

## Differential Pulse Voltammetry Technique, Using Ferrocene-Modified Carbon Paste Electrodes for the Determination of Pb(II) In *Kepok* Banana

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### Abstract

The voltammetry method is a field of electrochemistry used to measure electric current at a certain potential, and in turn, determine the concentration of inorganic and organic compounds able to undergo oxidation or reduction. This study therefore aims to improve the sensitivity of Pb(II) content measurement in the differential pulse voltammetry (DPV) technique, using the carbon paste electrode (CPE) and ferrocene-modified carbon paste electrode (CPE-Fc) as the working electrodes. The two parameters optimized were ferrocene composition and scan rate, and the validation parameters included the linear concentration range, detection limit, quantization limit, precision and accuracy. In addition, the optimum ferrocene composition was determined at 6%, and the scan rate was 15 mV/s using CPE, increased to 20 mV/s using CPE-Fc. The validation results showed the linearity using CPE-Fc was wider, compared to CPE at the peak potential of 0.515 V. Meanwhile, the detection and quantization limit values obtained using CPE were 0.1551 µg/L and 0.1556 µg/L, while the CPE-Fc counterparts were 0.1089 µg/L and 0.1090 µg/L. The Horwitz ratio was discovered to be less than two, indicating the precision determination for both CPE and CPE-Fc had good results. Also, the percentage of recovery using CPE-Fc was found to be  $85.59 \pm 8.18\%$ . CPE-Fc was used to determine the levels of Pb(II) in *kepok* banana at the optimum measurement conditions, and a value of  $4.4306 \pm 0.0009$  mg/kg, was obtained. The Pb content was also discovered to exceed the permissible limit of 0.5 mg/kg, as established by the Standard National Indonesia (ISN) No. 7387:2009.

**Keywords:** carbon paste electrode, differential pulse voltammetry, Pb(II) ion, , ferrocene, *kepok* banana

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### 1. INTRODUCTION

According to Skoog *et al.*, (1996) the voltammetry method is an electro-analysis method based on the electrolysis of an analyte in a solution. Differential pulse voltammetry (DPV) is a voltammetry technique commonly used for quantitative analysis due to low detection limit, easy sample preparation, short analysis time, low cost, and the ability to simultaneously determine the content of metal ions in sample (Arduini *et al.*, 2010).

Meanwhile, reduction or oxidation reactions occur in working electrodes. Several materials serve as working electrode, including glassy carbon and carbon paste, as well as platinum, gold, copper, and other solid metals. The carbon paste electrode is often used in voltammetry methods due to abundance, low

cost, high conductivity, and ability to be chemically modified to improve the performance of trace level sample detection. Carbon paste is often mixed with modifier to form a mixture (bulk modified), or coated with a modifier on the surface of working electrode (surface modified) (Wang, 2001; Raof, *et al.*, 2011). Some commonly used modifiers include crown ether (Flores *et al.*, 2017), hematite (Wang *et al.*, 2019), and ferrocene (Gonzalez *et al.*, 2009; Raof *et al.*, 2011; Wu *et al.*, 2010).

Raof *et al.* (2011) modified carbon paste electrodes using ferrocene and obtained an optimum ferrocene composition of 0.6% with a linear concentration range of 0.03-2400 µM and a detection limit of 0.0096 µmol/L. Ferrocene is a suitable modifier due to the

ability to function as an effective catalyst for redox reactions to oxidize various substrates (Liu *et al.*, 2013).

Meanwhile, Pb(II) is a heavy metal and a cause of environmental pollution, with serious health implications, including impaired kidney, heart and cerebrum functions (Adhani and Husaini, 2017; Zhang *et al.*, 2016). The accumulation of Pb(II) tends to originate from rocks resulting from non-ferrous mining and smelting, combustion of leaded gasoline, as well as wall paint (Alloway, 2013; Mielke *et al.*, 2011; Xing *et al.*, 2020).

