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A Highly Selective Copper(II) Electrode Based on PVC Membranes of 2-Acetylpyridine-(1*R*)-(-)-Fenchone Azine Ligand

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Plasticized membranes based on 2-acetylpyridine-(1*R*)-(-)-fenchone azine ligand (L) have been prepared and explored as Cu^{2+}–selective sensors. Effect of various plasticizers and anion excluder, sodium tetraphenylborate (NaTPB) was studied in detail and improved performance was observed at several instances. Optimum performance was observed with copper(II) ion-selective electrode having a membrane composition of L (6): PVC (40): DOP (56): NaTPB (1). The sensor works satisfactorily in the concentration range of 1.0×10^{-5} to 1.0×10^{-1}M with a detection limit of 4.0×10^{-6} M and a Nernstian slope of 30.0 ± 0.2 mV/decade. Wide pH range (4.0–5.0 and 6.0–10.0), fast response time (≤20s) and adequate lifetime (3 months) indicate the vital utility of the proposed sensor. This electrode was used for 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) selective electrode, 2-acetylpyridine-(1*R*)-(-)-fenchone azine ligand, PVC membrane, Potentiometry

1. INTRODUCTION

The existence of copper in our environment is very important as it is used for many industrial, agricultural and domestic purposes [1]. Copper is an essential element for human beings as it is needed in the formation of blood and several enzyme systems, including superoxide dismutase, which detoxifies free radicals [2–4]. Our body can receive maximum level up to 2.0 mg L^{-1} of copper ions [5]. Excessive concentration of copper may cause a toxic effect to our body. It is known to cause certain diseases in humans for example, Menke's syndrome and Wilson's disease [6,7]. So it is important for us to determine the copper ion in environmental samples in view of its utility as well as toxicity.

Nowadays the available method for low level determination of copper or other heavy metals in the solution include atomic absorption spectrometry (AAS) [8–10], inductively coupled plasma-optical emission spectroscopy (ICP-OES) [11,12], anodic stripping voltammetry [13], flame atomic absorption spectroscopy (FAAS) [14,15], stripping voltammetry [16], and inductively coupled plasma-mass spectrometry (ICP-MS) [17]. However, these methods provide accurate results but are not very convenient for analysis of a large number of environmental samples as they generally require sample pre-treatment, sufficient infrastructure backup and not very convenient for routine analysis of large number of environmental samples. Thus, sensitive, reproducible and accurate analytical techniques require in the determination of copper in the environment

Since the 1970s, it has been reported that ion selective electrodes (ISE) are part of a group of relatively simple and inexpensive analytical tools which are commonly referred to as sensors [18–21]. Many ion selective electrodes have been previously reported for copper ion [22–27]. Their differences are from the ionophore used as sensing element. Thus, in this study, 2-acetylpyridine-(1*R*)-(-)-fenchone azine ligand (L) (Figure 1) was investigated as an ionophore in PVC matrix in potentiometric determination of copper(II) ion.

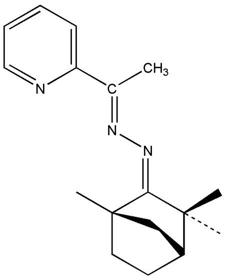

Figure 1. Structure of 2-acetylpyridine-(1*R*)-(-)-fenchone azine ligand (L).

2. EXPERIMENTAL

2.1. Reagents

All reagents used for the preparation of membranes were analytical–reagent grade and were used without further purification. High molecular weight poly(vinyl chloride) (PVC), fenchone hidrazone monohydrate, sodium chloride, sodium acetate, 2-asetiltiophene and sodium tetraphenyl borate (NaTPB) were obtained from Fluka (Switzerland). All analytical grade chloride salts of all cations, glacial acetic acid, ethanol, and tetrahydrofuran (THF) were obtained from Merck (Germany). All plasticizer, hydrazine monohydrate, (1R)-(-) fenchone, 2-acetylpyridine, acid hydrochloric (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 a pH/ion meter Orion 720A, Mass. (USA). 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.

