Int. J. Electrochem. Sci., 8 **(2013)** 11175 - 11185

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Development of New Copper(II) Ion-Selective Poly(vinyl chloride) Membrane Electrode Based on 2,6-Diacetylpyridine-(1R)-(-)-Fenchone Diazine Ligand

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Received: 18 June 2013 / *Accepted:* 16 July 2013 / *Published:* 20 August 2013

The construction and performance characteristics of polymeric membrane electrodes based on 2,6-diacetylpyridine-(1R)-(-)-fenchone diazine ligand (A) for quantification of copper ions, are described. Effect of various plasticizers and anion excluder, sodium tetraphenylborate (NaTPB) was studied and improved performance was observed at several instances. Best performance was obtained with the membrane having the following composition; A (7): PVC (50): TMDP (86): NaTPB (1). The membrane electrodes exhibits Nernstian response in the concentration range of 1.0×10^{-5} to 1.0×10^{-1} M with a detection limit of 2.5×10^{-6} M and wide pH range (4.0–8.0). The potentiometric selectivity coefficient values as determined by fixed interference method indicate excellent selectivity for copper ions over interfering cations. Each electrode possesses a fast response time of below 20s and a shelf life period of 3 months. The analytical utility of the proposed electrode was demonstrated by its application in the determination of copper in wastewater samples and the results were in agreement with those obtained with an atomic absorption spectroscopy (AAS) method.

Keywords: Copper(II) ion membrane electrode, 2,6-diacetylpyridine-(1R)-(-)-fenchone diazine ligand, PVC, Potentiometry

1. INTRODUCTION

Copper is a reddish metal that occurs naturally in rock, soil, water, sediment, and air. Copper(II) ion is third in abundance among the essential heavy metal ions in human body and plays an important role in various biological processes [1]. The Cu^{2+} at lower concentrations is an essential trace nutrient to all higher plant and animal life. In animals, including humans, it is found widely in tissues, with concentration in liver, muscle, and bone. It functions as superoxide dismutase, which detoxifies free radicals [2] and as a co-factor in various enzymes and in copper-based pigments [3]. Humans ingest about 1–3 mg/day. Copper may be stored in the liver, bound in part to metallothionein or secreted into plasma bound to ceruloplasmin, which transports 80% of plasma copper, or may be excreted in bile, perhaps bound to ceruloplasmin fragments. However, above a healthy limit it will accumulate in the liver, causing diarrhea, vomiting, transpiration, and death from bleeding [4]. The toxicity is generally attributed to the aquo-complexed "free" Cu^{2+} rather than its organic or inorganic complex [5]. In view of widespread use of Cu(II) and consequently, its occurrence in environments and its poisonous nature, its determination in environmental samples is very important.

A number of instrumental techniques such as atomic absorption spectrometry (AAS) [6,7], inductively coupled plasma-optical emission spectroscopy (ICP-OES) [8,9], flame atomic absorption spectroscopy (FAAS) [10,11], inductively coupled plasma-mass spectrometry (ICP-MS) [12,13] and voltammetric [14-16] are used for the determination of Cu(II) ions in any environmental samples. Even though these techniques provide accurate results, however they are time consuming, require adequate expertise and large scale infrastructure back up. Furthermore, their maintenance and operational costs are high and therefore they are not very appropriate for routine analysis involving large number of environmental samples. Thus, a reliable, low cost, quick and portable analytical technique is needed and such requirements are generally met with ion selective electrodes (ISEs) to a significant extent.

Numerous publications on neutral-carrier and ion-exchanger based ISEs and their application can be found in specialized publications as a part of the general area of chemical sensors or as a class of its own [17,18]. Recently, a number of attempts have been made to develop Cu^{2+} selective sensors [19-23] but most of them suffered from poor detection limits and poor interfering effect of cations such as $Li^{+,}$ K^{+}, $Hg^{2+,}$ Cd^{2+}, $Zn^{2+,}$ Ca^{2+}, Pb^{2+}, and Co^{2+}. Therefore, in the present work, a PVC membrane sensor incorporating 2,6-diacetylpyridine-(1R)-(-)-fenchone diazine ligand (Figure 1) was prepared, characterized and used for the determination of copper in real samples. This sensor offers the advantages of lower detection limit, fast response time, adequate lifetime, near-Nernstian slope over a wide range of concentrations, and remarkable selectivity for Cu^{2+} over most common cations.