In this study, ferrocene was used as a modifier in carbon paste electrode for determining Pb(II) content, and the optimized parameters were ferrocene composition and scan rate. Subsequently, measurements were validated using CPE and CPE-Fc, to determine the working electrode's performance, including the range of linear concentration, limits of detection and quantization, as well as precision and accuracy. The modified working electrode at the optimum condition was then used to determine the level of Pb(II) in kepok banana sample. Kepok bananas are widely consumed by people due to market availability, ability to be processed into various types of food, low cost. Meanwhile, Pb is a very poisonous heavy metal, often accumulated in air, soil as well as water, and this tends to pollute the surrounding environment, including banana plants.

## 2. MATERIALS AND METHODS

### Instruments and Materials

The equipment used for voltammetry measurement in this study include, a potentiostat Ingsens 1030 with a three-electrode system, Cu wire of 1.0 mm diameter (Nilaco) inserted in a teflon tube of diameter 2.0 mm as the working electrode, handmade Ag/AgCl reference electrode (KCl 0.1 M) with Ag wire diameter 0.5 mm (Nilaco) and glass tubes with a porous G3 membrane as the reference electrode tube, Pt coil diameter 0.5 mm (Nilaco) as counter electrode, analytical balance (Shimadzu ATY224), magnetic stirrer, micropipette, DC adapter, oven (Memmert), mortar agate, ZX metal block digester and glass wares.

Graphite powder, KCl, paraffin liquid, and ferrocene ( $\text{Fe}(\text{C}_5\text{H}_5)_2$ ) were procured from Wako, while HCl,  $\text{HNO}_3$ ,  $\text{Pb}(\text{NO}_3)_2$ , were obtained from Merck. All the chemicals were

of analytical grade and therefore used without further purification. Furthermore, double-distilled water was used to create stock and tested solutions, while the *kepok* banana samples were purchased from a local market in Denpasar, Bali, and all experiments were conducted at room temperature ( $25 \pm 1$ ) °C.

### Optimization of Measurement Conditions Fabrication Of Ferrocene Modified Carbon Paste Electrodes

Carbon paste electrode was created by mixing graphite and ferrocene with a composition of 0.0; 0.2; 0.4; 0.6; 0.7; 0.8; 0.9; 1.0; 1.2; and 1.4% of the total weight of 100 mg graphite and ferrocene, and adding 45  $\mu\text{L}$  of paraffin liquid. The mixture was then homogenized in an agate mortar and the carbon paste was pressed into the electrode body's cavity. Subsequently, the paste's surface was polished on a weighing paper until flat and shiny. The working, reference, and counter electrodes were then immersed into a voltammeter cell, containing 10.0 mL of standard solution Pb(II) 500  $\mu\text{g/L}$  dissolved in 0.1 M  $\text{HNO}_3$ , as supporting electrolyte, while the peak current was measured using DPV technique, in three replicates.

### Scan Rate Optimization

The scan rate was optimized by measuring peak current with scan rates variation of 5; 10; 15; 20; 25; and 30 V/s, using a 10.0 mL Pb(II) 500  $\mu\text{g/L}$  testing solution.

### Validation of Measurement

#### Linear Concentration Ranges, Limit of Detection and Limit of Quantization

The concentration ranges was observed with concentrations of 5, 10, 20, 50, 100, 200, 500, 1000, 1500, as well as 2000  $\mu\text{g/L}$ , and the linear concentration range was deemed acceptable in cases where the correlation coefficient ( $R^2$ ) was close to 1.00 (Miller and Miller, 2010). In addition, the limit of detection (LoD) and limit of quantization (LoQ) were calculated using the equation below (Miller and Miller, 2010).

$$L_oD = y_b + 3 S_B \quad (1)$$

$$L_oQ = y_b + 10 S_B \quad (2)$$

$$S_B = \frac{S_{y/x}}{\sqrt{\sum(x_i - \bar{x})^2}} \quad (3)$$

$$S_{y/x} = \sqrt{\frac{\sum(y_i - \hat{y}_i)^2}{n-2}} \quad (4)$$

Where,  $y_b$  denotes the blank solution's peak current response,  $S_B$  represents the standard deviation of slope,  $S_{y/x}$  represents a random error in the y direction, and the  $\hat{y}$ -values (or 'fitted' y-values) are the points on the calculated regression line corresponding to the individual x-values. The  $\hat{y}$  -value for a given value of x is readily calculated from the regression equation below.

$$\hat{y} = a + bx \quad (5)$$

Where, a and b represent the intercept and slope, respectively.

