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Application of *meso*-2,3-Dimercaptosuccinic Acid Self-assembled Gold Electrode for Voltammetric Determination of Copper

Pei Dao Ding,[a] Ling Mei Niu,[b,c] Hong Qun Luo,[b,c] and Nian Bing Li[a,b,c,*]

[a]*College of Material Science and Engineering,, Chongqing University, Chongqing, 400044, China*

[b]*School of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, China*

[c]*Key Laboratory of Eco-environments in Three Gorges Reservoir Region (Ministry of Education), Chongqing, 400715, China*

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Fabrication and electrochemical characteristics of the *meso*-2,3-dimercaptosuccinic acid (DMSA) self-assembled monolayer modified gold electrode were described. The modified electrode exhibited increased sensitivity and selectivity for Cu^{II} compared to the bare gold electrode by stripping voltammetry and the peak current was proportional to the concentration of Cu^{II} in the range of $8.0 \times 10^{-7} \sim 1.2 \times 10^{-4}$ mol/L with the detection limit of 1.1×10^{-7} mol/L. The influence of coexistent substances was investigated and the modified electrode showed good selectivity for copper determination. The DMSA/Au electrode was applied for Cu^{II} determination in a tap water sample with satisfactory results, with the recovery in the range from 99.7 to 101.1 %.

INTRODUCTION

Copper is important as an essential trace element in biological systems. In humans, copper is the third most abundant trace element, following iron and zinc and its presence is fundamental in many metabolic processes. However, the intake of copper excess may produce different toxic effects,[1] such as Wilson's disease, and copper deficiency can cause ischemic heart disease, anemia. The toxicity is generally attributed to the aquo-complexed "free" copper(II) ion rather than its organic or inorganic complex; therefore, measurement of free copper ions in environmental monitoring is important.[2]

Considering the importance of copper, many techniques for the quantification of copper in water have been developed, such as atomic adsorption spectrometry (AAS),[3] atomic emission spectrometry,[4] neutron activation analysis (NAA),[5] inductively coupled plasma-mass spectrometry (ICP-MS),[6] stripping voltammetry,[7–9] *etc*. Each method has its respective advantages. Among these techniques, stripping voltammetry is frequently used in copper detection,[7–9] and the use of the self-assembled monolayer (SAM), which is a good way to control the surface of electrodes at the molecular level,[10,11] has grown enormously in recent years, primarily due to its ease of fabrication, characterization, and manipulation. SAM electrodes are very promising for the construction of electrochemical sensors because they can enhance selectivity and sensitivity, improve the response time, decrease the overpotential of the redox process of analytes and have good stability.[12-14] Based on its prominent properties, the application of SAMs to the estimation of copper

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[*] Author to whom correspondence should be addressed. (E-mail: linb@swu.edu.cn)

has been investigated.[15-25] Rubinstein and co-workers demonstrated that a mixed functionalized SAM could recognize the Cu^{II} ion selectively in the presence of other ions.[15] Shen *et al.* used the bifunctional alkylthiols SAM-modified gold electrode to minimize the underpotential deposition effect during the stripping analysis of lead and copper.[16] Stora *et al.* developed a new impedance spectroscopy method to detect trace copper ion using self-assembled nitrilotriacetic acid-modified thioalkane monolayers.[17] Bontidean *et al.* reported the use of a protein immobilized in a mercaptosuccinic acid self-assembled electrode to copper analysis in aqueous solution.[18] Liu *et al.* have demonstrated the application of cysteine monolayers for electrochemical determination of Cu^{II}.[19] Arrigan *et al.* have reported a cysteine monolayer-coated gold electrode for copper determination.[20] Yang *et al.* also reported electrochemical determination of Cu^{II} employing Osteryoung square wave voltammetry at a cysteine monolayer-coated gold electrode.[21] Zeng *et al.* assembled a mixed monolayer of glutathione and 3-mercaptopropionic acid on gold surface, which showed a highly selective response to Cu^{II}.[22] Grégoire Herzog *et al.* reported direct comparison of two disorganized monolayer films (2-mercaptoethane sulfonate and mercaptoacetic acid) on a gold surface for selectively recognizing Cu^{II} ions.[23] Freire *et al.* reported a gold electrode modified with a SAM of 3-mercaptopropionic acid as a highly sensitive voltammetric sensor for copper ions.[24] Li and co-workers investigated the electrochemical characteristics of the 2,5-dimercapto-1,3,4-thiadiazol SAM-modified gold electrode and developed a new electrochemical method to detect trace copper ions using SAM.[25]

