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Determination of copper in food by stripping voltammetry using Cu(II)–[2-(2,3,5-triazolylazo)-5-dimethylaninobenzonic] complex

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Abstract

The electrochemical behavior of copper (II)-2-[2,3,5-triazolylazo]-5-dimethyl-aninobenzonic [Cu(II)–TZAMB] complex was studied. In 0.05 mol l^{-1} potassium hydrogenphthalate (PBS, pH 2.5) buffer solution, Cu(II) and TZAMB can form Cu(II)–TZAMB complex. This complex has adsorptive characteristics on hanging mercury drop electrode (HMDE) and can be reduced in an irreversible reduction step. The calibration graph for copper(II) was linear over the concentration range 9.5×10^{-9}mol l^{-1} to 4.7×10^{-7} mol l^{-1}; the detection limit of the method was 9.5×10^{-9} mol l^{-1}. The interference of some common ions was studied and the method was found suitable for the determination of copper(II) in rice and vegetables.

Keywords: Copper(II); Food; Stripping voltammetry

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1. Introduction

Copper is an essential trace element in biological systems. It exists in nature extensively, but the concentration in various samples is usually low, so developing sensitive and selective methods to determine copper are required. Several methods to determine copper in food and biological samples have been reported based on flame atomic absorption spectrometry and stripping voltammetry (Anzano & Gonzalez, 2000; Pournaghi-Azar & Dastangoo, 2000; Shamsipur, Rouhani, Ganjali, Eshghi, Sharghi, 1999). In particular, stripping-analysis following adsorption accumulation of the metal chelates has become a widely accepted analytical tool because of its high sensitivity (Ensafi & Abbasi, 2000; Girousi, Kaspentakis, & Voulgaropoulos, 2001; Osipova et al., 2000; Pournaghi-Azar & Dastangoo, 2000; Xiao & Jin, 1993). One of its main advantages is that after some time accumulation, metal and chelates can adsorb on the electrode by chelate complex, and it is can enhance the detection limit strongly. Thus highly selective and sensitive reagent to chelate with trace metal from samples can be exploited to determine trace metal in biological or environment samples.

Several adsorption voltammetric methods with different chealating reagents have been used to determine copper and all have some disadvantages. For example, in those methods, some used adapted extraction method to enhance the detection limits; some had narrow linear dynamic ranges and some used reagents that were too reactive in the atmosphere for routine use. Pournaghi-Azar and Dastangoo (2000) used BAE [bis-(acetylacetone)-ethylendiimine] as chelate to determine copper by differential pulse anodic stripping voltammetry, but an extraction step was adopted using dichloromethane as the solvent, which complicated the analysis procedure. Ensafi and Abbasi (2000) used α-benzylmonooxime to determine copper by differential pulse cathodic voltammetry, but the chelate was a reactive agent and could not be exposed in air for a long time. Necati, Saim, and Mustafa (2000) studied the electrochemical behavior of Cu(II)–5-Br-PADAP complex, but did not used it to determine copper in real samples.

In this paper, we found a highly sensitive and selective method to determine copper using a new chelate

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reagent, 2-(2,3,5-triazolylazo)-5-dimethylaninobenzonic (TZAMB). TZAMB is a ligand that has azo- and heterocyclic function groups (Fig. 1) making it a strong chelate agent for copper. Although this reagent has been reported for the determination of cobalt by spectrophotometry (Ye, Jing, Han, 2000), up to now, there has been no report in its use to determine copper in food sample by electroanalysis method. This method was applied to determine copper in rice and vegetables in this paper, and the results were consistent with those of spectrophotometry method (Hygienic Bureau of P.R. China, 1997).

2. Methods and materials

2.1. Apparatus and electrodes

Experiments were performed on a CHI604A Electrochemical Analyzer (CH Instrument, USA) equipped with a computer as control and recorder. A hanging mercury drop electrode HMDE was used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a Platium wire electrode as the counter electrode. A 50-ml beaker was used as the electrolytic cell. All potentials were measured versus the SCE.