### Determination of Repeatability Measurements

Repeatability describes the precision of within-run replicates. For this process, 10.0 mL of a standard solution of Pb(II) 500  $\mu\text{g/L}$  in 0.1 M HCl was used a test solution, with 10 replicates. The repeatability of measurements was determined by calculating the Horwitz Ratio (HorRat), and this is the ratio of the coefficient of variance (CV calculated) and CV Horwitz.

$$SD = \sqrt{\frac{\sum(x - \bar{x})^2}{n-1}} \quad (6)$$

$$RSD = \frac{SD}{\bar{x}} \quad (7)$$

$$CV \text{ calculated} = RSD \times 100\% \quad (8)$$

$$CV \text{ Horwitz} = 2^{1-(0.5 \log C)} \quad (9)$$

$$\text{Rasio Horwitz} = \frac{CV \text{ calculated}}{CV \text{ Horwitz}} \quad (10)$$

Where, SD represents standard deviation, RSD denotes relative standard deviation, and c signifies the mass ratio (e.g. mg/g=0.001), according to the approximate and empirical equation. A Horwitz Ratio value below 2 is generally regarded as a satisfactory performance (Miller and Miller, 2010; Horwitz and Albert, 2006).

Subsequently, the data from the determination of repeatability of

measurements were further analysed by Analysis of Variance (ANOVA) calculation to determine the significance of the measurement results, using the same electrodes (within CPE or CPE-Fc) and different electrodes (between CPE and CPE-Fc). The F value was then determined using the equation below.

$$MSB = \frac{SSB}{k-1} \quad (11)$$

$$SSB = \sum_{k=1}^k n_i (\bar{x}_i - \bar{x})^2 \quad (12)$$

$$MSW = \frac{SSW}{N-k} \quad (13)$$

$$SSW = \sum_{l=1}^K \sum_{j=1}^{N_j} (\bar{x}_l - \bar{x})^2 \quad (14)$$

$$F \text{ calculate} = \frac{MSB}{MSW} \quad (15)$$

$$F\alpha = F \text{ table in } \frac{df \text{ MSB}}{df \text{ MSW}} \alpha = 0.05 \quad (16)$$

Where, MSB represents Means Squares Between Variance, SSB denotes Sum of Squares Between, MSW signifies Mean Squares Within Variance, SSW connotes the Sum of Square Within. In addition, N represents the number of samples in the entire population,  $n_i$  signifies the number of samples in population i, and k connotes the total population. The measurement results were declared significantly different in cases where the calculated F value was greater, compared to the F table counterpart (Hseltman, 2012).

### Percent Recovery

The percent value of recovery was calculated to determine the accuracy of the measurement. This was carried out by comparing standard solution concentrations measured by the presence of sample solution as a matrix as well as the standard concentration of the counting result. The percentage value of acceptable recovery is in the range of 80-110% (AOAC, 1998).

### Pb(II) Metal Analysis in Kepok Banana Samples

*Kepok* banana samples were obtained from a traditional market in Denpasar, Bali, then peeled, cut into 2 mm thick flesh, weighed, and oven-dried at 80°C, for an hour. The dry sample was then cooled in a desiccator, weighed, re-heated in the oven,