2.3. Synthesis of 2-acetylpyridine-(1R)-(-)-fenchone azine ligand

A solution containing (1*R*)-(-)-fenchone hydrazone (16.75 g, 0.10 mol), 2-acetylpyridine (12.20 g, 0.11 mol) and acetic acid (0.1 cm^3) in ethanol (80cm^3) was heated at 80 °C for 5 hours. The reaction mixture was left standing at 20 °C for 1 hour, after which it was concentrated and cooled to -30 °C where the product precipitated out as a white solid. This was filtered off, washed with cold ethanol and dried. Yield 22.5 g, 84%. Found: C, 75.7; H, 8.7; N 15.7. $C_{17}H_{23}N_3$ requires C, 75.8; H, 8.6; N, 15.6%). m/z (EI): 469 (M^+). ^{13}C–{^1H} NMR (62.9 MHz. $CDCl_3$) δ_C: 12.8 (1C, s, methyl carbon from fench residue), 17.1 (2C, s, methyl carbon from fench residue), 22.2 (1C, s, methyl carbon from fench residue), 51.0 (1C, s, acetyl carbon), 120.6 (1C, s, pyridyl carbon with H), 123.4 (1C, s, pyridyl carbon with H), 135.9 (1C, s, pyridyl carbon with H) and 148.4 (1C, s, pyridyl carbon with H).

2.4. Electrode preparation

The general procedure to prepare the PVC membrane is similar to that previously described [28–30]. 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 a surface of 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 was developed by optimizing the ratio of membrane ingredients, time of contact and concentration of equilibrating solution [31–33].

2.5. Potential measurements

The performance of the electrodes was investigated by measuring the emf of copper(II) chloride solutions prepared with concentration range of 1.0×10^{-1} to 1.0×10^{-7} M serial dilution. Each solution was stirred and the potential reading was recorded when it became stable, and then plotted as logarithmic function of Cu^{2+} cation activity. All electromotive force (emf) 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. Optimization of membrane composition

The selectivity of the ligand toward Cu^{2+} ion over other metal ions that have rapid exchange kinetics and sufficiently lipophilic to prevent leaching of the ligand into the aqueous solution surrounding the membrane electrode should be fulfilled in order to used the ligand as ionophores for copper(II) ion selective electrode [34]. As no information about the coordination behavior of ionophore is available, a preliminary experiment was conducted by testing the potential responses of a polymeric membrane electrodes based on ligand L (with the same composition) for a variety of metal ions. As it can been seen from Figure 2, among different tested cations, Cu^{2+} with the most sensitive response seems to be suitably determined with the PVC membrane based on ligand L. The emf response obtained for all other cations are much lower than those expected by the Nernstian equation. This is probably due to both the selectivity behavior of the ionophore against Cu^{2+} in comparison to some other metal ions. The possible ion exchange mechanism at the membrane-solution interface of Cu^{2+} ion and 2-acetylpyridine-(1*R*)-(-)-fenchone azine ligand that is responsible for the potentiometric response is shown in Figure 3.