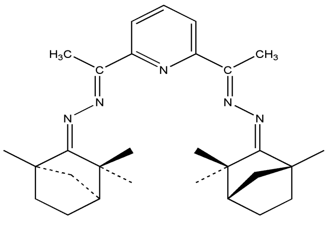

Figure 1. Structure of 2,6-diacetylpyridine-(1R)-(-)-fenchone diazine ligand (A).

2. EXPERIMENTAL

2.1. Chemicals and reagents

All reagents used for the preparation of membranes were of analytical–reagent grade and were used without further purification. All analytical grade chloride salts of all cations, glacial acetic acid, ethanol, and tetrahydrofuran (THF) were obtained from Merck (Germany). All plasticizers, high molecular weight poly vinyl chloride (PVC), hydrazine monohydrate, (1R)-(-)-fenchone, 2,6-diacetylpyridine, hydrochloric acid (HCl) and sodium hydroxide (NaOH) solution for pH adjustments, and anion excluder sodium tetraphenylborate (NaTPB) were obtained from Aldrich (Germany). Stock solutions of copper ion were freshly prepared by dissolving appropriate amount of copper (II) chloride in distilled deionized water.

2.2. Instrumentation

All solutions were prepared using distilled deionized water from EASYpure LF, Barnstead (USA). The potentiometric measurements were performed using an pH/ion meter Orion 720A, Mass. (USA). An Ag|AgCl electrode of BASi, MF-2052 (USA) with a fiber junction was used as a reference electrode. The pH value was determined by using Orion, 915600, Mass. (USA) glass-pH electrode. An Analyst 400 atomic absorption spectroscopy (AAS) was used to analyze copper(II) in real samples.

2.3. Synthesis of ionophore

A solution containing (1R)-(-)-fenchone hydrazone (779 mg, 4.68 mmol), 2,6-diacetylpyridine (348mg, 2.14 mmol) and acetic acid (0.1 cm^3) in ethanol (10cm^3) was heated at 80 °C for 28 hours in water bath. The reaction mixture was left to stand at 20 °C for 1 hour, after which it became concentrated and cooled to -30 °C for 2 days. The required product was precipitated out as a white solid. This was then filtered off, washed with cold ethanol and dried. The yielded product weighed 821 mg with 85% concentration. The following data were found: C, 75.55; H, 8.85; N 15.1. $C_{29}H_{41}N_5$ requires C, 57.7; H, 8.9; N, 15.2%; m/z (EI): 459 (M^+). ^{13}C–{^1H} NMR (62.9 MHz. $CDCl_3$) δ_C: 22.3 (2C, s, methyl carbon from fench residue), 22.8 (2C, s, methyl carbon from fench residue), 24.5 (2C, s, methyl carbon from fench residue), 48.5 (2C, s, acetyl carbon), 120.4 (2C, s, pyridyl carbon with H) and 136.1 (1C, s, pyridyl carbon with H).

2.4. Electrode preparation

The general procedure to prepare the PVC membrane is similar to that previously described [24–27]. The membrane electrode was prepared by thoroughly dissolving amount of PVC, plasticizers and ionophore in 5 ml THF. The mixture was vigorously stirred immediately after the addition of THF for an easy dissolution of PVC. After complete dissolution of all components, the homogeneous mixture obtained was then poured in a glass ring with an inner diameter of 3.5 cm, which sat on the surface of a glass plate. A filter paper was placed on top of the glass ring to prevent dust and air streams from spoiling the mixture. The mixture was then allowed to evaporate at room temperature. After 24 hours, the membrane was later peeled off from the glass. A membrane disc of 6 mm diameter was then cut and glued to one end of a Pyrex glass tube with Araldite. The glass tube was then filled with an internal solution of 1.0 M copper(II) chloride solution and electrical contact was done by immersing a gold wire in the solution. The sensor was conditioned for 24 hours by soaking in 1.0×10^{-4} M copper(II) chloride solution and rinsed well with distilled water when not in use. Membrane with reproducible, stable and noiseless potentials were developed by optimized the ratio of membrane ingredients, time of contact and concentration of equilibrating solution [28–30].

