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Novel potentiometric copper (II) selective membrane sensors based on cyclic tetrapeptide derivatives as neutral ionophores

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Abstract

Two novel membrane sensors sensitive and reasonably selective for Cu^{2+} ions are described. These are based on the use of newly synthesized cyclic tetrapeptide derivatives as neutral ionophores and sodium tetraphenylborate (NaTPB) as an anionic excluder in plasticized PVC membranes. The sensors exhibit fast and stable near-Nernstian response over the concentration range 1.0×10^{-6} mol l^{-1} to 1.0×10^{-2} mol l^{-1} Cu^{2+} with a cationic slope of 30.2–25.9 mV per decade at pH 4.5–7 with a lower detection limit of 0.05–0.13 μg ml^{-1}. Effects of plasticizers, lipophilic salts and various foreign common ions are tested. The sensors display long life-span, long term stability, high reproducibility, and short response time. Selectivity of both sensors is significantly high for Cu^{2+} over Fe^{3+}, Al^{3+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, alkaline earth and alkali metal ions. The sensors are used for direct measurement of copper content in different rocks and industrial wastewater samples from electroplating factories. The results agree fairly well with data obtained using atomic absorption spectrometry.

Keywords: Determination of Cu^{2+}; Cyclic tetrapeptides; Neutral ionophores; PVC membranes; Potentiometric sensors; Copper in rocks and wastewater

1. Introduction

Assessment of accumulation, deficiency and concentration of low levels of copper require sensitive, reproducible and accurate analytical techniques. Methods in current use for copper quantification include inductively coupled plasma/mass spectrometry [1,2], stripping potentiometry with matrix-exchange techniques [3], voltammetry [4], atomic absorption spectrometry [5–7], UV–vis spectrometry [8,9] and potentiometry with chemical sensors [10,11]. Although, the commercially available solid-state copper electrode based on CuS–Ag_2S membrane has been commonly used for determining Cu^{2+} ions in various matrices [12,13], the presence of Ag^+, Hg^{2+}, Cd^{2+}, Fe^{3+}, Cl^- and S^{2-} ions causes serious interference.

Plasticized poly(vinyl chloride) membrane sensors incorporating neutral carrier ionophores have been suggested, including thiacrown ethers [14], azathiacrown ethers, containing 1,10-phenanthroline moiety [15], thiuram disulfide [16], dithiocarbamate [17], dithioacetal [18], thiohydrazone and thiosemicarbazone [19], dithiodianiline [20], thio and dithiosalicylic acid [21], pyrimidinethione derivatives/carbon paste [22], macrocyclic diamide [23], Schiff's bases [24–27], ethambutol/copper complex [28], ribonucleic acid [29], hydrotris(3-isopropylpyrazolyl) methane [30], 9,10-anthraquinone derivatives [31] and calixazacrown ethers [32]. However, most of these sensors suffer from sever interferences from one or more of Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Ag^+ and Na^+ ions [14,19–21,23,25,28–30]. It seems that the chemical and structural features of macro cyclic metal ionophores varied by incorporating different soft and hard donor atoms in the chelating ring, thereby promoting the stability and selectivity of the resulting complexes, as

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well as forcing metal ions to adopt typical coordination geometry.

On the other hand, peptides are very effective and often specific ligands for a variety of metal ions due to the presence of potential donor atoms in their backbone. Acyclic amides and peptides exist in a variety of conformations and their binding to metal ions involving participation of either the carbonyl oxygen or the amide nitrogen [33]. It has been demonstrated, however that significantly stronger binding of metals to peptides is obtained when the amide nitrogen are involved [34,35]. This can be only achieved by using cyclic peptides. Spectroscopic studies on cyclic tetraaza ligands confirm coordination of copper with N-donor tetradentate (N_4) macrocyclic ligands [36]. Simple synthesis of different cyclic peptides renders these ligands highly attractive class of electroactive materials for developing potentiometric metal ion sensors [33].

In the present work, two polymeric membrane sensors incorporating novel synthesized cyclic tetrapeptide derivatives (I) and (II) were prepared, characterized, compared and used for determination of copper in real natural samples. The differences between the two ligands are that ionophore (I) is more hydrophobic with less ring size than ionophore (II), whereas the latter is more polar due to the presence of asymmetric substitution with an ester group. Sensors based on both ionophores offer the advantages of lower detection limit, fast response time, long term stability, near-Nernstian slope over a wide range of concentration, and remarkable selectivity for Cu^{2+} ions over most common cations.

