

## Selective potentiometric electrode for copper (II) ion based on Schiff-base chelate

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### ABSTRACT

Copper (II) selective electrode has been fabricated from polyvinyl chloride (PVC) matrix membranes using 2-(2-Hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)3-azabut-3-enyl]-1,3-imidazolidine copper (II) (I) as an ionophore. Effect of various plasticizers *viz.*, bis(2-ethylhexyl) sebacate (DOS), tri-*n*-butylphosphate (TBP), tris(2-ethylhexyl)phosphate (TEHP), *o*-Nitrophenyl octyl ether (NPOE) and anion discriminator, sodium tetraphenylborate (NaTPB) was studied in detail and improved performance was observed at several instances. The electrode having a membrane of composition (w/w) of I (1.5%): PVC (33%): NaTPB (1.5%): *o*-NOPE (64%) exhibited the best performance under various conditions such as working concentration range  $5.0 \times 10^{-7}$  to  $1.0 \times 10^{-1}$  M (~detection limit  $3.2 \times 10^{-7}$  M) with a Nernstian slope of 29.5 mV/decade of activity, wide pH range (3.0-8.5), fast response time (10s) and tolerance in partially non-aqueous media up to 20 % (v/v) content of methanol and ethanol. It could be used over a period of 9 weeks. The selectivity coefficients determined using the fixed interference method show that the electrode has excellent selectivity for  $\text{Cu}^{2+}$  over a large number of mono-, bi- and trivalent cations. The electrode has also been used as an indicator in potentiometric titration of  $\text{Cu}^{2+}$  with EDTA. The utility of the electrode has been tested for the estimation of copper in water samples.

**Keywords:** Potentiometric selectivity; PVC membrane electrodes; Copper-selective electrode; Chelating ionophore.

### INTRODUCTION

Copper is an essential trace element also present in human body and plays an important role in various biological processes [1, 2]. Higher concentration of copper in human body causes highly objectionable adverse effects on the human health. It causes dyslexia, hypoglycemia, gastrointestinal cataract and Wilson disease [3, 4]. Moreover, copper is widely used in industries, agriculture and for domestic purposes [5]. Due to its above utilities its estimation has been a matter of enormous interest among the analytical chemists.

A number of instrumental methods such as atomic absorption spectrometry (AAS), Inductively Coupled Plasma (ICP), Stripping Voltametry and Flame photometry are employed for the determination of copper at low concentration levels. Since, these methods are expensive, time consuming and require expertise, therefore, cheaper and more convenient methods are still required. In recent years, the ion selective electrodes based on ionophores have provided more

simple and economical approach for estimation of various metal ions. The primary requirement for a material to be used as ionophore is its high affinity towards a particular ion to be estimated. Due to frequent need of estimation of copper present in food, water samples, biological and environment samples, many electroactive materials have been used as ionophore [6-20]. Successful attempts have been made for the synthesis of selective ionophore as sensing molecules for copper ion but they show a poor detection limit [7, 8, 11], narrow working concentration range [10,13] and serious interference of other ions [14]. Due to above shortcomings of the reported electrodes, we synthesized 2-(2-Hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)3-azabut-3-enyl]-1,3-imidazolidine copper (II) (I) as an excellent ionophore for the preparation of sensitive and selective polymeric membrane electrode for copper ion detection and the results are being reported in this paper.

## 2. Experimental

### 2.1 Reagents

2-(2-Hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)3-azabut-3-enyl]-1,3-imidazolidine copper (II) (I) (Fig.1) was synthesized using a reported method [21]. Di-octyl sebacate (DOS), Aldrich (USA); high molecular weight polyvinyl chloride (PVC), Aldrich (USA); sodium tetraphenylborate (NaTPB), BDH (England); tri-n-butylphosphate (TBP), BDH (England); o-nitrophenyloctyl ether (o-NPOE), Merck (Germany); tris-2-ethylhexyl phosphate (TEHP), Merck (Germany) were used as received. Analytical reagent-grade tetrahydrofuran (THF), nitric acid and sodium hydroxide were purchased from Ranbaxy (India). Doubly distilled water was used throughout the experiment.