Our experiment showed that *meso*-2,3-dimercaptosuccinic acid (DMSA) could be used as a modified agent to fabricate the DMSA SAM on the gold electrode surface by virtue of the Au–S bond. This new chemically modified electrode has been applied to study the electrochemical properties of uric acid and epinephrine.[26] DMSA is also a molecule with two carboxyl groups and copper ion can be complexed by coordination with acidic functional groups; therefore, in this paper, a new electrochemical method has been developed for quantification of copper by using the DMSA/Au electrode.

EXPERIMENTAL

Reagents

DMSA solution (5.0×10^{-3} mol/L) was prepared by dissolving 0.0456 g of DMSA (Sigma) in water and diluting it to the mark in a 50-mL calibrated flask. Stock solution (5.8×10^{-3} mol/L) of Cu^{II} was prepared using water and the working solution of Cu^{II} for voltammetric investigation was prepared by diluting the stock solution with water. A phosphate buffer (0.1 mol/L), prepared with NaH_2PO_4 and Na_2HPO_4, was used to control the pH. All the other chemicals were of analytical-reagent grade and were used without further purification. Doubly distilled water was used throughout. All the experiments were carried out at room temperature (approx. 25 °C).

Instruments

Electrochemical measurements were carried out on a CHI 660 electrochemical analyzer (CH Instruments, USA). Electrochemical impedance measurement was carried out on a Model IM 6e (Zahner Elektrik Co., Germany). Electrochemical quartz crystal microbalance (EQCM) measurements were carried out on a CHI 440 electrochemical analyzer (CH Instruments, USA). AT-cut gold-coated quartz crystals with a resonant frequency of 7.995 MHz (5 mm diameter) were used for the EQCM measurements. Gold electrodes of the EQCM were cleaned in a Piranha solution. The three-electrode system used in the measurements consisted of a gold electrode (d = 2 mm) or DMSA/Au electrode as the working electrode, Pt as the counter electrode, and an Ag/AgCl electrode as the reference electrode. All potentials were given with respect to the Ag/AgCl electrode.

Preparation of DMSA/Au Electrode

A bare gold electrode was polished to a mirror-like surface with 0.3 μm or 0.05 μm Al_2O_3 powder and immersed in a Piranha solution (a mixed solution of 30 % H_2O_2 and concentrated H_2SO_4, volume ratio 1:3), and then rinsed ultrasonically with water and absolute ethanol for 3 min. This electrode was voltammetrically cycled between 0 and 1.6 V in 0.1 mol/L H_2SO_4 until a stable cyclic voltamogram was obtained. After washing with sonication, the electrode was immersed in an aqueous solution containing 5.0×10^{-3} mol/L DMSA for about 30 h at room temperature. Upon removal from the DMSA solution, the electrode was thoroughly rinsed with water to remove the physically adsorbed species.

Determination of Cu^{II}

A 10-mL volume of a solution containing an appropriate concentration of Cu^{II} and phosphate buffer (0.1 mol/L, pH = 5.4) was transferred into an electrochemical cell. The stirrer was switched on. The accumulation potential (–0.6 V) was applied to the DMSA/Au SAM electrode for 250 s. At the end of accumulation, the stirrer was switched off. The determination step was performed in a copper-free solution (phosphate buffer: pH = 5.0) employing stripping voltammetry at a scan rate of 50 mV s^{-1}. The peak height was measured at 0.26 V. After each electrochemical measurement, the electrode was scanned for five times from –0.6 to 0.2 V by electrocycling scan in a pH = 5.0 phosphate buffer to clean previous deposits.

