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New copper(II)-selective chemically modified carbon paste electrode based on etioporphyrin I dihydrobromide

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ABSTRACT

A new chemically modified carbon paste electrode (CMCPE) based on etioporphyrin I has been developed for the determination of Cu^{2+} in real samples. The performance of this electrode was investigated using potentiometric measurements. The developed sensor exhibits a good linear response with a slope of 30.30 mV per decade over the concentration range of 1.28×10^{-6}–1.28×10^{-2} mol L^{-1}. It has a very low limit of detection, 8.99×10^{-7} mol L^{-1}, with response time of 5 s. The proposed electrode revealed very good selectivities with respect to alkali, alkaline earth and some transition metal ions and could be used in pH range of 4.5–8.5. The thermal stability of the electrode was studied. This modified electrode was successfully applied as an indicator electrode for potentiometric titration of Cu^{2+} with EDTA and CDTA. Also the electrode was applied for direct determination of copper in different water samples, milk powder, brass powder and copper rod.

1. Introduction

Copper is an essential element and is also toxic at high concentration, the maximum tolerable level for copper is 2.0 mg L^{-1} [1]. Copper deficiency results in anemia while its accumulation results in Wilson disease (WD) [2]. Potentiometric determination of copper assumes high importance in view of the widespread occurrence of this element in the environment and the sophistications associated with the other instrumental techniques used for its determination. Reactivity and biological uptake of copper are strongly influenced by its free ion concentration. Potentiometric measurements with a copper selective electrode allow direct determination of free copper ion concentration in water samples [3–6]. For this reason researchers attempted to develop sensors for its determination at high selectivity and sensitivity.

In spite of availability of a number of Cu(II) sensors, their use for Cu(II) estimation is limited, because they have shown interference by K^+ [7], Pb^{2+} [8–12], Fe^{3+} [13], Ni^{2+} [14,15] and Co^{2+} [16] ions, working over narrow concentration range [8,17–19], and show non-Nernstian response [8,9,18], limited pH range [20] and high response time [18]. In order to achieve wider applicability, these limitations need to be removed or neutralized. Efforts in this direction are exerted to use different materials for preparing Cu^{2+} sensors. The essential requirements to impart selectivity to the ion sensor are to use specific ion-recognition elements which show strong affinity for the assayed metal ion and give poor response for all others. Continuing efforts in this direction, we tested several carbon pastes of varying compositions based on different reagents specific for Cu(II). It was found that the CMCP based on etioporphyrin I ligand is highly sensitive to Cu(II) over several alkali, alkaline earth, and transition metal ions. This work describes the preparation, characterization and analytical applications of new Cu(II) ion-selective modified carbon paste electrode using etioporphyrin as ion-recognition element.

2. Experimental

2.1. Reagents and materials

Sodium tetratphenylborate (NaTPB), sodium tetrakis (1-imidazolyl)borate (NaTImB), etiopophyrin I dihydrobromide 98.0%, potassium tetraphenylborate, o-nitrophenyloctyl ether (o-NPOE), dioctyl phthalate (DOP), dibutyl-butyl phosphonate (DBBP), tricresyl phosphate (TCP), dioctyl adipate (DOA), and dioctyl sebacate (DOS) were purchased form Aldrich chemical company. Copper nitrate trihydrate was purchased from Oxford laboratory products-Mumbai-India 95–103%.

2.2. Solutions

Deionized water was used for all preparations and throughout all experiments. Stock solution of Copper nitrate trihydrate solution (0.1 mol L^{-1}) (Oxford product) was prepared by dissolving 2.415 g $Cu(NO_3)_2 \cdot 3H_2O$ in 100 ml deionized water, and nitric acid

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was added for reservation to prevent hydrolysis and standardized by complexometry [21]. It was kept in glass bottles in refrigerator.

2.3. Apparatus

For potential measurements JENWAY 3010 digital pH/mV meter was used. A SENTEK R1/2MM Ag/AgCl electrode was used as the outer reference electrode. Millipore Elix S (Automatic Sanitization Module) (ASM) was used for obtaining the deionized water. Perkin–Elmer Optima 2000 ICP instrument was used for the atomic emission spectrometry measurements.

2.4. Preparation of modified carbon paste electrodes

A Teflon holder (12.0 cm, length) with a hole at one end (7.0 mm diameter, 3.5 mm deep) for the carbon paste filling served as the electrode body. Electrical contact is made through a stainless steel rod through the center of the holder. This rod can move up and down by screw movement to press the paste down when renewal of the electrode surface is needed. The modified paste was prepared by mixing the appropriate weight of ionophore and high purity graphite with acetone. The mixture is homogenized, left at room temperature to evaporate acetone, then a weighed amount of plasticizer is added and a very intimate homogenization is then achieved by careful mixing with agate pestle in agate mortar. The paste is then packed into the hole of the electrode body. The carbon paste was smoothed onto a paper until it had a shiny appearance and used directly for potentiometric measurements without preconditioning.

