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Preconcentration and Determination of Copper(II) at a Chemically Modified Electrode Containing Salicylaldehyde Thiosemicarbazone

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A chemically modified electrode (CME) containing salicylaldehyde thiosemicarbazone (TSCsal) was evaluated for the ability to preconcentrate copper(II) prior to quantification by voltammetry. The CME has been used for the very sensitive and selective analysis of trace amounts of copper(II). A detection limit of 0.1 ppb was obtained by applying anodic stripping voltammetry with a flow system. The parameters that affect the sensitivity and possible interference by other ions or chelating agents have been examined in detail. The CME exhibits high stability and the response could be reproduced for four preconcentration-determination-renewal cycles [10ppb Cu(II)] with a 2.87% relative standard deviation. The proposed method has been applied to the determination of copper(II) in tap water, drinking water, and NASS-3 standard reference sea water samples. The results gave satisfactory recoveries.

INTRODUCTION

Recently, considerable attention has been focused on electrochemical determinations using chemically modified electrodes (CMEs).[1,2] CMEs have been widely used in trace analysis, especially modified carbon paste electrodes. Their easy fabrication and good performance have resulted in many practical applications.[2-6] Electrode modification usually serves to enhance sensitivity and selectivity through the selective accumulation of the target analyte by the modifier. Substances with complexing properties - metal chelates, ion exchangers, inorganic sorbents, polymer etc. - are the most frequently used modifiers. Chelating agents are the most widely studied among many types of modifying agents.

The well known chelating agents dimethylglyoxime[7,8] and o-phenanthroline[9] have been used as modifiers of carbon paste electrodes for trace level detection of Ni^{2+} and Cu^{2+}, respectively. Other chelating ligands used as chemical modifiers have also been reported suitable for trace analysis, including di-8-quinolyl disulphide,[10] benzoin oxime,[11] salicylideneamino-2-thiophenol,[12] and 1-(2-pyridylazo)-2-naphthol[13] allowing the determination of copper ion with good selectivity and sensitivity. In this respect two analytical advantages can be achieved. One is that the electroanalytical quantitation might be extended to analytes that cannot be reductively deposited or require excessively negative deposition potentials. The other is that the selectivity of the chemical step used for the preconcentration might improve the overall selectivity of the entire analysis.[2]

This paper describes the accumulation behavior and stripping voltammetry of copper ion with a carbon-paste electrode modified with salicylaldehyde thiosemicarbazone (TSCsal). Since this compound is not soluble in water and has a strong affinity for heavy metal ions, it is suitable as an electrode-modifying reagent. The aim of this paper is to develop a highly selective method for the determination of copper ion in a flow injection measuring system.

EXPERIMENTAL SECTION

Apparatus

A polarographic analyzer (EG & G Princeton Applied Research, Princeton, NJ, USA; model 174A) coupled with a thin layer flow cell (BAS LC-44-0100) was used for the voltammetric measurements. The cell consisted of a BAS (MF-1004) dual carbon paste working electrode (modified by the procedure below), Ag/AgCl (3M KCl) reference electrode, and stainless steel auxiliary electrode. The peristaltic pump (Ismatic, Japan) was used with a flow rate of 1 mL min^{-1}. Voltammograms were recorded on an Omnigraphic X-Y recorder (Houston series, model 2000). A pH meter (Radiometer PHM 82, Copenhagen, Denmark) was used to measure the pH.

Reagents

Most chemicals were of reagent grade (E. Merck, Darmstadt, Germany). Water (18MΩ-cm) purified using the Milli-Q UltraPure Water System (Millipore, USA) was used for all solutions. The stock solution (ca 0.1 M) of copper ion was prepared by dissolving an appropriate amount of the copper salt in nitric acid (0.1 M), diluting with pure

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Dedicated to Professor Yu-Shia Cheng on the occasion of her 65th birthday.

water, adjusting to pH 1.6, and storing in polyethylene bottles. The concentration of copper ion was verified by EDTA complexometric titration. All solutions and standards were prepared under a class 100 laminar flow hood. The supporting electrolyte was nitric acid (0.02 M). Salicylaldehyde thiosemicarbazone (TSCsal) was prepared as in the procedures of Ghosh.[14] This product was recrystallized from hot absolute ethanol: yield: 65%, mp 221 °C dec. Anal. Calcd. for $C_8H_9N_3SO$: C, 49.23; H, 4.61; N, 21.35. Found: C, 49.26; H, 4.68; N, 21.54.