RESULTS AND DISCUSSION

Characterization of DMSA SAM in $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ Solution

Characterization of the DMSA SAM in a $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ solution was carried out by cyclic voltamo-

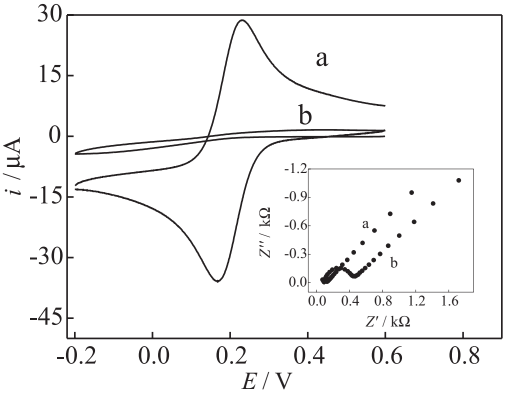

Figure 1. Cyclic voltamograms of a 5.0×10^{-3} mol/L $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ solution containing 0.1 mol/L KCl at a scan rate of 0.1 V s^{-1}. The inset represents complex impedance plots measured in a 1.0×10^{-2} mol/L $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ + 0.1 mol/L KCl + phosphate buffer (pH = 7.7) solution at the formal potential of 0.14 V; the frequency range is between $10^{-2} \sim 10^{6}$ Hz. (a) the bare gold electrode; (b) the DMSA/Au electrode.

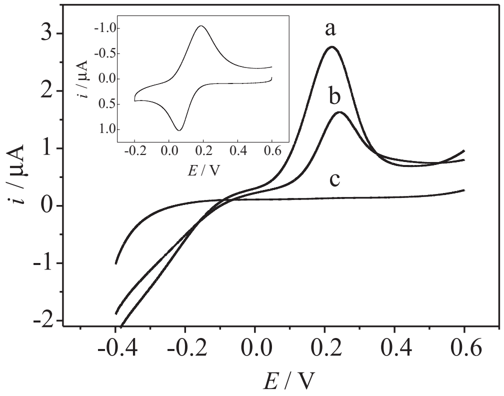

Figure 2. Linear sweep voltamograms. (a) in 8.0×10^{-5} mol/L Cu^{II} solution at the DMSA/Au electrode; (b) in 8.0×10^{-5} mol/L Cu^{II} solution at the bare Au electrode; (c) in the absence of Cu^{II} at the DMSA/Au electrode. Deposition pH: 5.4; stripping pH: 5.0; deposition time: 250 s; deposition potential: – 0.6 V; scan rate: 0.05 V s^{-1}. The inset is the cyclic voltamogram of a 4.0×10^{-5} mol/L copper solution.

grams and impedance methods. Figure 1 shows the cyclic voltamograms of the bare gold electrode and the DMSA/Au electrode in a 5.0×10^{-3} mol/L $[Fe(CN)_6]^{3-}$ solution containing 1.0 mol/L KCl. For the bare gold electrode, a couple of well-defined waves of $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ appeared and the peak-to-peak separation was 60 mV. However, there was no obvious current peak at the DMSA/Au electrode. This is because DMSA contains two carboxylate groups and the electrostatic force between the negative group of DMSA and the $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ couple inhibited electron transfer. Using the EQCM technology, we studied the adsorption of DMSA at the Au electrode in terms of the change of frequency. The adsorptive mass increased with time and reached the maximum after about 30 h because of the saturated absorptive quantity. The saturated mass is 89.1 ng.[27] Considering the adsorptive mass gained and the molecular weight, we calculated that the surface coverage (Γ) was 2.5×10^{-9} mol cm^{-2}.

The inset of Figure 1 displays complex impedance plots of the bare gold electrode and the DMSA-modified gold electrode. Comparison of complex impedance plots of the bare gold electrode and the monolayer-covered gold electrode shows the effect of the absorbed DMSA monolayer on the AC response. For the monolayer-covered electrode, R_{ct}, which is the diameter of the semicircle at high frequency, is clearly greater than that of the bare gold electrode due to inhibition of the DMSA SAM to electron transfer. This also proves the presence of DMSA on the gold electrode.

Electrochemical Response of Cu^II^ at the DMSA SAM Electrode

Figure 2 presents the linear sweep stripping voltamograms of under-potential deposits and the cyclic voltamogram for copper solution of 4.0×10^{-5} mol/L, which was obtained with the DMSA/Au electrode. In the presence of Cu^{II}, a single oxidation peak can be observed at 0.22 V (curve a in Figure 2), which was the same as that by the cyclic voltamogram (the inset figure). The peak results from the oxidation process of Cu since the DMSA/Au electrode does not exhibit any current wave in blank solution under the same conditions (curve c in Figure 2). It can be seen that a current peak appeared at 0.26 V at the bare gold electrode (curve b in Figure 2). Comparing curves a and b, the anodic peak current was obviously increased when the DMSA/Au electrode was used. As mentioned above, DMSA was assembled on gold by the Au-thiolate linkage, leaving carboxylic groups. The –COOH groups are well known as excellent metal ion chelating groups; therefore, Cu^{II} can interact with carboxylic groups of the DMSA self-assembled monolayer to form a Cu^{II}-DMSA complex. Thus, the voltammetric response of the DMSA/Au electrode to Cu^{II} should be attributed to the interaction between the DMSA self-assembled monolayer and the metal, which could greatly improve the sensitivity of Cu^{II} determination. In this paper, the anodic wave of Cu^{II} was systematically studied by anodic stripping voltammetry for analytical applications.