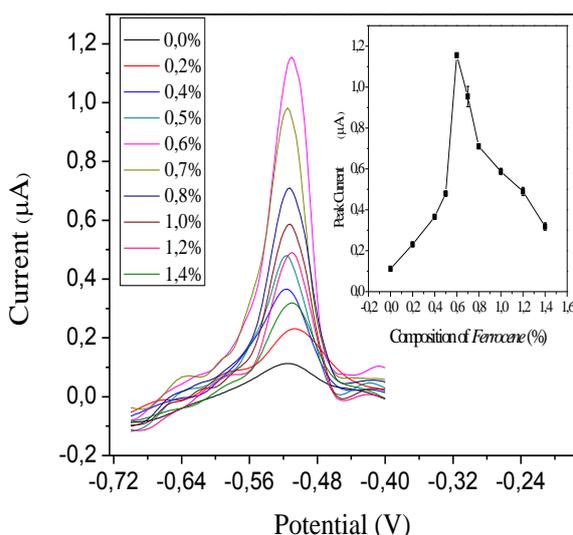
cooled, and weighed until a constant weight was obtained. Moisture content was determined by comparing the weight of the sample before and after heating.

Subsequently, the dried sample was mashed and 2.00 gram of the mashed sample was weighed and transferred into a digestion tube. This was followed by adding 16mL of Aqua regia ( $\text{HNO}_3:\text{HCl} = 4:12$  mL), then digesting in a metal block digester at  $120^\circ\text{C}$ , for  $\pm 1$  hour. After a clear color was observed, the solution was cooled and filtered into a 50.0 mL volumetric flask, then diluted to the mark with double-distilled water.

The Pb(II) content was determined by the standard addition method. For this assay, 2.0 mL digested sample solution was pipetted into five measuring flasks and a standard solution of Pb(II) 1 mg/L with various volume of 0.00; 1.00; 2.00; 3.00; and 5.00 mL, were added. Subsequently 0.1 M  $\text{HNO}_3$  solution was added until the limit mark was reached. The metal content was then measured at the optimum scan rate, using a ferrocene-modified carbon paste electrode as working electrode.

### 3. RESULTS AND DISCUSSION

The ferrocene composition in carbon paste as well as the highest peak response were ascertained. **Figure 1** shows the plot of the graph of ferrocene composition and respective peak current.

