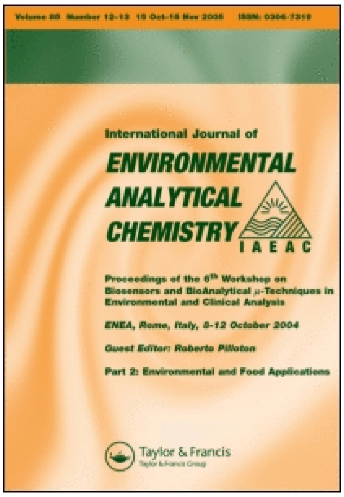

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Singh, Ashok K. , Jain, A. K. , Singh, Jitendra and Mehtab, Sameena(2009) 'Development of an electrochemical sensor based on Schiff base for Cu(II) determination at nano level in river water and edible materials', International Journal of Environmental Analytical Chemistry, 89: 15, 1081 — 1098
To link to this Article: DOI: 10.1080/03067310902719167
URL: http://dx.doi.org/10.1080/03067310902719167

Intern. J. Environ. Anal. Chem.
Vol. 89, No. 15, 20 December 2009, 1081–1098

Development of an electrochemical sensor based on Schiff base for Cu(II) determination at nano level in river water and edible materials

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(*Received 28 August 2008; final version received 4 January 2009*)

Plasticised membranes using 2-[{(2-hydroxyphenyl)imino}methyl]-phenol (L_1) and 2-[{(3-hydroxyphenyl)imino}methyl]-phenol (L_2), have been prepared and investigated as Cu^{2+} ion-selective sensors. Effect of various plasticisers, namely, dibutyl phthalate (DBP), dibutyl sebacate (DBS), benzyl acetate (BA), *o*-nitrophenyloctylether (*o*-NPOE) and anion excluders, oleic acid (OA) and sodium tetraphenylborate (NaTPB) was studied and improved performance was observed in several instances. Optimum performance was observed with membranes of (L_1) having composition $L_1:DBS:OA:PVC$ in the ratio of 6 : 54 : 10 : 30 (w/w, %). The sensor works satisfactorily in the concentration range 3.2×10^{-8}–$1.0 \times 10^{-1}\,mol\,L^{-1}$ with a Nernstian slope of $29.5 \pm 0.5\,mV\,decade^{-1}$ of $a_{cu^{2+}}$. The detection limit of the proposed sensor is $2.0 \times 10^{-8}\,mol\,L^{-1}$ ($1.27\,ng\,mL^{-1}$). Wide pH range (3.0–8.5), fast response time (7 s), sufficient (up to 25% v/v) non-aqueous tolerance and adequate shelf life (3 months) indicate the utility of the proposed sensor. The potentiometric selectivity coefficients as determined by matched potential method indicate selective response for Cu^{2+} ions over various interfering ions, and therefore could be successfully used for the determination of copper in edible oils, tomato plant material and river water.

Keywords: Schiff base; poly (vinyl chloride) membranes; copper-selective sensor; electrochemical sensors; potentiometric selectivity

1. Introduction

Copper is widely used for industrial, agricultural and domestic purposes and is therefore widely distributed in the environment. Though copper plays an important role in many biological processes, such as blood formation and functioning of various enzymes, its maximum tolerable level is $2.0\,mg\,L^{-1}$ [1]. Its excessive intake manifests in certain diseases in humans, such as Menke's syndrome and Wilson's disease [2,3]. Thus, the determination of copper is important in view of its utility as well as toxicity. A number of sophisticated instrumental methods such as atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-MS), stripping voltammetry and flame photometry are employed for the determination of copper at low concentration levels [4–9]. These methods generally require sample pretreatment, infrastructure backup, expertise and are thus not very convenient for routine analysis of a large number of environmental samples.

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310902719167
http://www.informaworld.com

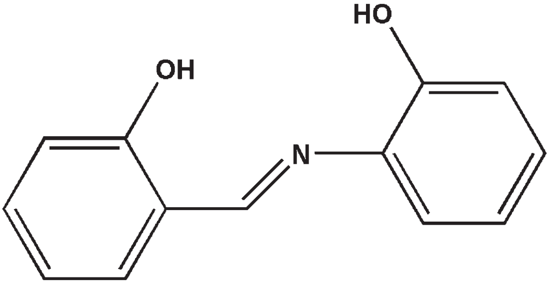

Figure 1. Structure of 2-[{(2-hydroxyphenyl)imino}methyl]-phenol (L_1).

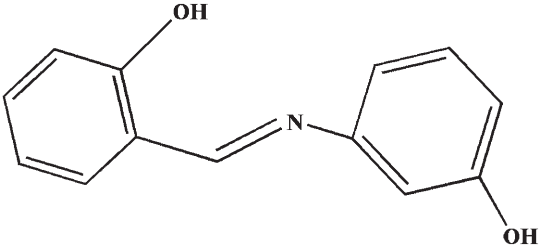

Figure 2. Structure of 2-[{(3-hydroxyphenyl)imino}methyl]-phenol (L_2).

Ion-sensors provide analytical procedures that overcome or minimise the above drawbacks since they are fast, convenient, can be handled easily and do not require sample pretreatment and large infrastructure backup.

The specific metal–ligand interaction is the most important recognition mechanism that can be utilised in the development of potentiometric sensors [10]. Due to urgent need for selective potentiometric determination of trace amounts of copper ions, especially in food and water samples, many coordination compounds have been used as ionophores in the construction of ion-selective electrodes (ISEs) for copper ion [11–30]. The Cu(II)–nitrogen–sulphur ligands frame have made remarkable contribution to the determination of copper in various samples [31]. Successful attempts have been made in the design and synthesis of highly selective ionophores for developing Cu^{2+} ion-selective sensors, but they show some limitations such as poor detection limit [15], narrow working concentration range [16], serious interfering effect of other ions [18], narrow useful pH range [19,20] and slow response [25]. A review of literature reveals that the Schiff bases are the excellent choice as ionophores for the fabrication of ion sensors due to their peculiar properties [32–40]. The lipophilic ability of Schiff bases provide geometric and cavity control for host guest complexation modulation and thus produces remarkable selectivity, sensitivity and stability for a specific ion. A number of Schiff bases have been employed in ion-selective sensors as cation carriers for the determination of several metal ions such as Cu^{2+} [18,21,41–43], Ni^{2+} [35], Al^{3+} [36], Hg^{2+} [37], Ag^{+} [38], Gd^{3+} [40], Yb^{3+} [44].

