous pollutants in the environment because of their toxicity, non-biodegradability and persistence. Continuous exposure to these elements may cause adverse effects in animals and humans (Flora et al., 2012; Jarup & Akesson, 2009; Lim et al., 2008). The concentration of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  in food and biological samples is generally low, so sensitive and selective methods for determination of these heavy metals are required. Analytical techniques such as cold vapor atomic fluorescence spectrometry (Leopold et al., 2009), atomic absorption spectrometry (AAS) (Bagheri et al., 2012), neutron activation analysis (Shams et al., 2004) and inductively coupled plasma mass spectrometry (D.S. Rajawat, 2012) are currently used to detect heavy metals. However, these approaches use sophisticated instruments that are expensive to operate and maintain and possess limited life span. In addition, these techniques require time-consuming manipulation steps, skilled manpower and are unsuitable for in situ measurements because of the complex instrumentation. Therefore, a low-cost, portable, highly sensitive and environmentally friendly method to quantify trace metals needs to be developed. Voltammetric techniques like square-wave anodic stripping voltammetry (SWASV) are most widely used method of stripping analysis for trace metals (Abbasi et al., 2011; Bernalte et al., 2011; Jovanovski et al., 2015; Laffont et al., 2015; Punrat et al., 2014). SWASV possesses various advantages such as rapid determination, good selectivity, sensitivity and accuracy, and the possibility of simultaneous analysis of analytes using inexpensive instrumentation. In past years, mercury (Hg) was commonly used as the working electrode because of its high sensitivity and reproducibility. However, the toxicity of Hg means that scientists are now focused on designing Hg-free electrodes. Carbon paste electrodes (CPEs) consisting of a mixture of carbonaceous material with a liquid binder have attracted attention for use in stripping techniques because of their easy preparation, low cost, porous surface, low toxicity and environmentally friendly components. Moreover, CPEs can be modified by various materials such as ligands, ion exchange species and functionalized nanoparticles to improve their sensitivity, selectivity, detection limit and other properties. Various kind of modified electrodes such as array of peptide-modified electrodes (Serrano et al., 2014), sputtered bismuth screen-printed electrode (Sosa et al., 2014) and antimony film screen-printed carbon electrode (Sosa et al., 2015) are successfully applied for the determination of heavy metals in natural samples. Modified CPEs with good

electrochemical behavior, high thermal stability, low vapor pressure, low melting temperature and high ionic conductivity have been fabricated (Nabid et al., 2012; Tarley et al., 2009). Schiff base ligands are suitable for use as modifiers in CPEs because they readily attach to metal ions through the formation of highly stable coordination compounds. Their ability to bind metal ions is a consequence of the great number of potential donor atoms they contain. The unique nature of a Schiff base may be enhanced by the presence of a well-delocalized  $\pi - \pi$  conjugation system. Several ligands have been used to modify electrodes for the determination of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$ . The binding of a metal ion to a Schiff base involves a number of passive accumulation processes, which may include adsorption, ion exchange, coordination, complexation, chelation and microprecipitation (Afkhami, Bagheri, et al., 2012; Afkhami, Madrakian, et al., 2012; Khudaish et al., 2013; Pérez-Ràfols et al., 2015; Serrano et al., 2015; Wei et al., 2014). Determination of  $\text{Pb}^{2+}$  in natural waters with 2-mercaptobenzimidazole-5-sulfonate (MBIS) chemically modified gold electrode was studied by Francesca Zavarise et al. (Zavarise et al., 2010). Similarly, Clara Pérez-Ràfols et al. (Pérez-Ràfols et al., 2015) and Chengguo Hu (Hu et al., 2003) applied penicillamine and diacetyldioxime modified electrode for the determination of heavy metals in natural samples. In this study, we modify a CPE with the Schiff base of 2-hydroxy-5-nitrobenzaldehyde with S-benzyl-dithiocarbazate (Figure 1) with the objective of developing a low-cost, highly sensitive electrochemical sensor based on a modified CPE for the rapid determination of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  using SWASV.

