Short Communication

Coated Wire Copper(II) Ion Selective Electrode Based On 5,6,14,15-Dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene

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Abstract
A coated wire copper ion selective electrode based on 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene as a neutral carrier in a polyvinyl chloride matrix was developed. Concentrations of Cu in synthetic samples, bath samples, cupro-nickel alloy and ore were determined. The electrode has a wide linear response to the activity of Cu(II) in the range of 1×10^{-1} to 1×10^{-6} M and the influence of pH on the membrane prepared is small.

Keywords: Copper wire electrode, 5,6,14,15-Dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene, Synthetic alloy and ore samples, Electroplating bath solutions

An attempt was made to develop a coated wire copper ion selective electrode based on 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene as a neutral carrier in a polyvinyl chloride matrix for the determination of Cu(II) ions. Several ion selective electrodes for alkali and alkaline earth metal ions based on crown ethers have been prepared and studied [1,2]. Ion selective electrode (ISE) for K(I), Sr(II), and Pb(II) based on benzo 18-crown-6 and its lariat ether derivatives were prepared by Christian et al. [3]. Substitution of sulfur and/or nitrogen atom in the coronand ring of the crown compound increases the affinity of the ligand towards the transition metal ions. Several oxa-thia crown ethers with bulky pinan groups were synthesized and studied for their selectivity towards silver ions [4]. Ag(I) selective sensor based on dodecylmonothia-16-crown-5 and Ni(II) selective sensor based on 5,7,12,14-tetramethyldibenzotetraazaannulene have been reported [5,6]. Coated wire ion selective electrode for Cd [7], Mg [8] and Ag [9] have been developed, but less work has been carried out for Cu detection at microlevel with coated wire electrodes [10 – 12]. Cu(II) forms a strong complex with 5,6,14,15-dibenzo-1,4-dioxa-8,12-diaza-cyclopentadeca-5,14- diene (stability constant of Cu(II) with this ligand in 90% DMSO + water was found to be 5.98) [13]. An attempt has been made to develop Cu(II) ISE using Cu(II)-5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca -5,14-diene complex as the electroactive material.

After conditioning the electrode for 20 min in 0.01 M solution of Cu(NO₃)₂ the electrode potential for a series of standard solutions was measured. The value of the potential was noted after every 15 s. For the first two months the bead showed a linear response with a slope of 28 ± 2 mV per decade in the activity range of 1×10^{-1} to 1×10^{-6} M Cu(NO₃)₂. With passage of time the slope deteriated to 26 ± 2 mV per decade change but the response was linear.

However, the electrode showed a proper Nernstain response after preliminary conditioning for 20 min with 0.01 M solution of Cu(NO₃)₂ before use, even when kept without conditioning for two months. The ISE response is due to the electron-exchange mechanism at the membrane contact (Pt) interface and the ion exchange at the membrane-solution interface, which has been explained before [9]. The cationic interference due to other ions was studied by the determination of selectivity coefficients. The selectivity coefficients (K_{ij}) of wire-coated ISE for a number of alkali, alkaline earth and transition metal ions are given in Table 1. In case of acid copper electroplating bath solutions when the samples were analyzed after decomposing the organic matter, the response was the same as when done without decomposing the organic matter, indicating that the organic components do not have deleterious effect on the membrane. The concentrations of Cu in the synthetic samples (Table 2), bath samples, cupro-nickel alloy and ore (Table 3) were determined by directly dipping the ISE in

Table 1. Selectivity coefficients with respect to the Cu(II) ion.

Sr. No.	Interfering ions	Selectivity coefficients
1	Cd (II)	1.0×10^{-2}
2	Co(II)	6.4×10^{-3}
3	Zn(II)	1.3×10^{-2}
4	Hg(II)	1.0×10^{-2}
5	Ni(II)	7.9×10^{-1}
6	Mn(II)	1.3×10^{-2}
7	Mg(II)	9.5×10^{-3}
8	Ag (I)	1.0×10^{-3}
9	Na(I)	9.7×10^{-3}
10	K(I)	7.6×10^{-3}
11	Pb(II)	1.1×10^{-2}
12	Ca(II)	1.0×10^{-2}

Table 2. Results obtained by direct potentiometry of synthetic samples.

