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Full Paper

New Potentiometric Sensor for Copper Determination in Waste Waters Based on a New Type of Modified GC Electrode

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Abstract- The potentiometrical analysis of Cu^{2+} using Nafion- modified electrode with Cu complex with DPABA (Methyl 3,5-bis{bis-[(pyridin-2-yl)methyl]amino}methyl)benzoate) incorporated, is described. Parameters and conditions such as the volume of 2% Nafion, pH, and the concentration of Cu complex with DPABA and pH of medium were optimized. Interference of Fe^{3+}, Co^{2+} and Zn^{2+} with Cu^{2+} were examined. Calibration curve was linear in the range of 1×10^{-7}-5×10^{-5} mol/L. The detection limit was 7×10^{-8} mol/L. A response time of the proposed electrode was 3 s.

Keywords- Modified Electrode, Potentiometry, Copper Determination, Cyclic Voltammetry

1. INTRODUCTION

Copper is important element in biological system. It is an essential micronutritient present in at least thirty enzymes. On the other hand it is toxic above a certain concentration. The European Water Quality Directive recommends that its concentration in drinking water does not exceed 2 mg/L. The concentration of copper is low in natural, environmental, biological and real sample. Finding a sensitive method for reliable detection of copper is of great

interest. Because of that, metal complexes as artificial metallonucleases attracted considerable interest due to their structural diversity and reactivity. Copper complexes are the most frequently studied species due to their nucleonase affinity and biologically accessible oxidative/reductive potential [1-3].

In recent years many substances have been used for electrode modification and determination of copper. A amoxicillin [4], cysteine [5], calix(4)arene[6], diquinolyl-8,8'-disulfide[7], hexacyanoferrate[8], tetraethylthiuram disulfide[9], tetraphenylporphyrin[10], p-tert-Butylcalix(4)arene[11], 1,2-bis-methyl (2-aminocyclopentene-carbodithioate) ethane[12], polypirrole pyrocatechol violet[13] and 2-aminothiazole organofunctionalized silica[14] have been used to make chemically modified electrodes for determination of copper. Cu^{2+} and other metal complexes with dipicolylamine and their derivatives are shown to be effective and selective in hydrolysis of 2'-5' and 3'-5' ribonucleotides [15], for fluorescence detection of flavin adenine dinucleotide in human eosinophilis [16], making ensemble system for detection of polyphosphates in water [17], for fluorescent artificial chemosensors for phosphorylated proteins and peptides [18], and other sensors. In papers which use modified electrodes, voltammetric methods are mainly used. It requires much expensive and complicated instrumentation as opposed to potentiometrical methods widely used in most analytical laboratories.

Potentiometry is well-known as a common method for determination of many metals. This can be very sensitive and useful [19-20]. Chemically modified electrodes have been recognized as one of the alternatives for reduction of detection limit for determination of metals. Chemically modified electrodes can be easily and conveniently made and have advantages in enhancing the selectivity and sensitivity due the chemical nature and structure of the modified electrode surface. Therefore, chemically modified electrodes are already widely used in analytical chemistry [21].

The aim of this work is to develop a new glassy carbon modified electrode for determination of copper by potentiometry. This study has led to the development of a new and sensitive potentiometric method for copper determination. Our intention was to develop an ion selective Cu^{2+} electrode based on modified glassy carbon (GC) electrode immobilized with Nafion using a simple construction procedure for performing Cu^{2+} determination in waste water.

2. EXPERIMENTAL

2.1. Reagents

All reagents were of analytical grade. Nafion perfluorinated (Aldrich, Steinheim, Germany) ion-exchange resin (2%) was used. All other reagents were p.a. quality, performed from Merck, Germany. DPABA was synthesized according to previously described

procedure [22]. Cu-DPABA was prepared by mixing solution of Cu^{2+}, and DPABA, of the same concentration (15 mg/mL).

A stock solution (1×10^{-3} mol/L) of Cu^{2+} for determination of copper was prepared in deionized water. A working solution for potentiometric investigations was prepared by dilution of the stock solution with deionized water using variable Eppendorf micropipettes. Buffer solutions were used to control the pH .

Samples

For application of the new Cu^{2+} modified electrode Danube river water from five different places were used without any prior preparation.

Instrumentation

The potential changes of the sensor were measured against a Ag/AgCl (3 M KCl) reference electrode using a JENCO electronics ltd. 6071 pH/mV meter. All measurements were taken at ambient temperature. During the measurements the sample was stirred using a magnetic stirrer. All results were extracted from calibration curve.

2.2. 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 ultasonic- treated in water for 3 min. Modifying compound was prepared by mixing of 10 μL 2% (v/v) Nafion-ethanol solution with 10 μL of Cu–DPABA solution (15 mg/mL), and applicating the 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.

2.3. Electrode evaluation

The potentiometric response characteristics of sensor were evaluated in terms of ionic sensitivity, detection limit, working concentration range, response time, lifetime and interfering cations.

