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Carbon Paste Electrode Modified by Dibenzo 18-crown-6 for the Determination of Pb in Carrot Using Differential Pulse Voltammetry

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Abstract: In this research, modification of carbon paste electrode (CPE) using dibenzo 18-crown-6 was carried out to detect Pb level in carrot. The purpose of this electrode modification is to increase the sensitivity of the measurement. The optimized parameters were scan rate, composition of dibenzo 18-crown-6 in carbon paste, and supporting electrolyte. Measurements were validated by determining the linear concentration range, detection limit (LoD), quantification limit (LoQ), repeatability, selectivity, and recovery. At the best measurement conditions, the modified CPE (CPE-Dbc) was applied to determine Pb in carrot. The optimum measurements conditions were obtained the optimum concentration of crown ether in carbon paste was 0.8%, the scan rate using CPE at 15 mV/s, increased to 20 mV/s, and H_2SO_4 solution as supporting electrolyte. The linear concentration was found in the range of 5-100 µg/L using CPE and became wider to 5-2000 µg/L using CPE-Dbc. The values of LoD and LoQ measurement using CPE were 0.3575 µg/L and 0.3583 µg/L, and decreased to 0.1265 µg/L and 0.1266 µg/L using CPE-Dbc. CPE and CPE-Dbc had good precision with Horwitz ratio values were 0.2231 and 0.2183, which is smaller than two. The percentage of recovery of Pb in the mixture of standard and sample solutions was (88.97 ± 2.76)%. The presence of Cu, Cd and Na in the solution did not interfere the measurement of Pb. The concentration of Pb in carrot sample was (1.8423 ± 0.0002) mg/kg, which was higher than the acceptable concentration according to SNI No. 7387:2009, which is 0.5 mg/kg.

Keywords: Carbon paste electrode, carrot, dibenzo 18-crown-6, differential pulse voltammetry, lead (Pb), validation

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1. INTRODUCTION

Voltammetry is one of the techniques of chemical analysis that is often used to determine metal concentrations in trace levels. The method has advantages, namely it is efficient, highly sensitive, and inexpensive compared to other methods (1). Several previous studies using voltammetry method in the analysis of Pb have been carried out by researchers (2-4). Determination of Pb levels in plants using anodic stripping voltammetry obtained a detection limit value of bare electrode was found at 112.10 µg/L and activated carbon from coconut husk modified CPE was found at 0.72 µg/L in the linear range concentration of 0-1100 µg/L (5). The result of Pb detection using crosslinked chitosan/carbon nanotubes thin film electrodes obtained at the concentration range of 0.63–3.70 mg/L with limit of detection 0.6 mg/L (R^2 = 0.972) (6). LoD and LoQ of Pb using silver nanoparticle modified graphene paste electrode were 12 µg/L and 36 µg/L in linear range concentration of 100-900 µg/L (R^2 = 0.9928) (7).

In voltammetry, the working electrode can be modified to improve the performance and lower the detection limit. Some of the modifier materials can be used to analyze Pb, such as activated clay, biopolymer lignin, and crown ether (8-10). Crown ether can bind metals and form stable complexes because they have a cavity in the middle so that able to trap metal ion in the appropriate size (11).

These properties of crown ether can increase the current response of Pb(II) measurement.

The previous studies of Pb(II) determination using modified carbon paste electrode were conducted by researchers, and found different LoD within certain linear range concentration. Measurement of Pb(II) ion using crown ether modified carbon paste electrodes (5% in graphite) had detection limit of 0.11 µg/L at the range of 0.5-60 µg/kg (12). 4-carboxybenzo-18-crown-6 graphite-epoxy composite electrodes for Pb(II) measurement had linear range concentration from 5.0- 186.5 µg/L and LoD value was 1.5. 4-carboxybenzo-15-crown-5 graphite-epoxy composite electrodes had linear range concentration of 10.9-186.5 µg/L and LoD at 3.3 (10). The voltammetric response of N-(2-hydroxypropyl)methacrylamide-co-N-acryloxysuccinimide with 2-aminomethyl-18-crown-6 (p(HPMA-NAS18C6))-modified electrode had linear response in the interval of 0.01–4.39 mg/L Pb(II), and LoD: 0.17 µg/L (13). Screen-printed carbon paste modified with siloxane–crown ether polyamide was used for Pb measurement and had linear concentration range from 50–2760 µg/L and LoD at 30 µg/L (14).

Dibenzo 18-crown-6 (crown ether) is a group of macrocyclic compounds, can form stable complexes with alkali metals, and bind metals and organic ammonium cations (11). These properties indicate that dibenzo 18-crown-6 can be used as a chelating agent with Pb to form a complex. The development of crown ether-based molecular assemblies for the analysis of alkali and heavy metal ions is getting increase. Crown ethers are often used as ionophores for ion-selective electrodes. Electrodes modified with dibenzo-18-crown-6 (CPE-Dbc) are capable for measuring of Pb(II) ion at concentrations below 10 mg/L in the presence of other interfering metal ions, except for Al(III) and Hg(II) which can affect the peak current of Pb(II) measurement significantly (15).