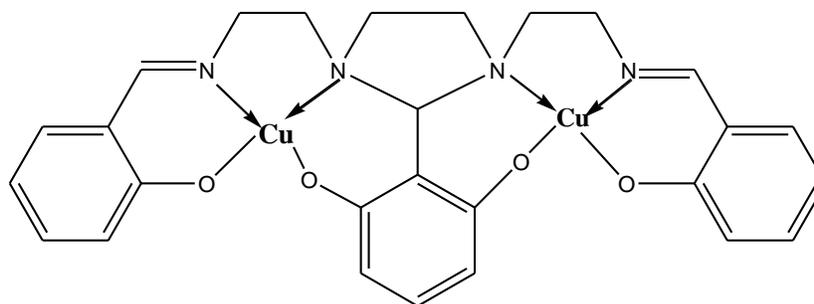


Fig. 1 Structure of 2-(2-Hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)3-azabut-3-enyl]-1,3-imidazolidine copper (II)

### 2.2 Preparation of membranes

The membrane was prepared using a reported method [22]. Homogenous membranes of the metal chelate were prepared when ionophore (I), anion excluder, solvent mediators (DOS, TEHP, TBP and o-NPOE) and PVC in THF (~10 mL) were mixed in their appropriate amount. The resulting homogenous mixture was vigorously stirred and after removing all air bubbles it was poured into rings made up of polyacrylate which were placed on a smooth glass plate. The

solution was then allowed to evaporate at room temperature. After 48 h, transparent membranes of 0.5 mm thickness were obtained. It was attached to “Pyrex” glass tube with the help of araldite. The membranes thus prepared were equilibrated for 2 days in 0.1M  $\text{Cu}^{2+}$  solutions. Thus, several membranes of various compositions were prepared and their performance was investigated. The membranes exhibiting the best performance characteristics with reproducible results were selected for subsequent studies.

### 2.3 Potential measurement and apparatus

The potential measurements were carried out at  $25 \pm 0.1$  °C with a digital potentiometer (Model 5652 A, ECIL, India) and Century Micro Voltmeter (Model CVM 301, India) by setting up the following cell assembly:

SCE / test solution / membrane / internal solution, (0.1M,  $\text{Cu}^{2+}$ ) / SCE

The saturated calomel electrodes (SCE) were used as internal and external reference electrodes. The concentration of metal ion in the test solutions was varied from  $1.0 \times 10^{-7}$  -  $1.0 \times 10^{-1}$  M. The activity of metal ion was calculated using Debye Huckel Procedure [23].

## 3. Results and discussion

Metal chelate (I) used as ionophore in constructing the PVC- membrane electrodes for a number of metal ions showed improved performance. The potential response of various electrodes is shown Fig 2. It showed that the best response was observed for  $\text{Cu}^{2+}$  ions among different metal ions. Therefore, the membrane was studied as copper selective electrode.

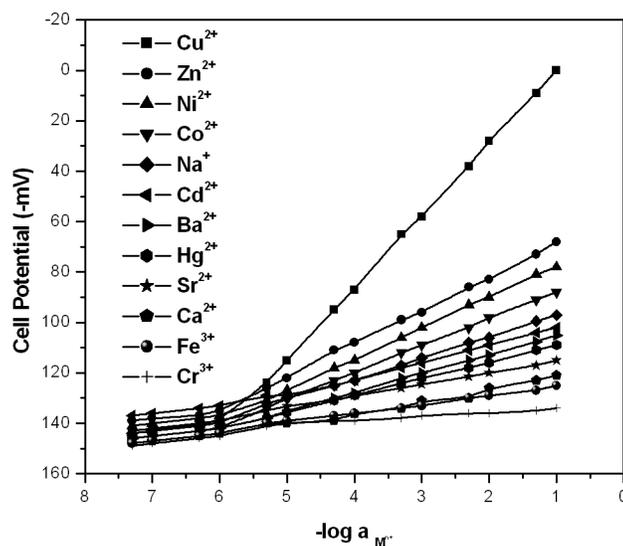


Fig.2. Potential response of the selective electrodes based on (I) to various metal ions.

