

Cu²⁺-selective Sensors Based on a New Ion-Carrier and Their Application for the Analysis of Copper Content of Water Samples

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The present work tends to introduce a new selective ion-carrier (i.e. 4-(2-hydroxy-benzylideneamino)-5-phenyl-4H-1,2,4-triazole-3-thiol (**L**)) for Cu²⁺ ions. The study, hence involved complexation studies in acetonitrile solutions of different ions which proved a selective interaction between the ion-carrier and copper as opposed to alkali, alkaline earth, and transition metal cations. Based on the complexation observations **L** was evaluated for use as a new sensing agent in copper selective membrane sensors and the optimal sensor responses were observed at a membrane composition of 30% PVC, 62% NPOE, 6% **L** and 2% NaTPB. The potentiometric sensors produced stable potential responses towards Cu²⁺ ion, and the slope of the calibration curve was 28.7±0.4 mV decade⁻¹ over the range of 1.0×10⁻⁶ to 1×10⁻² mol L⁻¹ for polymeric membrane electrodes (PMEs) and 28.5±0.3 for all solid state electrodes (ASSEs) in the range of 1.0×10⁻⁸ to 1×10⁻⁴ mol L⁻¹. The response time of the sensors was rather short (i.e. about 25s in the case of PMEs and 15 s for the ASSEs) and both devices showed acceptable life times of 5 weeks for the PMEs and 7 weeks in the case of the ASSEs. The electrodes were used for the determination of the copper content of some water samples, and the results proved to be acceptable.

Keywords: Copper, PVC membrane, Ion selective electrode, Potentiometry, Sensor, Water sample

1. INTRODUCTION

Copper has traditionally had various applications, a lot of which are currently being phased due to the increased consciousness about its toxicity and damage to the environment. Soluble forms of

copper may further be released into the environment as a result of mining and industrial processing of other elements.

Increased levels of copper in the blood, can lead to copper poisoning. Copper toxicity, called copperiedus, refers to excess amount of copper in the body [1]. Copperiedus can occur from eating acid foods cooked in uncoated copper cookware, or from exposure to excess copper in drinking water or other environmental sources. The main toxicity of copper can be due to its ability to accept and donate single electrons through changing oxidation state. Hence, it can catalyzes the production of very reactive radical ions, such as hydroxyl radical. This catalytic activity of copper is used by some metalloprotein enzymes. Thus, the copper is only toxic when unsequestered and unmediated. This increase in unmediated reactive radicals is generally termed oxidative stress, which is an attractive area of research in a variety of diseases where copper may play an important but more subtle role than in acute toxicity [2]. Some of the diseases may be associated with excess copper are Indian childhood cirrhosis (cirrhosis of the liver in children), which occurs by boiling milk in copper cookware; Wilson's disease, an inherited condition causes the body to retain copper, since it is not excreted by the liver into the bile. This disease, if untreated, can lead to brain and liver damage; Alzheimer's disease, where the elevated free copper levels can be observed [3], which has been hypothesized to be occurred due to the inorganic copper consumption [4]. Copper and zinc bind to amyloid beta proteins in Alzheimer's disease [5] and mediate the production of reactive oxygen species in the brain [6].

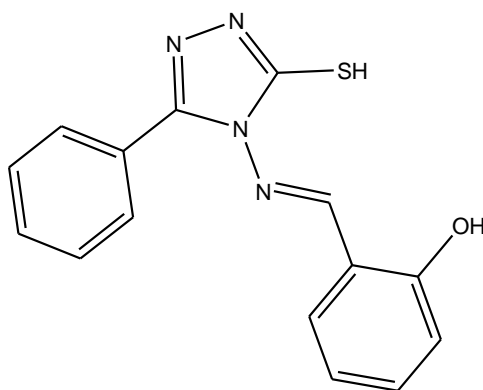
Copper-based paint is a common marine antifouling agent which can causes entering copper in to the environmental waters [7]. Too much copper in water may also damage marine and freshwater organisms such as fishes [8]. The chronic effect of sublethal concentrations of copper on fish and other creatures is damage to gills, liver, kidneys and the nervous system. It also interferes with the sense of smell in fish, thus preventing them from choosing good mates or finding their way to mating areas [9].