Electrode Preparation

Graphite powder (particle size < 50 μm, purity > 99.5%, Merck) (1 g) and salicylaldehyde thiosemicarbazone (0.8 g) were mixed to a paste with liquid paraffin (for spectroscopy, Merck) (about 0.6 mL) in a mortar. A part of the paste was filled into the surface of the electrode, which was then smoothed by a spatula or an ashless filter paper. Here dual electrodes were used, so the total active surface area was 0.56 cm^2.

Procedures

A portion of the sample solution was transferred to a volumetric flask and introduced directly to the thin-layer cell. The preconcentration was carried out at a potential of -0.6 V for 5 min by a peristaltic pump with a flow rate of 1 mL min^{-1}. After the accumulation stage was complete, the flow was stopped and the voltammograms were recorded after 1 min of quiescent time.

Renewal of the Electrode

After each electrochemical measurement, the electrode was treated for 2 min in a solution of 0.02 M nitric acid at +0.5 V, in order to free the bound metal and reactivate the surface.

RESULTS AND DISCUSSION

This is the first instance of the use of salicylaldehyde thiosemicarbazone in a chemically modified electrode. The cyclic voltammograms obtained after exposure of the modified electrode to copper (1 ppm) in nitric acid (0.02 M) is shown in Fig. 1. The electrode displayed two successive anodic responses near -0.15 V and +0.18 V, respectively. No cathodic wave was observed within the potential range studied. In an unmodified carbon paste electrode, there are no distinct redox waves. The optimum amount of TSCsal in the carbon paste electrode was determined. The highest sensitivity obtained for the CMEs was around 45% (w/w) TSCsal/graphite mixture (Fig. 2). Therefore such CMEs were used in all subsequent work.

Optimization of Experimental Conditions

The oxidation peak current of Cu(II) obtained with the carbon paste electrode modified with TSCsal depends on the sample concentration, accumulation potential, accumulation time, modulation amplitude, supporting electrolyte, and scan rate. The selection of a suitable supporting electrolyte system is an indispensable step for any voltammetric determination. Initially, various concentrations of acetate buffer, hydrochloric acid, nitric acid, and sodium chloride were selected for investigation. Under similar voltammetric measurement conditions, nitric acid (0.02 M) system exhibited a well-defined voltammetric peak and a consistently better sensitivity toward copper(II) than the other supporting electrolytes. More acidic solution would lead to the formation of hydrogen. The peak current for Cu(II) increased with the increase in amplitude, to a maximum at a pulse amplitude of 100 mV (Fig. 3A). Owing to the asymmetrical peak formation under the pulse amplitude greater than 50 mV, a value of 50 mV was chosen for this study. The height

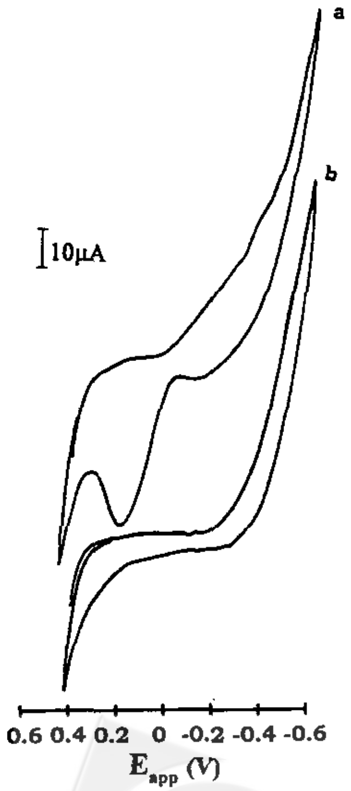

Fig. 1. Cyclic voltammograms for solution containing 50 ppb Cu(II) in 0.02 M nitric acid at scan rate of 20 mV s^{-1}. a. Carbon paste electrode modified with TSCsal; b. Carbon paste electrode.