2.5. Effect of interfering ions

The influence of some inorganic cations was investigated graphically by plotting the calibration curves for all ions tested and comparing them to the calibration curve of Cu^{2+} ion. The selectivity coefficient values were determined by applying the matched potential method [22,23] that depends neither on the Nicolsky–Eisenman equation nor on any of its modifications. This method was recommended in 2002 by IUPAC [24] as a method that gives analytically relevant practical selectivity coefficient values.

2.6. Potentiometric determination

The standard addition method was applied, in which a known incremental change is made through the addition of standard solution to the sample. This was achieved by adding known volumes of a standard copper(II) solution to 50 ml water containing different amounts of the copper(II) samples including, milk powder, brass powder, copper rods and different water samples. The change in mV reading was recorded for each increment and used to calculate the concentration of the copper(II) in sample solution using the following equation [25]:

$$C_x = C_s\left(\frac{V_s}{V_x+V_s}\right)\left(10^{n(\Delta E/S)} - \frac{V_x}{V_s+V_x}\right)^{-1}$$

where C_x is the concentration to be determined, V_x is the volume of the original sample solution, V_s and C_s are the volume and concentration of the standard solution added to the sample to be analyzed, respectively, ΔE is the change in potential after addition of certain volume of standard solution, and S is the slope of the calibration graph.

2.7. Sample analysis

For analysis of milk samples, 2.0 g milk powder was ashed at 400 °C in a crucible for 3 h and then 2 ml of conc. HNO_3 was added and the mixture was heated to dissolve residue. The resulting solution was diluted with deionized water in a 25.0 ml volumetric flask [16]. The Cu(II) content in the resulting solution was determined potentiometrically using the Cu(II)-CMCPE. Analysis of brass powder and red copper was done by dissolving the sample in conc. HNO_3 and the solution is transferred to a 100 ml volumetric flask and diluted to the mark with deionized water [14]. The resulting solutions were subjected to potentiometric determination of Cu(II) using the present Cu(II)-CMCPE.

3. Results and discussion

Etioporphyrin I (2,7,12,18-tetraethyl-3,8,13,17–tetramethyl-21H,23H-prophine) (Fig. 1) is an important member of porphyrins which are promising to be used in molecular electronics due to their rich electronic components/photonic properties [26]. Based on the unique configuration of etioporphyrin and the extremely high stability of its metal-complexes, the compound is considered highly attractive material for developing potentiometric metal ion-sensor. Incorporating etioporphyrin in carbon paste plasticized with a solvent such as DOA resulted in a novel sensitive sensor to Cu(II) ions. The sensor exhibits fast and stable Nernstian response over a wide concentration range with low limit of detection and high selectivity over wide variety of cations.

3.1. Composition of the electrode paste

3.1.1. Effect of the amount of ionophore

It is well known that the electrode response for specific metal ions depends on the amount and the nature of the electrode components [27]. The general characteristics of sensor are outlined by determining its sensitivity, detection limit, linear range and selectivity coefficients. Some important features of carbon paste electrode, such as the properties of the plasticizer, the graphite (G)/plasticizer (P) ratio, the nature and amount of the ionophore, are reported to significantly influence the sensitivity and selectivity of the sensor. The influence of amount of etioporphyrin as an ionophore on the potential response of the electrode was studied and the corresponding results are summarized in Table 1.

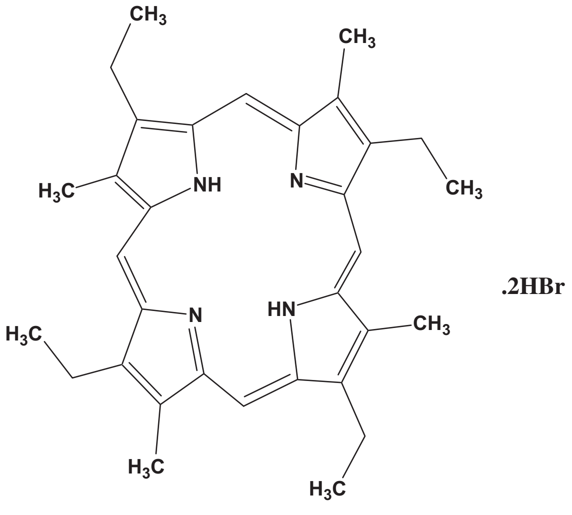

Fig. 1. Structure of etioporphyrin.