However, copper has been extracted and used by humans for a very long time, during which process miners were gradually poisoned by exposure and direct contact to the element and its accumulation in their bodies. The risks have been known for many years, but a thorough understanding their dimensions and the determination of the levels of copper which can lead to such problems is rather recent. New experiments have shown that even low amounts of the element can be dangerous to humans and blood copper levels, which were previously considered as being safe, are now known as hazardous for living organisms. The U.S. Environmental Protection Agency's declares Maximum Contaminant Level (MCL) of copper in drinking water is 1.3 milligrams per liter [10]. They lists copper as a micronutrient and a toxin too.

The modern standards on controlling the levels of environmental pollutants, on the other hand, have led to an increasing interest in the area of developing methods of analysis for different species including heavy metals like copper.

Given the toxic effects of this element on human health, the development of methods and tools for the determination of copper in various samples has been very necessary. The common routines applied to the determination of this element include instrumental techniques such as spectrophotometry [11,12], dispersive liquid-liquid microextraction (DLLM) [13,14], adsorptive stripping voltammetry (ASV) [15], sequential injection analysis (SIA) [16], solid phase microextraction-high performance liquid chromatography (HPLC) [17], and anodic stripping voltammetry [18,19].

Electrochemical methods on the other hand, enjoy figures of merit such as accuracy, portability, sensitivity and selectivity, low cost and ease of use, which have changed them to simple yet powerful tools for the analysis of various target species [20-24]. Among them, numerous Ion selective electrodes (ISEs) have been developed for the determination of different ions, based on the application of proper ionophores [25-39]. The significance of copper ions in biological, environmental and industrial systems necessitate the design and construction of fast, selective and sensitive ISEs for the copper based on various ionophores [40-49], and hence the present work focuses on the application of a new ion-carrier, i.e. 4-(2-hydroxy-benzylideneamino)-5-phenyl-4H-1,2,4-triazole-3-thiol (Scheme 1), in the development of potentiometric membrane and all-solid state electrodes for the determination of this species.



4-(2-hydroxy-benzylideneamino)-5-phenyl-4H-1,2,4-triazole-3-thiol

Scheme 1. Chemical structure of used **L**

All-solid state electrodes (ASSEs) [50-55] are known to have certain advantages over traditional PVC membrane electrodes (PMEs). These advantages, which arise from the asymmetric design of these devices, in which the inner and outer environments of the selective membrane are different, include the lack of the limitations caused by the internal filling solution in symmetrical devices, such as higher detection limits, lower life times, and inflexible application positions. These advantages, in addition to the potentials of using different solid substrates for the deposition of selective membranes and hence altering the sensor behavior have attracted a great deal of an increasing interest to the area in recent years. Another advantages of ASSEs is their enhanced mechanical stability. The improved detection limits of ASSEs are the result of eliminating the inner filling solution, which in turn eliminates the need for optimizing the solution properties, and the risks of its leaking. The increased mechanical stability of the ASSEs, on the other hand, makes it possible to use more flexible design, application of the devices in different directions and produce of disposable sensors.

In the light of the above mentioned and the need for the valid determination of traces of Cu^{2+} ion in aqueous samples, and the importance of finding new ion carrier for copper, the present work has been focused on the development of copper-selective PMEs and ASSEs based on the application of 4-(2-hydroxy-benzylideneamino)-5-phenyl-4H-1,2,4-triazole-3-thiol. The ASSEs were based on the

application of conductive polymeric composites (CPCs) comprising multi-walled carbon nanotubes (MWCNTs), graphite and an epoxy resin which coated on a copper wire to act as the solid contact of the ASSEs. The solid contact was next coated with a layer of the copper-selective PVC membrane.