2. Experimental

2.1. Equipment

Potentiometric measurements were performed at 25 ± 1 °C using an Orion pH/meter (model SA 720) and Cu^{2+} ion-PVC membrane sensor based on ionophores (I) and (II) in conjunction with an Orion Ag/AgCl single junction reference electrode (model 90-01) filled with 10% (w/v) KCl. A combination Ross glass pH electrode (Orion 81-02) was used for all pH measurements. The cell used for EMF measurements was of the type: Ag/AgCl/KCl (10^{-1} mol l^{-1})|sample test solution||sensor membrane||internal filling solution|AgCl/Ag. The potential readings of stirred 10^{-2} mol l^{-1} to 10^{-7} mol l^{-1} $CuSO_4$ solutions were measured, recorded after stabilization to ±0.5 mV and a calibration graph was constructed. Atomic absorption spectrometric measurements of Cu^{2+} ions were made with Perkin–Elmer spectrometer (model 3100) at 324.7 nm with a copper hollow cathode lamp using the recommended optimum conditions [6]. Copper ores were digested in a Microwave Sample Preparation System (Type MDS-2000), CEM Cooperation, U.S.A. Spectrophotometric measurements were made with SHIMADZU UV spectrophotometer (model UV-1601) using 1.00 cm quartz cuvettes.

2.2. Reagents

All reagents used were of analytical grade and doubly distilled deionized water was used throughout. High molecular weight poly (vinyl chloride) (PVC), *o*-nitrophenyloctylether (*o*-NPOE), dioctylphthalate (DOP), dibutylsebacate (DBS), sodium tetraphenylborate (NaTPB) and tetrahydrofuran (THF) were purchased from Fluka. Nitrate salts of all cations used (all from Merck) were of the highest purity available and used without any further purification. Ionophores (I) and (II) were prepared and purified by column chromatography according to the method previously published [37]. Purity of both compounds was verified by thin layer chromatography.

2.3. Membrane preparation and sensor construction

The general procedure used for preparation of the PVC membrane is similar to that previously described [38–40]. A 2.9 mg of the ionophores, 66.5 mg PVC, and 127 mg of dibutylsebacate (DBS) solvent mediator and 2.1 mg of sodium tetraphenylborate (NaTPB) were thoroughly mixed in a petri dish (3 cm diameter) and dissolved in 5 ml of dry freshly distilled THF until a homogeneous solution was obtained. The solvent was allowed to evaporate slowly at room temperature. A membrane was sectioned with a cork borer (10 mm diameter) and glued to a PVC tubing (∼3 cm length, 8 mm i.d.) using THF. The electrode body consisted of a glass tube attached to PVC tubing [41]. The internal reference solution was prepared by mixing equal volumes of 1.0×10^{-2} mol l^{-1} $CuSO_4$ and 1.0×10^{-2} mol l^{-1} KCl. An Ag/AgCl internal reference electrode (1.0 mm diameter) was immersed in the internal reference solution.

The sensors were calibrated by transferring 1.0 ml aliquots of 10^{-1} mol l^{-1} to 10^{-6} mol l^{-1} aqueous Cu^{2+} solutions to 50 ml beakers, containing 9.0 ml de-ionized double distilled water or 10^{-2} mol l^{-1} acetate buffer solution of pH 5.5 followed by insertion of the corresponding Cu^{2+}-PVC membrane sensor in conjunction with a single junction Ag/AgCl reference electrode. The potential readings were recorded after stabilization to ±0.2 mV and the emf readings were plotted as a function of logarithm Cu^{2+} concentrations. The calibration graphs were used for subsequent determination of unknown copper concentration.

2.4. Effect of interfering ions

Potentiometric selectivity coefficients ($K^{pot}_{Cu,B}$) were determined using the separate solutions method [42]. The log a_{Cu} versus E relations of the sensor for the primary and interfering ions were obtained independently. Then, the activities that correspond to the same sensor potential value were used to determine the $K^{pot}_{Cu,B}$ value. The emf values obtained were

plotted versus the logarithm of the activity of the interfering ion. The intersection of the extrapolated linear portions of this plot indicated the value of the concentration of interfering ion a_B used to calculate $K^{pot}_{Cu,B}$ from the equation:

$$K^{pot}_{Cu,B} = \frac{a_{Cu}}{a_B^{Z_{Cu}/Z_B}}$$

where a_{Cu} is the activity of Cu^{2+} ion, a_B the activity of the interfering ion, and Z_{Cu} and Z_B the charges of the primary and interfering ions, respectively.

2.5. Direct potentiometric determination of Cu^{2+} ions

Copper membrane sensors based on ionophores (I) and (II) with NaTPB as ion discriminator and Ag/AgCl single junction reference electrode were immersed into a 25 ml beaker, containing 10 ml aliquot of 10^{-2} mol l^{-1} acetate buffer of pH 5.5. The solution was stirred till a stable response within ±0.2 mV was obtained. Portions (10–100 μl) of 10^{-3}, 10^{-2} and 10^{-1} mol l^{-1} $CuSO_4$ solution were added to the test solution. After each addition, the potential response of the sensor was measured after stabilization and plotted against the logarithm Cu^{2+} concentration. The plot was used for subsequent determination of unknown Cu^{2+} test solutions. Alternatively, the known addition (spiking) technique was used by measuring the potentials of copper test solutions before and after addition of 1.0 ml of 10^{-2} mol l^{-1} standard Cu^{2+} solution [10].