In the development method, validation is very important to determine the performance of the modified working electrode. The validation parameters include a linear concentration range, limit of detection (LoD), limit of quantification (LoQ), precision, accuracy, and selectivity of measurements. Another factor in measuring the peak current of the analyte, is supporting electrolyte solution to reduce the migration current. The choice of a supporting electrolyte solution is very important because solution is a medium for ionization, reduction, and oxidation processes (1). The presence of ions with the same charge or similar atomic radius can produce current response, in addition to the response of the target analyte. The effect of interference ions can be observed by calculating the selectivity coefficient (Kij) (16). A modified carbon paste electrode with bigarreau burlat kernel shell (BBKS-CPE) was used for the simultaneous analysis of the same charge ions, i.e. Cd(II), Pb(II) and Cu(II) and obtained a good peak separation (17).

Pb can be produced from various human activities, such as forest fires, air pollution from fuel, industrial waste, and use of fertilizers and pesticides (18). If Pb accumulated in the human body, can cause acute and chronic health problems. Some of the effects of Pb to the human body are damage to the kidneys, testes, liver, nervous system, immune system, and blood (19). Therefore, the detection of Pb in the food and environment needs a selective and sensitive method.

In this study, dibenzo-18-crown-6 was use as a modifier in carbon paste electrode. The concentration of dibenzo-18-crown-6, scan rate, and supporting electrolyte were optimized. Linear concentration range, LoD, LoQ, precision, accuracy, and selectivity of measurement were observed to determine the performance of working electrode in Pb determination. Furthermore, working electrode modified with dibenzo 18-crown-6 were applied to determine the concentration of Pb in carrots from Bedugul vegetable plantation, Tabanan-Bali.

2. MATERIALS AND METHOD

2.1. Chemicals and Tools

The voltammograms were recorded by an Ingsens potentiostat 1030 (China), DC 12 V adaptor, Ag/AgCl electrode (KCl 0.1 M) as a reference electrode, platinum electrode as counter electrode (Nilaco), analytical balance (Ohaus PX224), magnetic stirrer (Thermoline), micro pipette (Socorex), copper wire Ø 2,0 mm (Nilaco), Teflon tube, Metal block digester ZX, oven, and mortar agate.

HNO_3, HCl, $Pb(NO_3)_2$, $3CdSO_4.8H_2O$, $CuSO_4.5H_2O$, $K_3Fe(CN)_6$, $K_4Fe(CN)_6.3H_2O$, H_2SO_4, H_3PO_4, $NaH_2PO_4.2H_2O$, $Na_2HPO_4.12H_2O$, $CH_3COONa.3H_2O$, and CH_3COOH were purchased from Merck, NaCl, KCl, graphite, liquid paraffin, and dibenzo-18-*crown*-6 were obtained from Wako, and carrot sample was taken from vegetable plantations in the Bedugul area, Tabanan, Bali.

2.2. Optimization of Dibenzo-18-crown-6 Concentration in Carbon Paste

The working electrode body was made by inserting a 1 mm Cu wire into a Teflon tube, and leaving an empty space at the bottom of about ±5 mm for the carbon paste. 100 mg of graphite and 45 µL of liquid paraffin were mixed until homogeneous in an agate mortar. The carbon paste was inserted into the empty space in the working electrode body. The surface of electrode was smoothed by polishing on the wax paper until shiny (CPE). A modified CPE was prepared by adding dibenzo 18-crown-6 to a carbon paste in concentration of 0.2; 0.4; 0.5; 0.6; 0.7; 0.8; 1.0; 1.2 and 1.4% of the total mass of graphite and dibenzo 18-crown-6, respectively, and continued with the same way with CPE. The working electrode, reference electrode, and counter electrode were immersed into a voltammetric cell containing 10.0 mL of Pb 500 µg/L. Next, the three electrodes were connected to a potentiostat and current measurements were made by DPV, as parameters in

Table 1. The measurement replicated three times for each concentration of dibenzo-18-crown-6.

Table 1: Parameters of current measurement in various concentrations of dibenzo 18-crown-6 in carbon paste.

Parameter	**Values**
Potential Range (mV)	650 s/d -400
Pulse increment (mV)	2.5
Pulse amplitude (mV)	37.5
Scan rate (mV/s)	15

The optimum concentration of dibenzo 18-crown-6 in carbon paste is the composition that produces the highest peak current.

2.3. Optimization of Scan Rate

The CPE/modified CPE at the optimum concentration of dibenzo-18-crown-6 as working electrodes, into a voltammetric cell containing 10.0 mL of a 500 μg/L metal standard solution. The solution was measured with various scan rate of 5; 10; 15; 20; 25; and 30 mV/s. The optimum scan rate was determined from the highest peak current.