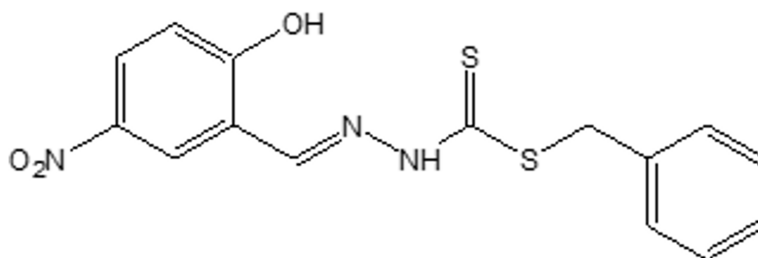


Figure 1: Chemical structure of 2-hydroxy-5-nitrobenzaldehyde Schiff base of S-benzyl-dithiocarbazate

## 2 Materials and methods

### 2.1 Chemicals and reagents

Pb, Cd, Hg and potassium nitrate were purchased from Merck, Germany. Potassium dihydrogen phosphate (Fluka, Singapore), potassium hydrogen phosphate (Fluka), sodium hydroxide (GCE, Singapore), hydrochloric acid (Sigma-Aldrich, Singapore) and stannous chloride dehydrate (Fluka) were of analytical grade and used without further purification. CPEs were prepared using graphite powder ( $< 20 \mu\text{m}$ , Sigma-Aldrich) and mineral oil (Sigma-Aldrich). Phosphate buffer solution (PBS) consisted of an aqueous of monosodium phosphate (0.1 M) and disodium phosphate (0.1 M) and was adjusted to the required pH with hydrochloric acid (0.1 M) or sodium hydroxide (0.1 M). Stock standard solutions of Cd, Pb and Hg ( $100 \mu\text{g mL}^{-1}$ ) were prepared and stored at  $4 \text{ }^\circ\text{C}$  when not in use. All aqueous solutions were prepared using double-distilled water at room temperature.

### 2.2 Preparation of modified and unmodified electrodes

The modifier was 2-hydroxy-5-nitrobenzaldehyde Schiff base of S-benzyl-dithiocarbazate, which was prepared according to the method described in ref. (Mohammad Akbar Ali, 2012). Briefly, to a boiling solution of 2-hydroxy-5-nitrobenzaldehyde (0.33 g,  $1 \times 10^{-3}$  M) in absolute ethanol (25 mL), a hot solution of S-benzyl-dithiocarbazate (0.41 g,  $1 \times 10^{-3}$  M) in absolute ethanol (25 mL) was added, which gave a pale yellow solution. A few drops of glacial acetic acid were added, and then the mixture was heated under reflux for 3 h. The reaction mixture was then decreased to half its original volume by heating on a water bath, resulting in the formation of yellow crystals. The modified CPE was prepared by homogenously mixing graphite powder (2.25 g) with modifier (0.45 g) in a Petri dish for 5 min. Mineral oil (0.3 g) was added and the components were hand mixed for 15 min to obtain a fine paste. The homogenized paste was inserted into a carbon tube with a diameter of 3 mm and length of 7.3 cm. The electrical connection was provided by a copper wire connected to the paste inside the tube. The modified CPE was dried overnight at room temperature before use. The surface of the sensing end of the modified CPE was polished with fine sandpaper (No. 2000) and rinsed with double-distilled water before use. An unmodified CPE was prepared by following the same procedure but omitting the modifier.

## 2.3 Electrochemical characterization

The electrochemical behavior of the modified and unmodified CPEs in 0.1 M HCl were investigated using cyclic voltammetry (CV). Measurements were performed at room temperature in a conventional three-electrode cell containing a silver/silver chloride reference electrode, platinum wire counter electrode and the modified or unmodified CPE as the working electrode. A potentiostat (ED401, Australia) equipped with the software EChem, eDAQ was used for all voltammetric measurements. Cyclic voltammograms were measured over a potential range of  $-1.5$  to  $+1.5$  V at a scan rate of  $100 \text{ mV s}^{-1}$ .

## 2.4 Anodic stripping voltammetry

Anodic stripping voltammetry (ASV) is one the most widely used stripping techniques to analyze metal concentration. The system was purged with nitrogen gas for 5 min before each experiment. SWASV was recorded positive scanning in the potential range of  $-0.9$  V to  $+0.3$  V vs Ag/AgCl. It has the features of electrochemically cleaning electrodes and surface regeneration. In this study, a fixed potential of  $+0.8$  V was applied for 60 s to clean the electrode surface in 0.1 M HCl supporting electrolyte (blank solution) and remove any accumulated analyte from previous experiments. Blank tests were performed after each measurement to ensure that there was no carryover between samples.