3. RESULTS AND DISCUSSION

The potentiometric curves using the procedure described above with a bare glassy carbon electrode and electrode modified with Cu-DPABA and Nafion showed that the sensitivity increased when the Cu-DPABA was used to modify the coating (Fig. 1). The results obtained for the modified electrode showed Nernstian response and that the potentiometric response characteristics (detection limit 7×10^{-8} mol/L, linear range 1×10^{-7}-5×10^{-5} mol/L) better than bare glassy carbon electrode.

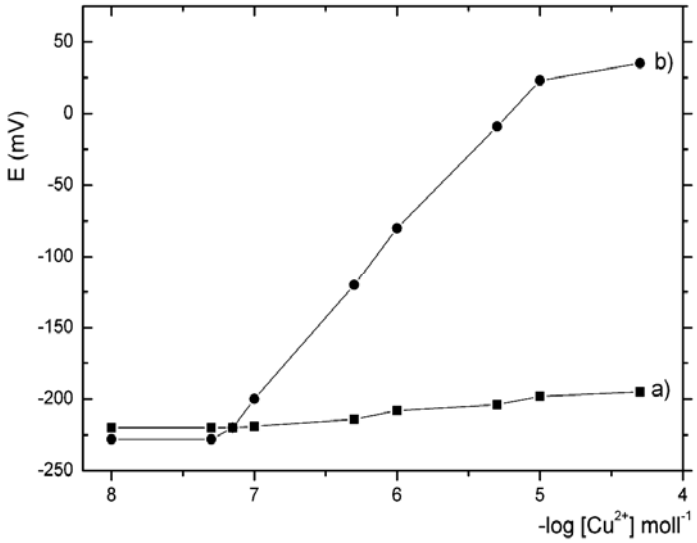

Fig. 1. Potentiometric calibration graph of glassy carbon electrodes: a) nonmodified GC electrode, b) modified GC electrode

3.1. Effect of volume of modifying mixture on response time

The effect of volume of modifying mixture on potentiometric response was studied, and the results shown in Fig. 2. The curve has better slope when the volume of 2% Nafion is 10 μL, mixed with 10 μL of Cu-DPABA with concentration of 15 mg/mL. The function of Nafion was to fix complex on glassy carbon electrode, and also to serve as a barrier to prevent interferents from reaching the electrode surface.

When used 30 μL of modifying mixture, thickness on the electrode surface increased, which leads to a higher concentration of detection limit and longer response time (8 s). So, the best volume of modifying compound for preparing modified glassy carbon electrode was 20 μL and that was used for all other experiments [23, 24, 25].

3.2. Effect of pH

The potentiometric response of Cu^{2+} in various electrolytes, such as different phosphate and acetate buffers was investigated. The effects of different pH values (adjusted with phosphate and acetate buffers) were examined (Fig. 3).

It was found that a well-defined and sensitive potentiometric response corresponded to chosen conditions (10 μL of Nafion, 10 μL of Cu-DPABA) in acetate buffer as electrolyte. The pH value 4 was selected as optimal when concentration of supporting electrolyte was 1×10^{-3} mol/L. On selected pH value calibration curve has Nernstian response, detection limit 7×10^{-8} mol/L and response time of 3 s. Higher pH is not taken into account because of low solubility product of metal hydroxides.

(K_{sp}: $Cu(OH)_2=4.8\times10^{-20}$, $Zn(OH)_2=5\times10^{-17}$, $Fe(OH)_3=5\times10^{-38}$, $Co(OH)_2=5.92\times10^{-15}$) .

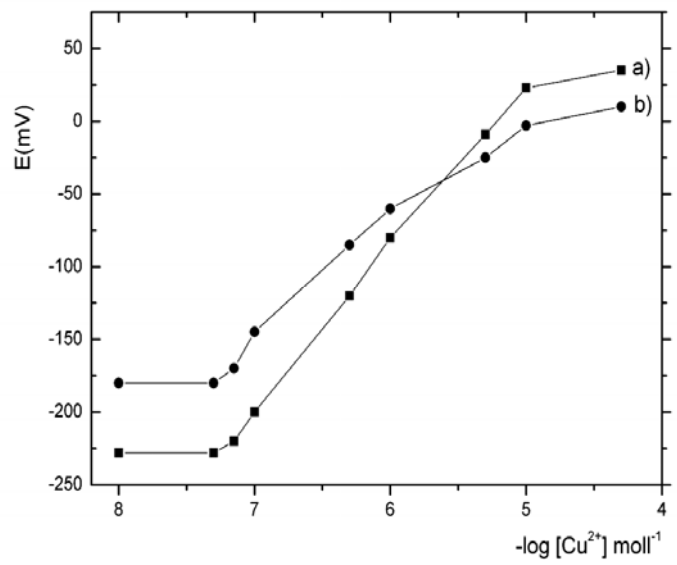

Fig. 2. Effect of the Nafion on the potentiometric response of modified glassy carbon electrode: a) 10 µl of Nafion; b) 5 µl of Nafion (volume of DPABA 10 µl, concentration 15 mg/mL , pH 4)

