

Short Communication

Determination of Trace Level Copper(II) in Malaysian Vegetables by Cyclic Voltammetry

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The sequential voltammetric measurement using ZLH-CPPA modified CNT paste electrode for the determination of Cu(II) in Malaysian vegetables is proposed. The digestion of vegetable samples was carried out using a concentrated HNO₃ (69 %) and 4×10^{-3} M of CH₃COONa was employed as supporting electrolyte at pH 2.5 and scan rate of 500 mV s⁻¹. The Cu(II) concentrations were found in the range of 0.04–6.88 µg g⁻¹. The levels of Cu(II) found were compared with the results obtained from other food studies in the world.

Keywords: Cu(II), voltammetry, vegetables, ZLH-CPPA modified CNT paste electrode

1. INTRODUCTION

Heavy metal contamination has become a severe threat to human health, because they tend to concentrate in all environmental matrices, in particular those involved in the food chain [1]. Heavy metal may be present in food either naturally or as a result of anthropic activities. They have deleterious effect to human health even at low concentration when ingested over a long period of time [2,3]. Hence, it is importance to ensure that such heavy metals contained in foods are kept below the maximum limit that is allowed by WHO in the milligrams per millilitre range [4].

Copper is an essential heavy metal for human metabolism at the trace level, but it is toxic at high quantities [5]. The excessive intake of copper would lead to accumulation of the metal in liver cells and haemolytic crisis, jaundice, neurological disturbances, and Wilson's disease [6]. Excess of

copper enters the body through pollutant present in water, food contamination and certain vegetables rich in copper. Vegetables are well known as bio-monitors which can take up a lot of essential nutrients along with certain trace elements in a short period [7,8]. Therefore, it is important to monitor the levels of copper in vegetables due to its toxicological effect on human health.

Several analytical methods for the determination of copper have been reported that include inductively coupled plasma-mass spectrometry (ICP-MS), X-ray fluorescence spectrometry (XRF), and atomic absorption spectrometry (AAS). However, their sophisticated instruments severely restrict their practical application and need high cost maintenance. Furthermore, the procedure is too time consuming and risk of sample contamination due to the strong interference of analytical matrix of vegetable samples [4].

Voltammetric method have shown numerous advantages, including speed of analysis, good selectivity and sensitivity, good performance with saline matrices like sea water, and low cost instrumentation. Recently, the modified CNT paste electrode using ZLH-CPPA has been successfully employed for determination of Cu(II). The previous work showed high sensitivity and selectivity of determination Cu(II) with detection limit of 1.0×10^{-10} M [9]. These results have been the rationales in proposing this present work. This present work used the ZLH-CPPA modified CNT paste electrode for the sequential voltammetric determination of Cu(II) in Malaysian vegetables.

2. EXPERIMENTAL

2.1. Reagents and chemicals

MWCNT (Timesnano), paraffin oil (Uvasol, Merck), sodium acetate (Merck), sodium hydroxide (Fluka), acetic acid (Merck), and copper(II) chloride dihydrate (Sigma–Aldrich) were used as received. The supporting electrolyte was 4.0×10^{-3} M CH_3COONa (Sigma–Aldrich), at pH 2.50 was chosen on the basis of previous study [9]. The complex of ZLH-CPPA was synthesized and purified as previously reported [10].

2.2. Apparatus

Cyclic voltammetry was performed with a Gamry Potentiostat Series-G750, USA, assembling three electrode cell systems, using ZLH-CPPA modified CNT paste electrode, a saturated Ag/AgCl reference electrode and a Pt wire counter electrode. The pH value was determined using glass electrode Orion 915600, USA. Prior to any measurement, the solutions were deoxygenated by bubbling oxygen free nitrogen (Nissan Oxygen, Malaysia) for 30 min.

2.3. Sample preparation

The vegetable samples were purchased from the local market in Tanjung Malim. The vegetables were washed thoroughly with tap water and deionized water. Then, the samples were cut into bar and dried at 105 °C for 24 h and grounded.