Effects of Different Support Electrolytes on Copper Response at the DMSA/Au Electrode

The effects of different support electrolytes including phosphate buffer, acetate buffer and Tris buffer solutions were studied at the step of copper deposition. As shown in Figure 3, curve a was a linear voltamogram in phosphate buffer, the peak current was 1.74×10^{-6} A. Curve b was that in acetate buffer with the peak current of 1.42×10^{-6} A and curve c was in Tris buffer, the peak current of which was 1.22×10^{-6} A. Copper deposition showed a better

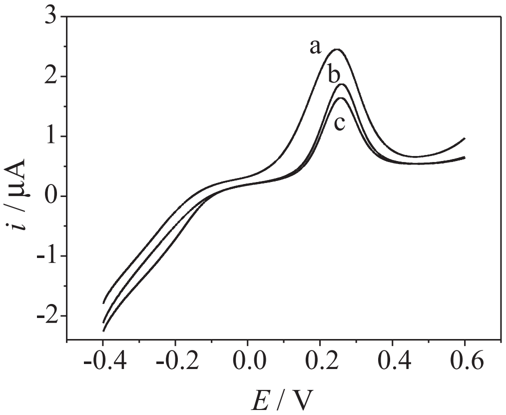

Figure 3. Linear sweep voltamograms of copper solution (8.0 × 10^{-5} mol/L) at the DMSA/Au electrode in phosphate buffer (a), acetate buffer solution (b) and Tris buffer (c). Deposition pH: 5.4; stripping pH: 5.0; deposition time: 250 s; deposition potential: –0.6 V; scan rate: 0.05 V s^{-1}; concentration of three different support electrolytes: 0.1 mol/L.

response in the phosphate buffer solution. Therefore, phosphate buffer solution was selected as the support electrolyte in the following studies.

Effects of Deposition pH and Stripping pH on Copper Stripping

This research was performed in two steps and the phosphate buffer (0.1 mol/L) with different pH was adjusted with NaH_2PO_4 and Na_2HPO_4 solutions of the same concentration. The first step involved deposition in copper solution (8.0 × 10^{-5} mol/L) of a series pH values. The second step involved stripping in blank phosphate buffer of different pH. It can be seen from Figure 4 that in the range of pH 2.6 ~ 6.2, the stripping current increased with raising the pH and reached the maximum at pH = 5.4, then decreased gradually as the pH increased. So pH = 5.4 was adopted as the deposition pH value. At a lower pH, the low response of the DMSA SAM electrode resulted from the protonation of carboxylic acid. The electrochemical response increased with the pH increase since the carboxylic acid was gradually deprotonated, facilitating the formation of copper complexation. At higher pH, the low response of the electrode could be ascribed to the hydrolysis of Cu^{II}, because it was not likely for the neutral $Cu(OH)_2$ or negatively charged Cu^{II}–hydroxide complexes to be taken up by the DMSA self-assembled monolayer.

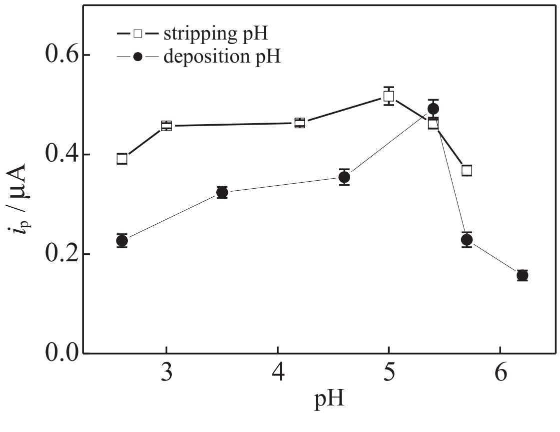

Figure 4. Effects of deposition pH on the peak current in phosphate buffer at the stripping pH of 4.6, and of stripping pH on the peak current in phosphate buffer at the deposition pH of 5.4. Cu^{II} concentration: 8.0 × 10^{-5} mol/L; deposition potential: –0.8 V; deposition time: 20 s; scan rate: 50 mV s^{-1}.