A 600 W MK-III(Guohua, 2000)microwave sample preparation system (Xin-Ke Institute of Applied Microwave Technology, Shanghai, China) was used for pretreatment of the samples. Airtight and pressure-resisting vessels made of Shanghai were employed to hold the samples and a turntable was used to hold the vessels. Adjusting the pressure controlled the extent of the samples decomposition.

2.2. Reagents

TZAMB was provided by Deman Han (Ye et al., 2000) and recrystallized with ethanol five times. Analytical calculated for TZAMB (%): C, 50.76; H, 4.65; N, 32.29. Found (%): C, 50.94; H, 4.57; N, 32.32 using element analysis method. Obviously the molecular formula of TZAMB we put forward is right based on the similitude of the two groups of values.

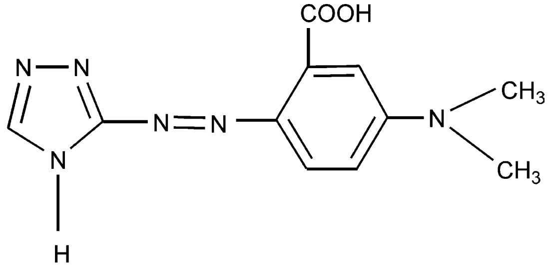

Fig. 1. The chemical structure of 2-(2,3,5-triazolylazo)-5-dimethylaninobenzonic (TZAMB).

A 1×10^{-3}mol l^{-1} TZAMB stock solution was prepared by dissolving 0.0130 g TZAMB in ethanol and then diluting with water in 50-ml volumetric flask. A 1×10^{-3}mol l^{-1} Cu^{2+} stock solution. All standard solutions were obtained by sequential diluting the stock solution with double-distilled water. Unless otherwise specified, all solutions were prepared from analytical grade reagents and double-distilled water.

2.3. Procedure

Each measurement was carried out after an accumulation step while the solution was stirring for a given time; the accumulation potential (E_{acc}) of 0.05 V was applied. After a rest period of 15 s, the response curve was recorded by scanning the potential to the negative direction. Each measurement was performed with a fresh drop and always of the same size.

2.4. Sample treatment

The samples (rice, celery etc.—all samples were obtained from the Center General Merchandise Supermarket) were grounded, sifted through 100-mesh, and dried in 70 °C for 2 h. After cooling, a 1–2 g sample was accurately weighted and transferred to the PTFE lined vessel. 4.0 ml nitric acid and 1.0 ml H_2O_2 solution was added to it. The vessel was placed on the microwave turntable, the pressure was increased to 2 MPa for 5 min. After completion, the vessel was taken out to cool to room temperature. When a clear solution was obtained, the solution was transferred to a beaker and heated to near dryness. After cooling, the solution was neutralized using 1 mol l^{-1} NaOH to weak acidic (pH = 2.5) and transferred to a 10-ml volumetric flask and diluted to volume with water.

3. Results and discussion

3.1. Effect of pH

Effect of pH on the peak height was studied in the range of 1.5–5.0 and an optimum pH of around 2.5 was found.

3.2. Effect of accumulation potential

Fig. 2 shows the effect of the accumulation potential on the peak current i_p and that i_p reaches maximum while the accumulation potential is 0.05 V (vs.SCE). So in samples analysis step, the accumulation potential was set at 0.05 V.

3.3. The properties of polargraphic peak

There were no redox peaks of TZAMB in PBS buffer solution (Fig. 3, curve A). Cu^{2+} did not give any redox

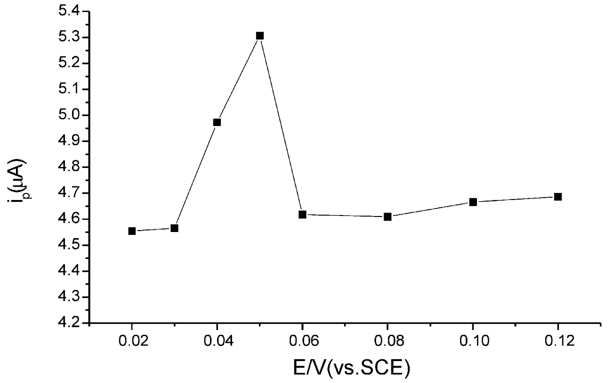

Fig. 2. The effect of the accumulation potential on the peak current. $C_{TZAMB} = 1\times10^{-6}$mol l^{-1}, $C_{Cu2+} = 1\times10^{-7}$mol l^{-1}, accumulation time is 30 s. pH = 2.5 (0.05 mol l^{-1} PBS solution), Scan rate is 100 mV s^{-1}.