2.4. The Effect of Supporting Electrolyte

The solution Pb(II) 500 μg/L was made in several types of 0.1 M supporting electrolytes i.e. HCl, HNO_3, H_2SO_4, H_3PO_4, acetic acid, NaCl, KCl, phosphate buffer, and acetate buffer. The peak current was measured for each supporting electrolyte and the current response was recorded by DPV technique. The supporting electrolyte with the highest peak current was used for the next experiment.

2.5. Linear Concentration Range, LoD, and LoQ

Linearity is a concentration range that has a correlation coefficient value close to 1.00 (20). In this work, the linearity was studied in the range of 5-2000 μg/L. The line equation obtained from the linear concentration range was used to calculate LoD and LoQ with the following equation.

$$\text{LoD} = y_B + 3\, s_B \quad (1)$$

$$\text{LoQ} = y_B + 10\, s_B \quad (2)$$

$$s_B = \frac{S_{y/x}}{\sqrt{\Sigma\left(x-\bar{x}\right)^2}} \quad (3)$$

$$S_{y/x} = \sqrt{\frac{\Sigma\left(yi-\hat{y}i\right)^2}{n-2}} \quad (4)$$

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

Description: y_B is the intercept, S_B is the relative error of the slope, $\hat{y}$ value obtained from the substitution of concentration value to the linear equation, y_i is the peak current measured, and n is the number of measurements (20).

2.6. Repeatability (Precision)

The repeatability of measurement was determined by measuring the concentration of Pb(II) 500 μg/L ten times, the Horwitz ratio value was calculated. A precision is acceptable if the value of the Horwitz ratio is less than two (21). The Horwitz ratio is calculated by the following equation.

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

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

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

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

$$\text{Horwitz Ratio} = \frac{CVcount}{CV\ Horwitz} \quad (10)$$

The variable of x is the peak current for each measurement, $\bar{x}$ is the average of peak currents, n is the number of measurements, and C is the concentration fraction of the standard solution. One Way Analysis of Variance (ANOVA) test was used to determine the significance of the peak current, between and within of measurement results. The peak currents were measured using the same type of working electrodes with several measurements (within CPE or CPE-Dbc), and different electrode (between CPE and CPE-Dbc), then the F value is calculated and compared with the F table. The calculated F value is determined by the following equation (22).

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

$$\text{MSW} = \frac{SSW}{N-k} \quad (12)$$

$$\text{SSB} = \sum_{i=1}^{k} n_i\left(\bar{x}_i-\bar{x}\right)^2 \quad (13)$$

$$\text{SSW} = \sum_{i=1}^{k}\sum_{j=1}^{nj}\left(\bar{x}_{ij}-\bar{x}_i\right)^2 \quad (14)$$

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

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

Description: MSB is the Mean Squares Between Variance, MSW is the Mean Squares Within Variance, SSB is the Sum of Squares Between, SSW is the Sum of Squares Within, N is the total sample of the entire population, ni is the number of population samples i, k is the total population or group, $\bar{x}$ is the total mean, and α is the error level. A good precision is obtained if the Fcount value is smaller than Ftable (22).

2.7. Percentage of Recovery (Accuracy)

The percent recovery was calculated by comparing the measured and known of standard concentration in the presence of sample as a matrix in solution. An accuracy value is good if the percentage of recovery is in the range of 80-110% (23).

$$\text{Recovery} = \frac{(concentration\ of\ sample + standard\ measured) - (concentration\ of\ sample)}{concentration\ of\ known\ standard} \times 100\,\% \quad (17)$$

2.8. Selectivity Coefficient

The selectivity of Pb(II) was determined by calculating the current response of Pb(II) in the presence of interference ions of Cu(II), Cd(II), and Na(I). The current response was measured in separated and mixed solution methods, as recommended by IUPAC (24). The main concentration of Pb(II), and the interfering ions Cd(II), Cu(II), and Na(I) were varied, i.e. 100; 300; 500; and 1000 µg/L. In the separated solution method, the voltammograms of target and interference ions were recorded separately, but in mixed solution method, the target and interference ions were mixed before measurement. The selectivity coefficient (K_{ij}) is calculated by:

$$\log K_{ij}^{pot} = \frac{E_{i-E_j}}{2{,}3030\,RT/zF} \quad (17)$$

$$K_{ij}^{pot} = \frac{\left(e^{\Delta E\, z_i/RT} - 1\right)_{a_i}}{a_j^{zi/zj}} \quad (18)$$

K_{ij}^{pot} is selectivity coefficient of target to interference ions, E_i is peak potential of target ion, E_j is the peak potential of interference ion, z is charge of ion, a_i and a_j are the acitivity of target and interference ions, R: the gas constant (8.314 J mol^{-1} K^{-1}), T: temperature (K), and F: 96.5 KJ mol^{-1}. A good selectivity or peak potential resolution is obtained if the value of K_{ij} is less than one (25).