The literature revealed that Schiff bases 2-[{(2-hydroxyphenyl)imino}methyl]-phenol (L_1 Figure 1) and 2-[{(3-hydroxyphenyl)imino}methyl]-phenol (L_2 Figure 2) form complexes with various metals. Stability constants of several metal complexes of L_1 and L_2 were determined by the sandwich membrane method [45] and given in Table 1.

Table 1. Stability constants of various metal ions with L_1 and L_2.

	Stability constants ($\log \beta_{Ln}$) ($n = 2$)	
Cation	L_1	L_2
Cu^{2+}	7.14 ± 0.8	4.38 ± 0.3
Co^{2+}	3.27	2.98
Ni^{2+}	3.82	3.62
Fe^{2+}	3.71	2.02
Hg^{2+}	1.76	1.61
Cd^{2+}	1.72	1.68
Mg^{2+}	1.62	0.74
Pb^{2+}	1.60	0.69
Zn^{2+}	1.57	1.32
Ag^{+}	1.43	0.85
Ca^{2+}	1.22	0.96
Na^{+}	0.97	0.72
La^{3+}	0.83	0.66

Note: n = Ligand to metal ratio.

The values show that the Schiff bases (L_1 and L_2) interact strongly with Cu^{2+} ion (stability constant 7.14 ± 0.8 for CuL_1 complex and 4.38 ± 0.3 for CuL_2 complex) but show moderately weak interaction with other metals such as Co, Ni, Fe, Hg, Cd, Mg, Pb, Zn, Ag, La, Na and Ca (having stability constant of metal complexes in the range 3.82–0.66). The PVC-based membranes of L_1 and L_2 were investigated as Cu^{2+} selective sensors and the results are presented in the present communication.

2. Experimental

2.1 *Reagents*

Reagent grade, oleic acid (OA), sodium tetraphenylborate (NaTPB), dibutyl phthalate (DBP, $\varepsilon = 8.5$), dibutyl sebacate (DBS, $\varepsilon = 4.0$), benzyl acetate (BA, $\varepsilon = 5.1$), *o*-nitrophenyloctylether (*o*-NPOE, $\varepsilon = 14$), tetrahydrofuran (THF), AR grade copper nitrate and high molecular weight PVC were procured from E. Merck (Mumbai, MH, India) and used as received. 2-Aminophenol, 3-aminophenol from Glaxo (Mumbai, MH, India) and salicylaldehyde from Loba Chemie (Mumbai, MH, India) were reagent grade materials. Double distilled water was used to prepare stock solution (0.1 M) of metals which was then diluted to prepare solutions of different concentrations.

2.2 *Synthesis of ionophores*

Schiff bases L_1 and L_2 were synthesised according to the reported method [46].

2.2.1 *Synthesis of 2-[{(2-hydroxyphenyl)imino}methyl]-phenol[L_1]*

2-Aminophenol (0.218 g, 2 mmol) was dissolved in 50 mL dried ethanol at elevated temperature under nitrogen atmosphere. Salicylaldehyde (0.244 g, 2 mmol) in ethanol was added drop-wise to this solution. The reaction mixture was heated under refluxing condition.

Orange precipitates were observed within 10 min. Reaction was continued for 1 h. Precipitates were filtered, washed with toluene and dried in a vacuum oven at 60°C, orange crystals were obtained: m.p. 110°C. Elemental Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.28; H, 5.33; N, 6.61%. IR(KBr, cm^{-1}) 1614 (s, $\nu_{C=N}$). 3453(m, $\nu_{O\text{–}H}$), ^1H NMR ($CDCl_3$, δ/ppm): 6.7–7.3 (m, 8H), 8.5 (s, 1H), 11.3 (s, br, 2H).

2.2.2 *Synthesis of 2-[{(3-hydroxyphenyl)imino}methyl]-phenol[L_2]*

3-Aminophenol (0.218 g, 2 mmol) was dissolved in 50 mL dried ethanol at elevated temperature under nitrogen atmosphere. Salicylaldehyde (0.244 g, 2 mmol) in ethanol was added drop-wise to this solution. The reaction mixture was heated under refluxing condition for 2 h. Orange yellow precipitates were observed. Precipitates were filtered and washed with toluene, and dried in a vacuum at room temperature (≈30°C), orange yellow crystals were obtained: m.p. 125°C. Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57. Found: C, 74.28; H, 5.14; N, 6.22%. IR (KBr, cm^{-1}) 1620 ($\nu_{C=N}$). 3664 (m, $\nu_{O\text{–}H}$), ^1H NMR ($CDCl_3$, δ/ppm): 6.8–7.8 (m, 8H), 8.3 (s, 1H), 11.3 (s, br, 2H).

2.3 *Electrode preparation*

Besides the critical role of the nature of ion carrier in preparing selective sensors, other important parameters of the PVC-based membrane sensors are the amount of ionophore, nature of plasticiser (solvent mediator), plasticiser/PVC ratio and the nature of the additive [47–50]. In order to prepare membranes of different compositions, varying amount of the ion-active phase and anion excluders OA/NaTPB and PVC were dissolved in 5 mL THF. To this solution, solvent mediators' namely DBP, DBS, BA and NPOE were added. The mixture was shaken thoroughly with a glass rod. When the solution became viscous it was poured into an acrylic ring placed on smooth glass plate. The solution was then allowed to evaporate for 24 h at room temperature. Transparent membranes of about 0.1 mm thickness were obtained, which were then cut to circular disc (diameter ≈5 mm) and attached to one end of a Pyrex glass tube with araldite. The ratio of membrane ingredients, time of contact and concentration of equilibrating solution was optimised so that the potentials recorded were reproducible and stable. Membrane-to-membrane reproducibility was assured by following carefully the optimum condition of fabrication. The membrane that gave reproducible results and best performance was selected for detailed studies.