### 3.1 Working Concentration Range and Slope

The PVC based membrane of metal chelate (I) was equilibrated with 0.1M  $\text{Cu}^{2+}$  solution in order to generate a stable potential for 2 days. The Nernstian response and slope were

constant. The performance of a membrane in terms of certain parameter, namely, sensitivity, linearity and selectivity for a given ionophore depends significantly on the composition of membrane and nature of plasticizer used [24-26]. Thus, various membranes were prepared with and without plasticizer. The potential of membrane of (I) was determined as a function of  $\text{Cu}^{2+}$  concentration ( $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-1}$  M) and the results are shown in Fig.3. The working concentration range and slopes have been determined from the plot and data is shown in Table 1. Fig. 3. indicates that the electrode no.5 having membrane of (I) without any plasticizer exhibits a slope ( $33.0 \text{ mV decade}^{-1}$ ) with concentration range from  $7.1 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M and a detection limit  $4.0 \times 10^{-6}$  M. The slope of the membrane was found nearly-Nernstian and the working concentration range was considerably narrow. The addition of plasticizers improved the selectivity and stability of electrode. A good plasticizer should exhibit high lipophilicity and capacity to dissolve the membrane components [27]. Thus, four plasticizers, namely, TBP, TEHP, DOS and o-NPOE were added in order to improve the performance of electrode. The addition of four plasticizers to the membranes of (I) (electrode no. 1-4) improved the working concentration range and slope (Fig.3 and Table 1). The best performance characteristic were obtained with the membrane having o-NPOE plasticizer (electrode no 1). The electrode exhibited Nernstian slope ( $29.5 \text{ mV decade}^{-1}$ ) over a wide concentration range ( $5.0 \times 10^{-7}$  to  $1.0 \times 10^{-1}$  M) with the detection limit  $3.2 \times 10^{-7}$  M. Electrode no.1 having a composition of (I) (1.5%), NaTPB (1.5%), PVC (33%), (o-NPOE) (64%) showed the best performance (widest working concentration range and near Nernstian slope) and therefore, it was used for further studies.

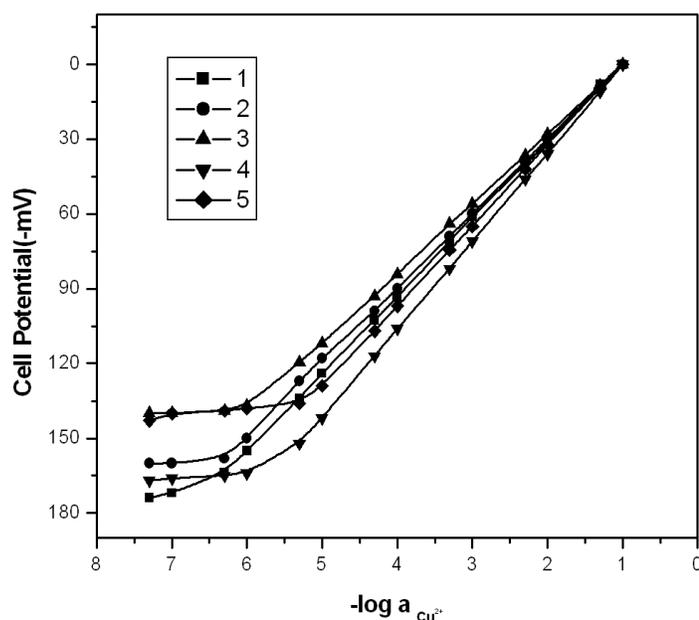


Fig.3. Potentiometric response of copper electrode based on (I) with plasticizers, o-NPOE (1), DOS (2), TEHP (3) and TBP (4) and without plasticizer (5).

Table1. Composition of PVC membranes of copper chelae (I) and performance characteristics of Cu<sup>2+</sup>-selective electrode based on them.

S. No.	Composition of membrane (w/w) (amount w/w % of different components added)						Working concentration range (M)	Slope (mV/decade of activity)	Response time (s)	Detection limit (M)
	I	PVC	NaTBP	<i>o</i> -NPOE	DOS	TEHP				
1	1.5	33	1.5	64			$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$	29.5	10	$3.2 \times 10^{-7}$
2	1.5	33	1.5		64		$7.9 \times 10^{-7} - 1.0 \times 10^{-1}$	30.0	20	$5.0 \times 10^{-7}$
3	1.5	33	1.5			64	$1.9 \times 10^{-6} - 1.0 \times 10^{-1}$	28.0	18	$1.1 \times 10^{-6}$
4	1.5	33	1.5				$3.2 \times 10^{-6} - 1.0 \times 10^{-1}$	35.0	25	$2.2 \times 10^{-6}$
5	1.5	33	1.5				$7.1 \times 10^{-6} - 1.0 \times 10^{-1}$	33.0	28	$4.0 \times 10^{-6}$