2.5. Potential measurements

The performance of the electrodes was investigated by measuring the electromotive force (emf) of copper(II) chloride solutions prepared with optimum pH 4.0 and a concentration range of 1.0×10^{-1} to 1.0×10^{-7} M serial dilution. All potential measurements were carried out with the following cells assemblies:

Ag, AgCl; KCl (3.0 M)//sample solution/membrane/copper(II) chloride (1.0 M)/gold wire.

3. RESULTS AND DISCUSSION

3.1. Working concentration range and slope

Ligand A tends to form a stable 1:1 complex with Cu^{2+} by coordination with nitrogen atom. Because of its solubility in an organic solvent and insolubility in water, this ligand was used as a sensing ionophore for PVC membrane electrode. In such a case the electrode response to Cu^{2+} may be the consequence of the complexation reaction at the membrane surface. The possible ion exchange mechanism at the membrane-solution interface of Cu^{2+} and 2,6-diacetylpyridine-(1*R*)-(-)-fenchone diazine ligand that is responsible for the potentiometric response is shown in Figure 2. Besides the critical role of the nature of ion carrier in preparing membrane-selective sensors, it is well known that some important features of the PVC based membranes, such as the nature and amount of ionophore, the properties of the plasticizer, the plasticizer/PVC ratio and, especially, the nature of additives used, significantly influence the sensitivity and selectivity of the ion-selective electrodes [31]. Thus, different aspects of membrane preparation based on ligand A for Cu^{2+} were optimized and the results were summarized in Table 1. In order to arrive at optimum composition for best performing electrode, first the variation in potential response with different amounts of ionophore was examined (sensor nos. 2–4). The quantity of ligand A was found to affect the sensitivity of the membrane electrode. The sensitivity of the electrode response increases with increasing ionophore content until a value of 7mg is reached (sensor no. 3). Further addition of ionophore (10mg) will, however, result in diminished response of the electrode (sensor no. 4). This electrode is not performing well as it works over limited working concentration range of 1.0×10^{-4} M to 1.0×10^{-1} M with a slope of 12.5±0.5 mV/decade. This is most probably due to some inhomogenities and possible saturation of the membrane. Therefore, a ligand A content of 7 mg was chosen as the optimum ionophore amount in the construction of copper(II) sensor electrode.

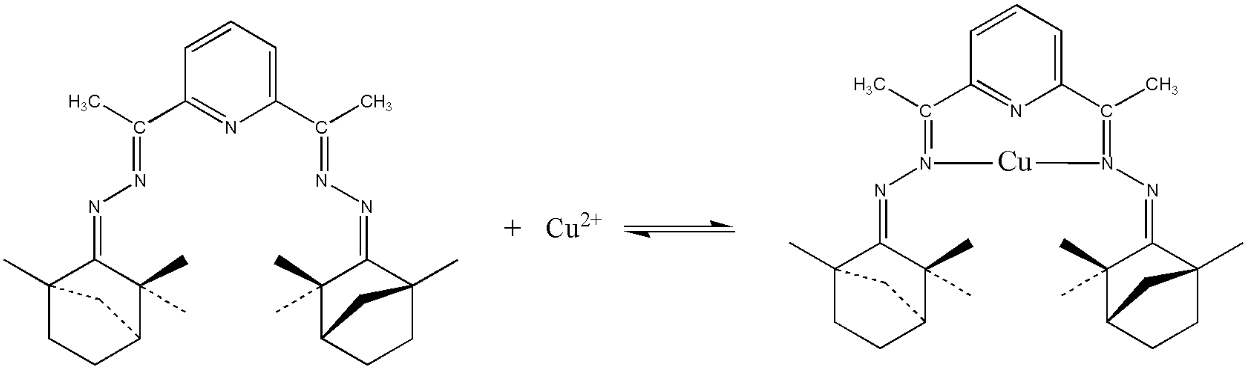

Figure 2. The possible ion exchange mechanism at the membrane-solution interface of Cu^{2+} and 2,6-diacetylpyridine-(1*R*)-(-)-fenchone diazine ligand.

Since the selectivity of ISEs is highly influenced by the membrane solvent nature (plasticizer) it is therefore expected to play a fundamental role in specifying the selective electrode characteristics. The lipophilicity, polarity, viscosity and dielectric constant of the plasticizer play a significant role in efforts to ensure the long and stable response by the sensor assembly. Thus, the addition of plasticizer will improve the sensitivity and stability of the sensor.