2.4 *Equilibration of membranes and potential measurements*

The membranes were equilibrated for 4 days in $1.0 \times 10^{-1}\,mol\,L^{-1}$ $Cu(NO_3)_2$ solution. The potentials were measured by varying the concentration of $Cu(NO_3)_2$ test solution in the range 1.0×10^{-8}–$1.0 \times 10^{-1}\,mol\,L^{-1}$. Each solution was stirred and the potential reading was recorded when it became stable, and then plotted as logarithmic function of Cu^{2+} ion activity. The potential measurements were carried out on Orion 4 star pH meter at 25 ± 0.1°C using saturated calomel electrode (SCE) as reference electrode with the following cell assembly:

$$Hg/Hg_2Cl_2 \mid KCl(satd) \mid 0.1\ M\ Cu(NO_3)_2 \parallel PVC\ membrane \parallel test\ solution$$
$$\mid Hg/Hg_2Cl_2 \mid KCl(satd).$$

The activities of Cu^{2+} ions were calculated according to the following modified Debye–Hückel approximation equation:

$$\log \gamma = -0.511 Z^2 \left[\frac{\mu^{\frac{1}{2}}}{1 + 1.5\mu^{\frac{1}{2}}} - 0.2\mu \right],$$

where γ is activity coefficient, μ is the ionic strength and z is charge on ion.

2.5 *Methodology of selectivity*

In this study, selectivity coefficients were determined by IUPAC recommended matched potential method (MPM) [51,52]. According to this method, the activity of the reference solution ($a_{Cu^{2+}} = 1.0 \times 10^{-4}\,\text{mol L}^{-1}$) was changed by adding a specified activity (concentration) of primary ions ($A = 5.0 \times 10^{-4}$ to $1.0 \times 10^{-2}\,\text{mol L}^{-1}$ of Cu^{2+} ion) and the potential was measured. In a separate experiment, interfering ions ($B = 1.0 \times 10^{-2}$ to $1.0 \times 10^{-1}\,\text{mol L}^{-1}$) were added to the identical reference solution until the potential matched the previous one obtained by adding the primary ions. In this method, selectivity coefficient $K^{\text{Pot}}_{\text{Cu},B}$ is calculated by the following equation:

$$K^{\text{Pot}}_{\text{Cu},B} = \frac{\Delta a_{\text{Cu}}}{a_B} = \frac{a'_{\text{Cu}} - a_{\text{Cu}}}{a_B},$$

where Δa_{Cu} is the chang in the activity of the reference solutions and a_B is the activity of the interfering ion.

2.6 *Methodology of dynamic response time*

Dynamic response time of an ISE is defined as length of time between the instant at which the ISE and a reference electrode are brought into contact with a sample solution and the first instant at which the cell gives a constant potential. The response time of a sensor is measured by changing the concentration of test solution successively from 1.0×10^{-7} to $1.0 \times 10^{-2}\,\text{mol L}^{-1}$ and each time the cell potential is measured. A similar procedure was adopted, in a sequence of high to low sample concentration, in order to evaluate the reversibility of the sensor.

3. Results and discussion

3.1 *Optimisation of membrane composition*

PVC-based membranes of two ionophores L_1 and L_2 of different composition were prepared and their potential response to Cu^{2+} ion in the test solution, in the concentration range 1.0×10^{-8}–$1.0 \times 10^{-1}\,\text{mol L}^{-1}$, was studied. The variation of membrane potential as a function of $-\log a_{\text{Cu}}$ for membranes of L_1 and L_2 was studied and the results are given in Table 2 along with composition of membranes and their performance characteristics. It is seen from the table that the blank membranes (Nos. 1 and 11) having only plasticiser, additives and PVC show very poor response to Cu^{2+} with a very small slope and short range. The membranes Nos. 2 and 12 which now have ionophore show an increase in slope and working concentration range indicating the selectivity of ionophores. Though in the presence of ionophore the response of membrane sensors is better as compared

Table 2. Potentiometric response characteristics of Cu(II) PVC membrane sensors based on ionophore L_1 and L_2.

Membrane No.	Composition of membrane (%, w/w)				Slope (mV decade^{-1} of $a_{Cu^{2+}}$)	Linear range (mol L^{-1})
	Ionophore	Plasticiser	Additive	PVC		
1	–	60	10, OA	30	<9.2	6.2×10^{-3}–1.0×10^{-1}
2	6, L_1	–	–	94	21.6	5.2×10^{-5}–1.0×10^{-2}
3	6, L1	54, DBS	–	40	27.9	4.0×10^{-7}–1.0×10^{-2}
4	6, L1	54, BA	–	40	23.9	7.4×10^{-6}–5.0×10^{-2}
5	6, L1	54, DBP	–	40	22.3	7.8×10^{-6}–2.0×10^{-2}
6	6, L1	54, NPOE	–	40	20.8	2.8×10^{-6}–3.0×10^{-2}
7	6, L1	54, DBS	10, OA	30	29.5	3.2×10^{-8}–1.0×10^{-1}
8	5, L1	54, DBS	10, OA	31	26.8	1.3×10^{-7}–1.0×10^{-2}
9	4, L1	54, DBS	10, OA	32	25.4	9.6×10^{-7}–1.0×10^{-2}
10	6, L1	–	10, OA	84	21.3	1.5×10^{-5}–1.0×10^{-2}
11	–	60	3, NaTPB	37	<14.2	1.5×10^{-3}–1.0×10^{-1}
12	8, L2	–	–	92	20.4	7.5×10^{-5}–1.0×10^{-2}
13	8, L2	58, DBP	–	34	27.3	3.1×10^{-6}–1.0×10^{-2}
14	8, L2	58, NPOE	–	34	33.1	8.3×10^{-6}–7.2×10^{-2}
15	8, L2	58, DBS	–	34	35.3	5.2×10^{-6}–4.0×10^{-2}
16	8, L2	58, BA	–	34	34.9	6.5×10^{-6}–7.0×10^{-2}
17	8, L2	58, DBP	3, NaTPB	31	29.6	2.2×10^{-7}–1.0×10^{-2}
18	7, L2	58, DBP	3, NaTPB	32	26.4	8.8×10^{-6}–1.0×10^{-2}
19	6, L2	58, DBP	3, NaTPB	33	24.8	4.2×10^{-6}–1.0×10^{-2}
20	8, L_2	–	3, NaTPB	89	20.5	1.0×10^{-5}–1.0×10^{-2}