### 3.2 Response and life time

Response time is one of the most important factors for an ion selective electrode. In the present study, the practical response time was recorded by changing  $\text{Cu}^{2+}$  concentration from  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-1}$  M. The response time remained unchanged on varying the concentration. This is due to the fast exchange kinetics of complexation/ decomplexation of  $\text{Cu}^{2+}$  ion with ionophore at the test solution-membrane interface [28]. The membrane was used over a period of 9 weeks and no significant change in the value of slope and working concentration range was observed. The sensing behavior of the membrane remained reasonably constant for a period of 9 weeks. Beyond the above duration a drift in potential was observed which may be due the fact that the membrane becomes mechanically weak and swelled up resulting the leaching of ions from the membrane phase. However, they were stored in  $0.1\text{M Cu}^{2+}$  solutions when not in use.

### 3.3 Effect of PH change

The variation in electrode potential response as function of pH has been investigated over the pH range (1.0-10.0) for  $\text{Cu}^{2+}$  solutions ( $1.0 \times 10^{-3}$  and  $1.0 \times 10^{-4}$  M) and the result is shown in Fig.4. The operational range was studied by varying the pH of test solution with nitric acid / sodium hydroxide. Fig.4. indicates that the potential is independent to pH in the range 3.0-8.5. The change in potential below pH 3.0 and above pH 8.5 is due to interference of  $\text{H}^+$  ions and hydrolysis of  $\text{Cu}^{2+}$  ions, respectively.

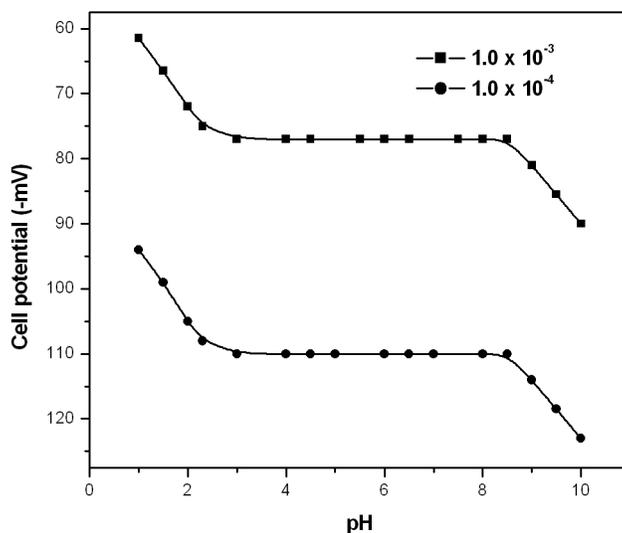


Fig.4. Effect of pH on cell potential;  $[\text{Cu}^{2+}] = 1.0 \times 10^{-3}$  and  $1.0 \times 10^{-4}$  M.

### 3.4 Solvent effect

Since the real sample may contain non-aqueous content, therefore, the performance of the electrode was also investigated in partially non-aqueous media using 10%, 15%, 20% and 25% (v/v) in methanol-water and ethanol-water mixtures and the results are given in Fig. 5 & 6, respectively. Working concentration range and slope were determined using these plots and the

data is shown in Table 2. which indicates that the electrode does not show any appreciable change in working concentration range and slope in mixture up to 20% (v/v) non-aqueous content. However, above to 20% (v/v) non-aqueous content, potential showed a remarkable drift with time. The drift in potential in non-aqueous content may be probably due to leaching of the ionophore at higher non-aqueous content.