Table 1. Optimized membrane composition of Cu(II) selective membrane electrode based on ligand A and their potentiometric responses.

Sensor no.	A	PVC	Plasticizer	Additive (NaTPB)	Slope (mV/decade)	Working range (M)	Detection limit (M)
1	-	50	86	Without	5.8 ± 0.5	1.0×10^{-4}- 1.0×10^{-2}	1.0×10^{-4}
2	5	50	Without	Without	13.1 ± 0.2	1.0×10^{-4}- 1.0×10^{-1}	6.3×10^{-5}
3	7	50	Without)	Without	17.0 ± 0.5	1.0×10^{-4}- 1.0×10^{-1}	7.1×10^{-5}
4	10	50	Without	Without	12.5± 0.5	1.0×10^{-4}- 1.0×10^{-1}	4.0×10^{-5}
5	7	50	86 (TMDP)	Without	23.6 ± 0.5	1.0×10^{-5}- 1.0×10^{-1}	5.0×10^{-6}
6	7	50	86 (TMDP)	1	29.1 ± 0.4	1.0×10^{-5}- 1.0×10^{-1}	2.5×10^{-6}
7	7	50	86 (BEHA)	1	20.6 ± 0.1	1.0×10^{-5}- 1.0×10^{-1}	5.0×10^{-6}
8	7	50	86 (*o*-NPOE)	1	19.0 ± 0.5	1.0×10^{-3}- 1.0×10^{-1}	3.2×10^{-4}
9	7	50	86 (DOPP)	1	25.4 ± 0.2	1.0×10^{-4}- 1.0×10^{-1}	5.6×10^{-5}
10	7	50	86 (DBP)	1	22.2 ± 0.3	1.0×10^{-5}- 1.0×10^{-1}	5.0×10^{-6}

From Table.1, membrane electrode without plasticizer shows a weak response but the presence of plasticizer affects the response characteristics of the electrodes, due to its influence on the dielectric constant of the membrane phase. As seen from Table 1, sensor no. 3 (without plasticizer) exhibits a poor response (slope; 17.0±0.5 mV/decade) to Cu^{2+} with working concentration range of 1.0×10^{-4} M to 1.0×10^{-1} M when compared to sensor no.5 with the presence of TMDP plasticizer which shows an increasing value in response (23.6±0.5 mV/decade) and working concentration range of 1.0×10^{-5} M to

1.0×10^{-1} M. The membrane electrode without ionophore and additive (sensor no. 1) was also investigated and it was observed that they generated low potential with slope of 5.8±0.5 mV/decade.

It is well understood that the presence of lipophilic negatively charged additives, improves the potentiometric behaviour of certain membrane electrodes, not only by reducing the ohmic resistance and improving the response behaviour and selectivity, but also in cases where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the membrane electrode. The data given in Table 1 also reveal that the presence of additive has a beneficial influence on the performance characteristics of the membrane electrode. Addition of NaTPB as a suitable additive increases the slope of the potential response of the sensor from a poor value of 23.6±0.5 mV/decade (sensor no. 5) to a Nernstian value of 29.1±0.4 mV/decade (sensor no. 6) and also improves the detection limits (2.5×10^{-6} M) of this membrane electrode. The influences of different plasticizers on the potentiometric behaviour of the polymeric membrane were also investigated by using a membrane composition of A (7): PVC (50): Plasticizer (86): NaTPB (1). Among five different plasticizers employed (TMDP, BEHA, *o*-NPOE, DOPP, and DBP), the membrane prepared with TMDP (sensor no. 6) had the best characteristic response. The replacement of TMDP with other plasticizer (sensor no. 7–10) led to a decrease or increase of the electrode's slope, working concentration range and detection limit. It seems that this is due to a synergism between lipophilicity and polarity, where the best results are obtained when these properties reach an intermediate value. Obviously, the best response characteristics are obtained with a membrane composition of A (7): PVC (50): TMDP (86): NaTPB (1). The calibration plot is shown in Figure 3 which indicates a working concentration range from 1.0×10^{-5} M to 1.0×10^{-1} M Cu^{2+} with a Nernstian slope of 29.1±0.4 mV/decade of Cu^{2+} concentration. Thus, sensor no. 6 was chosen for further electroanalytical investigation because the widest working concentration range and the lowest limit of detection.

