

Solid-state Cu (II) ion-selective electrode based on polyaniline-conducting polymer film doped with copper carmoisine dye complex

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Abstract A pencil graphite electrode coated by copper (II)–carmoisine dye complex in polyaniline (emeraldine base form) matrix (termed as PGE/PA/Cu-Car) was prepared and used as copper ion-selective electrode. The introduced electrode was found to have high selectivity toward copper ion (II) and exhibited wide working concentration range, low response time, and good shelf life. The sensor electrode showed a linear Nernstian response over the range of 5.0×10^{-6} to 1.0×10^{-1} M with a slope of 29.7 ± 1 mV per decade change in concentration. A detection limit of 2.0×10^{-6} M was obtained. The optimum pH working range of the electrode was found to be 4.0–7.0.

Keywords Pencil graphite electrode · Polyaniline · Carmoisine-Cu (II) complex · Copper (II) sensor electrode

Introduction

Copper is the third most used metal in the world. It is one of the most widely distributed elements in the environment of industrialized countries. It is present in all organisms, land, and marine. Most compounds of copper adopt oxidation states copper (I) and copper (II), which are often called cuprous and cupric, respectively. Copper (II) is the main form of copper encountered in its ores. Copper ion generally exists as Cu (II) oxidation state, and, less often as Cu (I) [1]. The occurrence of copper in environment is widespread as it is used for many industrial, agricultural,

and domestic purposes. Copper (II) ions are soluble in water, where they function at low concentration as bacteriostatic substances, fungicides, and wood preservatives [2]. The Cu (II) ion at lower concentrations is an essential trace nutrient to all higher plant and animal life.

It has been shown that copper is an important element for many biological processes, such as blood formation and the functioning of many important enzymes [3, 4]. This element plays a vital role as a catalytic cofactor for several enzymes including cytochromecoxidase, superoxide dismutase, and other multi copper oxidations [5]. Despite copper is an essential element for human beings, it is also toxic at elevated concentration and is known to cause gastrointestinal catarh, Wilson disease, hypoglycemia, and dyslexia [6]. The narrow window of concentration between essentiality and toxicity of copper ion and also because of its widespread use in industries and catalytic processes, the determination of copper ion in environmental monitoring becomes increasingly important [7–10].

A number of methods such as flame atomic absorption spectrometry (AAS), none flame atomic absorption spectrometry–electrothermal atomization (AAS-ETA) inductively coupled plasma/mass spectrometry, anodic stripping voltammetry, matrix exchange techniques, ion chromatography, UV-Vis spectrometry are used for copper ion determination at low concentration level [11–17]. However, these methods provide accurate results but are not very convenient for analysis of a large number of environmental samples and also from cost point of view.

Potentiometric measurements with copper ion-selective electrode allow directly the determination of free ion concentration in aqueous samples. Ion-selective electrodes provide analytical procedures for such situations as they are fast, convenient, require minimum sample pretreatment, and may also be suitable for online analysis. Further, ion-

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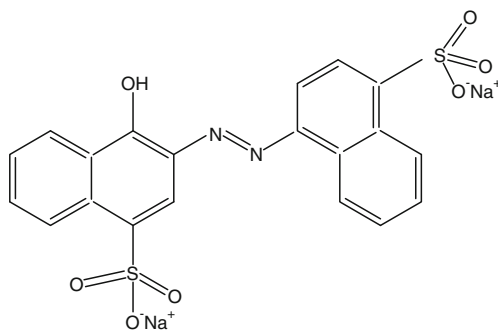


Fig. 3 Chemical structure of carmoisine

polyaniline-based membrane which allows better defined ion-to-electron transduction compared to the classical coated wire electrodes.