to blank membranes, the slope is sub-Nernstian (21.6 mV decade^{-1} and 20.4 mV decade^{-1} of activity, respectively) and the working concentration range is still much shorter (from 5.2×10^{-5} to 1.0×10^{-2} mol L^{-1} with L_1) and (from 7.5×10^{-5} to 1.0×10^{-2} mol L^{-1} with L_2).

It is well established that the selectivity, linearity and sensitivity for a given ionophore depends significantly on the membrane composition, nature of plasticiser [53] and additive used [54,55]. Therefore, it was thought desirable to improve the performance of these PVC-based membranes of L_1 and L_2. Therefore, the membranes Nos. 3–9 for L_1 having different compositions were prepared and investigated. The performance characteristics of these membranes are given in Table 2. In the case of carrier-type ion-selective sensors, the extraction equilibrium in the vicinity of the interface between the membrane and the aqueous layer affects the potentiometric response of membranes [56]. Therefore, the effect of amount of ionophore was also seen and it was found that 6% amount of the ionophore (L_1) is optimum with regard to all performance parameters. Both the slope and the working concentration range were affected as the amount of ionophore was changed.

The performance of an ion-selective sensor strongly depends on the nature of plasticiser. This is because the plasticiser forms a liquid organic phase through which the cations can easily extract into the membrane. Therefore, the effect of a set of plasticisers (DBS, DBP, NPOE and BA) was checked as shown in Figure 3 and the results are gathered in Table 2. A perusal of Table 2 shows that the addition of plasticisers (DBS, DBP, NPOE and BA) improves the slope and broadens the working concentration range. However, the membrane sensor No. 3 of L_1 with DBS plasticiser shows better characteristics in terms of slope (27.9 mV decade^{-1}) and working range

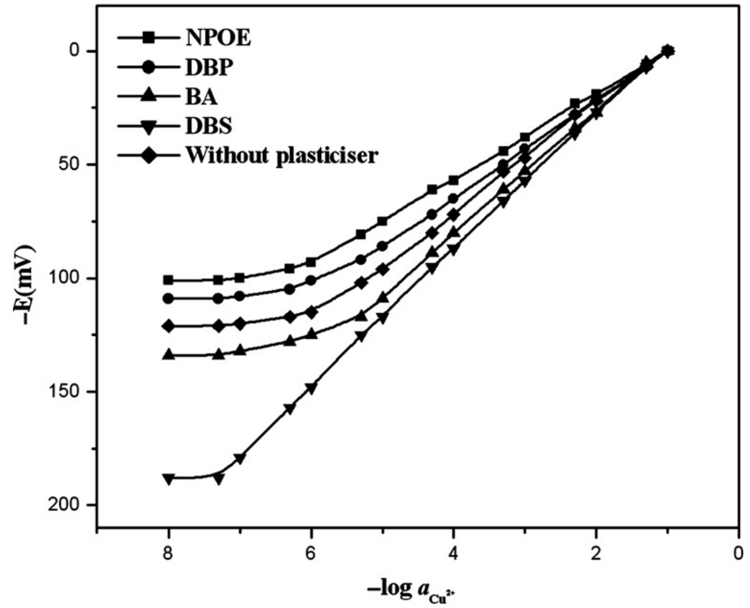

Figure 3. Potential responses of Cu^{2+} membrane sensors based on L_1 with different plasticiser.

(4.0×10^{-7}–1.0×10^{-2} mol L^{-1}). The performance of the membrane sensor was further improved by adding lipophilic anion additives. The use of 10% OA was found as a suitable additive for the sensor based on ionophore L_1, and the sensor No. 7 having membrane composition L_1 : DBS : OA : PVC ratio as 6 : 54 : 10 : 30 (%, w/w) shows the best performance characteristics with regard to Nernstian slope (29.5 mV decade^{-1}) and widest activity range (3.2×10^{-8}–1.0×10^{-1} mol L^{-1}).

Similarly the membrane Nos. 11–20 of L_2 having different compositions were also prepared. The additive used in these preparations was more lipophilic NaTPB (3%, w/w). The performance characteristics of these membranes are also gathered in Table 2. It is seen that in this case too the addition of plasticiser improves the performance characteristic of membrane sensor. However, the effect of DBP is the best and 8% amount of ionophore is optimum with regard to all performance parameters. Hence, the membrane No. 17 having composition L_2 : DBP : NaTPB : PVC ratio as 8 : 58 : 3 : 31 (%, w/w) performs best as it shows the widest working activity range (2.2×10^{-7}–1.0×10^{-2} mol L^{-1}) with Nernstian slope (29.6 mV decade^{-1}).

The experimentally determined results show that DBS gives better results for L_1 and DBP gives better results for L_2. It seems that this is due to a synergism between lipophilicity and polarity and the best results are obtained when these properties gain an intermediate value. The better results of NaTPB with L_2 show that it enhances the selectivity of the membrane electrodes and promote the exchange kinetics at the sample membrane interface.