2. EXPERIMENTAL SECTION

2.1. Reagents

Tetrahydrofuran (THF), dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), *o*-nitrophenyloctylether (NPOE), and sodium tetrapenyl borate (NaTPB), graphite powder (1–2 μm particle size), the MWCNTs (95%; 30–50 nm), were obtained from a local company in Iran. The epoxy resin (Macroplast Su 2227 epoxy) was procured from Henkel Co. and the hardener (desmodur RFE) was from Bayer Ag. High-molecular weight polyvinylchloride (PVC) was from Fluka and the 4-(2-hydroxy-benzylideneamino)-5-phenyl-4H-1,2,4-triazole-3-thiol (Scheme 1) was synthesized through the common Schiff's base synthesis procedure between 2-hydroxybenzaldehyde and 5-phenyl-4H-1,2,4-triazole-3-thiol amine as described elsewhere [56,57]. Reagent-grade nitrate salts (from Merck) were used for preparing the solutions in triple-distilled deionized water. The salts were not subjected to any treatments except for vacuum drying over P_2O_5 .

2.2. Preparing the Electrodes

The PVC membrane cocktails were prepared by dissolving 30 mg of PVC, 62 mg of the plasticizer NPOE, and 2 mg of NaTPB in 2 ml of tetrahydrofuran (THF). After thoroughly mixing the ingredients, 5 mg of the ion-carrier (**L**) were added to the solution and mixed, and the resulting homogenous mixture was poured into a 2 cm glass dish, where it was rested until a viscous cocktail was obtained through the evaporation of the THF. Next a Plastic tube (3–5 mm in diameter at the top) was inserted into the mixture for a short period until a 0.3 mm membrane was formed at its tip. The membrane was then allowed to dry in air before the tube was filled with a 1.0×10^{-3} M $\text{Cu}(\text{NO}_3)_2$ solution, and placed in an identical solution for 1 day to be ready for use. An Ag/AgCl reference electrode was inserted into the tube to act as the internal reference electrode and the overall system was used as an ISE. To optimize the sensor response the amounts and ratios of the membrane ingredients, the internal solutions, and conditioning times were monitored to evaluate the best conditions for preparing and using membranes with reproducible, noise-free and stable potentials [25–30].

The CPC, which was used to prepare the solid contact of the sensor, was made of a MWCNTs-loaded epoxy resin. To optimize the composition of the CPC different amounts of graphite powder, MWCNTs, the epoxy and hardener were mixed in THF and allowed to rest for 20–30 minutes in air, to yield a viscous mixture. Next a polished section of a shielded copper wire (0.5 mm diameter and 15 cm length) was dipped into the CPC mixture. The CPC coated wire was then left to dry in air for 6 hours and used as the solid contact of the ASSEs afterwards. The solid contacts were coated with the copper-selective PVC membranes through being immersed into the membrane cocktail three or four times, and

were finally left to dry for 1 day. The best ASSE responses were observed with membranes compositions of 6% wt. of L, 62% wt. of the optimal plasticizer (NPOE), 30% wt. of PVC, and 2% wt. of NaTPB, and the cocktails were prepared as described above. The dried ASSEs were conditioned in a 10^{-3} mol L⁻¹ Cu²⁺ solution for 48h [52, 53].

2.3. Measurements

The potentiometric studies of the samples were conducted in a cell assembly according to the illustration below, while a Corning 250 pH/mV meter ion analyzer was used for the measurements. The readings were performed at 25.0 ± 0.1 °C.

Ag-AgCl | KCl (3 mol L⁻¹) internal solution, 1.0×10^{-3} mol L⁻¹ Cu(NO₃)₂ | PVC membrane test solution | Hg-Hg₂Cl₂, KCl (satd).

As it is clear a double-junction saturated calomel electrode (SCE) filled with an ammonium nitrate solution was used as the reference electrode and the PME and acted as the indicator electrode.

In the case of the ASSEs, the potentiometric cell further included an Ag/AgCl double junction reference electrodes (Azar-Electrode Co., Iran) and the cell can be illustrated as below:

Cu wire/ASS layer/ion selective PVC membrane | sample solution || Ag-AgCl, KCl (satd.)