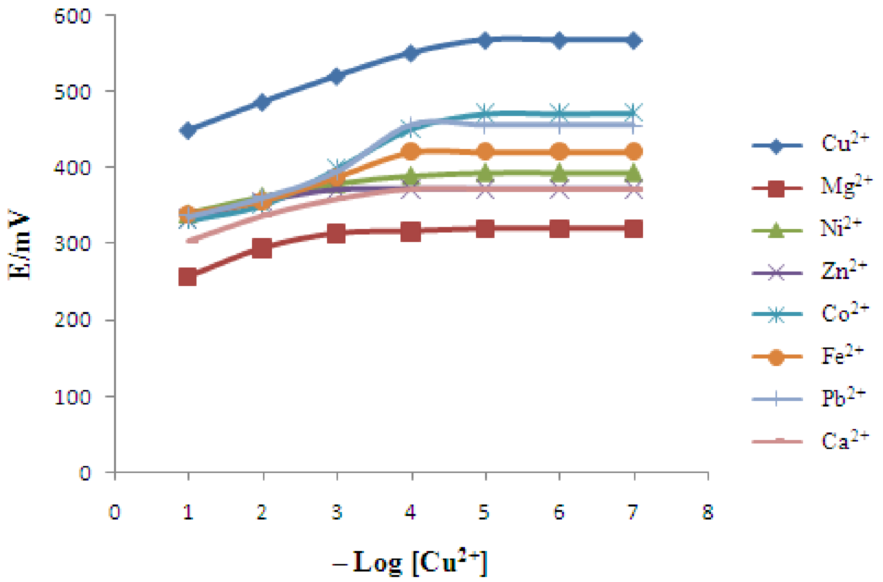

Figure 2. Potentiometric response of membrane sensors based on ligand L for various metal ions.

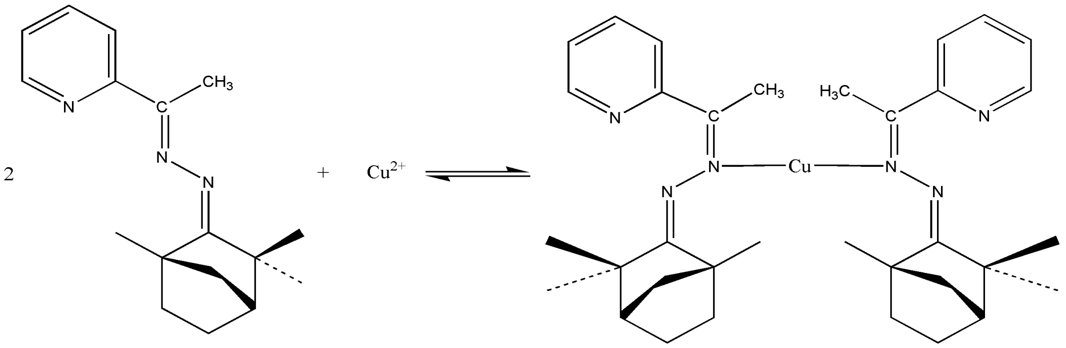

Figure 3. Possible ion exchange mechanism at the membrane-solution interface.

Other than the structure and the nature of ionophore that influence the selectivity behavior of ion selective electrode [35 – 37], it is also well known that some important features of the PVC based membranes, such as the amount of ionophore used, 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 [38 – 42]. Thus, the influence of several membranes compositions on the potential response of the Cu^{2+} ion selective electrode was investigated. The results obtained were summarized in Table 1 and its potential response as a function of copper ion concentration was plotted and shown in Figure 4(a) and 4(b).

Table 1. Optimized membrane composition of copper(II) membrane sensor based on ligand L and their potentiometric responses.

No.	Ion (L)	PVC	Plasticizer	Additive (NaTPB)	Slope (mV/decade)	Working range (mol L^{-1})	Detection limit (mol L^{-1})
1	6	40	–	–	27.7 ± 0.3	1.0×10^{-5}- 1.0×10^{-2}	7.5×10^{-6}
2	6	40	56 (DOP)	–	26.7 ± 0.3	1.0×10^{-5}- 1.0×10^{-1}	5.0×10^{-6}
3	6	40	56 (DOP)	1	30.0 ± 0.2	1.0×10^{-5}- 1.0×10^{-1}	4.0×10^{-6}
4	6	40	56 (TMDP)	1	25.9 ± 0.3	1.0×10^{-5}- 1.0×10^{-1}	8.9×10^{-6}
5	6	40	56 (BEHA)	1	32.7 ± 0.4	1.0×10^{-5}- 1.0×10^{-1}	4.5×10^{-6}
6	6	40	56 (*o*-NPOE)	1	28.3 ± 0.4	1.0×10^{-4}- 1.0×10^{-1}	2.5×10^{-5}
7	6	40	56 (BEHS)	1	15.9 ± 0.2	1.0×10^{-5}- 1.0×10^{-2}	7.9×10^{-6}
8	6	40	56 (DOPP)	1	31.5 ± 0.4	1.0×10^{-5}- 1.0×10^{-1}	6.3×10^{-6}
9	6	40	56 (DBP)	1	26.6 ± 0.3	1.0×10^{-5}- 1.0×10^{-1}	8.9×10^{-6}
10	6	40	56 (T2EP)	1	12.0 ± 0.3	1.0×10^{-4}- 1.0×10^{-2}	5.0×10^{-5}