3.2 *Potentiometric characteristics*

The calibration curve (Figure 4) for the two copper ion-selective sensors indicate that the sensor No. 7 based on L_1 exhibits Nernstian slope (29.5 ± 0.5 mV decade^{-1} of $a_{Cu^{2+}}$) over

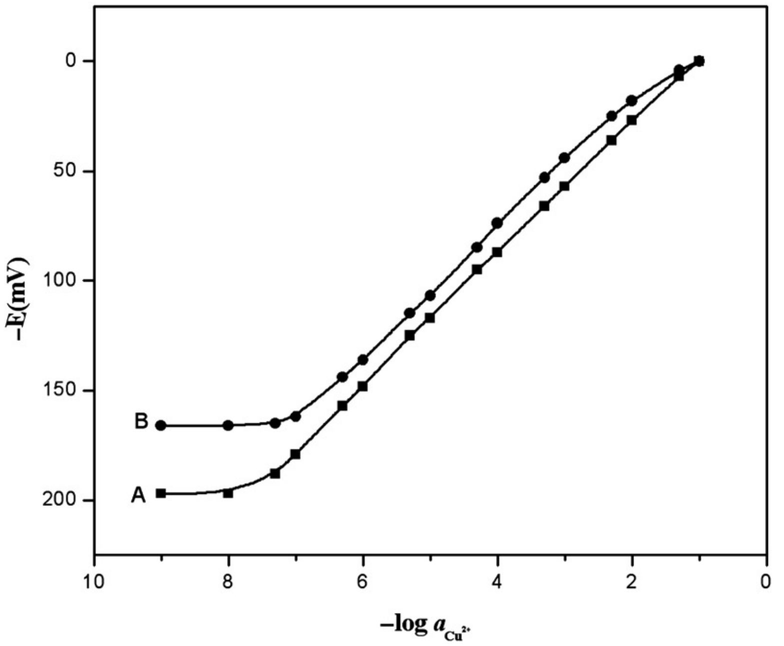

Figure 4. Calibration plot for Cu^{2+} ion-selective sensors: (a) for sensor No. 7 (b) for sensor No. 17.

a wide concentration range of 3.2×10^{-8}–$1.0 \times 10^{-1}\,\mathrm{mol\,L^{-1}}$ with a limit of detection $2.0 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$, while sensor No. 17 based on L_2 exhibits a Nernstian slope ($29.6 \pm 0.5\,\mathrm{mV\,decade^{-1}}$ of $a_{Cu^{2+}}$) and linear concentration range of 2.2×10^{-7}–$1.0 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$ with limit of detection $1.2 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$.

3.3 *Effect of soaking time and lifetime*

The performance of these sensors was seen as a function of time and it was found that sensor No. 7 shows adequate life time of 3 months while it is 1.5 months for sensor No. 17. Over this period the response of both the sensors were measured by recording the calibration graph, at 25°C at different time intervals, without appreciable change in slope and working concentration range. The results listed in Table 3 summarise the effects of soaking time on slope working concentration range and detection limit. However, when not in use the sensors were stored in 0.1 M copper nitrate solution. The lower lifetime of the sensor No.17 based on L_2 may be due to the leaching on membrane components into the solution.

3.4 *Effect of pH change*

The effect of pH on the performance of the sensors was also investigated in the pH range 1.0–12.0 for $1.0 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$ and $1.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ Cu^{2+} ion solution and the effect is shown in Figure 5. The operational range was studied by varying the pH of the test solution with HNO_3/NaOH. It is seen from Figure 5 that the potentials remain constant in

Table 3. Effect of soaking time on the potential response of the copper selective sensors.

Electrode type	Soaking time (days)	Slope (mV decade^{-1} of $a_{Cu^{2+}}$)	Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})
Sensor No. 7 based on L_1				
	15	29.5	3.2×10^{-8}–1.0×10^{-1}	2.0×10^{-8}
	30	29.5	3.2×10^{-8}–1.0×10^{-1}	2.0×10^{-8}
	45	29.3	3.6×10^{-8}–1.0×10^{-1}	2.2×10^{-8}
	60	29.2	3.6×10^{-8}–1.0×10^{-1}	2.3×10^{-8}
	90	28.9	4.1×10^{-8}–1.0×10^{-1}	2.9×10^{-8}
	95	23.8	8.7×10^{-7}–5.0×10^{-2}	1.9×10^{-7}
	100	26.3	9.6×10^{-6}–1.0×10^{-3}	5.3×10^{-7}
Sensor No. 17 based on L_2				
	15	29.6	2.2×10^{-7}–1.9×10^{-2}	1.2×10^{-7}
	30	29.2	2.2×10^{-7}–1.9×10^{-2}	1.3×10^{-7}
	45	28.5	6.8×10^{-7}–1.9×10^{-2}	7.1×10^{-7}
	60	27.2	2.5×10^{-6}–1.9×10^{-2}	1.9×10^{-6}
	90	26.9	3.5×10^{-6}–1.9×10^{-2}	2.3×10^{-5}
	95	25.2	2.3×10^{-5}–1.0×10^{-2}	1.5×10^{-5}
	100	24.4	7.3×10^{-5}–1.0×10^{-2}	4.5×10^{-5}

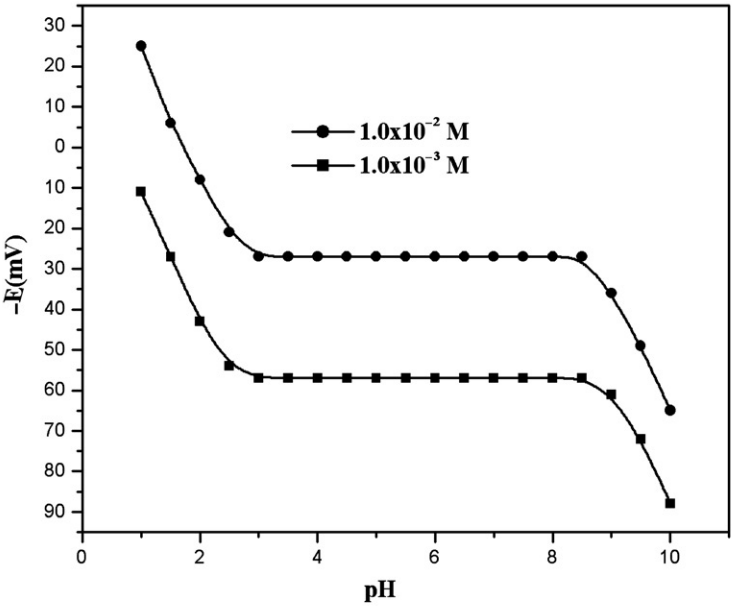

Figure 5. Effect of pH on cell potential of sensor No. 7 based on L_1 at 1.0×10^{-2} mol L^{-1} and 1.0×10^{-3} mol L^{-1}, respectively.