3. RESULTS AND DISCUSSION

3.1. Evaluation of the ion-carrier

Given that the ion-carrier has of one sulfur and nitrogen atoms which can act as soft bases, it was expected to form stable and selective complexes with soft acids such as transition and heavy metal ions as opposed to other metal ions. To validate this anticipation behavior of L in complexation reactions with some of transition and heavy metal ions was studied through conductometric tests in an acetonitrile solution at 25 ± 0.1 °C [27-33]. The formation constants (K_f) of the 1:1 complexes are calculated and summarized in Table 1, which clearly indicates that L formed the most stable complexes with copper ions. This was held as ground to expect L to form selective complexes and hence act as a specific ion-carrier Cu²⁺ ions. Accordingly the L further evaluated in this role and used in PVC membrane ion selective electrodes for copper ions. The results obtained simply proved the anticipations to be true, since the resulting sensors selectively responded to copper ion concentrations in different samples and revealed a Nernstian behavior in a very wide concentration window.

Table 1. The formation constants of $L - M^{n+}$ complexes

Ion	Log K_f	Ion	Log K_f
Na ⁺	<2.00	Ni ²⁺	2.77 ± 0.16
K ⁺	<2.00	Ag ⁺	<2.00
Mg ²⁺	<2.00	Cd ²⁺	3.37 ± 0.21
Ca ²⁺	2.31 ± 0.25	Pb ²⁺	2.74 ± 0.13
Fe ³⁺	2.05 ± 0.27	Fe ²⁺	<2.00
La ³⁺	2.78 ± 0.31	Pt ³⁺	2.71 ± 0.36
Zn ²⁺	3.44 ± 0.36	Mn ²⁺	2.41 ± 0.14
Ce ³⁺	2.72 ± 0.14	Nd ³⁺	2.22 ± 0.15
Cr ³⁺	2.53 ± 0.23	Gd ³⁺	2.53 ± 0.26
Hg ²⁺	3.75 ± 0.23	Sm ³⁺	2.73 ± 0.32
Cu ²⁺	5.12 ± 0.33	Eu ³⁺	2.22 ± 0.35

3.2. Membrane composition

Evaluation of the responses of the L-based membrane sensors with various composition were made and the potential response behaviors are illustrated in Table 2. The Table clearly shows that the sensor with the membrane composition no. 5, had most sensitive response towards copper ions, which as discussed earlier was attributed to the highly selective complexation interactions among L and Cu²⁺, as well as rapid exchange kinetics of the complexation reactions.

Table 2. Various membrane ingredients used in making PVC membrane sensor

No.	PVC (wt.%)	Ligand (wt.%)	NaTPB (wt.%)	Plasticizer (wt.%)		Slope (mV/decade)	Range (mol/L)
1	30	4	0	66	NPOE	20.4±0.8	5.0×10 ⁻⁵ -5.0×10 ⁻³
2	30	6	0	64	NPOE	23.2±0.6	5.0×10 ⁻⁶ -5.0×10 ⁻²
3	30	8	0	62	NPOE	19.8±0.7	5.0×10 ⁻⁶ -5.0×10 ⁻²
4	30	6	1	62	NPOE	25.5±0.5	5.0×10 ⁻⁶ -1.0×10 ⁻²
5	30	6	2	62	NPOE	28.7±0.4	1.0×10 ⁻⁶ -1.0×10 ⁻²
6	30	6	3	62	NPOE	27.2±0.5	1.0×10 ⁻⁶ -1.0×10 ⁻²
7	30	6	2	62	DBP	22.1±0.5	5.0×10 ⁻⁶ -1.0×10 ⁻³
8	30	6	2	62	NB	16.8±0.6	1.0×10 ⁻⁵ -1.0×10 ⁻²
9	30	6	2	62	BA	19.8±0.8	1.0×10 ⁻⁴ -1.0×10 ⁻²
10	30	0	0	70	NPOE	4.2±1.2	1.0×10 ⁻⁴ -1.0×10 ⁻²

