Determination of Lead(Ⅱ) at Nafion-DTPA-Glycerol-Modified Glassy Carbon Electrodes

Eun Heui Park[*1] · Chan Ju Park[2] · Keun Ho Chung[3]

*[*1,2]Department of Chemistry · [3]Department of Chemistry Education, Chonnam National University, Gwangju, 500-757 Korea*

Abstract

Determination of Lead(Ⅱ) using nafion-DTPA (diethylene triamine pentaacetic acid)-glycerol-modified glassy carbon electrodes is described. Lead(Ⅱ) is accumulated at the electrode by complexing with the DTPA, reduced, and detected by differential pulse voltammetry. In this study, we demonstrate that at a preconcentration time of 5min the nafion-DTPA-glycerol-modified glassy carbon electrode has a linear calibration curve at range 1.0×10^{-9}M~1.0×10^{-7}M in pH 4.0 buffer solution. The detection limit(3σ) is as low as 5.0×10^{-10}M. This method is applied to the determination of lead(Ⅱ) in certified reference material and the result agrees satisfactorily with the certified value.

Introduction

Chemically modified electrodes(CMEs) are electrodes which have been deliberately treated with some reagent, having desirable properties, so as to take on the properties of the reagent. The CMEs are the essential interface between target analyte and modifier which has a particular affinity for the analyte. The CME approch is considered more selective than conventional stripping analysis. This paper describes the determination of Lead(Ⅱ) at nafion-DTPA-glycerol-modified glassy carbon electrodes by differential pulse voltammetry. We selected glassy carbon as the working electrode because of its chemical inertness, easily renewable surface, large overvoltage for hydrogen, and high electrical conductivity. The polymer nafion serves as a matrix for electrode modification, DTPA is a selective complexing reagent for lead(Ⅱ), and glycerol is modifier to enhance the sensitivity. This has the advantages of low detection limit, low cost, and ease in operation.

Materials

All chemicals were purchased from Aldrich Co. and used without further purification. Lead (Ⅱ) certified reference material solution was obtained from Korea Research Institute of Standards and Science. A 0.1M acetate buffer solution(pH4.0) served as a supporting electrolyte. All solutions were prepared in doubly distilled water obtained from Sambo scientific Co.(Korea). BAS Model 100B/W Electrochemical Analyzer was used for voltammeric experiments. A three-electrode system consisting of a nafion-DTPA-glycerol-modified glassy carbon working electrode, a Pt wire auxiliary electrode, and Ag/AgCl reference electrode was used.

Methods

Preconcentration step

The modified electrode was immersed in 10㎖ of pH 4.0 buffer solution containing Pb(Ⅱ) ion, which was stirred by magnetic stirrer 1.0㎝ below the electrode surface for 5 min(open circuit).

Voltammetric determination step

After preconcentration, the electrode was taken out and rinsed with distilled water and was transferred to another cell containing blank pH4.0 buffer solution(10㎖). The quiet time was applied for 50s, the electrode was scanned from -0.9 to -0.3 V, and the peak current was measured.

Renewal step

After each determination the electrode was rinsed with distilled water and polished with a alumina slurry(0.05㎛) on a Buehler cloth. Ultrasonic vibration served to remove any alumina or other impurities that might adhere to the electrode surface.

Fabrication of nafion-DTPA-glycerol-modified GCE

A glassy carbon electrode coated with nafion-DTPA-glycerol mixture solution was prepared by drying at room temperature(10min) after dropping 2㎕ modifier solution onto the surface of a fresh glassy carbon electrode.

Results and Discussion

In order to find out the optimum conditions, we investigated various experimental parameters, such as the composition of modifier, preconcentration time, pH of electrolyte, and parameters of differential pulse voltammetry(DPV). The composition of modifier was nafion(1%), DTPA(5.0×10^{-4}M), and glycerol(0.14M). The pH of electrolyte was 4.0 and preconcentration time was 5 min. The DPV measuring conditions were as follows. Scan rate

: 20mV/sec ; quiet time : 50s ; pulse amplitude : 50mV. The relationship between the peak current and the concentration of Pb(Ⅱ) ion was examined. The calibration plot was obtained range 1.0×10^{-9}M~1.0×10^{-7}M in pH 4.0 buffer solution. The analytical application of the nafion-DTPA-glycerol-modified GCE was demonstrated in determination of Pb(Ⅱ) on certified reference material.

Conclusion

1. A linear calibration curve shows at range 1.0×10^{-9}M~1.0×10^{-7}M and correlation co-efficient of 0.9922. The detection limit(3σ) is as low as 5.0×10^{-10}M(0.1ppb).
2. This method is applied to the determination of Pb(Ⅱ) for certified reference material with relative standard deviation of 4.69%.

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