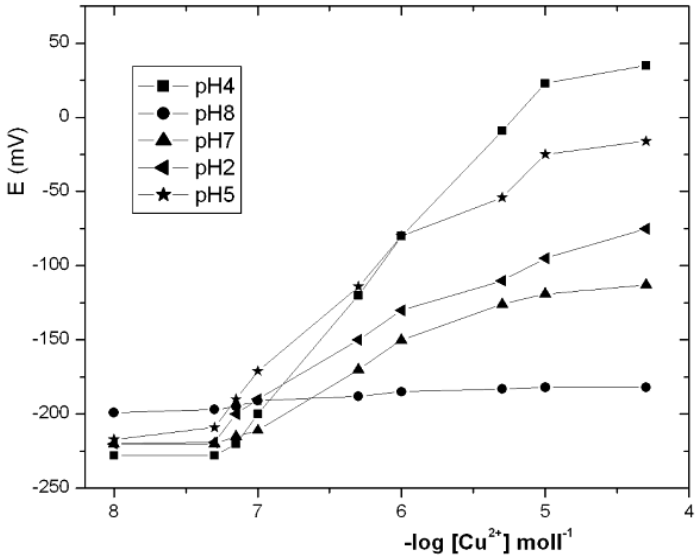

Fig. 3. Effect of the pH on the potentiometric response of the modified glassy carbon electrode

3.3. Effect of possible interfering cations on the response of the electrode

The influence of some cations on the potentiometric response of copper-selective electrode was investigated. Tested interfering cations are selected as the most common companions of copper in waste water. The results showed that cations such as Fe^{3+}, Co^{2+} and Zn^{2+}, in concentration of 1×10^{-7} mol/L have influence on the response of the modified electrodes. The detection limit was the same and the calibration curve was linear in the same range when cations were Fe^{3+} and Co^{2+} but when zinc was present in solution, electrode does not have good response to copper (Fig. 4). These results were expected for these cations because DPABA could not coordinate iron (III) and Co (II) ions. Reaction of copper (II) with DPABA could be suppressed completely in presence of zinc ions [22].

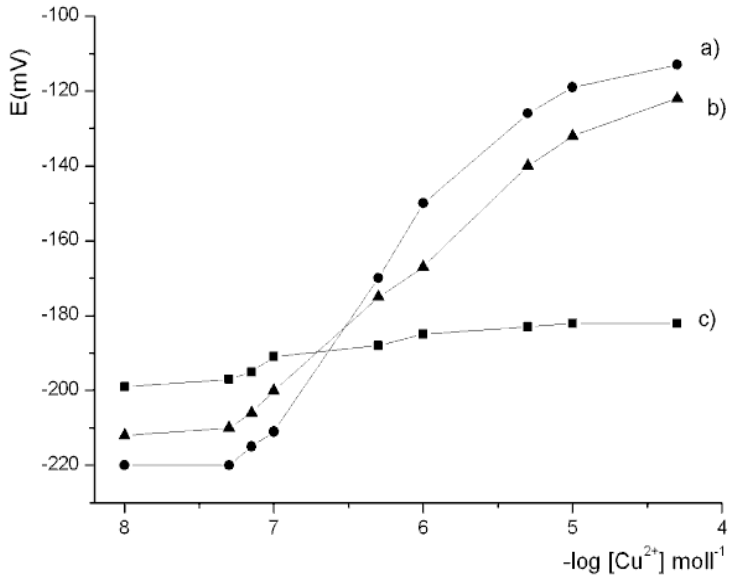

Fig. 4. Effect of the cations on the potentiometric response of modified glassy carbon electrode: a) Fe^{3+}, b) Co^{2+}, c) Zn^{2+}, concentration of all cations: 1×10^{-7} mol/L

3.4. Analytical applications

Application of the new Cu^{2+} modified electrode in real samples was one of the primary requirements for its validation. The concentration was estimated by direct potentiometry from the calibration curve of the proposed Cu^{2+} modified electrode. Accuracy was evaluated with recovery experiments (Table 1). It was found that the copper contents obtained from five measurements are in satisfied agreement with prepared solution.

Table 1. Results determination of copper in Danube water samples

Sample	Sample conc.	Cu^{2+}-added mol/L	Cu^{2+}-found mol/L	Recovery %
1.	ND	5×10^{-6}	5.01×10^{-6}	100.2
2.	ND	5×10^{-6}	4.97×10^{-6}	99.4
3.	ND	5×10^{-6}	5.02×10^{-6}	100.4
4.	ND	5×10^{-6}	5.00×10^{-6}	100
5.	ND	5×10^{-6}	4.95×10^{-6}	99

ND-non detectable

4. CONCLUSIONS

A new type of modified glassy carbon electrode for potentiometric determination of copper has been developed. The new potentiometric sensor is based on readily available Cu-DPABA. The results obtained shows that this modified electrode can be alternative to conventional electrode. New Nafion–Cu-DPABA modified glassy carbon electrode enhances the selectivity and detection limit (7×10^{-8} mol/L) for potentiometric determination of copper. In addition, the lifetime of suggested sensor is relatively long (more than hundred measurements) and it can be easily re-prepared for another determinations.

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