2.6. Determination of copper in rocks

About 1.0 g portion of a well ground copper-bearing rocks was transferred to a clean microwave vessel. A 2 ml portion of doubly distilled deionized water and 5 ml of 1 mol l^{-1} HNO_3 were added to get all sample particles on the vessel wall down in the solution, and allowed to stand overnight. The microwave vessel was placed in the microwave oven and subjected to rapid heating at elevated pressures; maximum temperature 1000 °C, pressure 170 PSI [43]. The contents of the vessel were quantitatively transferred to a 25 ml measuring flask, and shaken well. A 1.0 ml aliquot of the sample digestate was transferred into a 50 ml beaker followed by 1 ml of 10^{-2} mol l^{-1} acetate buffer solution of pH 5.5. The solution was completed with doubly distilled deionized water to a total volume of ~10 ml. Ionophore (I) membrane based sensor and a single junction Ag/AgCl reference electrode were immersed in the test solution and the concentration of Cu^{2+} was measured by direct potentiometry.

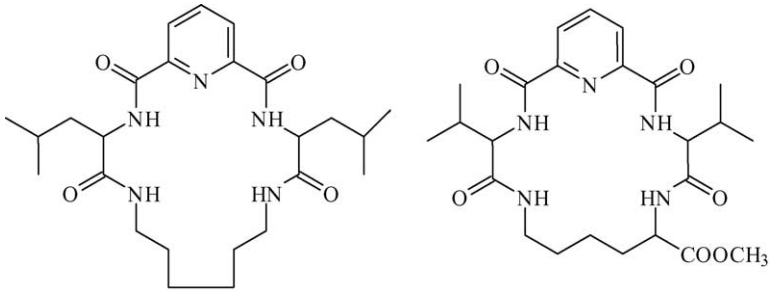
2.7. Determination of Cu^{2+} in industrial wastewater

A 10 ml aliquot of a well shaken wastewater sample obtained from electroplating factories and containing copper ions was treated with 10 ml of 1 mol l^{-1} HNO_3 and heated for boiling on a hot plate for 10 min to decompose the metal complexes. The solution was quantitatively transferred to 100 ml measuring flask and completed to the mark with 10^{-2} mol l^{-1} acetate buffer of pH 5.5. The copper sensor and the reference electrode were immersed in 10 ml of the test copper solution and the concentration of Cu^{2+} in the sample was determined by direct potentiometry.

3. Results and discussion

3.1. Characteristics of the sensors

Copper PVC membrane sensors based on ionophores (I) and (II) (Fig. 1) with the composition: 1.5 wt.% ionophore, 33.8 wt.% PVC and 64.7 wt.% plasticizer exhibits linear responses to Cu^{2+} ions within the concentration range 1.0×10^{-6} mol l^{-1} to 1.0×10^{-2} mol l^{-1} and 4.0×10^{-6} mol l^{-1} to 3.0×10^{-2} mol l^{-1} with lower detection limits of 9.0×10^{-7} mol l^{-1} and 2.0×10^{-6} mol l^{-1}, respectively. Increase or decrease the composition of the membrane constituents does not significantly affect the response of the sensors. In presence of 1 wt.% of NaTPB as a membrane additive, and 1.5 wt.% of ionophore, 33.5 wt.% PVC, 64 wt.% plasticizer, the limit of detection, linear range and calibration slope are improved. The detection limits are 7.5×10^{-7} mol l^{-1} and 2.1×10^{-6} mol l^{-1} and the linear ranges are 1.0×10^{-6} mol l^{-1} to 1.0×10^{-2} mol l^{-1} and 3.1×10^{-6} mol l^{-1} to 1.0×10^{-2} mol l^{-1} for membrane sensors incorporating ionophores (I) and (II), respectively. Both



Ionophore (I) **Ionophore (II)**

Fig. 1. Structural formula of cyclic tetrapeptide ionophores.

sensors exhibit near-Nernstian slope of 30.3 ± 1 mV per decade (correlation coefficient 0.9960), and 25.9 ± 1 mV per decade (correlation coefficient 0.9979), respectively ($n = 6$).