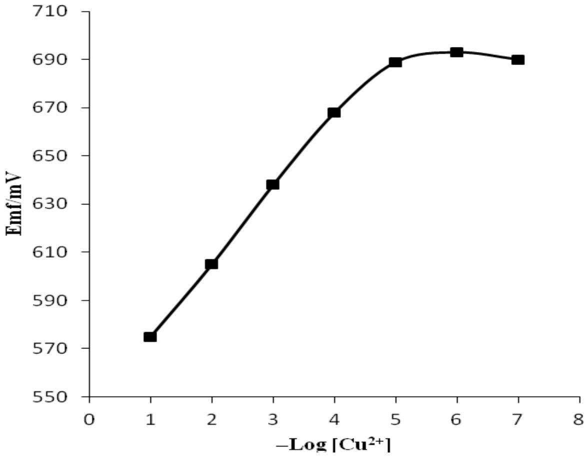

Figure 3. Calibration graph for the proposed Cu(II) selective membrane electrode (sensor no. 6).

3.2. Response time and lifetime

The fast exchanging kinetics of complexation–decomplexation of Cu^{2+} with the ionophore at the test solution–membrane interface is a factor that influences the response time of membrane electrode toward test solution. The response time of the electrode was determined by measuring the time required to achieve a 95% of the steady potential. The practical response time was recorded by changing the copper(II) chloride solution with concentrations from 1.0×10^{-5}M to 1.0×10^{-1}M. The response time recorded was less than 20s and decreased when proceeding from diluted to concentrated solutions. The high lipophilicity of ionophore and plasticizer ensures stable potentials and longer life time for the membrane [32]. Therefore, in order to determine the lifetime, the response of Cu(II) selective membrane electrode (sensor no. 6) was examined at regular intervals to check the reproducibility and lifetime of the sensor (Table 2). It was observed that during the long time period of three months, the slope of the sensor drifted only by 2.1 mV per decade from 29.1 to 27.0 mV per decade and detection limit was increased by a small factor. But after three months, the electrode characteristics significantly drifted away from the Nernstian behaviour. Therefore sensor no. 6 can be used over a period of three months without any considerable change in the value of the slope, working concentration range and detection limit.

Table 2. Potential response of Cu(II) selective membrane electrode (sensor no. 6) at different time intervals.

Time (days)	Slope (mV/decade)	Working range (M)	Detection limit(M)
2	29.1 ± 0.4	1.0×10^{-5}- 1.0×10^{-1}	5.0×10^{-6}
10	29.1 ± 0.4	1.0×10^{-5}- 1.0×10^{-1}	5.0×10^{-6}
25	29.0 ± 0.5	1.0×10^{-5}- 1.0×10^{-1}	5.6×10^{-6}
45	29.0 ± 0.5	1.0×10^{-5}- 1.0×10^{-1}	6.3×10^{-6}
70	28.6 ± 0.2	1.0×10^{-5}- 1.0×10^{-1}	7.1×10^{-6}
90	27.0 ± 0.2	1.0×10^{-5}- 1.0×10^{-1}	7.1×10^{-6}
95	25.5 ± 0.2	1.0×10^{-5}- 1.0×10^{-1}	1.0×10^{-5}

3.3. pH effect on the electrode response

The pH dependence of response of sensor no. 6 had been tested in the range of 2.0 to 12.0 at concentrations of $1.0\text{x}10^{-4}$M Cu(II) ions. The pH was adjusted with small drops of concentrated hydrochloric acid and sodium hydroxide solutions as per requirement. The potential of the sensor was determined as a function of pH and the results are shown in Figure 4. The potential remains constant over the pH range of 4.0–8.0, which may be taken as the working pH range of the sensor assembly. At pH lower than 4.0, the interference of H^+ ions is more which is due to the high rate of diffusion of H^+ ions from sample solution to membrane matrix (extract H^+ ion) where they interact with ionophore and it protonation takes place resulting in decreased selectivity of Cu(II) ions. In this case, the membrane sensor then responds to hydrogen ions. At pH higher than 8.0, the deviation in the electrode response is due to the formation of hydroxyl complexes of Cu^{2+} in solution.