of the Cu anodic peak increased nonlinearly with the scan rate when this was varied from 2 mV s^{-1} to 10 mV s^{-1}, and then decreased (Fig. 3B). The non-linear behavior might be due to the heterogeneous nature of the electrode process.[15] The dependence of deposition potential was investigated at a copper concentration of 50 ppb. The results are shown in Fig. 3C. The peak height obtained for Cu(II) using ASV with a deposition time of 3 min showed an increase with increasing deposition potentials between -0.2 V and -0.4 V, and remained nearly constant at potentials between -0.4 V and -1.0 V. In other words, the peak current of Cu(II) could be observed over a wide range, namely -1.0 V to -0.4 V. Moreover, a small peak around -0.3 V was indicated at values of the deposition potential larger than -0.7 V. This fact can be explained by the oxidation of TSCsal in carbon paste electrode. A more symmetrical and reproducible peak current, however, was obtained at -0.6 V, so a deposition potential of -0.6 V was considered optimum. The stripping current for Cu(II) was also measured as a function of the deposition time (Fig. 3D). A rapid increase of the peak with increasing preconcentration time was observed for the modified electrode, indicating an enhancement of the copper concentration on the surface. With 5 min preconcentration, a 4.5-fold peak current enhancement was observed. Longer times gave a higher peak current, but the slope was smaller.

The dependence of stripping current on flow rate was evaluated by alternating a supporting electrolyte (0.02 M nitric acid) and the same electrolyte solution with 50 ppb copper ion at a different flow rate. At flow rates of 0.5 - 1.5 mL min^{-1}, no significant difference of stripping current was found. For the system described, 1.0 mL min^{-1} was found to be a good choice for the time of quantitation.

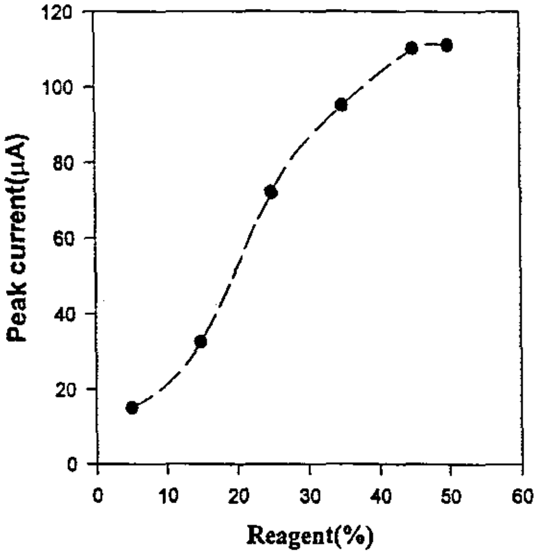

Fig. 2. Amount of modified reagent vs. the peak current on the determination of Cu(II). Modulation amplitude: 50 mV; Scan rate: 10 mV s^{-1}; Deposition potential: -0.5 V; Deposition time: 3 min; Equilibrium time: 1 min; Supporting electrolyte: 0.02 M HNO_3; [Cu(II)]: 50 ppb.

Mechanism of the Electrode Reaction

The above voltammetric behavior of Cu(II) on the CME (Fig. 1) can be explained as follows. In the preconcentration step, Cu(II) is accumulated by the TSCsal in the carbon paste electrode, forming a stable chelate. When it is electrolysed, the accumulated Cu(II) is reduced to Cu(0), which is reoxidized to Cu(II), giving an anodic peak during the anodic potential scan. In the subsequent cathodic scan no significant cathodic wave was observed. The phenomenon might be due to the irreversible and slow reduction of Cu(II). The electrode process could be as follows:
Cu(II) is accumulated on the electrode as the Cu(II)-TSCsal complex.

$$\mathrm{Cu(II) + TSCsal = Cu(II)\text{-}TSCsal + 2\,H^+}$$

The Cu(II)-TSCsal complex on the electrode is then reduced to give copper metal and free TSCsal ligand.

$$\mathrm{Cu(II)\text{-}TSCsal + 2H^+ + 2e = Cu(0) + TSCsal}$$

At the measuring step, the Cu(0) is reoxidized to Cu(II).