Copper PVC matrix membrane sensor incorporating ionophore (I) and different plasticizers having various dielectric constants (e.g. DBS, DOP and *o*-NPOE) were prepared and tested. Membrane sensor based on ionophore (I) plasticized with DBS ($\varepsilon = 4$), DOP ($\varepsilon = 7$) and *o*-NPOE ($\varepsilon = 24$) shows calibration slopes of 27.2, 17.1 and 16.4 mV per decade with lower detection limits of 9.0×10^{-7} mol l^{-1}, 1.8×10^{-5} mol l^{-1} and 5×10^{-5} mol l^{-1}, respectively. With membrane sensor based on ionophore (II), calibration slopes of 17.1, 17.8 and 12.3 mV per decade are obtained with DBS, DOP and NPOE membrane plasticizes, respectively. It can be seen that sensor based on ionophore (II) in DBS plasticized membrane shows lower slope and higher detection limit than that incorporating ionophore (I). This is probably due to the interaction of the polar ester moiety of ionophore (II) with the ester group of DBS.

In general, membranes incorporating DBS plasticizer, give more favorable linear range, slope and low detection limit than those, containing DOP and *o*-NPOE plasticizers. Low dielectric constant solvent mediators have been previously recommended for some divalent metal cation membrane sensors [29,44,45]. Table 1 shows the performance characteristics of copper membrane sensors based on ionophores (I) and (II) with different plasticizers in the presence of NaTPB. Typical calibration plots for these sensors are shown in Fig. 2. The dynamic response times of sensors based on ionophores (I) and (II) to reach ~95% of equilibrium response, are ~15 and 20 s, respectively. In general, ionophores (I) and (II)-based sensors exhibit similar response characteristics for Cu^{2+} ions. The slight differences in lipophilicity, ring size and polarity of the two ionophores do not significantly affect the general electrochemical performances of the sensors.

3.2. Effects of pH and foreign ions

A study of the potential-pH curves of Cu^{2+} membrane sensors based on ionophores (I) and (II) reveals that within the range 4.5–7, the potential does not vary by more than ±2 mV. At pH > 7 the emf of the sensors sharply decreases due to precipitation of $Cu(OH)_2$ and/or formation of hydroxyl copper complexes and competition of OH^- ion with the ionophores for Cu^{2+} ions. At pH < 4, interferences from H^+ ions is significant with subsequent increasing in the potential response. All subsequent potentiometric measurements of Cu^{2+} ions were made in 10^{-2} mol l^{-1} acetate buffer background of pH 5.5.

Potentiometric selectivity coefficients of the sensors towards different cationic species were evaluated using the separate solutions method (SSM) [42]. In this method, the selectivity coefficients of the copper sensors were evaluated graphically at a fixed potential of both Cu^{2+} ions and the interferent (Figs. 3 and 4). High concentrations of most cations, except Zn^{2+} and Pb^{2+}, do not affect the selectivity of the sensors towards Cu^{2+}. This is probably due to the stronger interaction of these ionophores with Cu^{2+}. Ionophore (I)-based membrane sensor exhibits higher selectivity for Cu^{2+} in the presence of Fe^{3+}, Al^{3+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, K^+, Na^+ and Ag^+ cations compared with membrane sensor based on ionophore (II). On the other hand, ionophore (II) displays high selectivity for Cu^{2+} in the presence of Mn^{2+}, Cs^+ and Li^+ ions (Table 2). In general, both sensors display a selectivity order of: $Cu^{2+} > Pb^{2+} \gg Zn^{2+} > Cd^{2+} > Hg^{2+} = Ni^{2+} > Mn^{2+} > Co^{2+} > Fe^{3+} > Al^{3+} \gg Cs^+ > Li^+$. Interference due to Pb^{2+} with both sensors is easily circumvented by addition of sulfate ion to the sample test solution prior to measurement. Other previously suggested sensors display superior selectivity in the presence of Pb^{2+} ions [15,23,31].

Variation of selectivity is probably due to the ability of the metal ion to cause deprotonation of the peptide-amide nitrogen. Metal induced deprotonation of the amide nitrogen increases the number of coordination points between the

Table 1
Potentiometric response characteristics of copper (II) PVC membrane sensors based on ionophores (I) and (II) using different plasticizers

Parameter	Ionophore (I)[a]				Ionophore (II)[a]			
	DBS	DBS + NaTPB	DOP	NPOE	DBS	DBS + NaTPB	DOP	NPOE
Slope (mV decade^{-1})	27.2	30.3	17.1	16.4	17.1	25.9	17.8	12.3
Correlation coefficient, r ($n = 6$)	0.9920	0.9960	0.9990	0.9980	0.9970	0.9979	0.9985	0.9960
Linear range (mol l^{-1})	1×10^{-6}	1×10^{-6}	1×10^{-5}	3.1×10^{-5}	4×10^{-6}	3.1×10^{-6}	3×10^{-5}	–
	1×10^{-3}	1×10^{-2}	1×10^{-2}	1×10^{-2}	3×10^{-3}	1×10^{-2}	3×10^{-3}	–
Detection limit (mol l^{-1})	9×10^{-7}	7.5×10^{-7}	1.8×10^{-5}	5×10^{-5}	2×10^{-6}	2.1×10^{-6}	1.5×10^{-6}	–
Working range (pH)	4.5–7	4.5–7	4.5–7	4.5–7	4.5–7	4.5–7	4.5–7	–
Response time (s)	<15	<15	<15	<20	<20	<20	<20	–
Standard deviation, δ_v (mV)	0.3	0.3	0.5	0.6	0.6	0.4	0.6	0.6
Accuracy (%)	98.7	99.1	97.6	96.8	97.1	99.5	96.4	96.2
Repeatability, Cv_w (%)	0.3	0.3	0.4	0.3	0.4	0.3	0.3	0.3
Between-day variability, Cv_b (%)	0.7	0.7	0.8	0.6	0.7	0.7	0.6	0.6
Life-span (week)	8	8	6	6	6	8	6	6

