Voltammetric Determination of Copper(II) Using Glassy Carbon Electrodes Modified with Nafion-DTPA-Glycerol

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Abstract

A glassy carbon electrode(GCE) modified with nafion-DTPA-glycerol was used for the highly selective and sensitive determination of a trace amount of Cu^{2+}. Various experimental parameters, which influenced the response of nafion-DTPA-glycerol modified electrode to Cu^{2+}, were optimized. The copper(II) was accumulated on the electrode surface by the formation of the complex in an open circuit, and the resulting surface was characterized by medium exchange, electrochemical reduction, and differential pulse voltammetry. A linear range was obtained in the concentration range 1.0×10^{-8}M~1.0×10^{-6}M Cu(II) with 7 min preconcentration . Further, when an approximate amount of lead(II) is added to the test solution, nafion-DTPA-glycerol modified glassy carbon electrode has a dynamic range of 2 orders magnitude(1.0×10^{-9}M~1.0×10^{-7}M). The detection limit(3σ) was as low as 5.0×10^{-10}M(0.032ppb). The interferences from other metal ions could be reduced by adding KCN into the sample solutions. This method was applied to the determination of copper(II) in certified reference material(3.23×10^{-7}M, 21ppb), sea water(9.50×10^{-7}M, 60ppb). The result agrees satisfactorily with the value measured by Korea Research Institute of Standard and Science.

Introduction

Chemically modified electrodes(CMEs) have been intensively studied in the field of analytical chemistry. One of the purposes for modifying electrodes is to improve its analytical performance by increasing sensitivity and selectivity. Advantages of CME are easy to fabricate in short time and can be readily prepared with a variety of modifier, highly sensitivity, and low cost. Selection of galssy carbon electrode is very useful because of chemically inertness, polishing of electrode surface easily, large overvoltage for hydrogen, and high conductivity. Reports on the analytical utilization of CMEs have included complexation, precipitation, bioaccumulation, potentiometric response, and others. Also many modification methods have been used to introduce modifiers onto the electrode surface. Recently, a number of studies on the use of chemically modified glassy carbon electrodes for analytical

determination have been reported. Baldwin and co-workers employed modified carbon paste electrode for the determination of Ni(II) and Cu(II) with excellent sensitivity and reproducibility. A microorganism for bioaccumulation and subsequent voltammetric quantitation of copper was reported by Wang et al. Other studies on the determination of metal ion have also appeared. This study describes determination of copper using a glassy carbon electrode modified with nafion-DTPA-glycerol.

Materials and Methods

Voltammetric measurements were performed with a BAS model 100B/W Electrochemical Analyzer. The three electrode system consisted of a modified glassy carbon working electrode, Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. All solutions were prepared with doubly distilled waster and all glassware were soaked in 6N HNO_3 and cleaned before use. All reagents were of analytical-reagent grade from Aldrich, Junsei pruducts. Seawater and river water filtered through a syringe filter with pore size of 0.45㎛. The glassy carbon electrode was polished with 0.05㎛ alumina on Buehler micro cloth to a mirror-like finish. Modification of glassy carbon electrode was performed by dropping 2㎕ solution containing nafion-DTPA-glycerol onto the electrode surface and drying for 10 min at room temperature. Preconcentration was accomplished by immersing a modified electrode into 10 ml of a stirred buffer solution(pH4.0) containing metal ion for 7 min without potential control. The modified electrode was removed, rinsed with distilled water and placed in the measurement cell containing buffer solution(pH4.0). A reduction potential of -0.4V was applied for 50s and then a positive scan was performed. Parameters of DPV was applied as follows. Scan rate : 20 mV/s ; pulse amplitude : 50mV ; potential range : +0.5V～-0.5V.

Results and Discussion

The reaction mechanisms at nafion-DTPA-glycerol-coated glassy carbon electrodes have been contemplated :

1) Preconcentration step(open circuit cell)

$$[\text{Carbon-nafion}(SO_3Na)_2\text{-glycerol-DTPA}] + Cu^{2+} \rightarrow [\text{Carbon-nafion}(SO_3^-)_2\text{- glycerol-DTPA } Cu^{2+}] + 2Na^+$$

2) Reduction step(closed circuit cell)

$$2e^- + [\text{Carbon-nafion}(SO_3^-)_2\text{-glycerol-DTPA } Cu^{2+}] + 2Na^+ \rightarrow [\text{Carbon-nafion}(SO_3Na)_2\text{-glycerol-DTPA } Cu^0]$$

3) Stripping step (closed circuit cell)

$$[\text{Carbon-nafion}(SO_3Na)_2\text{-glycerol-DTPA } Cu^0] \rightarrow 2e^- + [\text{Carbon-nafion } (SO_3^-)_2\text{-glycerol-DTPA } Cu^{2+}] + 2Na^+$$

The calibration plot was obtained range $1.0\times10^{-8}M\sim1.0\times10^{-6}$ for 7 min accumulation time at open circuit. The detection limit(3σ) was $5.0\times10^{-9}M$(0.32 ppb). Anodic peak current of Cu^{2+} ($2.5\times10^{-7}M$) was reduced(or increased) by about 15.4% in the presence of $1.0\times10^{-7}M$ Hg^{2+}. Additions of 1.0×10-7M Cd^{2+}, Ni^{2+}, and Pb^{2+} to Cu^{2+} ($2.5\times10^{-7}M$) solution resulted in 14.3%, 16.3%, and 17.6% increasing of the anodic peak currents of Cu^{2+}, respectively. Specially when Pb^{2+}(20.7ppb) was added in the sample solution, detection limit for Cu^{2+} was $5.0\times10^{-10}M$ (0.032 ppb). The analytical application of the nafion-DTPA-glycerol modified electrode was applied to the determination of copper(II) of river water and seawater. The results agree satisfactorily with the values measured by Korea Basic Science Institute.

Conclusion

A new chemically modified glassy carbon electrode has been developed using nafion-DTPA-glycerol for the determination of copper(II) at trace levels by differential pulse voltammetry. To enhance the sensitivity and reproducibility of the method, a second ion, e.g., Pb(II), was added to the test solution.

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