Calibration Curve

After choosing the optimum experimental conditions, the stripping voltammograms obtained after successive injections of Cu(II) solutions of ascending concentrations gave well defined sharp peaks (Fig. 4). The results indicate that the method allows convenient measurement of copper at the ppb level. The calibration graph was linear in the range 0.5 ppb to 10 ppb. Least squares treatment of these data yielded the equation I (μA) = 4.625 C (ppb) + 0.223 with a correlation coefficient of 0.9965. The Cu(II) blank level was around 0.5 ppb. Based on three times the standard deviation of the mean value obtained from seven determination of the blank level, the detection limit for Cu(II) is 0.1 ppb (1.7×10^{-9} M). The detection limit is similar to those reported for Cu(II) with other types of CME.[10-13]

Reproducibility

The reproducibility of the peak current after accumulation for 5 min from 10 ppb copper was tested for four runs at -0.6 V in 0.02 M nitric acid. The mean peak current found was 59.8 μA with a range of 58-62 μA and a relative standard deviation of 2.87%. These data indicate that the electrode renewal gives a relatively reproducible surface.

Interferences

Inorganic and organic substances present in the sample can interfere with the trace metal determination owing to their capability of accompanying the metal ion in the accumulation step. Possible interferences from coexisting metal ions capable of binding to TSCsal were evaluated. The influence of concomitant ions is shown in Table 1. In the determination of 10 ppb Cu(II) with a 5 min accumulation, little or no interference was found at the addition of 100-fold Cd(II), Co(II), and Tl(III). A slight interference was observed for the addition of 100-fold As(III) and Mn(II). As expected, the results indicate that the copper ion chelates very well with TSCsal in acidic solution. Compared with the conventional stripping procedure, which is based on electrolytic deposition, the CME procedure discriminated well against interference from many metal ions tested. However, the presence of a 10-fold excess in concentration of Pb(II) and Zn(II) gave observable interferences to the Cu(II) stripping peak, and a 10-fold excess of mercury(II) produced a larger than 40% decrease in Cu response. The phenomena mentioned might be due to the formation of stable complexes between the TSCsal in CME and these metal ions.

About 90% of aquatic organic components are macromolecules or particles, which may be proteins as well as peptides, polysaccharides, lipids, and fulvic/humic compounds.[16] In this study, humic substance, surfactants, and