2.9. Sample Analysis

The carrots sample was taken from a vegetable plantation in the Bedugul area, Baturiti District, Tabanan, Bali, Indonesia, with coordinates location at 8°15'15.2"S 115°09'27.7"E. The samples were washed and cut to a thickness of ± 2 mm and dried at room temperature for 24 hours. The samples were weighed and then dried in an oven at 80˚C for 1 hour. The sample was cooled in a desiccator and weighed, dried and weighed again until a constant mass was obtained. Furthermore, the water content in the sample was calculated.

The dry sample was crushed and weighed around 2 gram and transferred into a digestion tube. 16 mL of aqua regia (HNO_3: HCl= 4:12) was pipetted into a digestion tube to dilute the sample and heated in a metal block digester at temperature of 120 °C during ± 60 minutes. The digested sample solution was cooled, filtered, and the filtrate was moved into a 50.0 mL volumetric flask and diluted with double distilled water to the mark.

Sample solution was analyzed by standard addition method. 2.0 mL of sample solution was pipetted into 10.0 mL volumetric flask and added standard solution of Pb(II) 1 mg/L with various volume, then diluted up to the mark. The peak current for each solution were measured. The concentration of Pb(II) in the carrot sample was calculated by extrapolated the linear regression line to the axis. The analyte concentration in the sample is –Cs = Cx, Cs is the standard concentration and Cx is the sample concentration after dilution.

3. RESULTS AND DISCUSSION

3.1. Optimization of Dibenzo-18-crown-6 Concentration in Carbon Paste

The optimum concentration of dibenzo-18-crown-6 in carbon paste is shown in Figure 1.

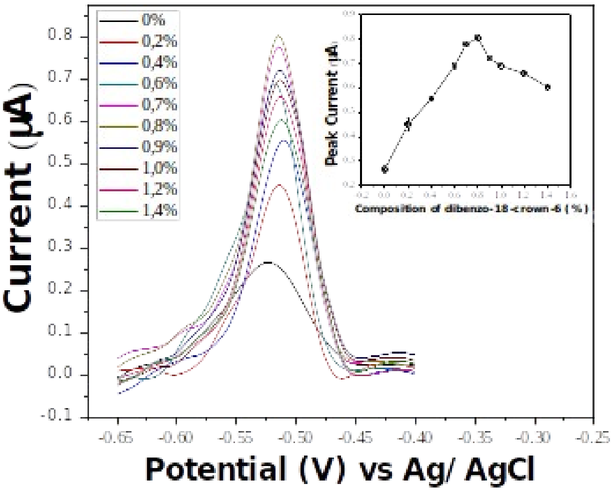


Figure 1: Voltammogram and plot between the concentration of the dibenzo 18-crown-6 in carbon paste, against the peak current.

Figure 1 showed the highest peak current was obtained at 0,8% dibenzo-18-crown-6 in carbon paste. The peak current increased from 0.2% up to 0.8% then decreased on the concentration higher than 0.8%. The peak current response using CPE-Dbc in various concentrations of dibenzo-18-crown-6 getting increased at the same potential around -0.50 V. It was indicated that the redox reaction of Pb(II) in presence of dibenzo-18-crown-6 in carbon paste was stable. The complex formation reaction of Pb(II) and dibenzo-18-crown 6 can be seen in Figure 2.

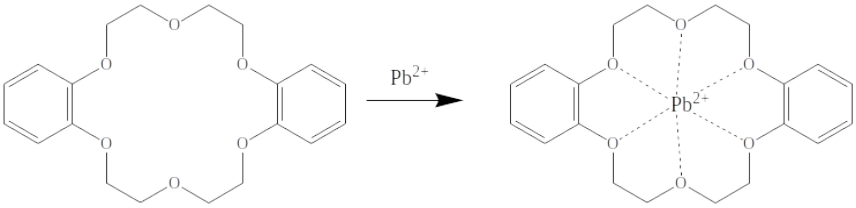
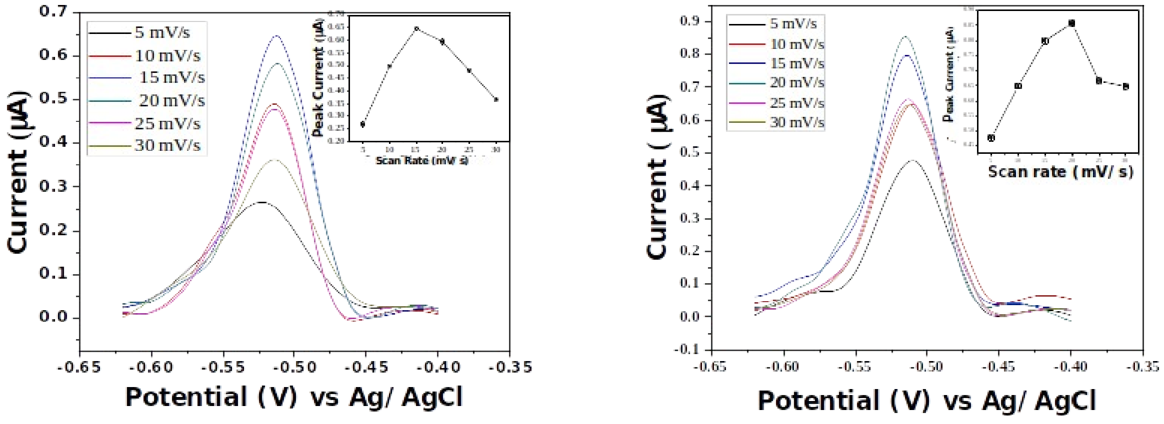


Figure 2: Complex formation reaction of dibenzo-18-crown-6 and Pb(II).