Sr. No.	Composition	Observed Cu concentration
1	0.0010 M $Cu(NO_3)_2$ + 0.01 M $NaNO_3$ + 0.01 M $Co(NO_3)_2$ + 0.01 M $Pb(NO_3)_2$	0.00097 M
2	0.0010 M $Cu(NO_3)_2$ + 0.01 M $Ni(NO_3)_2$ + 0.01 M $Mn(NO_3)_2$ + 0.01 M $Mg(ClO_4)_2$	0.00099 M
3	0.0010 M $Cu(NO_3)_2$ + 0.01 M $AgNO_3$ + 0.01 M $Cd(NO_3)_2$ + 0.01 M $Zn(NO_3)_2$	0.00102 M
4	0.0010 M $Cu(NO_3)_2$ + 0.01 M $Zn(NO_3)_2$ + 0.01 M $NaNO_3$ + 0.01 M KCl	0.00950 M

Table 3. Comparison of the present ISE method and voltammetric methods in real samples.

a) Electroplating bath solutions.

Sample		ISE method (g dm^{-3})	Voltammetric method (g dm^{-3})
Bath solution 1.	a) acid copper	53.79	53.74
	b) cyanide copper	20.39	20.35
Bath solution 2.	a) acid copper	54.01	53.95
	b) cyanide copper	19.87	19.90

b) Alloy and ore samples.

Samples	ISE method (%)	Titrimetric method (%)
Cupro-Nickel	73.12	73.03
Chalcocite	79.89	79.87

the sample solution after appropriate dilutions. The results obtained by the ISE were confirmed by differential pulse voltammetry and standard titration procedures [14, 15]. To study the effect of pH on the Nernstain slope, the potentials of solutions of different concentrations were measured between pH 1.5 to 6.7 and it was found that there was negligible effect on the Nernstain slope in this range of pH. It was observed that above pH 6.7 the potential of the wire coated membrane electrode decreases and at low pH the potential increases as experienced by Satsuo et al. [10]. The sharp break point and the fast response time in the potentiometric titration of Cu(II) against EDTA corresponds to Cu-EDTA stoichiometry which shows that this sensor can be used for the determination of Cu(II) by titrimetric methods. The titration curve obtained is not standard sigmoid, but a "L" shaped curve (Fig. 1). It may be because of the high sodium concentration and its interfer-
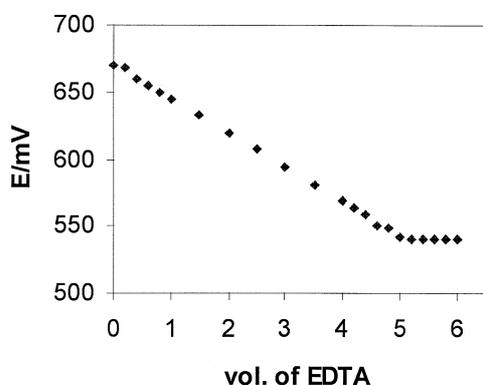
ence ($K_{Cu,Na} = 9.7 \times 10^{-3}$), as disodium salt of EDTA was used for potentiomeric titration. Similar nature of the curve has been reported for the potentiometric titration of Ni^{2+} against EDTA with nickel selective potentiometric sensor based on 5,7,12,14-tetramethyldibenzotetraazaanulene [6].

Because of the greater stability of the cyclam-Cu complex (stability constant = 20.66 in 90% DMSO-water) [13], it was also used as an ionophore to coat the platinum (Pt) substrate for the same purpose. The electrode showed a linear Nernstain response for two weeks after which the slope deteriorated and the electrode could not be used further.