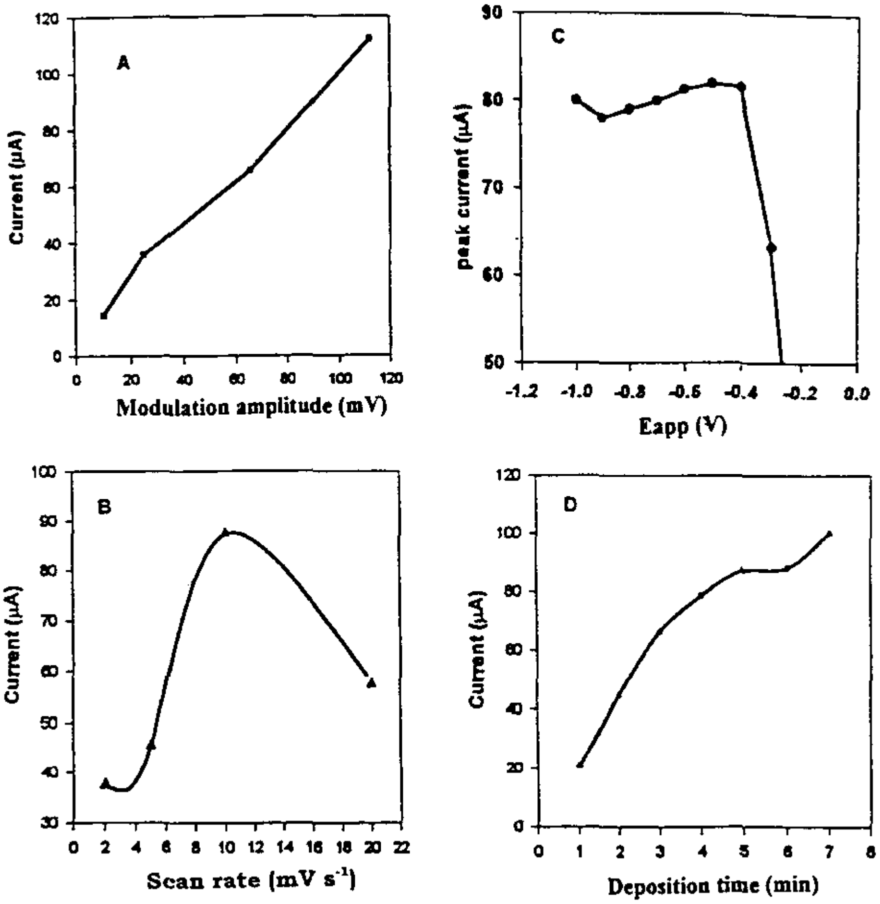

Fig. 3. Optimization of experimental conditions. A. Effect of modulation amplitude on the determination of Cu(II). Scan rate: 10 mV s^{-1}; Deposition potential: -0.5 V; Deposition time: 3 min; Equilibrium time: 1 min; Supporting electrolyte: 0.02 M HNO_3; Flow rate: 1 mL min^{-1}; [Cu(II)]: 50 ppb. B. Effect of scan rate on the determination of Cu(II). Modulation amplitude: 50 mV; Deposition potential: -0.5 V; Deposition time: 3 min; Equilibrium time: 1 min; Supporting electrolyte: 0.02 M HNO_3; Flow rate: 1 mL min^{-1}; [Cu(II)]: 50 ppb. C. Effect of deposition potential on the determination of Cu(II). Modulation amplitude: 50 mV; Scan rate: 10 mV s^{-1}; Deposition time: 3 min; Equilibrium time: 1 min; Supporting electrolyte: 0.02 M HNO_3; Flow rate: 1 mL min^{-1}; [Cu(II)]: 50 ppb. D. Effect of deposition time on the determination of Cu(II). Modulation amplitude: 50 mV; Scan rate: 10 mV s^{-1}; Deposition potential: -0.5 V; Equilibrium time: 1 min; Supporting electrolyte: 0.02 M HNO_3; Flow rate: 1 mL min^{-1}; [Cu(II)]: 50 ppb.

some chelating agents were used as model compounds for the assessment of the proposed method in trace analysis of natural water, since they could possibly influence the behavior of the electrode surface activity.[17] The electrochemical processes of Cu in the presence of humic acid, Triton X-100, sodium lauryl sulfate (SDS) or starch and EDTA were examined. Starch at 15 ppm gave no significant interference. Neutral surfactant (Triton X-100) interferes more severely than anionic surfactant (SDS). EDTA at 1×10^{-5} M, humic acid and Triton X-100 (both at 5 ppm) cause serious interference. Here a slower dissociation kinetics of the metal complexes might be formed.[18] Since the concentrations of these substances in natural water are much lower than the tested values,[16] interferences from them in real samples could be suppressed and even neglected.

Analytical Application

In order to study the performance of the CME in a practical analytical situation, the proposed procedure was demonstrated by determination of copper in spiked drinking-, tap-, and NASS-3 sea water. Recovery experimemts for Cu(II) with 10 ppb conducted on these samples produced satisfactory results (Table 2). Quantitative results were obtained by a standard-additions approach, then from a calibration graph obtained by the analysis of standard Cu(II) solution. The results for the certified reference material agreed well with the recommended value (Table 2).