It is noteworthy that the lipophilicity of plasticizer influences both the dielectric constant of the polymeric membranes and the mobility of the ionophore and its metal complex [43–45]. The presence of lipophilic anions in cation-selective membrane electrodes not only diminish the ohmic resistance [46] and enhance the behavior and selectivity but also in cases where the extraction capability is poor, increase the sensitivity of membrane electrodes [47]. So, it is clear from Table 1 that the addition of plasticizer DOP and additive NaTPB (sensor No. 3) exhibits a good Nernstian response (30.0 ± 0.2 mV/decade) to Cu^{2+} ions and also improves the working concentration range (1.0×10^{-5} M to 1.0×10^{-1} M) and detection limits (4.0×10^{-6} M) of this sensor. The influences of the plasticizer on the potentiometric behavior of the polymeric membrane were also investigated by using a membrane composition of L (6): PVC (40): Plasticizer (56): NaTPB (1). Among eight different plasticizer employed (DOP, TMDP, BEHA, *o*-NPOE, BEHS, DOPP, DBP and T2EP), the membrane prepared with DOP (sensor no. 3) had the best characteristic response. The replacement of DOP with other plasticizer (sensor No. 4 – 10) leads 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 was obtained when these properties reached an intermediate value.

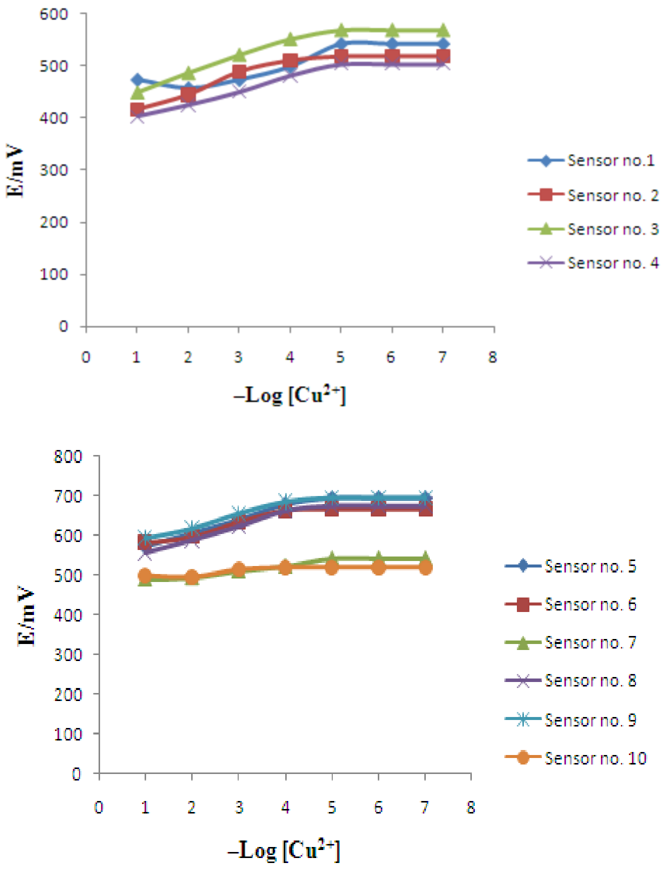

Figure 4(a) and 4(b). Potentiometric response of membrane sensors based on ligand L at different membrane composition and plasticizer.