Experimental

Chemicals

All chemicals used were analytical grade reagents and prepared in distilled water. Aniline were obtained from Merck and distilled before use. N-methylpyrrolidone (NMP, as solvent), NaOH, nitric acids, carmoisine dye (disodium 4-hydroxy-2-[(E)-(4-sulfonato-1-naphthyl) diazenyl] naphthalene-1-sulfonate), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and nitrate salts of the interfering cations were of analytical reagent grade, purchased from Merck and were used as received. Cu (II) (0.100 M) was prepared as stock solution by dissolving AR grade metal nitrates in double distilled water and standardized wherever necessary. The working solutions with different concentration were prepared by diluting the stock solution.

Apparatus

A Metrohm pH meter (model 827) with a combined double junction glass electrode, calibrated against two standard buffer solutions at pH 4.0 and 7.0, was used for showing pH values and potentiometric measurements. The pH of the solutions was adjusted with 0.10 M HNO_3 and NaOH. All potentiometric measurements were carried out at 25 °C with a cell of the following type: $\text{SCE} \parallel \text{Cu}^{2+} (a_A) \mid \text{PGE/PA/Cu-Car}$ using a pH/mV meter (Metrohm). A double junction-saturated calomel electrode was used as reference electrode.

Preparation of electrode and procedure

Polyaniline was first synthesized chemically and changed into an EB form of polyaniline (PA) in order to make it

possible for preparing it as a thin film on the electrode via casting [47]. Copper complex dye powder was prepared by adding 30 mL of 0.010 M of copper (II) into 10 mL of 0.002 M carmoisine. The mixture was heated at 80–90 °C for 14 h. The solution was then cooled at room temperature and the solid was separated. In order to have a good comparison, we also examined uncomplexed dye incorporated in polyaniline for the determination of Cu (II). The coating was performed from a cast solution containing dye/PA or Cu-Dye/PA. Cast solution was prepared in an NMP solvent. To prepare the electrodes, cleaned PGE were coated by dye/PA and Cu-Dye/PA via dip-coating method. The coated electrodes were allowed to dry at 50 °C for 3 h in an oven. The electrodes were conditioned for 24 h in 5.0×10^{-2} M Cu (II) solution before use. Selectivity coefficient ($K_{A,M}^{\text{Pot}}$) values for a range of common interferents cations were calculated by separated solution method [48]:

$$\log K_{A,M}^{\text{Pot}} = \frac{(E_M - E_A)Z_A F}{RT \ln 10} + \left(1 - \frac{Z_A}{Z_M}\right) \log a_A \quad (1)$$

Where a_A is the activity of the primary ion [Cu (II)] and a_M is the activity of an interfering ion with the same activity ($a_A = a_M$). E_A and E_M are the potential of the solution of target and interfering ions, Z_A and Z_M are the charges of the analyte and interfering ion, respectively. The concentration of the interfering ions used in the present study was 1.0×10^{-2} M. For preparing the calibration curve, standard solutions of Cu (II) (1.0×10^{-6} to 1.0×10^{-1} M) were prepared and the potentials were recorded after 30 s or less until the readings were stable to within ± 0.1 mV. The spectra of the copper ion, carmoisine dye, and metal–carmoisine dye complex were further studied using UV-Vis spectroscopy. The UV-Vis spectra of the Cu (II) ($\lambda_{\text{max}} = 800$ nm), carmoisine dye ($\lambda_{\text{max}} = 515$ nm), and Cu-Car complex ($\lambda_{\text{max}} = 470$ nm) are shown in Fig. 4. As the spectra show, complexing of the copper ion with the carmoisine dye leads some decrease (blue shift) in the maximum absorption wavelength of the dye (about 45 nm).