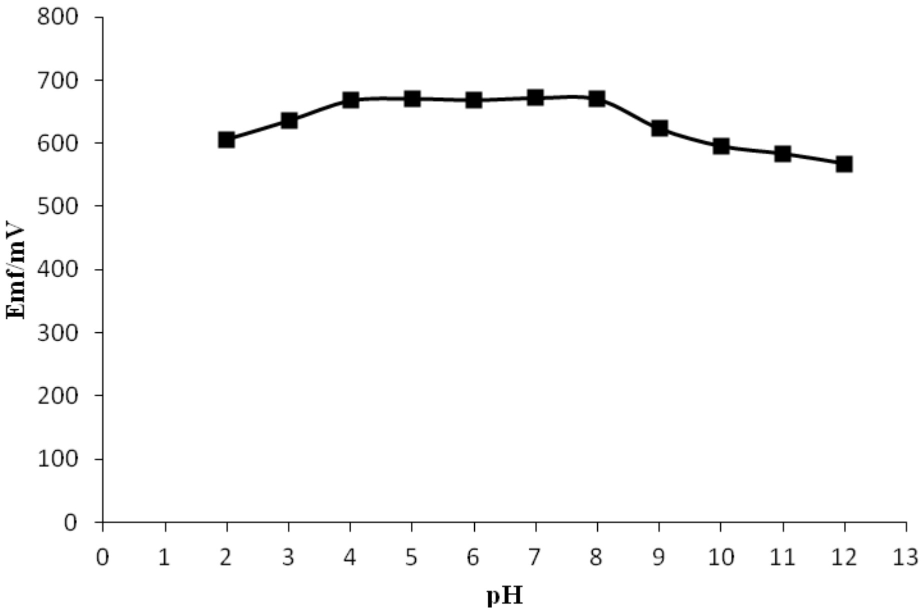

Figure 4. Effect of pH on the performance of sensor no. 6 (1.0×10^{-4} M Cu^{2+}).

3.4. Potentiometric selectivity

Selectivity is the most important characteristic as it determines the extent of utility of any sensor in real sample measurements. It gives the response of ion-sensitive sensor for the primary ion in the presence of other ions present in solution, which is expressed in terms of the potentiometric selectivity coefficients. Therefore, the response of the developed electrode has been evaluated in the presence of various cations. According to IUPAC, the fixed interference method is the preferred experimental choice for characterizing selectivity since it closely reflects the final application of the electrode. Thus, in this work the selectivity coefficients of the electrode towards different cationic species were evaluated by using the fixed interference method (FIM) [33].A fixed concentration of interfering ions (1.0×10^{-3} M) and varies concentration of primary ions (1.0×10^{-1} to 1.0×10^{-7} M) was used in this method. The selectivity of the membrane towards primary ion in the presence of interfering ion was obtained by plotting electromotive force (emf) values versus the logarithm of the primary ion concentration. The intersection of the extrapolated linear portions of this plot indicated the value of concentration of primary ions and was then used to calculate selectivity coefficient by Nicolsky–Eisenman equation:

$$K_{A,B}^{pot} = \frac{a_A}{(aB)^{zA/zB}}$$

where a_A is the activity of the primary ion (Cu^{2+}) and a_B is the activity of the interfering ions, and z_A and z_B are their respective charges on A and B. The resulting selectivity coefficients are summarized in Table 3. As can be seen, selectivity coefficient are in the order of 10^{-3} or smaller, indicating that all diverse ions would not significantly disturb the functioning of the membrane electrode. It is possible to determine Cu^{2+} in the presence of interfering ions at a concentration level smaller or slightly higher than the Cu(II) concentration. It is important to point out that the concentration level of the interfering ion, which the electrode can tolerate, depends on the numerical value of the selectivity coefficient. The smaller the value of the selectivity coefficient, the higher is the concentration of interfering ion(s), which can be tolerated by the sensor. The above results clearly demonstrate that the proposed electrode has shown the best selectivity for Cu^{2+}. In Table 4 the selectivity coefficients for the proposed sensor are compared with selectivity coefficients of previously reported PVC-membrane Cu(II) selective membrane electrodes based on different neutral carriers. As can be seen, the proposed electrode shows somewhat similar values in some cases and superior in most cases especially for Li^+, K^+ and Hg^{2+}.