3.2. Effect of pH on sensor performance

Since pyridine can be protonated or deprotonated depending on pH of the solution, thus the solution pH is certainly affecting the response of electrode [48]. The influence of the pH of the test solution on the potential response of the membrane sensor for a solution containing 1.0×10^{-4} M Cu^{2+} ions was considered in the pH range of 2.0–12.0 (pH was adjusted by introducing small drops of concentrated HCl and NaOH as per requirement) and the results are shown in Figure 5. As can be seen, the potential remains constant over a pH range of 4.0–5.0 and 6.0–10.0, beyond which the potential changes considerably. The observed drift at higher pH values could be due to the formation of a hydroxyl complex of Cu^{2+} ion in solution such as copper(II) hydroxide ($Cu(OH)_2$) [49,50]. The observed decrease in potential at low pH values indicates that the membrane may give response to hydrogen ions and possesses a poor response to the copper ions in solution [51].

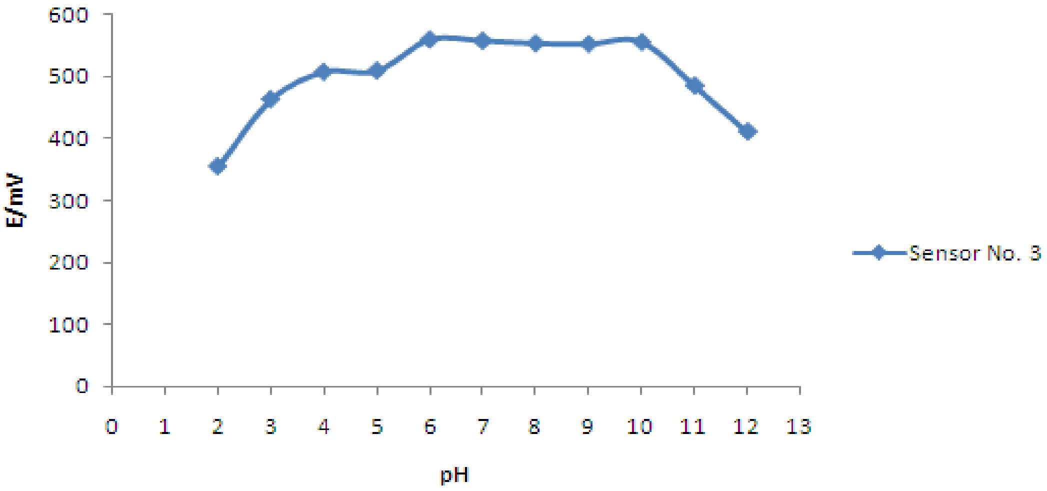

Figure 5. Effect of pH on the performance of sensor No. 3.

3.3. Response time and lifetime

Table 2. Potential response of Cu^{2+} selective electrode No. 3 at different time intervals.

Time (days)	Slope (mV/decade)	Working range (mol L^{-1})	Detection limit (mol L^{-1})
2	30.0 ± 0.2	1.0×10^{-5}- 1.0×10^{-1}	4.0×10^{-6}
10	30.0 ± 0.2	1.0×10^{-5}- 1.0×10^{-1}	4.6×10^{-6}
25	29.8 ± 0.3	1.0×10^{-5}- 1.0×10^{-1}	4.8×10^{-6}
45	29.5 ± 0.2	1.0×10^{-5}- 1.0×10^{-1}	5.1×10^{-6}
70	29.3 ± 0.2	1.0×10^{-5}- 1.0×10^{-1}	6.0×10^{-6}
90	29.1 ± 0.2	1.0×10^{-5}- 1.0×10^{-1}	6.5×10^{-6}
95	26.8 ± 0.2	1.0×10^{-5}- 1.0×10^{-1}	7.9×10^{-6}