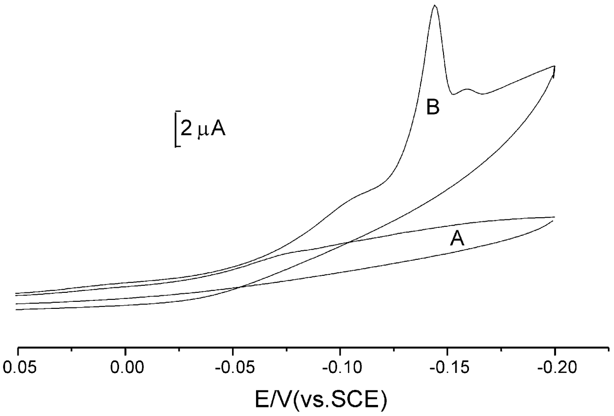

Fig. 3. The typical voltammograms of TZAMB and Cu(II)–TZAMB. A: $C_{TZAMB} = 1\times10^{-6}$mol l^{-1}; B: $1 + 1\times10^{-8}$mol l^{-1}Cu^{2+}.Other conditions are the same as in Fig. 2.

peaks also. When a micro-amount of Cu^{2+} was added to the solution containing TZAMB, a new peak appears at −0.13V (Fig. 3, curve B). This suggests that the Cu(II)–TZAMB complex causes this peak. The peak height increases with increasing Cu^{2+} concentration so this peak can be applied to the determination of trace Cu^{2+}. The repetitive voltammograms are shown in Fig. 3. Scanning four cycles, it was found that the peak current of first cycle (curve A) is much higher than those of the next cycles (curves B, C, D), which indicates that the complex has adsorptive characteristics. As shown in Fig. 3 (curve B) and Fig. 4, cathodic peak was observed during the scan in the negative direction. Scanning in the reverse direction did not produce an anodic peak, indicating the irreversibility of the oxidation process.

3.4. Electrode reaction mechanism

As shown in Section 3.3, there were no peaks observed when Cu^{2+} (2×10^{-8}mol l^{-1}) or TZAMB were alone in PBS buffer solution, but when Cu^{2+} and TZAMB co-existing, a sensitive peak was observed. This indicates that Cu(II)–TZAMB complex produced was reasonable for the peak. In order to obtain some information, electrolysis was used. The working electrode was a large area, mercury electrode. An electrolysis potential of −0.14 V (vs.SCE) was applied. After electrolysis for 4 h, reduction peak current of Cu(II)–TZAMB had dropped down to zero. A defined amount of TZAMB was added to the cell, by using cyclic voltammetry, reduction peak (−0.13 V, vs. SCE) of Cu(II)–TZAMB in this solution was obtained again. It is evident that the reactant is TZAMB in the Cu(II)–TZAMB. According to the reference (Li, Zhang, Luo, Song, & Lu, 2002; Lu & He, 1992), this reduction peak (−0.13 V) was produced by the azo group (–N=N–) to hydrozoa group (–NH–NH–).