## 2.5 Analysis of real samples

To demonstrate the applicability and reliability of the proposed sensor, two different river water samples were collected, filtered and diluted twice with distilled water to remove any matrix effects. Then, each sample was analyzed using the modified CPE. The concentrations of metal ions were evaluated using standard calibration curves. An atomic absorption spectrometer (AAS-6701F, Shimadzu) was used to measure the concentrations of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ , and a different atomic absorption spectrometer (AAS-7000, MVU-1A, Shimadzu) was used to determine the concentration of  $\text{Hg}^{2+}$ . The results obtained from AAS were compared with those from the modified CPE

## 3 Results

### 3.1 Cyclic voltammetry (CV)

The electrochemical behavior of modified and unmodified electrodes were investigated via CV. CV measurements were obtained by sweeping the potential from  $-1.5$  to  $+1.5$  V at a scan rate of  $100 \text{ mV s}^{-1}$  (Figure 2). The modified electrode showed a single oxidation and single reduction at  $+0.98$  and  $-1.09$  V, respectively. The reaction involved in oxidation process (forward scan) is assigned to one-electron oxidation of the metal centre, while the reduction (reverse scan) also involves a one-electron metal-centered process. The observed cyclic voltammograms are characterized by quasi-reversible behavior as seen by wide separation of anodic and cathodic peaks; whereas the electrochemical behavior of unmodified electrode did not show any redox peaks.

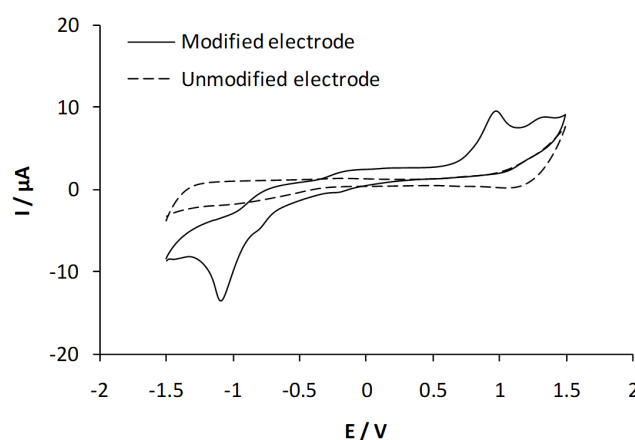


Figure 2: Cyclic voltammograms of modified and unmodified CPEs in 0.1 M HCl measured at a scan rate of  $100 \text{ mV s}^{-1}$

### 3.2 Sensor response

Preliminary experiments were carried out to identify the responses of the modified and unmodified electrodes to metal ions. SWASV in solutions containing  $1 \mu\text{g mL}^{-1}$   $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ions and positive scans in the potential range of  $-0.9$  to  $+0.3$  V vs. Ag/AgCl are shown in Figure 3. The Modified CPE exhibited three peaks at  $-0.76$ ,  $-0.47$  and  $+0.15$  V corresponding to the oxidation of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  at the electrode surface, respectively.

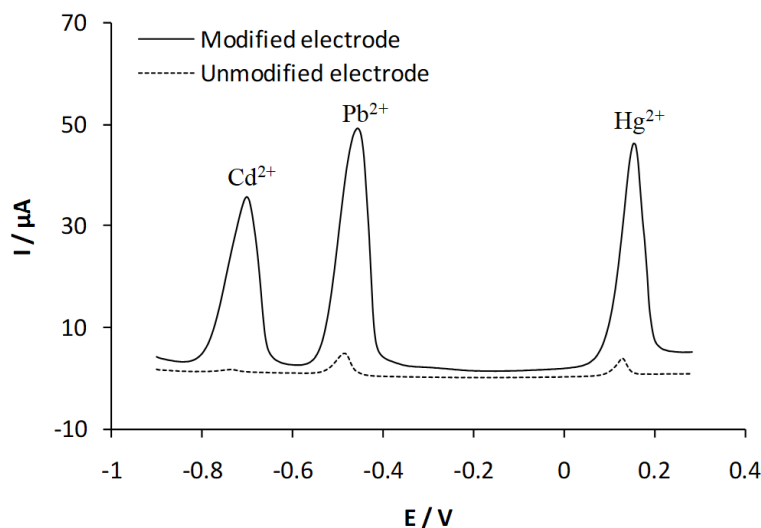


Figure 3: Cyclic voltammograms of modified and unmodified CPEs in 0.1 M HCl measured at a scan rate of  $100 \text{ mV s}^{-1}$

### 3.3 Optimization of parameters

The parameters applied during the stripping process influenced the sensing characteristics of the modified electrode. The effects of modifier composition, deposition time and pH of the solution need to be optimized to obtain an efficient sensor.

#### 3.3.1 Effect of deposition time

Deposition time is crucial factor for stripping voltammetry method that influences the sensitivity and selectivity of the determination (Yi et al., 2012). The electrochemical response of the modified electrode towards  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  in 0.1 M HCl solution containing  $1.0 \mu\text{g mL}^{-1}$  of each metal ion was investigated by SWASV. The variation of the stripping peak current with respect to deposition times of 5 to 80 s is presented in Figure 4.