the pH range 3.0–8.5 for sensor No. 7 based on L_1 while the pH range for sensor No. 17 based on L_2 was observed as 3.2–7.5. Therefore, the same was taken as the working pH range of the sensor assemblies. The change in potential below pH 3 is apparently due to interference of H^+ and above pH 8.5 due to strong hydrolysis of Cu^{2+} ions.

Table 4. Selectivity coefficients of various interfering ions.

	Selectivity coefficient ($-\log K_{\mathrm{Cu},B}^{\mathrm{Pot}}$)	
Interfering ions	L_1	L_2
Co^{2+}	2.2	2.1
Ni^{2+}	3.6	2.9
Fe^{2+}	3.8	2.7
Hg^{2+}	4.1	4.6
Cd^{2+}	4.3	4.3
Mg^{2+}	4.5	5.0
Pb^{2+}	4.6	5.1
Zn^{2+}	4.7	4.5
Ag^{+}	4.9	4.4
La^{3+}	5.1	5.1
Na^{+}	5.1	5.1
Ca^{2+}	4.2	3.5

3.5 *Potentiometric selectivity*

Selectivity is the most important characteristic as it determines the extent of utility of any sensor in real sample measurements. MPM, used in the present study has an advantage of removing limitations imposed by Nicolsky–Eisenman equation while calculating selectivity coefficient by other methods. These limitations include non-Nernstian behaviour of interfering ion and problem of inequality of charges of primary and interfering ions.

The selectivity coefficients so calculated for the sensors based on two ionophores are listed in Table 4. A value of 1.0 for selectivity coefficient shows equal response of the sensor both to primary and interfering ions. The values of selectivity coefficient those are smaller than 1.0, show that the sensor is selective to primary ions over interfering ions. It is seen from the Table 4 that the selectivity coefficients are of the order of 10^{-3} or smaller, indicating that the sensor is appreciably selective to Cu^{2+} ions over a number of foreign ions studied.

It is further seen from the table that the sensor No. 7 based on L_1 shows smaller selectivity coefficients to those of sensor No. 17 based on L_2. So in terms of selectivity sensor No. 7 it is better as compared to the sensor No. 17. Therefore, all further studies were carried out with this sensor only.

3.6 *Effect of non-aqueous solvent*

The real samples may contain non-aqueous content, so the performance of the sensor was also investigated in partially non-aqueous media as 10%, 20%, 25%, 30% and 35% (v/v) using non-aqueous content in methanol–water, ethanol–water and acetone–water mixtures. The results are summarised in Table 5. It was found that the sensor did not show any appreciable change in working concentration range and slope in mixtures up to 25% (v/v) non-aqueous content. However, above 25% non-aqueous content, the potentials showed drift with time both in working concentration range and slope which may be probably due to leaching of the ionophore at higher organic content.

Table 5. Effect of partially non-aqueous medium on the working of Cu^{2+} sensor based on L_1 (sensor No. 7).

Non-aqueous content (%, v/v)	Working concentration range ($mol\,L^{-1}$)	Slope (mV decade^{-1} of $a_{Cu^{2+}}$)
0	3.2×10^{-8}–1.0×10^{-1}	29.5 ± 0.5
Methanol		
10	3.2×10^{-8}–1.0×10^{-1}	29.5
20	3.2×10^{-8}–1.0×10^{-1}	29.5
25	5.0×10^{-8}–1.0×10^{-1}	29.1
30	9.2×10^{-7}–5.0×10^{-3}	24.2
35	3.2×10^{-6}–1.0×10^{-3}	22.6
Ethanol		
10	3.2×10^{-8}–1.0×10^{-1}	29.5
20	3.2×10^{-8}–1.0×10^{-1}	29.5
25	3.8×10^{-8}–2.3×10^{-1}	29.3
30	6.2×10^{-7}–5.0×10^{-2}	24.6
35	5.0×10^{-6}–2.0×10^{-3}	23.9
Acetone		
10	3.2×10^{-8}–1.0×10^{-1}	29.5
20	5.1×10^{-8}–1.0×10^{-1}	29.1
25	6.2×10^{-8}–3.0×10^{-1}	28.9
30	8.2×10^{-6}–2.4×10^{-2}	25.6
35	7.3×10^{-6}–5.0×10^{-2}	22.8

3.7 *Dynamic response time*

It is well known that the dynamic response time of a sensor is one of the most important factors in its evaluation. It was determined as described in Section 2.5. The results depicted in Figure 6 show that the time needed to reach a potential within ±1 mV of the final equilibrium value after successive immersion of a series of Cu^{2+} ions, each having a 10-fold difference in concentration, is 7 s for sensor No. 7. This indicates a fast exchange kinetics of complexation–decomplexation of Cu^{2+} ions with the L_1 ionophore at the test solution-membrane interface. The reversibility of the sensor was checked by changing the sample concentrations successively from 1.0×10^{-2} to $1.0\times10^{-7}\,mol\,L^{-1}$ and the results showed that the potentiometric response of the sensor was reversible; although the time needed to reach equilibrium values (58 s) was longer than that of low-to-high sample concentrations. Reproducibility of the sensor was examined by using six similar constructed sensors under the optimum conditions. The result showed good reproducibility (±0.6 mV) for the sensor.

4. Analytical applications

The high selectivity and sensitivity showed by the sensor No. 7 based on L_1 for Cu^{2+} makes it potentially useful for monitoring the concentration of Cu^{2+} in various samples. Trace levels of copper, present in edible oils and tomato plant material and river water were analysed by AAS and the proposed sensor.