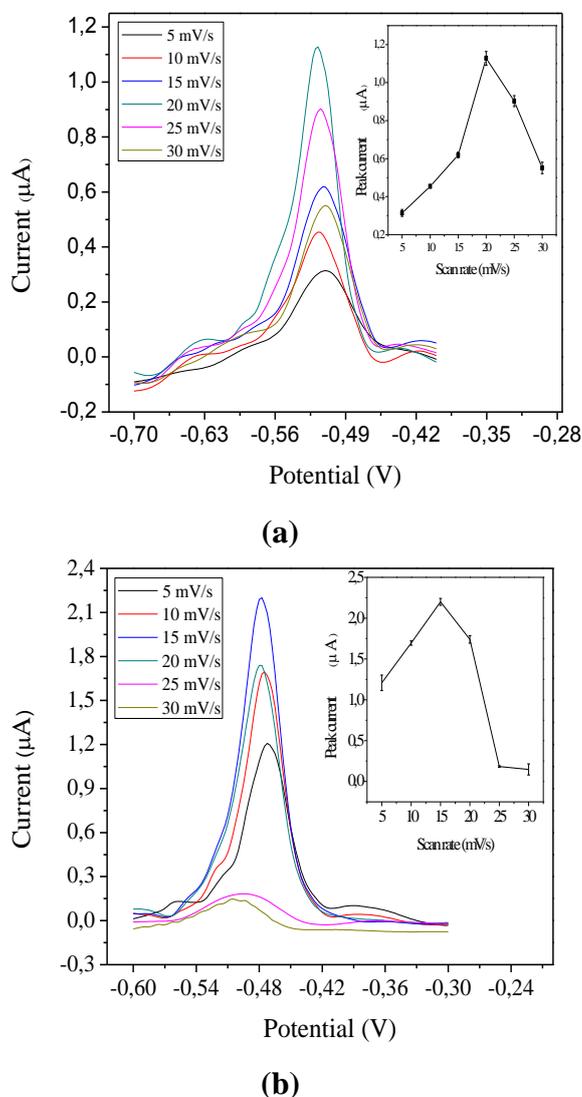


**Figure 1.** Optimize composition of Ferrocene in CPE, the concentration of Pb(II) 500 µg/L, and scan rate at 20 mV/s

According to **Figure 1**, the composition of ferrocene producing an optimum

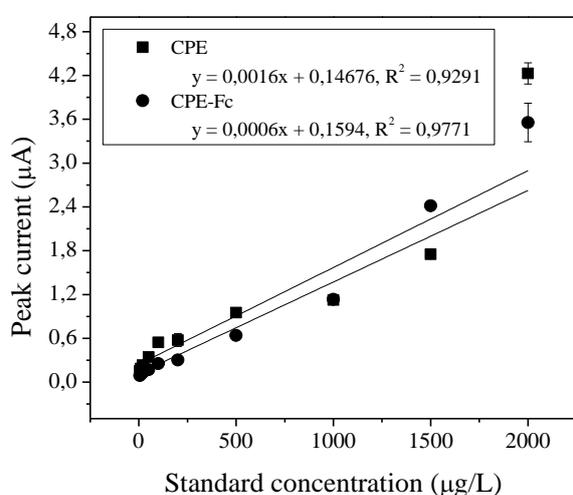
current is 0.6%. Furthermore, the peak currents increased with ferrocene addition, from 0.0% to 0.6%, and decreased after 0.6%. The peak current increased at the ferrocene composition below 0.6%, because the presence of ferrocene aids charge transfer from the solution to the electrode surface. Meanwhile, the peak current decreases at the ferrocene composition greater than 0.6%, because ferrocene blocks the distance of the graphite particles, causing a reduction in conductivity.

A comparison of the peak potential of carbon paste electrode without modification with the counterpart modified by different ferrocene compositions showed the same value of 0.5 V. Thus, there was no energy difference from the reactions occurring on the surface of electrodes using CPE and CPE-Fc.

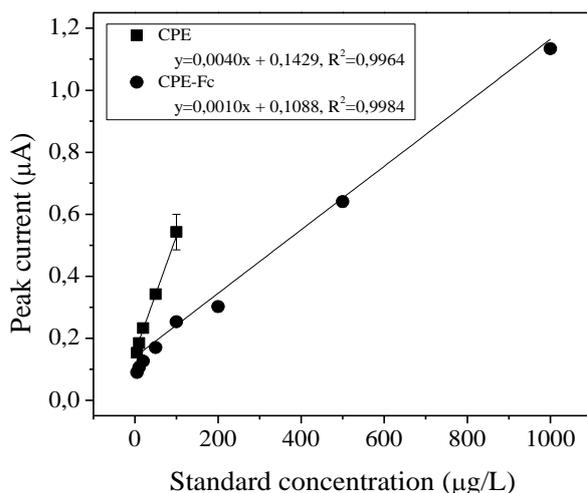


**Figure 2.** Voltammogram and plot between scan rate and peak current using CPE (a) and CPE-Fc (b). The concentration of Pb(II) 500 µg/L and 0.6% ferrocene in carbon paste (CPE-Fc)

The scan rate optimization was performed to find out the best scan rate with the highest peak current. Figure 2 shows the results of optimization of scan rate measurement of Pb(II). The optimum scan rate using CPE was found to be 15 mV/s, while the CPE-Fc counterpart was 20 mV/s. The presence of ferrocene as a modifier in the carbon paste electrode increased the electron transfer rate, and consequently, the scan rate. The peak potential obtained using CPE was -0.48 and a left shift to -0.51 was observed using CPE-Fc. This shows the modifier of CPE was able to reduce the energy transfer of electrons on the electrode surface (Liu *et al.*, 2013).



(a)



(b)

**Figure 3.** Observed concentration ranges between 5-2000 µg/L (a) and linear concentration ranges for CPE at 5-100 µg/L and CPE-Fc at 5-1000 µg/L.

The linear concentration range was calculated to determine the concentration range relating significantly with the signal produced by the instrument. **Figure 3** show the results of determination of linear concentration range, using CPE and CPE-Fc.