[a] Mean of six measurements. Membrane composition: type 1: PVC, 33.8 wt.%, ionophore, 1.5 wt.%, plasticizer, 64.7 wt.%; type 2: PVC, 33.5 wt.%, ionophore, 1.5 wt.%, DBS, 64 wt.%, NaTPB, 1.0 wt.%.

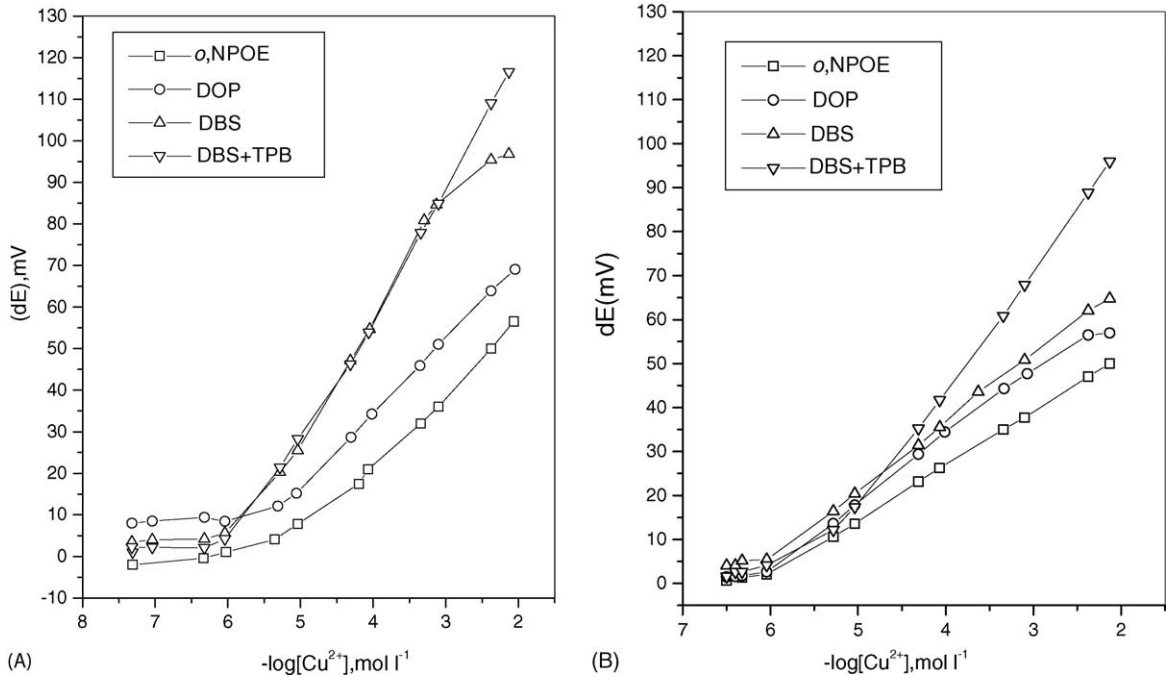


Fig. 2. Potentiometric response of copper PVC membrane sensors based on: (A) ionophore (I) and (B) ionophore (II) using different plasticizers.

metal and peptide. It has been reported that the order of peptide hydrogen displacements by metal ions is in the order $Cu^{2+} > Ni^{2+} > Co^{2+}$ [35] which is in a good agreement with the obtained selectivity data.

Table 2 shows a comparison of the performance characteristics of some previously reported Cu^{2+} membrane sensors with those described in this work. Selectivity coefficients of the proposed sensors for most ions were in the order of 10^{-3} or smaller, indicating superior selectivity over other sensors [14,16,18–21,23,25,28–30] especially in the presence of Cd^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, Ba^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Na^{+}, K^{+}, Cs^{+}, Ca^{2+}, Fe^{3+} and Ag^{+} ions. Wider working concentration range and lower detection limit are also offered by the proposed sensors compared with some of those previously suggested [14,15,19,23,31,32].