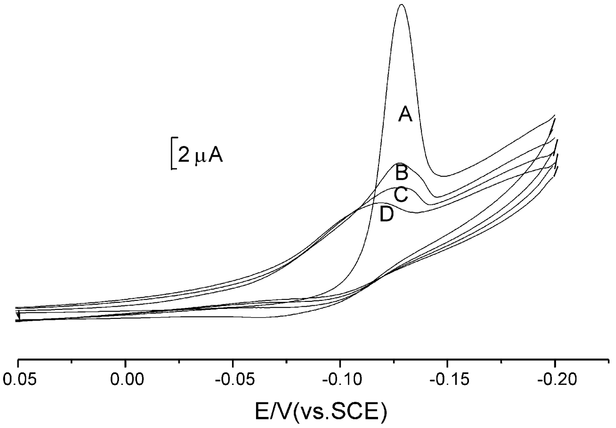

Fig. 4. The repetitive voltammograms of Cu(II)–TZAMB complex. $C_{TZAMB} = 1\times10^{-6}$mol l^{-1}, $C_{Cu2+} = 1\times10^{-7}$mol l^{-1}.Other conditions are the same as in Fig. 2.

3.5. Analytical application

The greatest advantage of the measurement of Cu^{2+} by adsorption voltammetry is its inherent sensitivity. The signal enhancement associated with the adsorptive accumulation time results in significantly lower detection limits compared with those obtained by conventional measurement. Using this method to determine copper, the calibration graph is: $y = 1.206 + 1.520x$ (y: peak current, i_p/μA; x: the concentration of Cu^{2+}, C_{Cu2+}/mol l^{-1}), correlation coefficient is 0.9985. The concentration of Cu^{2+} range from 9.5×10^{-9}mol l^{-1} to 4.7×10^{-7}mol l^{-1} can be determinated and the detection limit is 9.5×10^{-10}mol l^{-1}.

To evaluate the selectively of this method, the interference of other ions on the determination of copper(II) with the presence of 1×10^{-7}mol·l^{-1} Cu^{2+} at optimum reagent concentrations was studied. The tolerance ion concentration is about 10 000 fold for Na^{+}, NH$_4^{+}$, Mg^{2+}, Ca^{2+}, Cl^{-} and SO$_4^{2-}$; 100 fold of Zn^{2+}, Al^{3+}, Mo^{4+}, Ni^{2+}, Se^{4+}; 10 fold of Fe^{3+}, Cd^{2+} and equally amount of Co^{2+} do not interfere with the determination of copper (II).

The determination is made by the procedure described above. The results obtained are given in Table 1. Compared to the results of spectrophotometry (The samples were prepared according to Section 2.4), this method was reliable. Also, the merits of this method compared to other methods are given in Table 2.

Table 1
Results of samples analysis (means of triplicate determination)

Samples	Mean value ($P^{a}=95\%$) (μg/g)	Previous (μg/g) (Hygienic, 1997)
Rice (Hubei)	2.84±0.10	2.81
Cabbage (Hubei)	0.20±0.04	0.23
Celery (Hubei)	0.86±0.09	0.89
Mung bean (Hubei)	3.41±0.05	3.20
Medlar[b] (Hubei)	8.99±0.09	8.61

[a] P, Confidence interval.

[b] Medlar, A kind of Chinese traditional medical plant producing in native China.

Table 2
Comparing the analytical figures of various methods for determination of copper by adsorption stripping analysis

Reagents	LOD[a] (μg/ml)	LDR[b] (μg/m)	Interference	Reference
BAE[c]	0.05	0.06–2	Fe^{3+}	(Pournaghi-Azar & Dastangoo, 2000)
8-HD[d]	0.03	$1–10\times10^{-3}$	–	(Girousi et al., 2001)
BME[e]	0.3×10^{-3}	$1–850\times10^{-3}$	I^-,Br^-,SCN^- (1500)	(Ensafi, & Abbasi, 2000)
TZAMB	0.06×10^{-3}	$0.6–30\times10^{-3}$	Zn^{2+},Se^{4+} (100)	This method

[a] Limit of detection.

[b] Linear dynamic range.

[c] Bis(acetylacetone)ethylendiimine.

[d] 8-HD = 8-Hydroxyquinoline.

[e] α-Benzylmonooxime.

4. Conclusion

A novel method to determine Cu^{2+} using a new reagent TZAMB was discussed in this paper. Using different electroanalysis methods, the electrochemical behavior of this complex was studied. This method was applied to determine Cu^{2+} in real samples, such as rice and cabbages, and the results were compared with published data for these foods, obtained using the spectrophotometry.

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