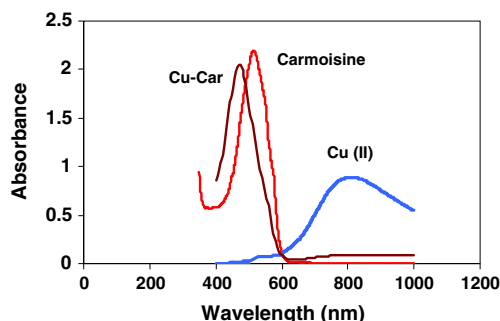


Fig. 4 UV-Vis spectra of the Cu (II), carmoisine dye, and Cu-Car complex

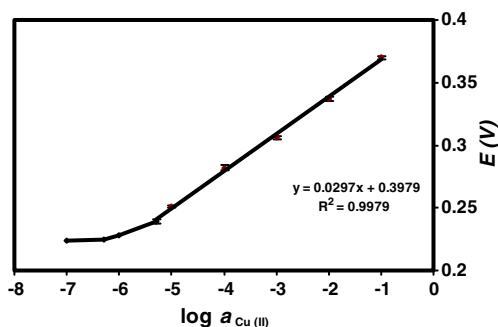
Table 1 Effect of preparation conditions of the electrode on the linearity of the sensor response toward copper (II) ion measurement

Electrode number	Composition (g)			Slopes (mV/decade)	Linear range (M)	R^2
	EB	Copper dye complex	Carmoisine			
1	0.040	–	–	20.1	10^{-4} to 10^{-1}	0.8120
2	0.040	–	0.010	20.2	10^{-5} to 10^{-1}	0.8697
3	0.040	–	0.012	22.1	10^{-5} to 10^{-1}	0.8597
4	0.040	–	0.015	28.2	10^{-5} to 10^{-1}	0.8506
5	0.040	–	0.018	30.3	10^{-5} to 10^{-1}	0.8357
6	0.040	–	0.020	33.5	10^{-5} to 10^{-1}	0.8930
7	0.040	0.010	–	21.4	5×10^{-6} to 10^{-1}	0.9475
8	0.040	0.012	–	25.4	5×10^{-6} to 10^{-1}	0.9475
9*	0.040	0.015	–	29.7	5×10^{-6} to 10^{-1}	0.9979
10	0.040	0.018	–	30.0	5×10^{-6} to 10^{-1}	0.9654
11	0.040	0.020	–	32.1	5×10^{-6} to 10^{-1}	0.9642

Results and discussion

Electrode performance parameters

The electrodes with different amounts of polyaniline (EB), carmoisine dye, and carmoisine complex with copper ions (Cu-Dye/PA) were prepared under different conditions employing various amounts of the ingredients in order to find out the optimized conditions with regard to sensitivity and working range. Carmoisine is an anionic dye molecule which has been found that it can be strongly adsorbed by conducting polymers [49]. It can also make a selective and stable complex with copper (II) ion. Carmoisine and its complex form with copper ion are both anionic species so they can be used as dopant for polyaniline in order to make the polymer composite both conductive and electrically charged balanced. The results obtained from using different experimental conditions for preparing sensor electrode with different coating compositions are summarized in Table 1.

**Fig. 5** Calibration curve of Cu (II) using PGE/PA/Cu-Car indicator electrode

As the data show, based on the Nernstian response, linearity and the dynamic range, the potentiometric response of the prepared electrodes was greatly improved when the metal dye complex was used as Cu (II) ion-sensing material. Using coated electrode with polyaniline (EB form), the response was neither Nernstian nor linear. Some improvements were observed when the coated electrode was prepared from a cast solution containing both dye and polymer. However, better response characteristics were observed when a cast solution prepared by mixing copper dye complex (Cu-Car) and PA.

The optimum weight ratio for obtaining an electrode slope closer to the theoretical value was found to be 0.015/0.040 (dye complex/polymer). The electrode response deviated from Nernstian slope when other weight ratios were used. So, our further investigations in order to study the effect of other operational parameters such as working concentration, sensitivity, selectivity, lifetime, response

Table 2 Effect of storage time of MPGE/EB/CACu electrode on its Nernstian response

Storage time (day)	Slope (mV per decade)	Intercept (E/V)
1	29.7	0.3979
5	29.7	0.3979
15	29.5	0.3985
20	29.3	0.3988
25	29.3	0.3988
30	29.0	0.3990
35	28.9	0.3995
40	28.6	0.3980
50	28.5	0.4005
60	28.5	0.4015