3.3. Direct determination of Cu^{2+} ions

Determination of Cu^{2+}, containing solutions using copper PVC membrane sensors-based ionophores (I) or (II) was validated according to the quality assurance standards [46]. The assay method for Cu^{2+} ions over the concentration range 0.5–10 μg ml^{-1} was validated using six batches (six determinations each) for measuring accuracy, precision, range, lower

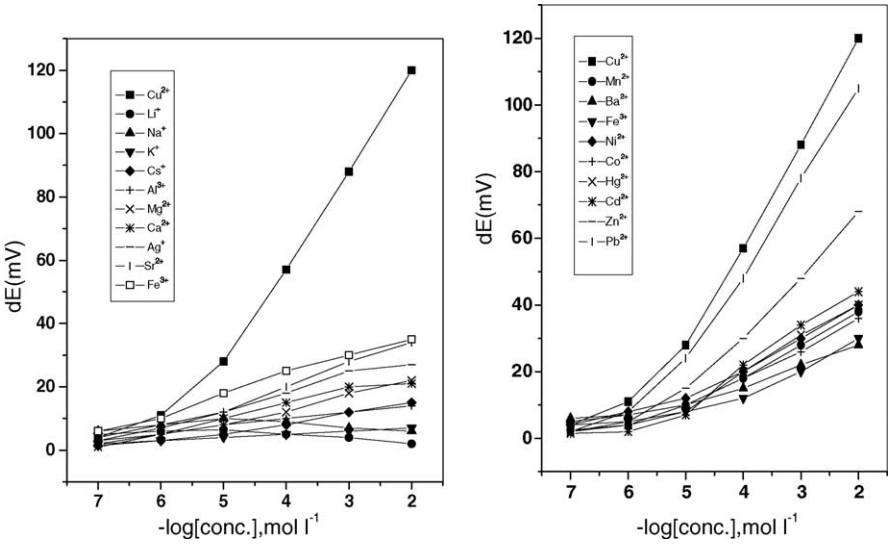


Fig. 3. Potential response of copper PVC membrane sensor based on ionophore (I) for various metal ions.

Table 2
General characteristics of some potentiometric copper membrane sensors based on neutral ionophores