Dibenzo-18-crown-6 has an effect on the peak current in the voltammogram was caused by the presence of two benzene rings can reduce the polarity. Therefore dibenzo-18-crown-6 can be dissolved in paraffin (26). Dibenzo-18-crown-6 formed a stable complex compound with Pb(II) metal due to the cavity, which is able to trap appropriate size of metal ion (11) as shown in Figure 2.

3.2. Optimization of Scan Rate

Optimum scan rate was measured to determine the redox reaction rate which has highest current response. The voltammogram of Pb(II) at various scan rates was showed in Figure 3, using CPE and CPE-Dbc.



(a) **(b)**

Figure 3: Voltammogram in the determination of optimum scan rate using CPE (a) and CPE-Dbc (b).

Figure 3 showed the optimum scan rate using CPE was found at 15 mV/s, with a peak current of 0.6470, and optimum scan rate become faster to be 20 mV/s with a higher peak current of 0.8561 using CPE-Dbc. The addition of dibenzo-18-crown-6 in carbon paste can accelerate the transfer of electrons at the electrode surface.

3.3. The Effect of Supporting Electrolyte

The current response of Pb(II) measurement using different supporting electrolyte as shown in Figure 4.

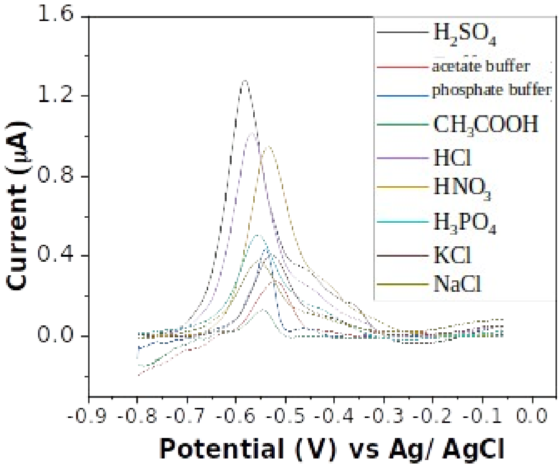


Figure 4: Voltammogram of Pb(II) Measurement in Different Supporting Electrolytes.

The order of peak currents from the highest to the lowest were H_2SO_4> HCl > HNO_3> H_3PO_4> phosphate buffer > KCl > NaCl > acetic buffer > acetic acid. The result showed the higher peak current response was found in strong acid electrolyte solutions, compared to the weak acids, inorganic salts, phosphate, and acetic buffer solutions. This is caused by Pb(II) completely dissociating in low pH, and strong acid solution has high concuctivity as well. Sulfuric acid solution has higher peak current than HCl and HNO_3 because H_2SO_4 is a diprotic acid which can deliver the current more than others.

3.4. Linear Concentration Range, LoD, and LoQ

The significant current response and concentration can be determine from the linearity of regression line. The observation of linear concentration range can be seen in Figure 5.

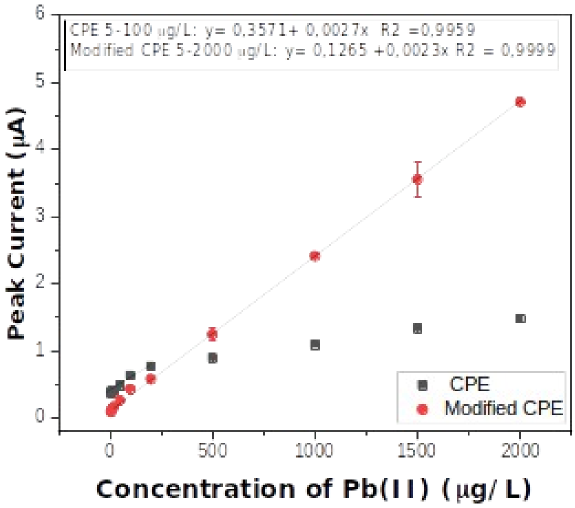


Figure 5: Linear Concentration Range of Pb(II) using CPE and modified CPE with dibenzo-18-crown-6.

Figure 4 shows that the linearity using CPE as working electrode was found in the range of 5-100 g/L with R^2= 0.9959 and increased to 5-2000 g/L using modified CPE by 18-crown-6 dibenzo, with R^2= 0.9999. This shows that the addition of dibenzo 18-crown-6 in carbon paste can cause the peak current increase significantly with increasing of concentration. The values of determination coefficient (R^2) showed excellent linearity of the calibration curve for the method.