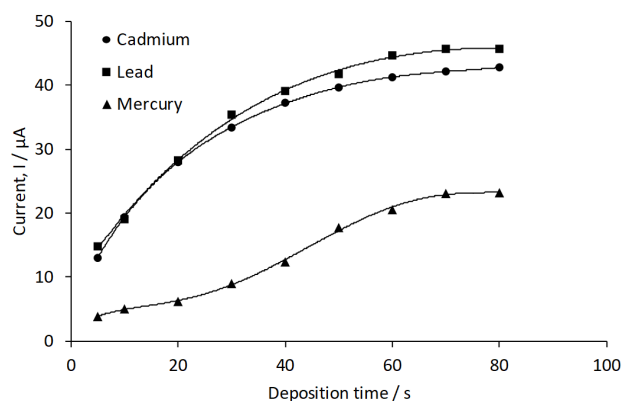


Figure 4: SWASV peaks of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ( $1 \mu\text{g mL}^{-1}$  each) using various deposition times. Conditions: potential from  $-0.9$  to  $+0.3$  V, 0.1 M HCl supporting electrolyte, scan rate  $75 \text{ mV s}^{-1}$ , square-wave frequency 15 Hz, step potential 5 mV, square-wave amplitude 25 mV and resting time 10 s.

### 3.3.2 Effect of pH on electrode response

The influence of pH on the electrochemical response of the modified electrode to metal ions was studied in PBS at pH from 1 to 7. All solutions contained a fixed concentration of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  of  $0.5 \mu\text{g mL}^{-1}$ . The peak current generated by the modified CPE at different pH is shown in Figure 5. The highest peak currents were observed for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  at pH 5, 1.8 and 4, respectively. Therefore, these pH values were used in subsequent studies.

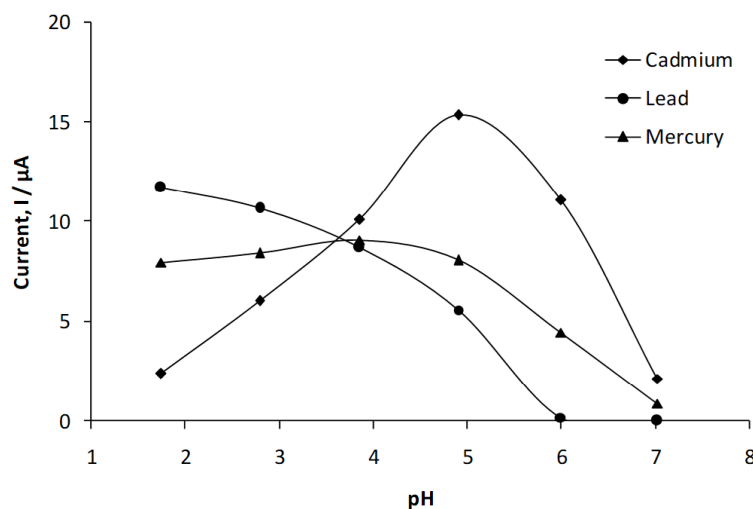
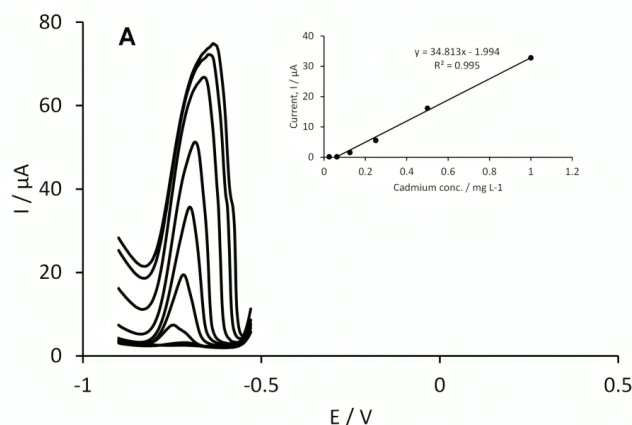


Figure 5: Effect of pH on the stripping current of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ( $0.5 \mu\text{g mL}^{-1}$ ). Conditions: potential  $-0.9 \text{ V}$ , deposition time 60 s, scan rate  $75 \text{ mVs}^{-1}$ , square-wave frequency 15 Hz, step potential 5 mV, square-wave amplitude 25 mV and resting time 10 s