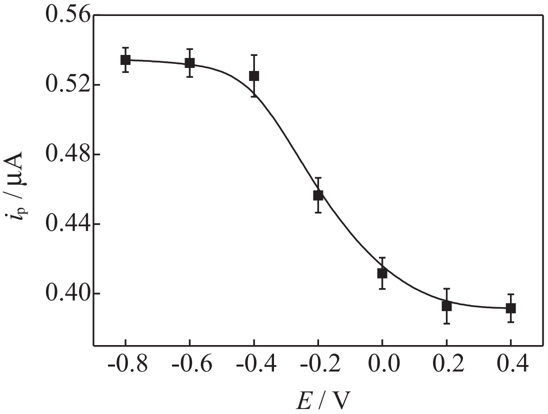

Figure 5. Effect of deposition potential on the peak current. Cu^{II} concentration: 8.0 × 10^{-5} mol/L; deposition pH: 5.4; stripping pH: 5.0; deposition time: 20 s; scan rate: 0.05 V s^{-1}.

For the second step, the peak current increased with the phosphate buffer pH changing from 3.0 to 5.0, and reached a maximum value at pH = 5.0. When the solution pH was further increased, the peak current decreased. Therefore, the pH value of 5.0 was selected for further studies in the stripping step.

Effect of Deposition Potential on Copper Stripping

The dependence of the anodic stripping peak current on the accumulation potential was examined over the potential range of 0.4 to –0.8 V. Figure 5 shows the effect of the accumulation potential on the stripping peak current. It can be seen from Figure 5 that the maximum response for copper occurred with the potential equal to, or more negative than, –0.4 V. Therefore, –0.6 V was chosen as the accumulation potential in our measurements.

Effect of Deposition Time on Copper Stripping

Another factor influencing copper stripping was deposition time. In this paper, the deposition time of two copper ion concentrations were investigated. The dependence of the peak current on the accumulation time is shown in Figure 6 for two different copper concentrations (8.0 × 10^{-5} mol/L and 1.0 × 10^{-5} mol/L). For the two different concentrations of copper ion, the peak current increased at first with increasing accumulation time, indicating an enhancement of the copper ion concentration at the surface of DMSA/Au electrode. When the deposition time exceeded 250 s, the peak current almost kept constant for the higher concentration of copper. But for the lower concentration of copper, the peak current did not reach the maximum until the deposition time was over 300 s. Consequently, the deposition of a lower concentration of copper ion will take more time to reach the maximum value of the stripping current.

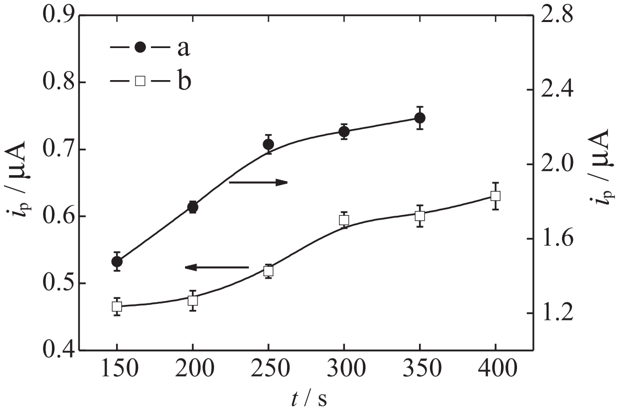

Figure 6. Effect of accumulation time on the peak current. Cu^{II} concentration: (a) 8.0 × 10^{-5} mol/L; (b) 1.0 × 10^{-5} mol/L; deposition pH: 5.4; stripping pH: 5.0; deposition potential: –0.6 V; scan rate: 0.05 V s^{-1}.

Stability of the Self-assembled Electrode

The DMSA SAM electrode showed good reproducibility and stability. If the modified electrode was placed in phosphate buffer (pH = 5.0) for 5 days, the relative error of peak current values was in the range of 5 %. Copper concentration of 8.0 × 10^{-5} mol/L was determined 10 times, and the relative standard deviation was 3 %.