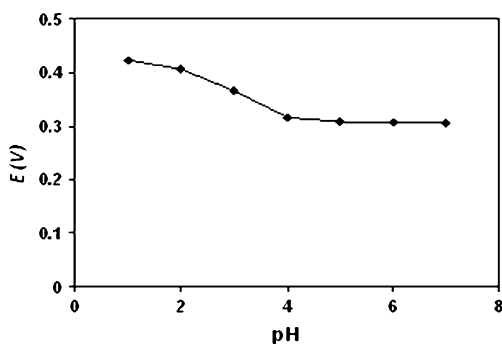


Fig. 6 Effect of pH on the electrode response, the solution contains 1.0×10^{-3} M Cu (II)

time, and pH were carried out using the aforementioned Cu-Car/PA weight ratio. The existence of donating oxygen and nitrogen atoms in the carmoisine dye (bidentate-chelating sites) as well as donating nitrogens in polyaniline is expected in the selective complexation behavior of the fabricated electrode for Cu^{2+} over other metal ions. The ISE response is due to the inherent electrical conductivity of the polyaniline [50] and the ion exchange process at the electrode–solution interface.

Working concentration range and slope

The potential of the cell set-up with solid state copper (II) electrode was determined as a function of Cu (II) activity. The calibration curve for the analysis of Cu (II) prepared using standard solutions of Cu (II) ion and the indicator electrode (PGE/PA/Cu-Car) is shown in Fig. 5.

Table 3 Selectivity coefficients for various interfering ions for electrode obtained by separate solutions method

Interfering ion	$K_{\text{Cu, M}}^{\text{Pot}}$
Na^+	9.1×10^{-4}
K^+	8.2×10^{-3}
NH_4^+	3.2×10^{-4}
Zn^{2+}	3.2×10^{-3}
Mg^{2+}	1.3×10^{-3}
Ca^{2+}	5.3×10^{-3}
Mn^{2+}	8.3×10^{-3}
Pb^{2+}	6.8×10^{-3}
Co^{2+}	7.3×10^{-3}
Ag^+	1.2×10^{-2}
Hg^{2+}	8.5×10^{-3}
Ba^{2+}	1.3×10^{-3}
Ni^{2+}	5.3×10^{-3}
Al^{3+}	4.2×10^{-3}
Fe^{3+}	4.6×10^{-2}
Cd^{2+}	3.9×10^{-3}

It is seen from Fig. 5 that the electrode no. 9 exhibits linear response over a working concentration range of 5.0×10^{-6} to 1.0×10^{-1} M with a slope of 29.7 mV per decade of activity. The limit of detection was calculated from Fig. 5 as the concentration of copper ion obtained when extrapolating the linear region of the calibration plot to the base-line potential was 2.0×10^{-6} M. The repeatability of the electrode response (readings) was quite high when the concentrations of the copper ion were changed. In order to find out the repeatability of the potential measurements with the copper (II) selective electrode, each concentration was analyzed for five times. The maximum standard deviation (SD) obtained was less than 2.0 mV.

Response and lifetime

The response time of the sensor was determined by measuring the time required to achieve a steady potential for different Cu (II) ion concentrations (5.0×10^{-6} to 1.0×10^{-1} M). The recorded response time of the PGE coated by polyaniline/metal dye complex was 20 s for each measurement. Maximum potential changes were ± 1 mV at least for 3 min. The lifetime of electrode no. 9 was further investigated by performing periodic calibration with standard solutions and calculating the response and slope over the range of 5.0×10^{-6} to 1.0×10^{-1} M Cu (II). The data obtained are summarized in Table 2. The tests performed in different time intervals (2 months) show that there were no observed considerable changes in the slope of the electrode response and the observed drift in potential was 4%. During storage, the electrodes were soaked in a 5.0×10^{-2} M Cu (II) solution.

