Full Paper

SW Anodic Stripping Voltammetry Determination of Copper with New Tape of Modified GC Electrode

Dalibor Stankovic*, Goran Roglic, Ivan Andjelkovic, Sandra Skrivanj, Jelena Mutic and Dragan Manojlovic

Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia

*Corresponding Author, Tel.: +381 11 3336745; Fax: +381 11 2184330
E-Mail: dalibors@chem.bg.ac.rs

Received: 5 November 2011 / Accepted: 14 December 2011 / Published online: 30 December 2011

Abstract - The analysis of Cu(II) by anodic stripping voltammetry using a Nafion-modified glassy Carbon electrode incorporated with Cu-DPABA complex (DPABA is Methyl 3,5-bis{bis-[((pyridin-2-yl)methyl]amino}methyl)benzoate) (Cu-DPABA–NA/GCE) is described. Cu(II) was accumulated in Hac-NaAc buffer pH=4 at potential of -0.3 V (vs. Ag/AgCl ref. electrode) and then determined with SWASV. Under the optimum conditions the calibration curve was linear in the range 15×10^{-8} – 5.6×10^{-5} mol/L. The detection limit was 8.9 x10^{-8} mol/L. Different parameters and conditions, such as volume of Nafion and Cu-DPABA, accumulation time and pH value was optimized. A study of the interfering substances was also performed. A significant increase in current was achieved at the modified electrode compared to a bare glassy carbon electrode. For explanation of voltammetric behavior of modified electrode in copper solution, cyclic voltammograms were recorded. The electrode has been used in the direct determination of Cu(II) in water.

Keyword- Modified Electrode, Square Wave, Anodic Stripping Voltammetry, Copper

1. INTRODUCTION

Chemically modified electrodes (CMEs) provide an active research area in many aspects of science and technology [1-3]. Extraction of trace analytes by complexation is an efficient technique for voltammetric determination at chemically modified electrodes. Many of the
selective ligands used for non-electroanalytical determinations can be employed successfully with CMEs, and retain their selectivities in the immobilized form [4-6]. Polymer coating is one of many different methods (such as adsorption [7], covalent attachment [8], or incorporation into carbon paste matrix [9]) used to immobilize the modifier onto an electrode surface [10-12]. Electrodes modified with polymer containing complexing ligands have been employed for determination of transition metals, and the factors affecting their electrochemical behavior have been studied [13-15].

Voltammetric methods involving an accumulation process, such as stripping voltammetry and adsorptive voltammetry, are generally very sensitive for the determination of trace metal ions. However, their application to practical samples is limited by the interferences from the sample matrix. In order to solve this problem, it is necessary to accumulate the analyte on an electrode selectively. For this purpose, chemically modified electrodes (CMEs) have been used; for example, a glassy carbon electrode the surface of which was modified by a ligand [16-17].

In this paper, the accumulation and voltammetric behavior of Cu(II) using a GCE modified with Cu-DPABA complex (DPABA is Methyl 3,5-bis{bis-[(pyridin-2-yl)methyl]amino}methyl)benzoate ) (Cu-DPABA–NA/GCE) is described. Hence it should be possible to develop a highly sensitive and selective method for the determination of Cu(II) by using a GCE modified with Cu-DPABA. The influence of concomitant ions on the method was found to be negligible. The method was applied to the determination of Cu (II) in water samples without prior preparation.

2. EXPERIMENTAL

2.1. Reagents

Nafion (5%) perfluorinated ion-exchange resin was purchased from Aldrich. 2% Nafion working solution was prepared after dilution with absolute ethanol. Methyl 3,5-bis{bis-[(pyridin-2-yl)methyl]amino}methyl)benzoate (DPABA) was synthesized according to previously described procedure[18]. Cu-complex was prepared by mixing solution Cu(II) c15 mgmL⁻¹ and DPABA, in same concentration. A stock solution (1×10⁻³ mol/L) of Cu was prepared in deionized water. A working solution for SWASV investigations was prepared by dilution of the stock solution with supporting solution. Buffers solutions were used to control the pH. All other reagents were of analytical grade.