### 3.4 Individual determination of $\text{Cd}^{2+}$ , $\text{Pb}^{2+}$ and $\text{Hg}^{2+}$

The analytical performance of the modified electrode was investigated by individual analysis of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  under optimized experimental conditions. Figure 6 shows the SWASV response of the modified electrode towards different concentrations of metal ions. The response of the modified electrode varied with the concentration of metal ions; linear relationships were observed in the range of  $25 - 1000 \text{ ng mL}^{-1}$  for  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ , and  $25 - 2500 \text{ ng mL}^{-1}$  for  $\text{Pb}^{2+}$  using an accumulation time of 70 s under optimum conditions. SWASV resulted in voltammograms containing peaks currents corresponding to the oxidation of  $\text{Cd}(0)$ ,  $\text{Pb}(0)$  and  $\text{Hg}(0)$ .



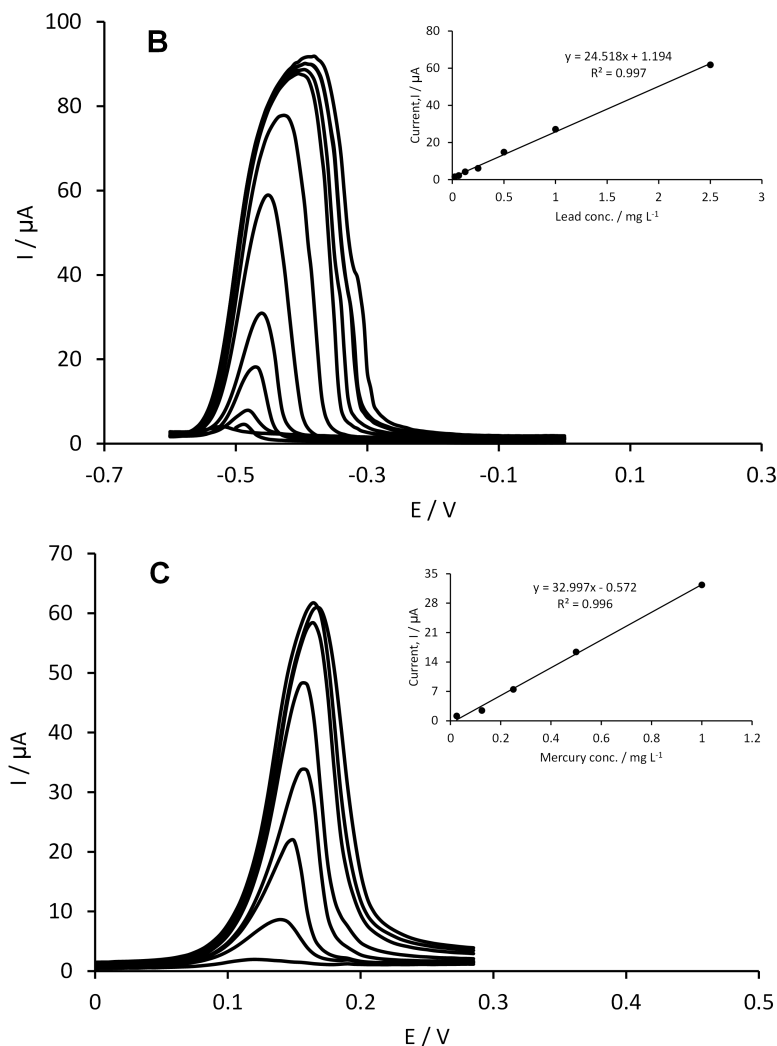


Figure 6: Calibration curves for (A)  $\text{Cd}^{2+}$  at pH 5, (B)  $\text{Pb}^{2+}$  at pH 1.8 and (C)  $\text{Hg}^{2+}$  at pH 4 at the modified CPE. Conditions: potential from  $-0.9$  to  $+0.3$  V, deposition time 70 s, scan rate  $75 \text{ mV s}^{-1}$ , square-wave frequency 15 Hz, step potential 5 mV, square-wave amplitude 25 mV and rest time 10 s