The LoD and LoQ values were obtained using CPE at 0.3575 g/L and 0.3583 g/L, and down to 0.1265 g/L and 0.1266 g/L using CPE-Dbc, respectively. This shows that the modified CPE can be able to detect Pb(II) at lower concentrations, compared with CPE without modification.

3.5. Repeatability (Precision)

The precision determination of Pb(II) measurement using CPE and CPE-Dbc was carried out by ten times peak current recording, performed in different days. The plot between peak current and measurement repeatability as shown in Figure 6.

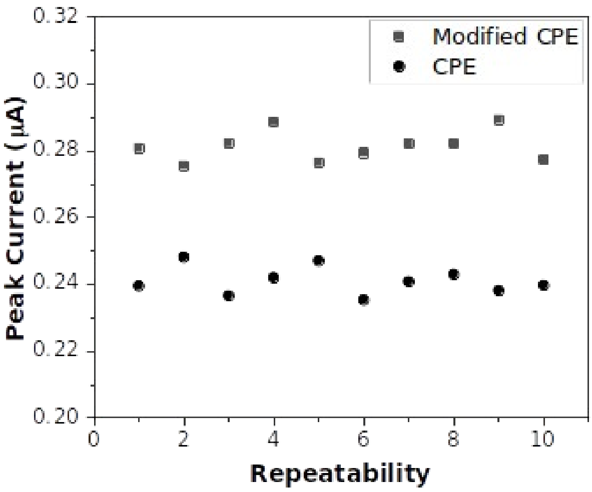


Figure 6: Repeatibility measurements of Pb(II) using CPE and modified CPE.

Measurement repeatability is a measure of the spread of measurement data and can be expressed as variance (27). Measurement of the repeatability of CPE and modified CPE resulted in the Horwitz ratio of 0.2231 and 0.2183, respectively. A good repeatability value is obtained if the Horwitz Ratio (HorRat) value is less than two (21). Both of CPE and modified CPE had good repeatability and met the specified requirements. The result of statistic calculation to determine the significant of peak current in ten times measurements is shown in Table 2.

Table 2: One Way ANOVA on Recurrence using CPE and CPE modified by dibenzo-18-crown-6.

MS Within Group	5.98×10^{-5}
SS Within Group	0.0011
MS Between Group	0.21
SS Between Group	0.2084
$F_{calculated}$	3485.88
FTable	4.41

The obtained result for $F_{calculated}$ is greater than the F_{table} values. This means that the addition of a modifier in the working electrode has a significant different peak current.

3.6. Percentage of Recovery (Accuracy)

The accuracy of an analytical method is based on the closeness of the test results obtained using the proposed method and the true value (20). The accuracy was accessed from three replicate measurements of Pb(II) 50 µg/L. The value of the recovery from standard solution of Pb(II) using CPE-Dbc was (88,97 ± 2,76%). It is evident that the proposed method is accurate within in acceptable range.

3.7. Selectivity Coefficient

Selectivity of measurement is determined by observing the current response of analyte in the presence of interference ions. The calculation of the selectivity coefficient (K_{ij}) aims to show the level of selectivity of the method for measuring the analyte against the interfering ions. The voltammogram of Pb(II) measurements in the presence of Cu(II) and Cd(II) as interference ions were shown in Figure 7 (separated solution), Figure 8 and Figure 9 (mixed solution).

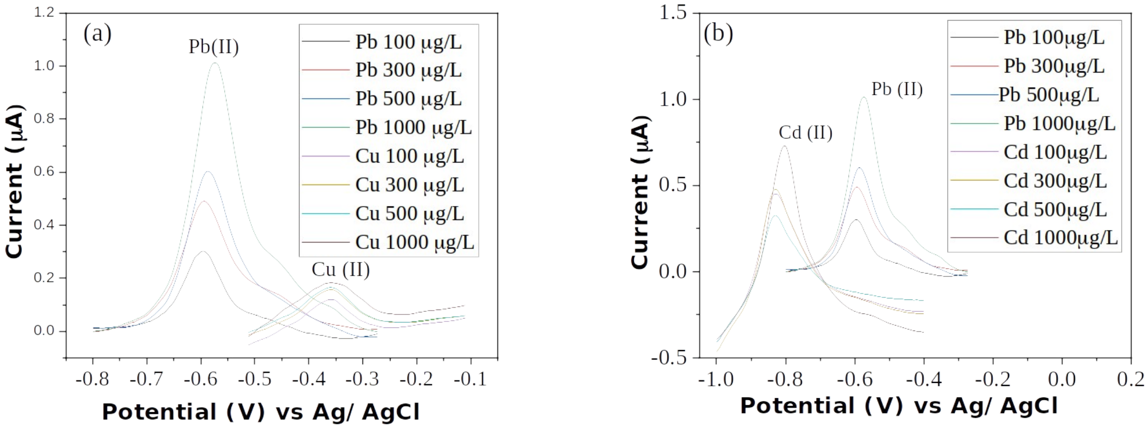


Figure 7: Voltammogram of Determination of Selectivity Coefficient of Pb (II) in the presence of Cu(II) (a) and Cd(II) (b) in Separated Solution.