Further to the role ion-carrier in the behavior of ISEs other critical features including the amounts of the different ingredients, the nature of solvent mediator and additives, and the plasticizer/PVC ratio leave significant influences on the sensitivity and selectivity of ISEs [25-30], and hence these parameters were evaluated and the results are summarized in Table 1. The amount of the

ion-carrier is also known to influence the sensitivity of membrane electrodes and as revealed by compositions 1-3 in Table 1, the sensitivity of the ISE actually increased with increasing this parameter up to 6% wt. The adverse effects on the sensor response above this value could be attributed to inhomogeneity of the membrane composition due to its saturation. As with the solvent mediators the results in this table (items 7-9) proved that benzyl acetate (NPOE) leads to better results as opposed to other tested plasticizers. The role of solvent mediators is greatly dictated by their dielectric constants as well as the mobility they provide for the ionophore-target species complex. The table further reveals that the presence of the additive improved the response of the membrane electrode. As already reported, presence of about 2% wt. of NaTPB as an additive increases the potential response of the sensors, as in the case of the present work in which the poor response of 19.8 mV/decade (No. 2) was enhanced to the Nernstian value of 28.7 mV/decade (No. 5). Also the incorporation of anionic additives like tetraphenyl borate (TPB) leads to the reduction of the Ohmic resistance of ISEs as well as improving their selectivity [22-29]. Such additives may also catalyze the kinetics of the ion exchange phenomena at the sample–membrane interface. Based on the studies, it was concluded that the best response could be obtained with PME having a composition of 30% PVC, 62% NPOE, 6% ionophore L, and 2% NaTPB (No. 5).

The effect of the different internal solutions on the response of the Cu^{2+} ISE was evaluated, and it was found that the concentration of these solutions does not leave any significant influences in the potential response of the electrodes, except for the anticipated changes in the intercept of the calibration curves, and hence a $1.0 \times 10^{-3} \text{ mol L}^{-1}$ solution was chosen and used in all studies. The optimized PME composition was next used as the starting point for preparing the ASSEs based on conductive epoxy supports [50-53].

3.3. Calibration

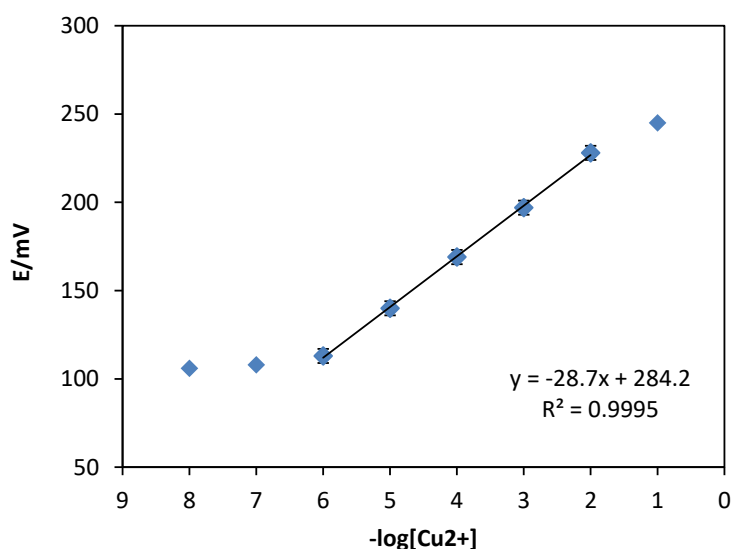


Figure 1. Calibration curve of the PME (based on membrane no. 5)

The characteristics of the electrodes were evaluated based on the protocols proposed by IUPAC. In the case of the emf response of the sensors toward the concentration of Cu^{2+} (Fig. 1), the plot of the sensor response was found to be linear in the range of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} , and the curve had a slope of 28.7 ± 0.4 mV per decade of copper concentration. The detection limit of the PME's were calculated from the intersection of the extrapolation of the two linear segments of the calibration graph at low concentrations and was found to be 1.0×10^{-6} mol L^{-1} .

With the ASSEs the potential response was assessed in the concentration window of 1.0×10^{-9} to 1.0×10^{-3} mol L^{-1} and the potential vs. $-\log [\text{Cu}^{2+}]$ plot were found to be linear from 1.0×10^{-8} – 1.0×10^{-4} mol L^{-1} (Fig. 2) and the curve had a slope of 28.5 ± 0.3 mV per decade of copper concentration.