3.5. Analytical application

To assess the applicability of proposed Cu(II) membrane selective electrode (sensor no. 6) in real samples, an attempt was made to determine the presence of copper in different wastewater samples obtained from the nearest industrial area in Selangor.

Table 3. Selectivity values for Cu(II) selective membrane electrode (sensor no. 6) for several interference cations.

Interfering ion	Selectivity coefficient
Ni^{2+}	6.6×10^{-3}
Fe^{2+}	5.6×10^{-4}
Zn^{2+}	5.0×10^{-3}
Co^{2+}	5.0×10^{-3}
Mg^{2+}	5.6×10^{-3}
Ca^{2+}	6.3×10^{-3}
Pb^{2+}	3.5×10^{-3}
Hg^{2+}	2.5×10^{-4}
Cd^{2+}	3.2×10^{-3}
Ba^{2+}	1.3×10^{-3}
K^+	6.3×10^{-3}
NH_4^+	4.0×10^{-3}
Li^+	7.9×10^{-4}
Na^+	6.3×10^{-3}
Ce^{3+}	5.0×10^{-3}
Fe^{3+}	7.9×10^{-3}

The samples were acidified with 0.1M HCl to adjust stable pH at 4.0. The results obtained from the triplicate measurement of proposed copper sensor were compared with that determined by atomic absorption spectroscopy (AAS) and are summarized in Table 5. From the given data, it is observed that there is satisfactory agreement between the results obtained by the proposed electrode and those by AAS. Thus, the sensor can be employed for Cu^{2+} quantification in real samples.

Table 4. Comparison of the selectivity coefficient of proposed Cu(II) selective membrane electrode (sensor no. 6) with the reported Cu(II) selective membrane electrodes.

Reference	Method	Potentiometric selectivity coefficient							
		Li^+	K^+	Hg^{2+}	Cd^{2+}	Zn^{2+}	Ca^{2+}	Pb^{2+}	Co^{2+}
[21]	FIM	2.0×10^{-2}	3.8×10^{-2}	3.0×10^{-2}	1.2×10^{-1}	3.5×10^{-2}	3.3×10^{-2}	2.5×10^{-2}	2.2×10^{-2}
[22]	FIM	-	6.3×10^{-2}	-	6.3×10^{-2}	1.9×10^{-2}	3.2×10^{-2}	4.1×10^{-2}	-
[23]	MPM	4.5×10^{-3}	6.0×10^{-2}	4.5×10^{-1}	8.2×10^{-2}	8.1×10^{-2}	6.3×10^{-2}	-	8.0×10^{-2}
[34]	MSM	3.2×10^{-2}	1.3×10^{-1}	3.9×10^{-3}	2.6×10^{-2}	4.5×10^{-3}	2.3×10^{-2}	6.3×10^{-3}	2.4×10^{-2}
[35]	FIM	6.3×10^{-2}	6.3×10^{-2}	9.4×10^{-3}	3.2×10^{-2}	1.2×10^{-2}	3.8×10^{-2}	6.5×10^{-2}	1.0×10^{-2}
This work	FIM	7.9×10^{-4}	6.3×10^{-3}	2.5×10^{-4}	3.2×10^{-3}	5.0×10^{-3}	6.3×10^{-3}	3.5×10^{-3}	5.0×10^{-3}

Table 5. Determination of Cu^{2+} in wastewater samples by Cu(II) selective membrane electrode (sensor no. 6) and by atomic adsorption spectroscopy (AAS).

Method	Samples		
	Sample 1	Sample 2	Sample 3
Membrane electrode (ppm)	8.0±0.5	5.7±0.2	5.5±0.5
AAS (ppm)	8.5±0.2	5.9±0.1	5.8±0.2

4. CONCLUSIONS

The proposed sensors are very easy to prepare and show sensitivity and wide dynamic range. High selectivity, low detection limit and rapid response make these electrodes suitable for measuring the concentration of copper ion in wide variety of samples, including biological and industrial samples without the needs for preconcentration or pretreatment steps and without significant interaction from other cationic species present in the samples.

ACKNOWLEDGEMENTS
The authors would like to thank the Ministry of Higher Education, Malaysia and Universiti Pendidikan Sultan Idris for financial supports (Grant No. FRGS2010-02-102-04 and 2012-0079-102-01).

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