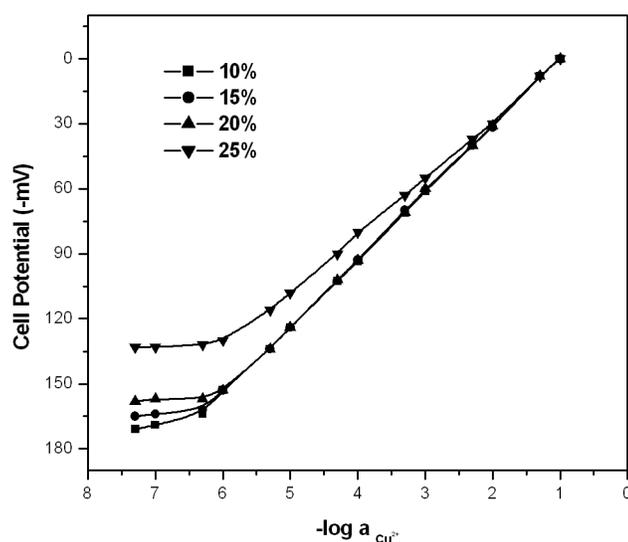


Fig.5. Potential response of the electrode in the presence of 10%, 15%, 20% and 25% Methanol.

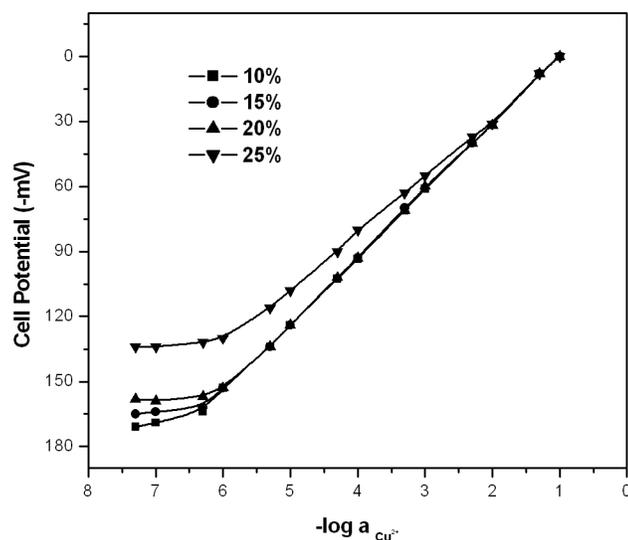


Fig.6. Potential response of the sensor in the presence of 10%, 15%, 20% and 25% Ethanol  
Table 2. Performance of  $Cu^{2+}$  selective electrode no. 1 in non-aqueous medium.

Non-aqueous content (% v/v)	Working concentration range (M)	Slope (mV/decade of activity)
0	$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$	29.5
Acetone		
10	$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$	29.5
15	$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$	29.3
20	$6.3 \times 10^{-7} - 1.0 \times 10^{-1}$	29.0
25	$1.6 \times 10^{-6} - 1.0 \times 10^{-1}$	25.0
Ethanol		
10	$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$	29.5
15	$5.0 \times 10^{-7} - 1.0 \times 10^{-6}$	29.4
20	$7.9 \times 10^{-7} - 1.0 \times 10^{-1}$	29.1
25	$3.2 \times 10^{-6} - 1.0 \times 10^{-1}$	24.0

### 3.5 Potentiometric selectivity

Selectivity of the membrane is measured in terms of selectivity coefficients which were determined by the Fixed Interference Method (FIM) as suggested by sa'ez de Viteri and Diamond [29]. The selectivity coefficients so calculated by this method are summarized in Table 3. It showed that the electrode exhibits selective response toward  $\text{Cu}^{2+}$ . A value of selectivity coefficient equal to 1.0 indicates that the membrane responds equally to primary as well as interfering ion. A value smaller than 1.0 indicates that it responds more to primary ion than interfering ion and in such a case the electrode is said to be selective to primary ion over interfering ion. Further, smaller selectivity coefficient value reflects higher selectivity order. Table 3. revealed that the selectivity coefficients are in order of  $10^{-4}$  or lower for almost all diverse ions tested. Thus, these ions would not cause significant interference in the estimation of  $\text{Cu}^{2+}$  ions by this electrode unless present in large amounts. Thus the electrode can be used for the determination of  $\text{Cu}^{2+}$  by direct potentiometry even in presence of foreign ions.

Table 3. Selectivity coefficients of electrode no. 1 as determined by Fixed Interference Method (FIM).