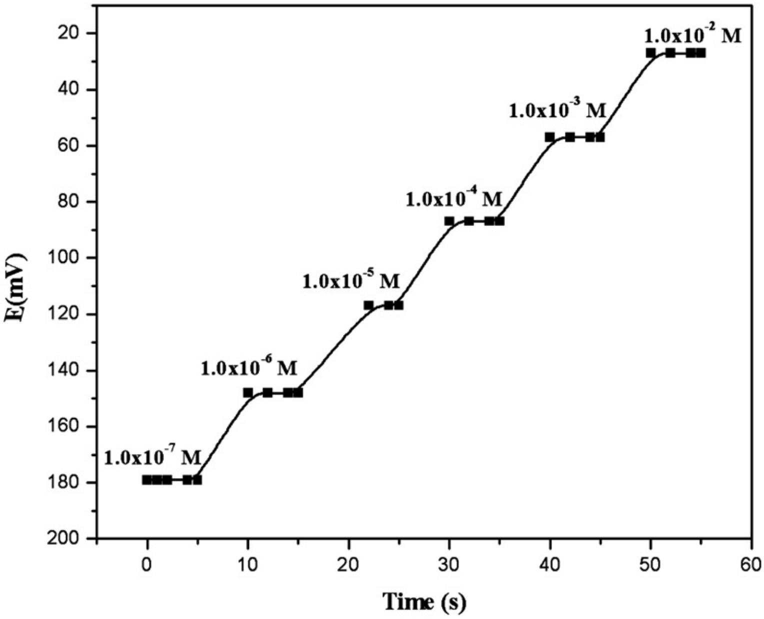

Figure 6. Dynamic response time of the copper sensor based on L_1 (sensor No. 7) for step changes in concentration of Cu^{2+} ion.

Table 6. Quantification of copper in edible oils, plant material and water samples using AAS and proposed Cu^{2+} sensor based on L_1 (sensor No. 7).

Name of sample	Copper found by AAS (μg/mL)[a]	Copper found by ISE (μg/mL)[a] (%, RSD)
Soya bean oil	0.90 ± 0.06	0.93 ± 0.02 (2.15)
Sunflower oil	0.97 ± 0.08	0.96 ± 0.02 (2.08)
Tomato plant material	121 ± 2.1	122 ± 1.3 (1.06)
River water sample	14.9 ± 0.5	15.3 ± 0.7 (4.57)

Note: [a]Average of three replicates.

4.1 *Estimation of Cu^{2+} in edible oils and plant material*

The oil and plant samples were ashed and the residue was dissolved in dilute hydrochloric acid and diluted to 50 mL. The pH of this solution was adjusted to 5 and Cu^{2+} concentration was determined by AAS and the proposed sensor. The results are compiled in Table 6.

4.2 *Determination of Cu^{2+} river water*

The sensor was also successfully applied to determine copper directly in the river water sample taken from Ganga. The water samples were acidified with 0.1 M HCl to adjust stable pH at 5.5. The results obtained from the triplicate measurements are compared with those determined by AAS and are summarised in Table 6.

Table 7. Comparison of the proposed Cu^{2+}-selective electrodes (sensor No. 7) with the reported electrodes.

Ref no.	Linear range (mol L^{-1})	Slope (mV decade^{-1} of activity)	Detection limit (mol L^{-1})	Selectivity coefficients ($-\log K^{Pot}_{Cu,B}$)	pH range	Response time (s)	Analytical applications
[13]	8.0×10^{-6}–1.0×10^{-1}	29.5	3.0×10^{-6}	Ca^{2+}(2.6), Mg^{2+}(2.3), Sr^{2+}(2.1), Ba^{2+}(2.1), Ni^{2+}(2.4), Co^{2+}(2.2), Cd^{2+}(2.2), Pb^{2+}(0.5), Zn^{2+}(2.3), Na^{+}(3.78), NH_4^+(2.74), Zn^{2+}(2.25), K^{+}(2.02)	3.0–6.5	15	Black tea, multivitamin and mineral capsule
[15]	7.9×10^{-6}–1.0×10^{-1}	29.9	7.0×10^{-6}	Ca^{2+}(1.0), Mg^{2+}(0.9), Sr^{2+}(0.8), Ba^{2+}(0.6), Ni^{2+}(0.8), Co^{2+}(0.2), Cd^{2+}(0.7), Pb^{2+}(0.6), Zn^{2+}(1.0), Hg^{2+}(0.9), Ag^{+}(0.6), NH_4^+(0.6), Li^{+}(0.7), Na^{+}(0.2), K^{+}(0.2)	2.1–6.3	11	Indicator electrode and in real samples
[19]	1.0×10^{-5}–1.0×10^{-2}	25.9	2.1×10^{-7}	Li^{+}(5.1), Na^{+}(5.2), K^{+}(5.1), Mg^{2+}(3.2), Ca^{2+}(3.4), Ag^{+}(3.1), Sr^{2+}(2.8), Ba^{2+}(3.0), Ni^{2+}(2.5), Co^{2+}(2.7), Hg^{2+}(2.52), Cd^{2+}(2.4), Zn^{2+} (1.7), Pb^{2+} (0.5)	4.5–7.0	15	Rocks and industrial wastewater samples
[20]	1.0×10^{-6}–1.0×10^{-1}	28.2	5.0×10^{-7}	Ca^{2+}(2.9), Ni^{2+}(3.0), Co^{2+}(3.0), Cd^{2+}(2.9), Pb^{2+}(4.7), Zn^{2+}(1.7), Hg^{2+}(4.1), Ag^{+}(3.7), NH_4^+(2.5), Li^{+}(2.3), K^{+}(2.9), Mg^{2+}(2.4)	3.0–6.5	10	In milk powder and indicator electrode

(*Continued*)

Table 7. Continued.