The upper detection limit of the electrodes was observed to be 10^{-2} mol L^{-1} and 10^{-4} mol L^{-1} , respectively, which was attributed to the saturation of its active at this concentration. In case of symmetrical sensor, it is higher than those of the asymmetrical sensors that have a smaller surface area.

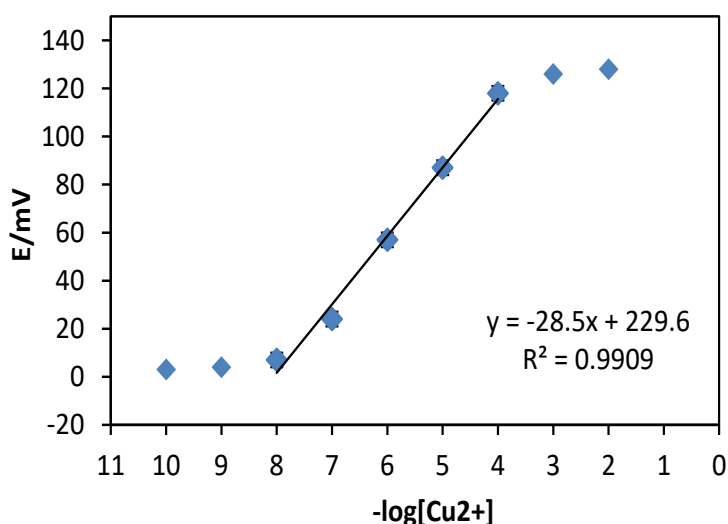


Figure 2. Calibration curve of the ASSE (based on membrane no. 5)

3.4. The potential-pH behavior of the sensors

The potential-pH behavior of the PME's and ASSEs was assessed through monitoring the response of the sensors in a 1.0×10^{-5} mol L^{-1} solution of copper ions while varying the pH from 2.0 to 12.0 using concentrated NaOH or HCl solutions. The resulting plots (Fig. 3) proved that the response of both sensors did not considerably change as a function of the solution pH in the range of 4.0 to 8.5. The drifts beyond these two limiting values were attributed to the formation of soluble $\text{Cu}(\text{OH})^+$ or $\text{Cu}(\text{OH})_2$ species at higher and protonation of the nitrogen atoms present in the structure of L, at lower pH values.

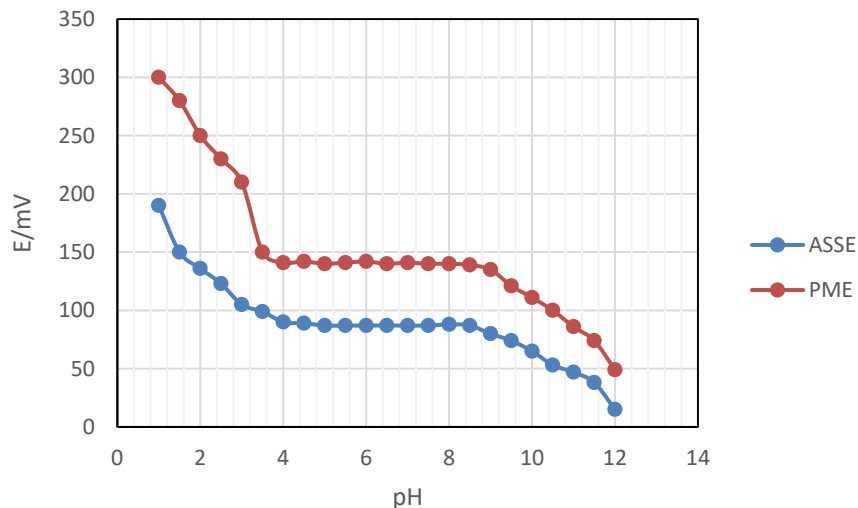


Figure 3. pH effect on potential response of the PME and ASSE in a 1.0×10^{-5} mol L⁻¹ solution of copper ions