### 3.5 Simultaneous determination of metal ions

In order to further study how sensitive the modified CPE in the present study, simultaneous determination of different concentrations of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  was carried out. The purpose of this was to investigate if the detection of a given analyte interferes with that of the other. When the concentrations of the three metal ions were increased simultaneously, all three metal ions exhibited separate oxidation peaks over the range from 25 – 1000  $\text{ng mL}^{-1}$  for  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  and 25 – 2500  $\text{ng mL}^{-1}$  for  $\text{Pb}^{2+}$ . The electrochemical method used for simultaneous determination of different metal ions was based on simultaneous pre-concentration/reduction of metal ions at the modified CPE at  $-0.9$  V vs. Ag/AgCl in PBS at pH 3.6 for 70 s. The calibration equations and correlation coefficients were  $y = 31.38x - 3.211$ ,  $R^2 = 0.986$  for  $\text{Cd}^{2+}$ ,  $y = 25.97x + 6.481$ ,  $R^2 = 0.870$  for  $\text{Pb}^{2+}$  and  $y = 36.52x - 0.593$ ,  $R^2 = 0.974$  for  $\text{Hg}^{2+}$  (Figure 7). Simultaneous determination of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  gave a linear response between the peak height and the concentration of the metal ions implying that the modified CPE can as well be applicable for the detection of all metal ions with no reasonable interference in their respective signals (Figure 7). Thus, the modified CPE sensor can detect  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  simultaneously.

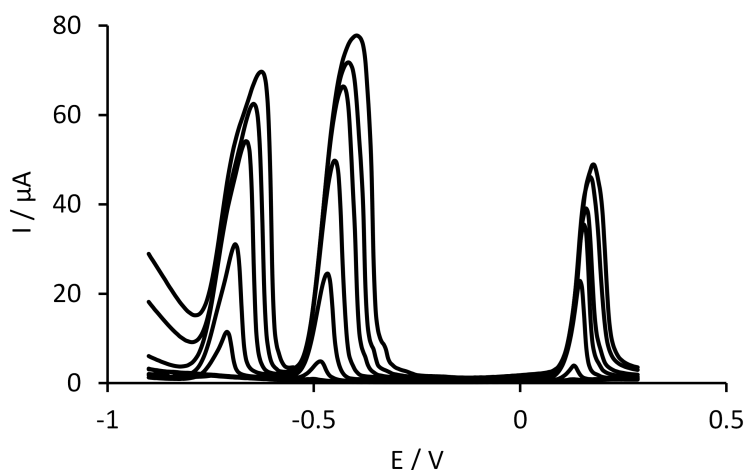


Figure 7: Simultaneous determination of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  by the modified CPE. Conditions: potential from  $-0.9$  to  $+0.3$  V, PBS (pH 3.6) as supporting electrolyte, deposition time 70 s, scan rate  $75 \text{ mV s}^{-1}$ , square-wave frequency 15 Hz, step potential 5 mV, square-wave amplitude 25 mV and rest time 10s

## 4 Discussion

The composition of the carbon paste made of graphite powder and modifier influences the peak current of the electrode during SWASV measurements. The presence of modifier in the carbon paste can greatly improve the sensitivity of the electrode because of its functional sites that can interact with metal ions. The peak current increased as the amount of modifier was increased until the highest peak current was obtained when the ratio of graphite to modifier to mineral oil was 75:15:10 (w/w/w). When the amount of modifier in the composite was increased further, the peak current started to decrease because the modifier may decrease the conductivity of the electrode. Hence, 75:15:10 (w/w/w) ratio of graphite, modifier and mineral oil was applied for further study.

Examining the result in Figure 3, we observe a corresponding increase in the square wave signals as the metal loading in the modified electrode increases indicating an increase in sensitivity towards  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  detection. The unmodified electrode also exhibited a response in square wave signals, but it was much weaker than that of the modified electrode. This result suggests that the modified electrode has higher conductivity and a more intense electrochemical response to metal ions than the unmodified electrode.

The length of the deposition time to accumulate metal ions on the electrode surface influenced the behavior of the modified electrode. Deposition time dependence on the peak height was also investigated at modified electrode by varying the deposition time from 5 s to 80 s. Long deposition time can lead to fouling of the electrode's surface thereby affect its analytical performance, as was evidenced in this study. For shorter deposition times, peak current increases linearly with lengthening deposition time because the amount of metal ions on the surface of the modified electrode increased. For longer deposition times, the peak current became constant because of the saturation of the modified electrode with metal ions binding sites on the modified electrode surface (Choudhary et al., 2020). Hence, a deposition time of 70 s was selected as the optimum.