Effect of pH

The pH dependence of response of the sensor no. 9 has been tested in the range of 1.0–7.0 at Cu (II) concentration of 1.0×10^{-3} M. An adjustment of pH was performed using dilute NaOH and HNO_3 solutions. The potential of the sensor electrode was determined as a function of pH is illustrated in Fig. 6. As the results indicate that the

Table 4 Comparison of the present ISE method and AAS methods in real samples

Sample	Concentration of Cu (II) determined by AAS (mg kg^{-1})	Concentration of Cu (II) determined by the electrode (mg kg^{-1})
Green tea leaves	6.38 ± 0.20	6.27 ± 0.40
Black currants	5.20 ± 0.30	5.08 ± 0.50
Sour cherry juice	0.55 ± 0.02	0.64 ± 0.05

potentiometric response for this electrode depends on the pH of the test solution.

The suitable pH ranges for the determination of Cu (II) were obtained between pH 4.0 and pH 7.0, which may be taken as the working pH range of the sensor assembly. Variation of the potential at pH < 4.0 could be related to some decrease in the metal–dye complex stability in polymer matrix coated onto electrode. Therefore, all of our further measurements were performed at pH 6.0. Applying higher pH values (pH > 7.0) was avoided because of the possible formation of the copper hydroxide precipitation. Furthermore, polyaniline is changed into an insulator material at neutral or alkaline media which affect its sensing properties.

Potentiometric selectivity

The selectivity of sensors is one of the most important performance parameters that determines the utility of a potentiometric sensor. The concentration level of the interfering ion, which an electrode can tolerate, depends on the numerical value of selectivity coefficient. The smaller the value of selectivity coefficient, the higher is the concentration of interfering ion(s), which can be tolerated by the sensor. The selectivity studies were carried out using sensor electrode no. 9, which exhibited the best performance characteristics in terms of working concentration range, slope, response time, shelf life, and storage stability. The selectivity coefficients of the electrode against a series of ions were evaluated under identical conditions using the separate solutions method.

In the separate solutions method, the influence of variation of primary ion and interfering ions concentrations on electrode response are investigated separately. The resulting selectivity coefficients are also presented in Table 3.

As the results show, the electrodes are very selective to Cu (II) ions over all the interfering ions listed in Table 3. Thus, because of the low selectivity of the electrode toward the tested interfering ions, it can be concluded that the introduced electrode can be successfully used for measurement or analysis of Cu (II) in real samples. Among the investigated metal ions, Ag^+ and Fe^{3+} ions showed some more interference, if present at higher concentration. The selectivity obtained for the electrodes employed in this study indicates that the extent of complex formation of carmoisine with copper ion and the structure of this complex are the major factors in determining its high selectivity.

Analytical applications

The utility of the copper sensor electrode prepared under optimized conditions (no. 9 in Table 1) was used to measure the concentration of copper ion in some real

samples that normally have copper in them such as green tea leaves, black currants, and sour cherry juice. The samples were air-dried in porcelain crucibles using an oven (105 °C, 24 h). Known amounts of dried samples were completely burned in the electric furnace (500 ± 20 °C). The ashes obtained were treated with a dilute HCl (0.10 M) for dissolving. The ash solutions were neutralized before analysis by AAS and potentiometry methods. For potentiometry analysis of sour cherry sample, the liquid sample was used directly. The results obtained are summarized in Table 4. As the results interestingly show, the data obtained with AAS technique are very close to those obtained using the copper selective sensor electrode introduced in the current paper.

Conclusions

The introduced indicator electrode based on polyaniline-conducting polymer can be easily prepared via simple dip-coating method. The copper sensor electrode fabricated in the current study showed response characteristics with almost Nernstian behavior over the concentration range 5.0×10^{-6} – 1.0×10^{-1} M of Cu (II). The response time was also fast enough (20 s). The low detection limit, low cost, high repeatability, high shelf life, together with the good selectivity and high sensitivity of the sensor to copper ions, make this electrode, potentially useful for measurement of free Cu (II) ions in the samples at low concentrations with high accuracy and precision using direct potentiometry. Due to the high toxicity of copper ions to aquatic life, the finding in this study is very important from both analytical and environmental point of views.

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