Interfering ion (B)	Selectivity coefficient ( $K_{Cu^{2+},B}^{Plot}$ )
Na <sup>+</sup>	$3.6 \times 10^{-3}$
Sr <sup>2+</sup>	$8.3 \times 10^{-4}$
Ag <sup>+</sup>	$7.6 \times 10^{-4}$
Mg <sup>2+</sup>	$3.5 \times 10^{-4}$
Ca <sup>2+</sup>	$9.5 \times 10^{-4}$
Ba <sup>2+</sup>	$7.9 \times 10^{-4}$
Hg <sup>2+</sup>	$8.2 \times 10^{-4}$
Pb <sup>2+</sup>	$8.6 \times 10^{-4}$
Cd <sup>2+</sup>	$7.8 \times 10^{-4}$
Zn <sup>2+</sup>	$5.4 \times 10^{-3}$
Ni <sup>2+</sup>	$4.4 \times 10^{-3}$
Co <sup>2+</sup>	$4.9 \times 10^{-3}$
Cr <sup>3+</sup>	$3.6 \times 10^{-4}$
Fe <sup>3+</sup>	$9.3 \times 10^{-4}$

### 3.6 Potentiometric titration

The proposed electrode was also used as an indicator electrode in the titration of Cu<sup>2+</sup> with EDTA. A 40 mL sample of  $1.0 \times 10^{-3}$  M Cu<sup>2+</sup> was titrated against  $1.0 \times 10^{-1}$  M EDTA solution at constant pH 5, and the change in potential was recorded and plot is shown in Fig. 7. The titration plot obtained was found sigmoid in shape, which indicates that the electrode is highly selective to Cu<sup>2+</sup> ions. The inflexion point of the plot was corresponding to 1:1 stoichiometry of copper-EDTA complex. Thus, the electrode can be used to determine copper by Potentiometric titration.

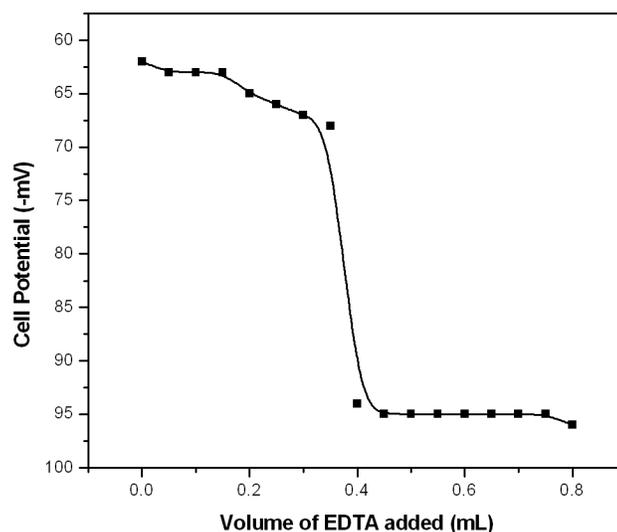


Fig.7. Potentiometric titration curve for 40 ml  $1.0 \times 10^{-3}$  M  $\text{Cu}^{2+}$  with  $1.0 \times 10^{-1}$  M EDTA at constant range 5 using the proposed electrode.

*Analytical applications*

The electrode was also used to determine the concentration of copper ion in drinking and river water samples. The water samples were acidified by adding a few drops of nitric acid and were kept at pH 5. The results obtained by the proposed electrode were found in good agreement with that of AAS (Table 4).

Table 4. Quantification of copper in water samples by proposed electrode no.1, and AAS

Sample	Average $\text{Cu}^{2+}$ concentration (mg/L)	
	Determined by (Proposed electrode)*	Determined by (AAS)*
Drinking water	$1.7 \pm 0.06$	$1.8 \pm 0.05$
River water	$16.5 \pm 0.05$	$16.3 \pm 0.04$

**Conclusion**

The proposed electrode based on Schiff-base metal chelate showed excellent response towards copper ions exhibiting good Nerstian slope ( $29.5 \text{ mV decade}^{-1}$ ) working concentration range ( $5.0 \times 10^{-7}$  to  $1.0 \times 10^{-1}$  M) and detection limit ( $3.2 \times 10^{-7}$  M). The electrode showed a lowest response time of (10 s) and operates in a pH range 3.0-8.5 with good selectivity for  $\text{Cu}^{2+}$  over a large number of mono, bi and trivalent cations. In view of the good selectivity of the electrode, it was able to work successfully in high-ionic-strength solutions and, therefore, with a

variety of real samples. Thus, the electrode can be used for  $\text{Cu}^{2+}$  determination in presence of other ions by potentiometry.

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