2.4. Dissolution of vegetable samples

One gram of samples was placed in a 100 mL beaker, and 15 mL of concentrated HNO_3 (69% w/w) was added to the beaker. The mixture was evaporated on a hot plate at about $130\text{ }^\circ\text{C}$ for 4 h. After cooling to room temperature, 8 mL of deionized water was added. Then, the mixture was filtered through Whatman N. 541 filter paper, and then diluted to 50 mL with deionized water. Ten millilitre of each sample solution was transferred to a voltammetric flask for the determination of Cu(II) via the recommended procedure under the established optimum conditions [9].

3. RESULTS AND DISCUSSION

Figure 1 shows cyclic voltammograms (CVs) of the vegetable samples containing Cu(II) using ZLH-CPPA modified CNT paste electrode with voltammetric measurement parameters and conditions previously set up [9]. The well defined anodic peak was obtained in the range of potentials measured for Cu(II) by voltammetric measurement. As discussed previously [9], the voltammetric behaviour of Cu(II) in the ZLH-CPPA modified CNT paste electrode is quasi-reversible process.

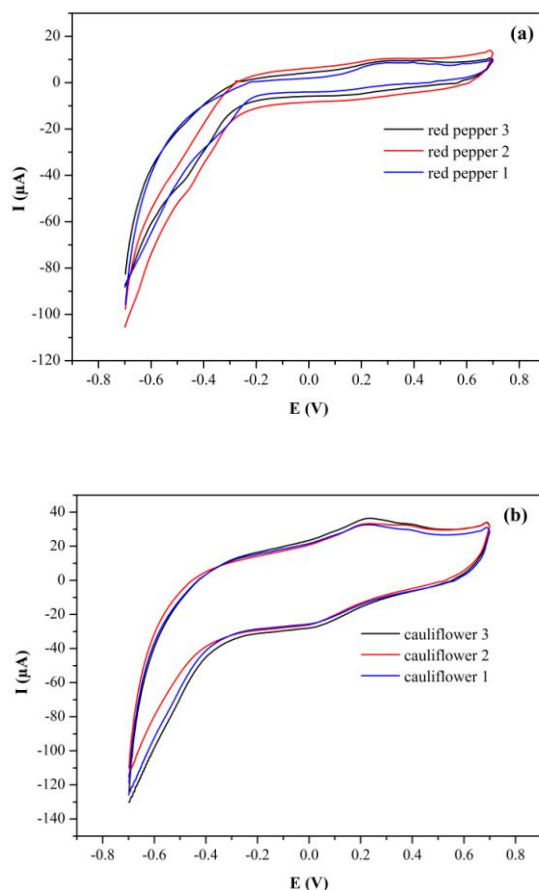


Figure 1. Cyclic voltammogram at ZLH-CPPA modified CNT paste electrode of Cu(II) in (a) red pepper and (b) cauliflower in 4×10^{-3} M CH_3COONa buffered at pH 2.5 and scan rate of 500 mV s^{-1} .

3.1. Concentration of copper in vegetable samples

The variation of Cu(II) concentration in vegetable samples is listed in Table 1. The copper levels in vegetables were found in the range of 0.04–6.88 $\mu\text{g g}^{-1}$. The maximum and minimum Cu(II) concentration in vegetables were found to be 6.88 $\mu\text{g g}^{-1}$ in broccoli and 0.04 $\mu\text{g g}^{-1}$ in potato. The copper concentration varies among different vegetables due to different nature of vegetable species and environmental conditions [11]. The uptake of copper by plants is an avenue of their entry into the human food chain. This may cause an excessive build up of copper in the human body with harmful effects on health [3]. The Cu(II) levels found in this study were lower than the limit value of 9.4 $\mu\text{g g}^{-1}$ set by FAO/WHO [12], which indicated that all the vegetables sampled accumulated low concentration of Cu(II) and were safe to enter the food chain.