2.2. Instrumentation

The voltammetric changes of the sensor were measured with instrument Metrohm 797 VA Computance (Herisau, Switzerland). The triple-electrode system consisted of a working electrode, modified GC electrode, a reference Ag/AgCl potassium chloride (3 M) and
auxiliary platinum electrode. Cyclic voltammogram were recorded on a CHI760B instrument (CHIInstruments, USA). The cell was equipped with modified GC electrode, an accessory platinum electrode of larger area (Model CHI221, cell top including Pt wire counter electrode) and an Ag/AgCl reference electrode (Model CHI111). All measurements were taken at ambient temperature. During the measurements the sample was stirred. All results were extracted from calibration curve.

2.3. Procedure

All measurements were carried out in acetic buffer (pH 4.0). Accumulation potential of -0.3 V (vs. Ag/AgCl electrode) was applied to the working electrode. The differential pulse anodic stripping voltammogram were recorded between -0.2 to 0.2 V. The accumulation time was 120 s. After recording the background voltammograms, standard solutions were added to the cell and measurements were repeated three times. All experiments were performed at room temperature.

2.4. Preparation of modified glassy carbon electrode

Prior to each experiment, the glassy Carbon electrode was polished with alumina powder (0.5 μm), rinsed with deionized water and ultrasonicated in water for 3 min. Modifying compound was prepared by mixing 5 μL 2% (v/v%) Nafion-Ethanol solution with 5 μL solution of Cu–DPABA c=15 mg mL$^{-1}$, and add freshly prepared mixture onto the dry electrode surface with micropipette. The electrode was dried (2 h) to evaporate the solvent and rinsed with deionized water. Their detection limit was 8.9×10$^{-8}$ mol/L.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry behavior of modified glassy carbon electrode

Sweep for modified glassy carbon electrode from -0.5 V to +0.6 V showed one cathodic peaks (0.3 V) and backwards anodic sweep (+0.6 to -0.5 V) showed one anodic peak (-0.36 V) (Fig. 1). Modified electrode has very good reproducibility (RSD=3.7% was for n=5, concentration 50μmol, scan rate 100 mV, average Ipa 45.8 μA, standard deviation 1.68 μA). Since the cyclic voltammogram of Cu(II) solution with nonmodified electrode did not show any wave in the same potential range, the Nafion–Cu-DPABA modified electrode can be used for voltammetric determination of copper (Fig. 1).
Fig. 1. Cyclic voltammogram of Cu(II) solution with modified electrode concentration of Cu(II) was $1 \times 10^{-5}$, scan rate 50 mVs$^{-1}$, supporting electrolyte acetic buffer

3.2. Optimization of membrane ingredients

The effect of volume of plasticizer on the peak current was study and the results shown in Fig. 2. They were mixed in ratio 1:1. The peak current reached its maximum when the volume of plasticizer (2% Nafion) was Cu-DPABA complex was 10 μL. The function of Nafion was to fix complex on glassy carbon electrode, and also to serve as a barrier to prevent interferences from reaching the electrode surface. When used more than 10 μL of modifying compound layer thickness on the electrode increased which leads to an increase of accumulation time and peak current decreases. Coating the glassy carbon electrode surface with films thinner than those created by adding 10 μL of modifying compound decreased the signal. So, the ideal volume of modifying compound for preparing modified glassy carbon electrode was 10 μL and it was used for all others experiment[19].