The electrolyte's pH plays an important feature in the electroanalytical behavior of the composite electrodes. In this study, and as can be seen from Figure 5, there was a rise in the peak height from pH 1.0 to 5.0, and then a sudden drop at higher pH values (5.0–7.0) for  $\text{Cd}^{2+}$ ; decrease in the peak height from pH 1.8 to 7.0 for  $\text{Pb}^{2+}$ ; and rise in the peak height from pH 1.0 to 4.0, and then a sudden drop at higher pH values (4.0 – 7.0) for  $\text{Hg}^{2+}$ . The voltametric signal of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  at the composite electrodes depends on how well the electrode's surface could sense and detect the existence of free  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ions in the solution. The low peak currents obtained during investigation of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  at low pH can be attributed to the competition between the binding of protons and metal ions to the donating atoms of the Schiff base ligand at the surface of the modified electrode. Proton can compete with metal ions for binding to the donating atoms of the modifier, the ligand at the surface of the electrode. Furthermore, at lower pH values the ligand can slowly dissolve in acidic solution and lose its ability in bind to  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  (Afkhani et al., 2013). The decrease in the intensity of peak current as the pH became more basic was probably caused by the formation of cadmium hydroxide, lead hydroxide or mercury hydroxide, which decreased the content of free ions available to bind to the modifier of CPE.

In square wave voltammetry, peak intensity depends on the concentration of the analyte present as shown in Figure 6. A linear calibration plot was obtained with the calibration curves of  $I_p(\mu\text{A}) = 34.81 [\text{Cd(II)}] (\text{mgL}^{-1}) - 1.994$  and a correlation coefficient of 0.995 for  $\text{Cd}^{2+}$ ,  $I_p(\mu\text{A}) = 24.51 [\text{Pb(II)}] (\text{mgL}^{-1}) + 1.194$  and a correlation coefficient of 0.997 for  $\text{Pb}^{2+}$  and  $I_p(\mu\text{A}) = 32.99 [\text{Hg(II)}] (\text{mgL}^{-1}) - 0.572$  and a correlation coefficient of 0.996

for  $\text{Hg}^{2+}$ . Under optimum conditions, SWASV also showed an excellent sensitivity of modified electrode towards detection of metal ions. The limit of detection, LOD, of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  were determined based on  $3\sigma/m$ , where  $\sigma$  is the standard deviation of a least metal ion concentration and  $m$  is the slope of the standard calibration graph. Standard deviations were estimated using six replicate determinations of the lowest concentration signals. Calculated LOD for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  were 9.50, 17.09 and 13.16  $\text{ng mL}^{-1}$ , respectively. The functional groups in the chemical structure of modified electrode attract the metal ions from the solution and form a metal-ligand complex on the modified electrode surface. This metal-ligand complex leads to the accumulation of a large amount of metal ions on the modified electrode and hence it gives high peak currents during the stripping/oxidation process compared to the unmodified electrode (Tefaye et al., 2022). Comparing the result with those reported in the literature showed how sensitive the fabricated electrode in this study is towards the voltammetric detection of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ions in aqueous samples as shown in Table 1.

The stripping peak current shifted to more positive potential with increasing concentration of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ions which might be related to an increase of the ohmic drop ( $iR$ ) in the electrochemical cell. Since the electrochemical cell has an internal resistance  $R$ , the ohmic drop  $iR$  increases with increasing concentration of the electrochemically active species (Bard & Murray, 2012).

Table 1: Comparison of the figure of merits of the proposed Modified CPEs and the others modified CPEs reported in the literature for determination of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$

Modifier	Metal ions	Technique	Linear range	LOD	Ref
Poly(GMA-MMA-DVB)-ATAL	$\text{Pb}^{2+}$ $\text{Hg}^{2+}$	SWASV	10.4 – 828.8 $\text{ng mL}^{-1}$ 10.0 – 1204 $\text{ng mL}^{-1}$	4.5 $\text{ng mL}^{-1}$ 12.3 $\text{ng mL}^{-1}$	(Şar et al., 2008)
SBA-15 nanostructured silica	$\text{Pb}^{2+}$ $\text{Hg}^{2+}$	DPASV	0.3 – 0.7 $\mu\text{mol L}^{-1}$ 2.0 – 10.0 $\mu\text{mol L}^{-1}$	0.04 $\mu\text{mol L}^{-1}$ 0.40 $\mu\text{mol L}^{-1}$	(Cesarino et al., 2008)
CB-15-crown-5-GEC	$\text{Pb}^{2+}$ $\text{Cd}^{2+}$	DPASV	10.9 – 186.5 $\text{ng mL}^{-1}$ 15.7 – 191.1 $\text{ng mL}^{-1}$	3.30 $\text{ng mL}^{-1}$ 4.70 $\text{ng mL}^{-1}$	(Serrano et al., 2015)
$\text{Na}_2\text{Mn}_2\text{Cr}(\text{PO}_4)_3$ -CPE	$\text{Pb}^{2+}$	SWASV	40 – 2050 $\text{ng mL}^{-1}$	51.8 $\text{ng mL}^{-1}$	(Benhsina et al., 2021)
TC4/AuNPs/SPCE	$\text{Pb}^{2+}$	SWASV	20 – 100 $\text{ng mL}^{-1}$	7.98 $\text{ng mL}^{-1}$	(Mei et al., 2021)
2-hydroxy-5-nitrobenzaldehyde Schiff base of S-benzyl-dithiocarbamate	$\text{Pb}^{2+}$ $\text{Cd}^{2+}$ $\text{Hg}^{2+}$	SWASV	25 – 2500 $\text{ng mL}^{-1}$ 25 – 1000 $\text{ng mL}^{-1}$ 25 – 1000 $\text{ng mL}^{-1}$	17.09 $\text{ng mL}^{-1}$ 9.50 $\text{ng mL}^{-1}$ 13.16 $\text{ng mL}^{-1}$	This study