Table 1. Concentrations of Cu(II) in vegetable samples (n = 3)

Samples	Mean concentration ($\mu\text{g g}^{-1}$)	Samples	Mean concentration ($\mu\text{g g}^{-1}$)
Red pepper	0.84 ± 0.17	Green bean	1.26 ± 0.37
Green pepper	0.110 ± 0.002	Water spinach	0.10 ± 0.01
Chinese lettuce	0.67 ± 0.08	Lettuce	0.82 ± 0.02
Carrot	0.15 ± 0.01	Chinese celery	0.080 ± 0.003
Tomato	0.12 ± 0.02	Scallion	4.75 ± 0.03
Cabbage	0.27 ± 0.07	Pumpkin	0.35 ± 0.01
Bitter guard	0.30 ± 0.01	Corn	2.02 ± 0.05
Long bean	3.31 ± 0.21	Cauliflower	2.04 ± 0.09
Garlic chive	5.67 ± 0.38	Lady finger	1.77 ± 0.08
Sweet potato	5.27 ± 1.02	Garlic	2.00 ± 0.03
Cucumber	4.13 ± 0.55	Onion	0.150 ± 0.002
Spinach	4.95 ± 0.26	Ginger	2.82 ± 0.56
Broccoli	6.88 ± 0.31	Potato	0.04 ± 0.03
Jicama	0.090 ± 0.003	Eggplant	0.290 ± 0.003
Chinese broccoli	0.53 ± 0.08	Luffa	4.66 ± 0.91

3.2. Comparison with the other country studies

In Table 2, comparison between the Cu(II) levels obtained in this study and the result obtained from the other countries is reported. The Cu(II) levels found in the vegetables here are higher than those found in Brazil [13] and China [14]. While, the Cu(II) concentrations in Ethiopia [15], Turkey [3], Saudi Arabia [16], India [17], Egypt [18], and Bangladesh [19] are higher than that found in similar vegetables grown locally.

The observed variation of Cu in vegetable species in the different countries could be due to variable capabilities of absorption and accumulation [20]. The uptake and accumulation of Cu by different vegetable species depend on their environmental conditions, such as soil pH, cation exchange capacity, soil organic content, soil texture and the interaction of soil–plant root–microbes which play important roles in regulating heavy metal movement from soil to the edible parts of vegetables [15]. The additional micronutrient fertilizers and copper based fungicides may sometimes increase the Cu levels that might pose risk for consumption.

Table 2. Comparison of Cu(II) ($\mu\text{g g}^{-1}$) in vegetable samples found in this study with those in literature

Samples	Mean concentration ($\mu\text{g g}^{-1}$)								
	Present study	Turkey [3]	Egypt [18]	Saudi Arabia [16]	India [17]	Ethiopia [15]	Brazil [13]	China [14]	Bangladesh [19]
Red pepper	0.84	2.82							5.00
Green pepper	0.11	2.45	4.53	4.49		5.62	0.9		
Carrot	0.15	2.94	1.51	0.94			0.7		1.50
Tomato	0.12	3.43	1.83	4.47	1.60	4.10	0.6	0.13	1.60
Cabbage	0.27			0.43		2.66	0.3	0.08	
Bitter guard	0.30				2.00				
Sweet potato	5.27						1.4		
Cucumber	4.13	2.51	5.69	2.48			0.4	0.22	
Spinach	4.95	5.88	4.48	2.71	2.00		0.6	0.44	
Broccoli	6.88	1.64					0.6		
Green bean	1.26		2.27		4.80				
Lettuce	0.82	6.54	1.97	0.90	3.60	5.30	0.4		
Chinese celery	0.08							0.13	
Scallion	4.75							0.32	
Pumpkin	0.35								2.7
Cauliflower	2.04	0.40			2.80		0.4	0.29	
Garlic	2.00	2.07	1.80					0.21	
Onion	0.15	1.71	1.49			2.48	0.8		1.70
Potato	0.04	0.79	0.83	0.88	3.40	2.52	1.1	0.53	
Eggplant	0.29	1.26	1.41	2.93	6.40		1.0	0.20	2.80

4. CONCLUSION

In this work, a selective and low cost analytical procedure for the determination of Cu(II) in vegetables has been successfully applied. The highest Cu(II) concentrations were found in broccoli ($6.88 \mu\text{g g}^{-1}$). The Cu levels in vegetables were lower than the maximum limit allowed. However, continuous efforts should be made to monitor copper concentration in vegetables grown locally in order to ensure safe consumption for human.

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