3.5. Response time

The time required for the sensor to reach the required stability for being used in analytical procedures upon condition in a 1.0×10^{-3} mol L⁻¹ Cu(NO₃)₂ solution was determined to be 24 h for PME and 48h for ASSE. After spending required time for conditioning the electrodes were found to be capable of generating stable potential responses. Further, the average time required by the electrodes to reach a potential values with the ± 1 mV range of the equilibrium potential corresponding to the solution concentration, upon successive immersions of the devices in a series of copper ion solutions with 10-fold concentration differences, is known as the response time of the sensor. The experiments showed the static response time of the PMEs to be 20s through the linearity range of the electrodes.

The dynamic response time of the ASSEs was also evaluated through the successive immersions of the electrodes into different solutions in the range of 1.0×10^{-8} to 1.0×10^{-4} mol L⁻¹, indicated that the ASSEs can reach equilibrium in less than 10s.

3.6. Selectivity

The effect of the presence of other ions on the response an ISE is expressed in terms of the so-called selectivity coefficients (K_{sel}). Here the matched potential selectivity coefficients were determined [33-39] and the results are reported in Table 3. It is clear that the selectivity coefficients of the PME and ASSE are in the order of 1.0×10^{-4} or less. This can be translated as the lack of significantly disturbances from the tested interfering ions even when these species are 1000 times more concentrated than the target ion.

Table 3. The selectivity coefficients of various interfering cations for Cu²⁺ PME and ASSE

Cation	Selectivity Coefficients for PME	Selectivity Coefficients for ASSE
Na ⁺	<10 ⁻⁵	<10 ⁻⁵
K ⁺	<10 ⁻⁵	<10 ⁻⁵
Mg ²⁺	<10 ⁻⁵	<10 ⁻⁵
Ca ²⁺	<10 ⁻⁵	<10 ⁻⁵
Hg ²⁺	5.2×10 ⁻³	3.3×10 ⁻³
Zn ²⁺	2.0×10 ⁻⁴	1.0×10 ⁻⁴
Co ²⁺	3.0×10 ⁻⁴	3.0×10 ⁻⁴
Cd ²⁺	2.3×10 ⁻³	1.1×10 ⁻³
Pb ²⁺	8.8×10 ⁻⁴	8.5×10 ⁻⁴
Ag ⁺	1.7×10 ⁻⁴	1.0×10 ⁻⁴
Fe ³⁺	3.5×10 ⁻⁴	3.2×10 ⁻⁴
Fe ²⁺	3.9×10 ⁻⁴	3.9×10 ⁻⁴
Ni ²⁺	4.3×10 ⁻⁴	4.1×10 ⁻⁴
La ³⁺	2.0×10 ⁻⁴	1.0×10 ⁻⁴
Ce ³⁺	3.2×10 ⁻⁴	2.2×10 ⁻⁴

3.7. Lifetime

Life time studies were conducted by recording calibration curves and potential responses of the devices on a daily basis using standard solutions. During the period of studies which was 12 weeks the three PME and three ASSEs were used separately for 1 hour /day and the life time of the devices was found to be in the range of 4–10 weeks as previously reported [42-50]. After 10 weeks the slope of the calibration curves gradually decreased and the detection limit were increased, which was attributed to the loss of the plasticizer, ion-carrier and the ionic additive from the membranes.

The proposed PME could be used for at least 5 weeks and ASSE for 7 weeks. After this time, the slope of the electrode reduces (from 28.7 and 28.5 to 24.4 and 25.1 mV per decade respectively).

3.8. Analytical applications

The proposed sensors were tested and found to work well in the determination of the concentration of copper ions in some water samples. The tests were performed by taking 2.0 ml of each sample adding 5.0 ml of sodium acetate/acetic acid buffer (pH=5.0) to it and next diluting the solution to 100 ml in volumetric flask. These samples were analyzed using the developed copper sensors through the standard addition method. The results were compared with ICP-OES results (Table 4) and a good consistency was observed between the two sets of data, i.e. statistically the differences are not significant at a 95% confidential interval.