In Figure 3(a), the correlation coefficient ( $R^2$ ) obtained in the range of 5-2000 µg/L for CPE and CPE-Fc were 0.9291 and 0.9771, respectively. In Figure 3(b), the correlation coefficient ( $R^2$ ) of CPE in the range at 5-100 µg/L was 0.9964, while CPE-Fc had a wider range at 5-1000 µg/L, with a correlation coefficient ( $R^2$ ) of 0.9984. This shows the addition of ferrocene in carbon paste increased the significance between the rise in concentration and the resulting peak current.

Generally, an analyte's limit of detection of an is described as the concentration where an instrument signal ( $y$ ) significantly different from the 'blank' or 'background' signal, is obtained. The limit of quantitation (or limit of determination) is regarded as the lower limit for precise quantitative measurements (Miller and Miller, 2010). In this study, the LoD and LoQ values generated at CPE were 0.1551 and 0.1564 µg/L, while the CPE-Fc counterparts, 0.1089 and 0.1091 µg/L, were lower. Thus, the sensitivity of measurements using CPE-Fc was concluded to be better, compared to CPE.

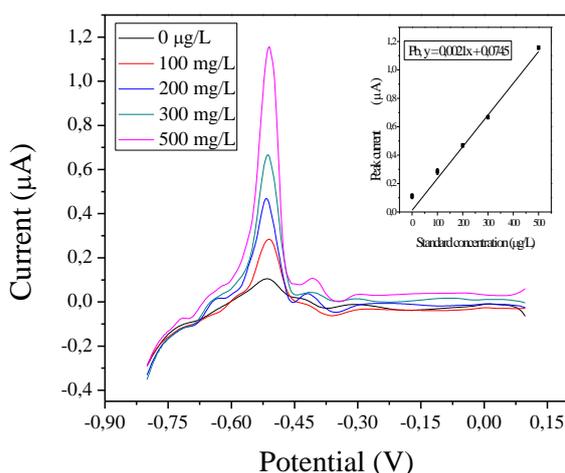
The measurement repeatability showed the degree of concordance between same individual test results, measured through the distribution of individual results from the average in cases where the procedure was performed repeatedly (Horwitz and Albert, 2006). In this study, the measurement of the peak current of the 500 µg/L standard Pb(II) solution was repeated ten times, using CPE and CPE-Fc. The results of HorRat values obtained were 0.1419 and 0.1568, respectively, and both are below 2. Thus, the results of determining the repeatability of the measurement were adequate (accuracy).

The result of Analysis of Variance (ANOVA) calculation gave an F value for Pb(II) of 976.5541 and this is much greater than the F table counterpart of 4.4139. This shows the addition of a modifier to the working electrode has a significant effect on the peak current generated (Hseltman, 2012).

The percentage recovery value was discovered to be  $85.59 \pm 8.18\%$ , using CPE-Fc. This value was within the range of

acceptable precision of 80-110% (AOAC, 1998), and therefore indicates the accuracy of the measurement results obtained using CPE-Fc. Thus, the results of determining the percentage of recovery are acceptable.

**Figure 4** shows the voltammograms of Pb(II) content determination in kapok banana, and the standard addition calibration curve, using CPE-Fc 0.6% as working electrode. The linear regression equation obtained was  $y = 0.0021x + 0.0777$ , with a correlation coefficient of 0.9966. Based on the calculation result obtained, the concentration of Pb(II) in the kapok banana was  $4.4306 \pm 0.0009$  mg/kg. According to the Indonesian Standard National (ISN) No. 7387: 2009, for the Maximum Limit Contamination of Heavy Metals in Food, the acceptable value for Pb(II) content is below 0.5 mg/L. Therefore, the Pb(II) content of kapok banana exceeds the permissible limit.



**Figure 4.** Voltammogram and standard addition curve of Pb(II) measurement in kapok banana.

#### 4. CONCLUSION

The addition of ferrocene as modifier in carbon paste electrode is able to increase the response of peak current. Furthermore, the validation of the Pb(II) measurements using CPE-Fc as working electrode is better, compared to CPE. Also, the metal concentration of Pb(II) in kapok banana is beyond the acceptable limit.

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