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 concentration from 1.0×10^{-5}M to 1.0×10^{-1}M. The response time was less than 20 s and decrease when proceeding from diluted to concentrated solutions. This is most probably due to the fast exchanging kinetics of complexation – decomplexation of Cu^{2+} ion with the ionophore at the test solution–membrane interface [52]. The high lipophilicity of ionophore and plasticizer ensures stable potentials and longer life time for the membrane [53,54]. Therefore, in order to determine the lifetime, the performance of the electrode was determined from time to time on daily basis over a period of 3 months. Performance characteristics of the same electrode at different time intervals are summarized in Table 2. It is seen from Table 2 that over a period of 3 months the slope, working concentration range and detection limits have not changed significantly. Thus, it can be said that the lifetime of the electrode is 3 months.

3.4. Sensor selectivity

The potentiometric selectivity is an important characteristic of the electrode that defines the nature of devices and the range to which it may be successfully employed and can determine whether a target species can be estimated accurately in the presence of diverse ions by using the proposed electrode [55].

Table 3. Selectivity coefficient values of Cu^{2+} selective electrode No. 3 for several interference cations.

Interfering ion	Selectivity coefficient Kpot
Ni^{2+}	7.9×10^{-3}
Fe^{2+}	7.9×10^{-3}
Zn^{2+}	$4.0.\times10^{-3}$
Co^{2+}	4.0×10^{-3}
Mg^{2+}	6.3×10^{-3}
Ca^{2+}	5.0×10^{-3}
Pb^{2+}	6.3×10^{-3}
Hg^{2+}	7.9×10^{-3}
Cd^{2+}	3.2×10^{-3}
Ba^{2+}	4.0×10^{-2}
K^{+}	3.1×10^{-3}
NH_4^{+}	5.6×10^{-3}
Li^{+}	4.0×10^{-3}
Na^{+}	5.0×10^{-3}
Ce^{3+}	6.3×10^{-3}
Fe^{3+}	7.9×10^{-2}

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) [56].

A fixed concentration of interfering ions (1.0×10^{-3} M) and varies concentration of primary ions (1.0×10^{-1}–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:

$$K_{A,B}^{pot} = \frac{a_A}{(aB)^{zA/zB}} \qquad (1)$$

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. It is observed from Table 3, the selectivity coefficients determined are much smaller than 1.0. Thus, it clearly indicates that the electrodes are selective to Cu^{2+} over other cations tested. In general, the interfering effect of the ions is in the following order: $Fe^{3+} > Ba^{2+} > Ni^{2+} = Fe^{2+} = Hg^{2+} > Mg^{2+} = Pb^{2+} = Ce^{3+} > NH_4^+ > Ca^{2+} = Na^+ > Zn^{2+} = Co^{2+} = Li^+ > Cd^{2+} > K^+$.

3.5. Analytical application

The analytical utility and sensitivity of the proposed membrane sensor was verified by analysis of Cu^{2+} ions in different wastewater samples obtained from the nearest industrial area in Selangor. 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 4. 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. Determination of Cu^{2+} in water samples by Cu^{2+} selective electrode No. 3 and by atomic adsorption spectroscopy (AAS).

Method	Samples		
	Sample 1	Sample 2	Sample 3
Membrane electrode (ppm)	8.3±0.2	6.2±0.2	5.4±0.2
AAS (ppm)	8.5±0.2	5.9±0.1	5.8±0.2

4. CONCLUSIONS

On the basis of the results 2-acetylpyridine-(1*R*)-(-)-fenchone azine ligand can be used as a neutral carrier for construction of a PVC-based membrane ion-selective electrode for determination of copper ions. The best composition of the proposed electrode was found to be ionophore:PVC:DOP:NaTPB = 6:40:56:1 (w/w). The sensor exhibits good reproducibility over a period of 3 months and performs high sensitivity, stability, response time and detection limit. The proposed electrode was then successfully used in the determination of Cu^{2+} ion in wastewater samples.

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