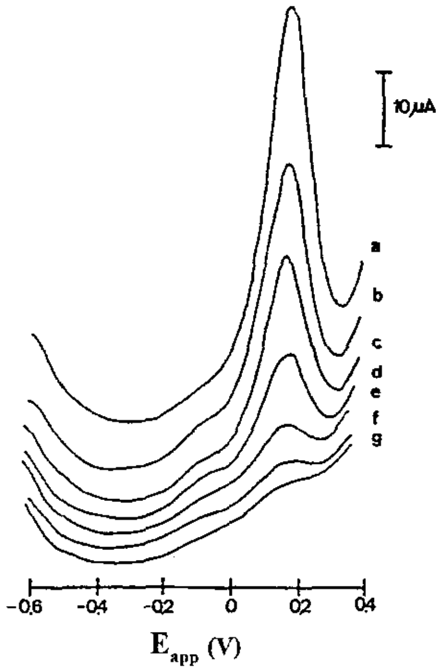

Fig. 4. DPASV voltammograms for various concentrations of copper in pure water. Modulation amplitude: 50 mV; Scan rate: 10 mV s^{-1}; Deposition potential: -0.5 V; Deposition time: 5 min; Equilibrium time: 1 min; Supporting electrolyte: 0.02 M HNO_3; Flow rate: 1 mL min^{-1}. a. 10ppb; b. 7.5 ppb; c. 5 ppb; d. 2.5 ppb; e. 1 ppb; f. 0.75 ppb; g. 0.5 ppb.

Table 1. Influence of Other Metal Ions and Chelating Agents on the Determination of Copper(II)[a]

Interference	Molar ratio, [M]/[Cu]	Signal ratio(%)
As(III)	100	92
	1000	81
Cd(II)	1	100
	10	100
	100	100
Co(II)	100	100
	1000	21
Hg(II)	1	80
	10	54
	100	54
Mn(II)	100	92
Pb(II)	1	108
	10	119
	100	118
Tl(III)	100	100
	1000	95
Zn(II)	1	121
	10	115
	100	129
EDTA	(1×10^{-5} M)	70
Humic acid	(15 ppm)	22
	(5 ppm)	55
Starch	(15 ppm)	96
SDS	(15 ppm)	84
Triton X-100	(15 ppm)	27
	(5 ppm)	64

[a] Deposition potential: -0.6 V; Deposition time: 5 min; Modulation amplitude: 50 mV; Scan rate: 10 mV s^{-1}; Equilibrium time: 1 min; Supporting electrolyte: 0.02 M nitric acid; [Cu(II)]: 10 ppb.

CONCLUSIONS

The incorporation of TSCsal into the carbon paste matrix appears to provide a promising method for preconcentration/voltammetric measurements of copper(II) in nitric acid solution. Several advantages of the flow system have been demonstrated. A switching valve allows injection of the sample and the system to be flushed clean more quickly. Medium exchange between deposition and the stripping steps is easy. Moreover, medium exchange is not necessary in the proposed system. Sample deoxygenation can be omitted. The small volume of flow cell decreases the time for one electrolysis/stripping cycle. Additionally, larger

Table 2. Determination of Cu(II) in Spiked Sample by DPASV at a Carbon Paste Electrode Modified with TSCsal[a]

Sample	Cu(II) added (ppb)	Total Cu(II) found (ppb)	Certified value for Cu(II) (ppb)
Drinking water	10	9.87 ± 0.12	
Tap water	10	9.76 ± 0.15	
NASS-3 sea water	10	9.17 ± 0.20	
NASS-3 sea water[b]		0.119 ± 0.022	0.109 ± 0.011

[a] Deposition potential: -0.6 V; Deposition time: 5 min; Modulation amplitude: 50 mV; Scan rate: 10 mV s^{-1}; Equilibrium time: 1 min; Supporting electrolyte: 0.02 M nitric acid.

[b] With standard addition method.

signal to background ratios were obtained than with the batch system. The method would be an attractive technique for continuous analysis, especially for monitoring environmental copper.

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Key Words

Chemically modified electrode; Salicylaldehyde thiosemicarbazone (TSCsal); Anodic stripping voltammetry; Flow system.

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