The coated wire ion selective electrode developed in the present work has a wide linear response to the activity of Cu(II) in the range of 1×10^{-1} to 1×10^{-6} M and the influence of pH on the membrane prepared is small. Copper ion selective electrode based on water-soluble copper phthalocyanine is reported [16] which shows as linear range between 1×10^{-5} and 0.1 M, moreover the electrode suffers form the interference of cobalt and works within the pH range of 1–5. Recently developed another Cu(II) selective membrane electrode based on mixed aza-thiaether crowns containing a 1,10-phenanthroline subunit showing a linear range of 2×10^{-1} to 1×10^{-5} M [17]. Present electrode works in the pH range 1.5 to 6.7 which also has an advantage over other Cu(II) ion selective electrodes based on 13,14-benzo-1,5-tetrathiacyclopentadecane (BTTCP), 7,8-benzo-1,5-dithiacyclononane (BDTCN) and other sulfur containing complexing compounds [10,11]. The longer life time shown by it is quite satisfactory over other Cu(II) ion selective membrane electrodes reported [10–12]. Complications arise in the presence of high halides with solid state electrode based on $CuS + Ag_2S$ which suffers form Hg^{+2} and Ag^+ interference [1]. Present electrode was successfully

Fig. 1.   Plot of emf vs. volume of EDTA.

used in halide medium, which was quite difficult for CuS + Ag$_2$S electrodes. Moreover, this sensor has successfully been used as an indicator electrode in the potentiometric titration of Cu(II). Finally, the electrode in the present work holds promise for real sample analysis with appreciable selectivity over the other metal ions, especially in the field of metal finishing, as it is free from interference from the common organic compounds used in this industry.

Experimental

Chemicals: Nitrates of copper (II), cobalt(II), cadmium(II), nickel(II), lead(II), zinc(II), silver(I), sodium(I) and potassium(I), tetrahydrofuran(THF), diethyl phthalate, ethylenediaminetetraaceticacid disodium salt (EDTA) and nitric acid were analytical grade chemicals and were used as such. Calcium and magnesium perchlorates were prepared by general methods described elsewhere [18]. Polyvinyl chloride (PVC) and 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-dine were purchased from Fluka. Standard solutions of metal salts were prepared in double distilled deionized water; working solutions were prepared as required by suitable dilution with the same water. The pH of the solutions was adjusted with 0.1 M nitric acid.

Preparation of ionophore: Equal volumes of equimolar solutions of 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene and Cu(NO$_3$)$_2$ in 80% ethanol-water were mixed and kept overnight for precipitation. The bluish color precipitate obtained the next day was filtered washed and dried at room temperature to obtain the ionophore. A slurry of 5% w/w ionophore, 33% PVC and 62% diethyl pthalate plasticizer was made in THF. To prepare the electrode a platinum wire was coated by dipping it several times in the slurry until a bead was formed and was kept for drying in air for 24 h. Before using, the electrode was dipped in distilled water for 20 min and after every 15 days it was conditioned with 0.01 M Cu(NO$_3$)$_2$ for 24 h. All solutions were prepared using a digital single-pan balance (Mettler Toledo AB204).

Apparatus and emf measurements: A Cyberscan 2500 pH meter having ±0.1 mV accuracy with a SCE as a reference electrode and KNO$_3$ salt bridge was used for potential measurements. All the measurements were carried out at 25 °C with a cell of type:

Hg, Hg$_2$Cl$_2$; KCl(satd) // Cu (II) / ion-selective membrane (bead) / Pt wire.

The performance of the electrode was investigated by measuring the emf's of copper ion solutions over a range of 1×10^{-1} to 1×10^{-8} M. To check the Nernstian response, standard solutions of Cu(NO$_3$)$_2$ in 0.05 M NH$_4$NO$_3$ were prepared. The measurement time varied between 1 to 5 min and after every 15 seconds readings were noted. The

selectivity coefficients (K_{ij}) were calculated by mixed solution method [19]. A constant concentration of interfering ions M(I) and M(II) was kept at 1×10^{-2} M. The titration methods being more accurate and easily automated, the sensor was also used as an indicator electrode in the potentiomertic titration of Cu(II) against EDTA.

5.0 cm^3 of 1×10^{-2} M Cu(NO$_3$)$_2$ solution was titrated against 1×10^{-2} M EDTA solution.

Sample preparation: Samples from cyanide copper electroplating baths were treated with HNO$_3$ and boiled off near to dryness, followed by HClO$_4$ to decompose the cyanides and organic matter. All these processes were done inside the fume chamber. In case of acid copper bath solutions the measurements were done directly after appropriate dilution and also by treating as above. The cupro-nickel alloy and chalcocite ore samples were treated with aqua-regia and nitric acid respectively. In all the cases the resulting solution was diluted by 0.05 M NH$_4$NO$_3$ and was used for analysis.

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