Ionophore	Range (mol l^{-1})	Slope, mV per decade	Lower limit of detection (mol l^{-1})	Selectivity coefficient (log $K^{pot}_{Cu,B}$)	Reference
Thiacrown ethers	1×10^{-5} to 1×10^{-1}	22.3	1.4×10^{-7}	Co^{2+} (−1.0), Ni^{2+} (−1.4), Pb^{2+} (+0.1), Cd^{2+} (−1.5)	[14]
Aza-thio ether crowns containing 1,10 phenanthroline	1×10^{-5} to 2×10^{-1}	29.4	8×10^{-6}	Ag^{+} (−2.13), Pb^{2+} (−2.69), Tl^{+} (−2.92)	[15]
Thiuram disulphides		31	4×10^{-7}	K^{+} (−0.8), Na^{+} (−1.5), Zn^{2+} (−1.0), Pb^{2+} (−0.9)	[16]
Dithiocarbamate	1×10^{-6} to 1×10^{-1}	28–29	4×10^{-7}	Cd^{2+} (−2.1), Co^{2+} (−1.9), Mn^{2+} (−2.4), Mg^{2+} (−2.8)	[17]
Dithioacetal	3×10^{-6} to 5×10^{-2}	29 ± 1	1×10^{-6}	Ag^{+} (−0.6), Hg^{2+} (−1.3)	[18]
Thiohydrazone and thiosemicarbazone	1×10^{-5} to 1×10^{-1}	27.2	6.3×10^{-6}	NH_4^{+} (−1.69), Ca^{2+} (−1.09), Mg^{2+} (−1.49), Zn^{2+} (−0.15), Ba^{2+} (−0.76), Pb^{2+} (−0.79), Cd^{2+} (−0.60), Hg^{2+} (+2.2)	[19]
2,2'-Dithiodianiline	7×10^{-7} to 5×10^{-2}	30 ± 1	6×10^{-7}	Pd^{2+} (−0.28), Fe^{3+} (−3.27), Cd^{2+}, Ni^{2+}, Hg^{2+} (<−3.5), Ag^{+} (<−4.01)	[20]
Thio and dithiosalicylic acids	$10^{-7.6}$ to $10^{-3.2}$	68.7	$10^{-7.9}$, $10^{-6.3}$	Pb^{2+} (+0.61), Mg^{2+} (+0.18), Cd^{2+} (+0.03), Ca^{2+} (−0.29), Al^{3+} (+0.32), Fe^{3+} (−1.16)	[21]
Pyrimidine thione derivatives/carbon paste	9.7×10^{-7} to 7.6×10^{-2}	30 ± 2	7.7×10^{-7}	NR	[22]
Macrocyclic diamides	3.2×10^{-5} to 1×10^{-1}	30	1.2×10^{-5}	Hg^{2+} (−2.4), Cd^{2+} (−1.58), Pb^{2+} (−2.2), Ni^{2+} (−2.01), Zn^{2+} (−2.3), Sr^{2+} (−1.03), Cs^{+} (−0.79), K^{+} (−0.88), Na^{+} (−0.48), Sr^{2+} (−1.03), Ca^{2+} (−1.63)	[23]
Schiff's base	6×10^{-8} to 1×10^{-1}	29.1	3×10^{-8}	K^{+} (−2.2), Ag^{+} (−2.1), Na^{+} (−2.21)	[24]
	8×10^{-6} to 1×10^{-1}	29.5	1.0×10^{-6}	Pb^{2+} (−0.5), Sr^{2+} (−2.09), Al^{3+} (−1.31).	[25]
	1×10^{-6} to 1×10^{-2}	30.0	$>10^{-7}$	Li^{+} (−1.50), Na^{+} (−1.75), Ag^{+} (−1.81), K^{+} (−1.85)	[26]
	1×10^{-6} to 1×10^{-2}	27.6 ± 0.1	2.5×10^{-7}	(Hg^{2+}, Li^{+}, Na^{+}, Ag^{+}) NR	[27]
Ethambutol–copper (II) complex	7.9×10^{-6} to 1.0×10^{-1}	29.9	7.0×10^{-6}	Hg^{2+} (−0.1), K^{+} (−0.2), Co^{2+} (−0.87), Pb^{2+} (−0.81), Al^{3+} (−0.68), Ni^{2+} (−0.59), Na^{+} (−0.48)	[28]
Ribonuclic acid	1.0×10^{-5} to 1.0×10^{-2}	31.3	2.0×10^{-6}	Hg^{2+} (−1.34), Mg^{2+} (−1.25), Cd^{2+} (+0.21), Mn^{2+} (−1.11), Cr^{3+} (+0.52), Fe^{2+} (+1.17), Ag^{+} (−1.50)	[29]
Hydro tris(3-isopropylpyrazolyl)methan	1×10^{-6} to 5×10^{-3}	29.1	2×10^{-6}	Pb^{2+} (0.00), Cd^{2+} (−3.5)	[30]
9,10 Anthraquinone derivatives	1.0×10^{-5} to 1.0×10^{-1}	27.3	8×10^{-6}	Zn^{2+} (−1.49), Cd^{2+} (−2.27), Pb^{2+} (−1.37), K^{+} (−2.44), Ni^{2+} (−2.18), Ag^{+} (−2.10)	[31]
Calixazacrown ethers	$1 \times 10^{-4.5}$ to $1 \times 10^{-2.5}$	27.2	1×10^{-5}	Fe^{3+} (−1.22), Ni^{2+} (−1.72), Cd^{2+} (−1.92), K^{+} (−1.60), Rb^{+} (−1.1)	[32]
Ionophore (I)	1×10^{-6} to 1×10^{-2}	30.3	7.5×10^{-7}	Li^{+} (−5.10), Na^{+} (−5.15), K^{+} (−5.10), Cs^{+} (−4.30), Al^{3+} (−4.06), Mg^{2+} (−3.22), Ca^{2+} (−3.40), Ag^{+} (−3.09), Sr^{2+} (−2.82), Fe^{3+} (−3.20), Mn^{2+} (−2.69), Ba^{2+} (−3.00), Fe^{2+} (−2.84), Ni^{2+} (−2.52), Co^{2+} (−2.71), Hg^{2+} (−2.52), Cd^{2+} (−2.39), Zn^{2+} (−1.70), Pb^{2+} (−0.52)	This work
Ionophore (II)	3.1×10^{-6} to 1×10^{-2}	25.9	2.1×10^{-6}	Li^{+} (−5.51), Na^{+} (−4.30), K^{+} (−4.41), Cs^{+} (−4.42), Al^{3+} (−3.97), Mg^{2+} (−2.85), Ca^{2+} (−3.00), Ag^{+} (−2.60), Sr^{2+} (−2.70), Fe^{3+} (−3.06), Mn^{2+} (−2.82), Ba^{2+} (−3.10), Fe^{2+} (−3.05), Ni^{2+} (−2.52), Co^{2+} (−2.60), Hg^{2+} (−2.39), Cd^{2+} (−2.15), Zn^{2+} (−1.52), Pb^{2+} (−0.39)	This work

NR: not reported.