Table 4. Results of copper analysis in waste water samples

Sample	Found by the PME* (mg/L)	Found by the ASSE* (mg/L)	Found by ICP-OES (mg/L)
Sample 1	2.1±0.4	1.9±0.3	1.7±0.2 **PME ($t_{exp}=2.00$) ASSE ($t_{exp}=1.24$)
Sample 2	3.5±0.3	3.6±0.3	3.8±0.3 **PME ($t_{exp}=1.58$) ASSE ($t_{exp}=1.05$)
Sample 3	2.5±0.4	2.0±0.3	2.2±0.3 **PME ($t_{exp}=1.34$) ASSE ($t_{exp}=1.05$)

* The results are based on five replicate measurements.

** $t_{calculated}=2.3$ (df=8; CI: 95%)

To show the superiority of the proposed sensor with the other previous reported ion selective sensor, a comparison table was provided. Table 5 listed the characterizations of some best reported ion selective electrodes for copper determination and the proposed electrodes here.

Table 5. Comparison of the proposed Copper selective sensors with the best previous ones

Selectophore	Electrode Type	Linear Range (mol L ⁻¹)	Response time	Slope (mV/decade)	pH range	[Ref.]
1-cyano-1-piperidino-2-(N-piperidino methyl)-cyclohexane	PME	1.0×10^{-8} - 1.5×10^{-2}	10 s	28.4	5-8.5	[40]
2-(1'-(4'-(1''-Hydroxy-2''-naphthyl)methyleneamino)butyliminomethyl)-1-naphthol	ASSE	1.0×10^{-8} - 1.0×10^{-3}	8 s	29.5	4-8.5	[41]
1,10-phenanthroline sub-unit	PME	1.0×10^{-5} - 2.0×10^{-1}	15 s	29.4	2.5-5.5	[42]
1-(2-hydroxybenzylidene)thiosemicarbazide	PME	1.0×10^{-5} - 1.0×10^{-1}	25 s	28.6	3.5-7.5	[43]
4-amino-6-methyl-1,2,4-triazin-3,5-dithione	PME	1.0×10^{-6} - 1.0×10^{-1}	15 s	29.2	3-7.5	[44]
Bis(2-hydroxyacetophenone)butane-2,3-dihydrazone	PME	5.0×10^{-8} - 1×10^{-2}	15 s	29.6	2.8-5.8	[45]
4-(2-hydroxybenzylideneamino)-5-phenyl-4H-1,2,4-triazole-3-thiol	PME ASSE	PME: 1.0×10^{-6} - 1×10^{-2} ASSE: 1.0×10^{-8} - 1×10^{-4}	PME: 20 s ASSE: 7 s	PME: 28.7 ASSE: 28.5	4-8.5	This work

As can be seen, combination of ASSE with PME can provide a wide linear range for determination of copper ions.

4. CONCLUSION

A new compound was evaluated in terms of its behavior towards different ions through complexation studies in acetonitrile. The studies showed selective interactions among this compound (i.e. 4-(2-hydroxy-benzylideneamino)-5-phenyl-4H-1,2,4-triazole-3-thiol (**L**)) and copper ions, as compared with alkali, alkaline earth, and other transition metal ions and hence **L** was tested as a new ion-carrier for use in copper selective PME and ASSEs. The optimal sensor responses were observed for devices based on a membrane composition of 30% PVC, 62% NPOE, 6% **L** and 2% NaTPB. The proposed devices had stable potential responses toward Cu^{2+} ion. The potential response of the PME was found to be $28.7 \pm 0.4 \text{ mV decade}^{-1}$ over a concentration range of 1.0×10^{-6} – $1 \times 10^{-2} \text{ mol L}^{-1}$, and that of the ASSE was 28.5 ± 0.3 in the concentration window of 1.0×10^{-8} – $1 \times 10^{-4} \text{ mol L}^{-1}$. The sensors revealed short response times of about 20s (PME) and 10s (ASSE) and their respective life times were 5 and 7 weeks. Further evaluations proved the devices to be fit for practical use in the determination of the copper content of water samples.

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