## 5 Sensor reproducibility, repeatability and stability

To examine the accuracy and practicability of the modified CPE sensor, its reproducibility, repeatability and stability were investigated by SWASV. The sensor response exhibited good repeatability, with relative standard deviations (RSD) of 2.83%, 5.40% and 5.44% for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$ , respectively, for five successive runs. The reproducibility of the sensor was investigated by measuring the peak current of three different sensors prepared under identical conditions. The observed RSD of 8.33%, 2.11% and 6.11% for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$ , respectively, revealed that the performance of the sensor was reproducible.

The modified CPE sensor possessed good stability, retaining its performance characteristics over a period of time and during repeated use. One modified electrode can be used for metal ion detection in more than 80 samples without any considerable change in response. After this period, the electrode retained 88.9%, 92.2% and 95.1% of the initial peak current signal of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$ , respectively. The modified electrode was kept in PBS at pH 7 for a short period, and dry for a longer period of time. These results indicate that the repeatability, reproducibility and stability of the sensor for the determination of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  are acceptable.

## 6 Selectivity

The proposed modified electrode showed high selectivity towards  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$ , with no interference from metal ions such as cobalt, iron, sodium, nickel and zinc at ten times higher concentration than the target ions. Analysis of variance was performed to reveal if the interfering ions had any significant effect on the performance of the sensor. The statistical results gave p-values of 0.52, 0.87 and 0.81 for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$ , respectively. These values are higher than 0.05 in the presence of the interfering ions, suggesting there is no significant difference between the results obtained with and without interfering ions at the 95% confidence level. These results indicate that the sensor does not suffer from interference by foreign ions and has high selectivity.



## 7 Analysis in real samples

The analytical performance of the developed voltammetric sensor was evaluated by using it to measure the content of metal ions in river water samples obtained from the Tutong and Kampong rivers. The results of these measurements are presented in Table 2 together with the reference results obtained from atomic absorption spectrometry (AAS). The results obtained using the modified electrode showed good agreement with those determined by AAS.

Table 2: Comparison of the content of Cd<sup>2+</sup>, Pb<sup>2+</sup> and Hg<sup>2+</sup> in river water determined using the modified CPE and AAS (n = 3)

Analyte	Sample	Modified CPE (ng mL <sup>-1</sup> )	AAS (ng mL <sup>-1</sup> )
Cd <sup>2+</sup>	Tutong River	64.3 ± 3.9	65.1 ± 0.4
	Kampong River	78.5 ± 1.6	79.6 ± 0.5
Pb <sup>2+</sup>	Tutong River	15.4 ± 1.4	16.2 ± 0.9
	Kampong River	300.6 ± 7.9	301.3 ± 1.3
Hg <sup>2+</sup>	Tutong River	28.9 ± 0.8	28.6 ± 0.5
	Kampong River	312.2 ± 12.4	312.9 ± 1.1

## 8 Conclusion

In this study, a CPE chemically modified with a Schiff base was found to act as a highly sensitive electrochemical sensor for the determination of Cd<sup>2+</sup>, Pb<sup>2+</sup> and Hg<sup>2+</sup> in aqueous solutions. The response of the sensor was influenced by measurement conditions such as pH, deposition time, and electrode composition. The modified CPE sensor possesses advantages like simple design, low cost and short measurement time, as well as high sensitivity and selectivity for the target analytes in aqueous solutions. Moreover, contamination on the electrode surface can be removed by electrochemical cleaning. The modified electrode displayed good repeatability and reproducibility with detection and quantification limits at the ng mL<sup>-1</sup> level. The sensor was successfully used to determine the metal ion content of real samples, revealing that it is a promising analytical tool to detect pollutant metal ions.

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### Authors' contribution:

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