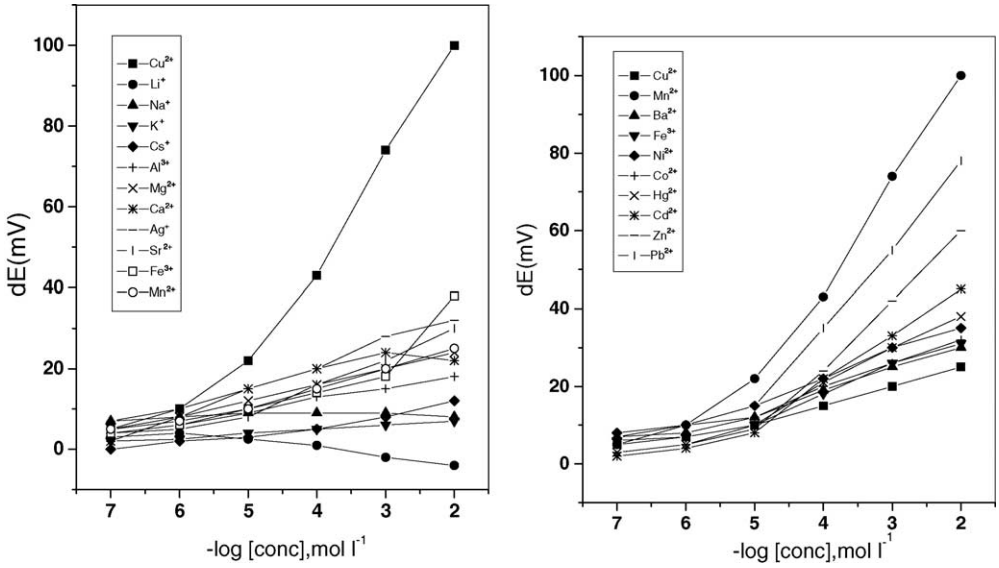


Fig. 4. Potential response of copper PVC membrane sensor based on ionophore (II) for various metal ions.

limit of detection, repeatability (Cv_w) and between-day variability (Cv_b). The results obtained are presented in Table 1. A statistical analysis of the results indicates that at the 95% confidence level, the method shows no statistical difference.

3.4. Determination of copper in ores

The copper contents of some natural rocks (Cu-bearing shale and Cu-oxides in basement rocks) taken from different geological areas were assessed. The rocks were grinded, digested with nitric acid and their contents of copper were measured by direct potentiometry using membrane sensor based on ionophore (I). The results obtained show an average Cu content ranging from 13 to110 mg g^{-1} of rocks. The mean standard deviation is ±0.6%. Similar results are obtained using atomic absorption spectrometry (Table 3).

3.5. Determination of Cu^{2+} ions in wastewater

Ionophores (I) membrane-based sensor was used for potentiometric determination of Cu^{2+} ions in some industrial wastewater samples obtained from local electroplating factories. The samples were treated with nitric acid to dissociate the metal complexes, and the Cu^{2+} content was determined by direct potentiometry using the proposed copper membrane sensor. Data obtained using atomic absorption spectrometry at wavelength 324.7 nm show a close agreement within 3 mg l^{-1} (i.e. 97.7 ± 0.7%) (Table 4).

Table 3
Determination of copper in some rocks using potentiometry with copper PVC membrane sensor based on ionophore (I) and atomic absorption spectrometry (AAS)

Sample	Copper content (mg g^{-1})[a]		
	Potentiometry	AAS	Difference
Cu-bearing shales (1)	30.9 ± 0.7	30.5 ± 0.8	0.4
Cu-bearing shales (2)	41.7 ± 0.6	42.5 ± 0.9	0.8
Cu (loea Gabbro from oxidation zone)	109.8 ± 0.6	110.4 ± 0.7	0.6
Cu-oxide basement rocks	13.8 ± 0.7	14.3 ± 0.8	0.5

[a] Mean of six measurements.

Table 4
Determination of copper in electroplating baths using potentiometry with copper PVC membrane sensor based on ionophore (I) and atomic absorption spectrometry (AAS)

Sample	Copper content (mg l^{-1})[a]		
	Potentiometry	AAS	Difference
Bath (1)	88.4 ± 0.9	90.1 ± 0.7	1.7
Bath (2)	112.5 ± 0.6	110.2 ± 0.5	2.3
Bath (3)	125.6 ± 0.2	128.6 ± 0.4	3.0

[a] Mean of six measurements.

4. Conclusions

Copper poly(vinyl chloride) matrix membrane sensors based on cyclic tetrapeptide ionophores are prepared, characterized and used for Cu^{2+} measurements. The sensors exhibit fast response, wide working pH range, high sensitivity, long-term stability and good selectivity. Advantages and limitations of many of the previously suggested potentiometric membrane copper sensors are given in Table 2, for comparison. It can be seen that the sensors suggested in the present work have several inherent advantages over many of those previously described. The sensors are used for determining copper in ores and for monitoring copper ions in industrial wastewater. The results favorably compare with data obtained using atomic absorption spectrometry.

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