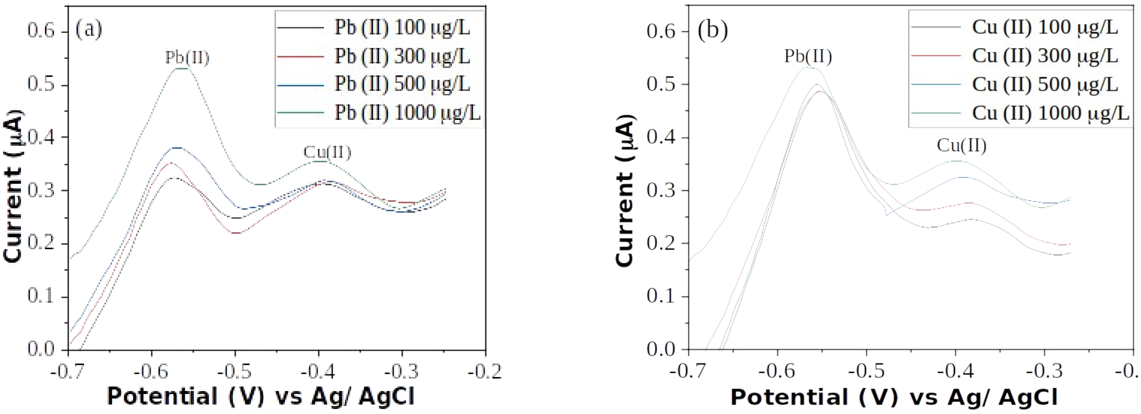


Figure 8: Voltammogram of Determination the Selectivity Coefficient of Pb (II) to Cu(II) with Various Concentration of Pb(II) (a), and Various Concentration of Cu(II) (b) in Mixed Solution

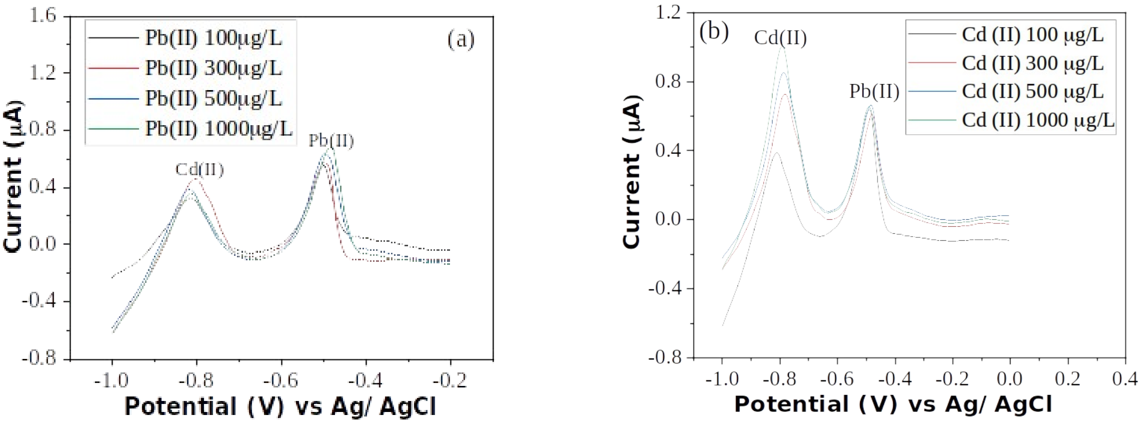


Figure 9: Voltammogram of Determination the Selectivity Coefficient of Pb (II) to Cd(II) with Various Concentration of Pb(II) (a), and Various Concentration of Cd(II) (b) in Mixed Solution

The peak potentials for measurements of Pb(II), Cd(II), and Cu(II) were obtained at -0.5879 V, -0.8288 V, and -0.3585 V, respectively. The peak potential values indicated that the measurement of ion Pb(II) in the presence of interfering ions of Cd(II) and Cu(II) using a dibenzo-18-crown-6 modified carbon paste electrode had good resolution. This is in accordance with the research of Hermouche et al (2021) which found that there was good separation peak potential for Cd(II), Pb(II) and Cu(II) ion simultaneously (17). There was no peak in Na(I) measurement at the potential range of Pb(II) because the standard reduction potential value (E˚) of Na(I) (E˚=-2.73 V) and Pb(II) (E˚=-0.13 V) totally different. The standard reduction potential of Cd(II) (E˚=-0.40 V) and Cu(II) (E˚ =+0.34 V) are close to E˚of Pb(II), and produce peaks in the potential range of measurements. This shows that the standard reduction potential values of ions is the important factor in determining selectivity. The results of selectivity coefficient measurement Pb(II) in the presence of Cu(II) and Cd(II) can be seen in Table 3.