Calibration Plot

According to the optimum experimental conditions and the procedure described above, the relationship between the stripping peak current and the Cu^{II} concentration was examined by determining eight standard solutions of different concentrations and each standard solution was determined three times. The dependence of the current response on the concentration of Cu^{II} was linear in the range of 8.0 × 10^{-7} mol/L to 1.2 × 10^{-4} mol/L. The linear response equation for the peak current (i) and the Cu^{II} concentration (c) was:

$$i_p \ / \ \mu A = 0.363 + 0.203 \ c \ / \ 10^{-5} \ \text{mol L}^{-1},$$

with the correlation coefficient of 0.9936. The relative standard deviations of the slope and intercept were 2 % and 4 %, respectively. The detection limit (three-times signal to noise) for Cu^{II} was 1.1 × 10^{-7} mol/L.

Effects of Other Ions

The interference of various foreign metal ions on the determination of 8.0 × 10^{-5} mol/L Cu^{II} was investigated. These species were added to the sample and the tolerable limit of a foreign substance was taken as the relative error not greater than 5 %. The tolerated ratio of foreign substances to 8.0 × 10^{-5} mol/L Cu^{II} was 10 for Pb^{II}, Cr^{III}, Fe^{III} and Ni^{II}; 20 for Al^{III}; 40 for Mg^{II}. The anti-interference capability could be improved greatly after adding citric acid as a masking reagent. For example, when the concentration of Cu^{II} was 8.0 × 10^{-5} mol/L, the relative error for Fe^{III} (1.0 × 10^{-3} mol/L) was 13 % before adding citric acid and 4 % after its addition.

Analytical Application

Tap water was used as the sample of Cu^{II} solution. Different concentrations of Cu^{II} solutions were acquired by adding standard solutions of various Cu^{II} concentrations. The determination results are listed in Table I, in which the original concentration was obtained by determining tap water directly with the modified electrode. The recoveries of sample solution of different concentrations were between 99.7 and 101.0 %. The feature of convenience and time-saving indicates that the DMSA/Au electrode can be applied in the determination of Cu^{II} in real samples.

CONCLUSIONS

The DMSA SAM modified gold electrode was prepared and based on this modified electrode, a novel approach for the determination of Cu^{II} was developed by the stripping voltammetry method. The DMSA/Au electrode exhibited a selective voltammetric response to Cu. The proposed method was applied to the determination of Cu^{II} in a water sample with satisfactory results.

TABLE I. Results of Cu^{II} determination in a water sample

$c(Cu^{II})_{orig.}$ [(a)] / 10^6 mol L^{-1}	$c(Cu^{II})_{added}$ / 10^{-5} mol L^{-1}	$c(Cu^{II})_{total}$ / 10^{-5} mol L^{-1}	$c(Cu^{II})_{found}$ [(b)] / 10^{-5} mol L^{-1}	Recovery / %	RSD / %
2.16	3.00	3.22	3.21	99.7	3
2.16	9.00	9.22	9.30	101.0	2

[(a)] The original concentration was obtained by determining Cu^{II} in tap water directly with the modified electrode.

[(b)] Found after Cu^{II} addition.

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SAŽETAK

Voltametrijsko određivanje bakra primjenom zlatne elektrode prekrivene samoorganiziranim slojem *meso*-2,3-dimerkaptosukcinične kiseline

Pei Dao Ding, Ling Mei Niu, Hong Qun Luo i Nian Bing Li

Opisana su elektrokemijska svojstva i priprava zlatne elektrode modificirane samoorganiziranim monoslojem *meso*-2,3-dimerkaptosukcinične kiseline (engl. DMSA, meso-*dimercaptosuccinic acid*). U usporedbi sa čistom zlatnom elektrodom, modificirana elektroda je osjetljivija i selektivnija u odnosu na bakarne ione. U voltametriji s akumulacijom, maksimalna struja linearno je proporcionalna koncentraciji Cu^{II} iona u rasponu od 8.0×10^{-7} mol/L do 1.2×10^{-4} mol/L. Granica detekcije je 1.1×10^{-7} mol/L. U prisutnosti konkurentnih iona i spojeva, modificirana elektroda je visoko selektivna za Cu^{II} ione. DMSA/Au elektroda korištena je za mjerenje koncentracije Cu^{II} iona u vodovodnoj vodi s preciznošću od 99.7 do 101.1%.