Ref no.	Linear range (mol^{-1})	Slope (mV decade^{-1} of activity)	Detection limit (mol L^{-1})	Selectivity coefficients ($-\log K^{\mathrm{Pot}}_{\mathrm{Cu},B}$)	pH range	Response time (s)	Analytical applications
[21]	5.0×10^{-6}–5.0×10^{-2}	29.8	3.1×10^{-6}	Ca^{2+}(3.0), Mg^{2+}(3.0), Ba^{2+}(3.1), Ni^{2+}(1.5), Co^{2+}(2.1), Cd^{2+}(2.1), Zn^{2+}(2.1), Na^+(1.3), Hg^{2+}(1.2), K^+(3.9), Pb^{2+}(2.4)	4.0–7.0	5	Indicator electrode
[22]	1.0×10^{-6}–1.0×10^{-1}	29.8	6.0×10^{-7}	Ca^{2+}(3.4), Mg^{2+}(3.5), Ni^{2+}(3.7), Co^{2+}(3.6), Cd^{2+}(3.5), Zn^{2+}(3.4), Na^+(4.0), Ag^+(4.0), K^+(3.7), Li^+(4.4), Pb^{2+}(3.7)	3.0–7.5	15	In black tea and in wastewater
[23]	1.0×10^{-6}–1.0×10^{-1}	29.0	1.4×10^{-7}	Ca^{2+}(3.6), Ni^{2+}(3.2), Co^{2+}(4.0), Cd^{2+}(4.5), Pb^{2+}(0.7), Zn^{2+} (2.2), K^+(2.3), Mg^{2+}(3.6), Na^+(2.6)	3.2–5.5	9	–
[24]	5.0×10^{-8}–1.0×10^{-2}	29.5	4.0×10^{-8}	Ca^{2+}(3.5), Mg^{2+}(4.5), Sr^{2+}(3.9), Ba^{2+}(4.2), Ni^{2+}(2.9), Co^{2+}(1.1), Cd^{2+}(2.2), Pb^{2+}(1.5), Zn^{2+}(2.4), Hg^{2+}(0.8), Ag^+(0.5), Li^+(4.7), Na^+(2.9), K^+(4.9), Ce^{3+}(4.7)	3.0–9.5	12	Milk powder and water samples

[25]	6.0×10^{-8}–1.0×10^{-1}	29.1 ± 0.1	3.0×10^{-8}	Co^{2+}(3.48), Pb^{2+}(3.48), Zn^{2+}(3.77), Ni^{2+}(3.64), Cd^{2+}(3.96), Hg^{2+}(5.46), Ag^{+}(4.24), Ca^{2+}(4.12), Sr^{2+}(4.10), Na^{+}(4.01), K^{+}(4.00)	2.8–5.8	<15	Black tea and indicator electrode
[26]	1.0×10^{-7}–1.0×10^{-3}	28.1	6.3×10^{-8}	Ag^{+}(0.0), Ni^{2+}(4.2), Co^{2+}(5.2), Zn^{2+}(4.7), Fe^{3+}(4.9), Mn^{2+}(5.2), Cd^{2+}(4.3)	5.3–7.2	6	FET Cu^{2+} checker and indicator electrode
[27]	5.0×10^{-8}–1.0×10^{-2}	29.6	3.0×10^{-8}	Co^{2+}(4.45), Pb^{2+}(4.64), Zn^{2+}(4.54), Ni^{2+}(4.55), Cd^{2+}(5.04), Hg^{2+}(4.96), Ag^{+}(5.14), Rb^{+}(5.39), Li^{+}(5.74), Tl^{+}(5.04), Mg^{2+}(5.51), Sr^{2+}(5.57), Ce^{3+}(4.96), Gd^{3+}(4.68)	2.8–5.8	<15	Water samples and indicator electrode
Present work	3.2×10^{-8}–1.0×10^{-1}	29.5 ± 0.5	2.0×10^{-8}	Co^{2+}(2.2), Ni^{2+}(3.6), Fe^{2+}(3.8), Hg^{2+}(4.1), Cd^{2+}(4.3), Mg^{2+}(4.5), Pb^{2+}(4.6), Zn^{2+}(4.7), Ag^{+}(4.9), La^{3+}(5.1), Na^{+}(5.1)	3.0–8.5	7	Edible oil, tomato plant material and river water

It is seen from the table that there is a close agreement between the results obtained by AAS and the proposed sensor which show that the estimations by the proposed sensor are reliable. Thus, this sensor can be used successfully to determine Cu^{2+} ion concentration in tomato plant, edible oils and river water and possibly in other samples.

5. Conclusions

The PVC-based membranes of Schiff bases, namely L_1 and L_2 act as Cu^{2+} selective sensors. Of the two membranes, the sensor No. 7 based on L_1 is found better as it shows better selectivity and wider working concentration range (3.2×10^{-8}–$1.0 \times 10^{-1}\,\mathrm{mol\,L^{-1}}$) with low response time (7 s). This sensor shows good selectivity, high sensitivity and is better than many reported Cu^{2+} selective sensors. A comparison of the proposed sensor with reported sensors (Table 7) show that the proposed sensor is better than most reported sensors in terms of working concentration range, detection limit, response time and selectivity. Most reported sensors show interference to Na^{+} [15], Cd^{2+} [15,24], Ag^{+} [24,26], Hg^{2+} [21,24], Pb^{2+} [13,15,23], Zn^{2+} [19,20], Co^{2+} [15,24] whereas the proposed sensor show better selectivity to these ions, therefore superior to them. However, there are only few reported sensors [24–27] which show similar selectivity and slightly higher detection limit as the proposed sensor. Thus, the proposed sensor is better when compared to the reported sensors in terms of working concentration range, detection limit and response time.

As the proposed sensor show high sensitivity wider working concentration range and good selectivity it could be used for the determination Cu^{2+} in various samples (edible oils, tomato plant material and river water), and is therefore a good addition to the family of Cu^{2+} selective sensors.

Acknowledgements

J. Singh is grateful to the Council of Scientific and Industrial Research, New Delhi, for providing financial assistance for this work.

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