In the separated solution, Kij values were found between 10^{-8} -10^{-9} and in the mixed solution it is between 10^{-5}-10^{-3} for the interfering ions of Cu(II) and Cd(II). The selectivity coefficient in separated solution is smaller than that of the mixed solution. In the mixed solution, there is interaction of analyte and interference in the measurement. In separated solution, no interaction of analyte and interference when measuring current. Theoretically, the electrode is declared selective for interfering ions if selectivity coefficient (Kij) value is less than one (25). The results obtained indicate that the Kij values was less than one from both of separated and mixed solutions. Therefore, this method provides good selectivity for the measurement of Pb(II) in the presence of interfering ions of Cu(II) and Cd(II).

Table 3: Selectivity coefficient of Pb(II) measurement to Cu(II) and Cd(II) at various concentrations.

Concentration of Pb(II) (μg/L)	Concentration of Interference Ions (μg/L)		Selectivity Coefficient(Kij)	
	Cu(II)	Cd(II)	Separated Solution	Mixed Solution
100		500	1.45×10^{-8}	1.23×10^{-3}
300		500	1.45×10^{-8}	1.10×10^{-3}
500		500	8.09×10^{-9}	1.12×10^{-3}
1000		500	3.08×10^{-9}	1.14×10^{-3}
500	100		1.87×10^{-8}	2.23×10^{-4}
500	300		2.00×10^{-8}	2.23×10^{-4}
500	500		2.27×10^{-8}	2.20×10^{-4}
500	1000		1.54×10^{-8}	2.10×10^{-4}
500		100	8.09×10^{-9}	1.12×10^{-3}
500		300	7.59×10^{-9}	1.19×10^{-3}
500		500	8.09×10^{-9}	1.16×10^{-3}
500		1000	7.59×10^{-9}	1.24×10^{-3}
100	500		1.27×10^{-8}	1.04×10^{-4}
300	500		1.64×10^{-8}	1.03×10^{-4}
500	500		2.27×10^{-8}	9.66×10^{-5}
1000	500		6.37×10^{-8}	9.98×10^{-5}

3.8. Sample Analysis

To evaluate the analytical performance of the CPE-Dbc, the quantitative determination of Pb(II) was explored by DPV technique. Before measurement, the water content of carrot sample was observed at (82.8 ± 2.75)%. The digested sample was measured by standard addition method, obtained the voltammogram as shown in Figure 10.

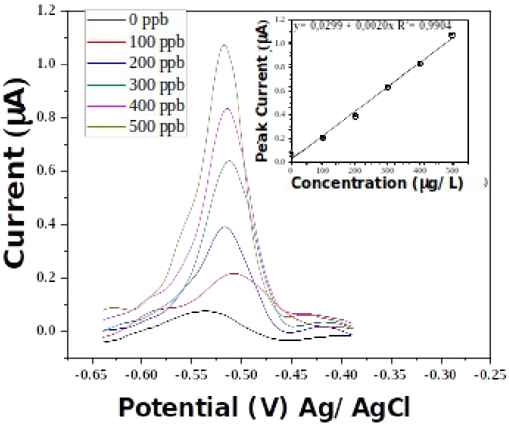


Figure 10: Differential Pulse Voltammogram of CPE-Dbc after the addition of Pb(II) into Sample Solution, and Calibration Plot of Oxidation Peak Currents againts the Concentration of Pb(II).

The potential peak currents were increased with increase in the Pb(II) concentration. The peak current showed a good linear relationship with Pb(II) concentration over the range between 0 to 500 μg/L. The regression line equation from calibration curve was found at y= 0,0299 + 0,0020x and R^2= 0,9904. The obtained result was satisfactory with the recovery range at (88.97 ± 2.76%). The content of Pb(II) in carrot sample was obtained at 1.8423 ± 0.0002 mg/kg. The content of Pb(II) in this sample is due to the location of the plantation close to the highway, so the residual exhaust fumes from motor vehicles containing Pb(II) can be absorbed into the plants. Based on the Indonesian National Standard (SNI) No. 7387:2009, concerning the maximum limit for Pb contamination in fruits and vegetables and their processed products, the acceptable value is maximum 0.5 mg/kg. The concentration of Pb(II) in the carrot sample exceeded the maximum specified limit.

4. CONCLUSION

In summary, CPE modified by 0,8% dibenzo 18-crown-6 was prepared for the detection of Pb(II) in the solution as well as in the real sample of carrot. This working electrode is a highly sensitive, stable, and good electrochemical sensor for Pb(II). The excellent performance of CPE-Dbc is due to the properties of dibenzo-18-crown-6 for complex formation, and excellent conductivity for fast electron transport. Based on the results, CPE-Dbc as working electrode is suitable due to its low cost, high sensitivity, easy preparation, and short time measurement.

5. CONFLICT OF INTEREST

All authors declared no conflicts of interest.

6. ACKNOWLEDGMENT

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