3.3. Effect of accumulation time

As expected for anodic stripping experiment the peak current increased with the increasing of accumulation time (Fig. 3). At longer deposition time than 120 s the stripping signals became almost constant. Because the preconcentration time depends on the analyte concentration, it takes longer for the peak current to level off at lower concentration of metal ions. With longer deposition time, the signal intensity grows slowly, but increases the time required for analysis, so that the optimal duration of analysis and intensity of the signal is 120 s.
Fig. 2. The effect of volume of modifying compound on the peak current at optimized measurements parameters: electrolyte acetic buffer pH=4, accumulation potential -0.3 V, accumulation time 120 s

Fig. 3. Effect of accumulation time on peak current at optimized measurements parameters: electrolyte acetic buffer pH=4, accumulation potential -0.3 V
3.4. Effect of pH

The peak current in various electrolytes, such as HCl, different acetate buffers and KCl, was investigated. To cover the entire range of pH different supporting electrolyte of the same concentration (1×10⁻³ mol/L) were used. For lowest pH used HCl, then acetate buffer and for pH 7 KCl. It was found that a well-defined and sensitive anodic stripping peak current were with acetic buffer. The effect of different pH values were examined (Fig. 4). The pH value 4 was selected as optimum.

![Graph showing effect of pH on peak current at optimized measurements parameters: different electrolyte, accumulation potential -0.3 V, accumulation time 120 s.]

3.5. Interferences

Perhaps the main advantage of the modified electrode for determination of metals ions lays in its inherent selectivity. Any electroactive species that forms a precipitate with DPABA might present an obstacle for the successful analysis. No alteration of the voltammetric signals of copper was found in excess of following ions: Li, Na, K, Cs, Mg, Ca, Ba, Mn, Zn, Cr, Pb, Cd and Ni for what is credited potential window in which was recorded. However in the presence of Hg and Bi ions the stripping response has altered significantly because there is a match signal and increase the peak current of copper.

3.6. Analytical applications

Application of the new Cu(II) modified electrode in real samples was one of the primary requirements for its validation. The concentration was estimated by ASV from the calibration curve of the proposed Cu(II) modified electrode. The SWASV for different concentrations of
Cu and calibration curve was presented in Fig. 5 and Fig. 6, respectively. The corresponding equation and correlation coefficient was \( I = -0.056 + 0.146 \, C \), \( r = 0.9922 \), where \( C \) is concentration in \( \mu \text{gL}^{-1} \) and \( I \), current in \( \mu \text{A} \). The resulting calibration plots were linear over the range from \( 15 \times 10^{-8} - 5.6 \times 10^{-5} \) mol/L. The detection limit was \( 8.9 \times 10^{-8} \) mol/L based on three times the background noise. Accuracy was evaluated with recovery experiments (Table 1). It was found that the copper contents obtained from three measurements are in satisfied agreement with prepared solution.

![SWAS voltammograms for different concentration of Cu with Cu-DPABA–NA/GCE in acetate buffer (pH 4.0), scan rate 50 mVs⁻¹, \( E_{\text{acc}} = -0.3 \) V and \( t_{\text{acc}} = 120 \) s](image)

**Fig. 5.** SWAS voltammograms for different concentration of Cu with Cu-DPABA–NA/GCE in acetate buffer (pH 4.0), scan rate 50 mVs⁻¹, \( E_{\text{acc}} = -0.3 \) V and \( t_{\text{acc}} = 120 \) s

**Table 1.** Results of determination of copper in samples of river water

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample conc. µg/L</th>
<th>Cu(II)-added µg/L</th>
<th>Cu(II)-found µg/L</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>ND</td>
<td>15.00</td>
<td>15.06</td>
<td>100.4</td>
</tr>
<tr>
<td>2.</td>
<td>ND</td>
<td>15.00</td>
<td>14.95</td>
<td>99.67</td>
</tr>
<tr>
<td>3.</td>
<td>ND</td>
<td>15.00</td>
<td>15.04</td>
<td>100.27</td>
</tr>
</tbody>
</table>
4. CONCLUSION

A new type of modified glassy carbon electrode for SWASV determination of copper has been developed. The new sensor is based on readily available Cu(II)-complex. The results obtained shows that these modified electrodes are comparable with other conventional electrode. The realization of new Cu-DPABA–NA/GCE modified glassy carbon electrode enhances the selectivity and detection limit for SWASV determination of copper. Although the life time of suggested sensor is relatively long (hundred measurements) and it can be easily prepared for another determinations.

Acknowledgements

This paper was supported by the Ministry for Science, Republic of Serbia, Project No 172030.

REFERENCE