

Full Paper

Nano-molar Monitoring of Copper ions in Waste Water Samples by a Novel All-Solid-State Ion Selective Electrode (ASS-ISE)

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Abstract- The focus of this work is on the preparation of a Cu²⁺ all-solid-state ion selective electrode (ASS-ISE) to be used in the analysis of copper ions in complex samples. The ASS-ISE was composed of a conductive substrate of graphite-epoxy resin on a copper wire. This conductive substrate was further coated with a layer of Cu²⁺-selective PVC membrane, comprising 32% of PVC, 57% of nitrobenzene (NB) as the plasticizing solvent, 2% of an ionic additive (i.e. sodium tetraphenyl borate (NaTPB)), and 9% of an organic ligand named 3-(2-methyl-2,3-dihydrobenzothiazol-2-yl)-2H-chromen-2-one (L) as the selective ionophore. The device with the optimal composition had a Nernstian response of 29.3±0.3 mV/decade from 1.0×10⁻⁸ M to 1.0×10⁻³ M of the analyte and its lower detection limit was estimated at be 4.0×10⁻⁹ M. The ASS-ISE showed excellent selectivity for the target ion in the presence of various common interfering ions, and was found to be satisfactorily applicable to the analysis of copper electroplating waste water samples.

Keywords- Sensor, All solid state, Potentiometry, Copper, Waste water

1. INTRODUCTION

Cu^{2+} ion is found in high concentrations in sea water. The ion has been proven to have a role in the lifetime of phytoplanktons [1,2]. Cu^{2+} ion further plays vital roles in animal husbandry and human health. In this light and given that even traces of the ion has toxicological effects on different organisms [3,4], the analysis of Cu^{2+} ion has always been an important analytical target, and this significance has been further intensified due to the enhanced emission of Cu^{2+} into the environment from various industrial sources, which can in turn increased the dangers caused to public health as a result of the presence of the element in the environment [5,6]. For ecological assessments and comprehension the dissemination of pollutants environmental monitoring of heavy metals is of great importance [7]. Copper is one of the heavy metals that need precise control in the environment that has a biological action at low doses (~1 mg/kg) and a toxic effect when ingested in larger quantities (3–4 mg/kg) [8,9].

It is ineluctable to state that the development of sensitive, accurate and precise analytical techniques constitute the platform for the determination of analytes in various samples. Conventionally the analysis of copper ions has been carried out by instrumental approaches like spectrophotometric techniques [10-12], stripping voltammetry [13-15], solid phase microextraction-high performance liquid chromatography (HPLC) [16]. The advantages like accuracy, portability, sensitivity and selectivity, reasonable costs and ease of operation, that are the inherent properties of ion selective electrodes (ISEs), have changed these devices into powerful rivals for the mentioned techniques, and hence the development and application of ISEs based on various natural and synthetic ionophores has been an interesting area of research on the analysis of different analytes including Cu^{2+} ion [17-25].

ASS-ISE, on the other hand, present various figures of merit [26-30] ranging from the lack of limitations arising from the internal solutions in symmetrical devices (i.e. detection limits, life time, and applications position of the devices) to the possibility of using various subd substrates as the ASS element of the devices, which have incrementally attracted the interest in the area. Further figures of merit offered by ASS-ISEs include improved detection limits and mechanical stability. The improved detection limits are actually achieved through the elimination of the inner filling solution (IFS), which subsequently eliminates the need for optimization IFS and risks of its leaking. The enhanced mechanical stability on the other hand makes it possible to have higher flexibility in designing the electrodes, and makes it possible to produce disposable devices.

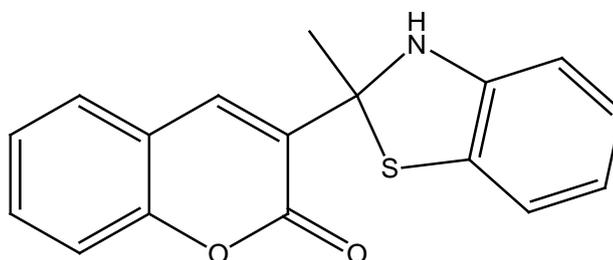
Also given the wealth of knowledge on the structure and chemistry of various ligands used as the ionophores in the construction of precise, accurate and selective polymeric ISEs for monitoring trace amount of Cu^{2+} ion in aqueous samples, and given that devising portable, easy-to-use devices with low detection limits for the online monitoring of Cu^{2+} ion concentration in different samples through the construction of ASS-ISE is of great interest in

quality control, as well as environmental and biological applications, the present work was focused on the design and preparation of a novel copper selective ASS-ISE. The device has been based on a conductive polymeric composite (CPC) as the ASS element. The CPC comprised multi-walled carbon nanotubes (MWCNTs) and an epoxy resin and a layer of this composite was coated on a copper wire to form the ASS, which was then coated with a layer of a copper selective PVC membrane to provide the required selectivity.

2. EXPERIMENTAL SECTION

2.1. Reagents

Analytical reagent grade, tetrahydrofuran (THF), dibutyl phthalate (DBP), benzyl acetate (BA), *o*-nitrophenyloctylether (*o*-NPOE), nitrobenzene (NB), potassium tetrakis (p-chlorophenyl) borate (KpCITPB) and sodium tetrapenyl borate (NaTPB), graphite powder (1–2 μm particle size), the MWCNTs and all nitrate or chloride salts of the cations used were from Merck Co. and used without any further treatment. High molecular-weight polyvinylchloride (PVC) was obtained from Fluka Co. and the ionophore L, 3-(2-methyl-2,3-dihydrobenzothiazol-2-yl)-2H-chromen-2-one (Scheme 1), was synthesized as expressed elsewhere [31]. Macroplast Su 2227 epoxy and the desmodur RFE hardener were from Henkel Co. and Bayer Ag.



Scheme 1. Chemical structure of L

2.2. ASS-ISE Preparations

The first step was the preparation of the CPC (i.e. MWCNTs-loaded epoxy resin) to be used as the internal contact and transducer. To do this various mixtures of graphite powder, MWCNTs, epoxy, and hardener were prepared in THF. The mixture was left for about 20-30 minutes in air, and after a mixture of proper viscosity a segment of a shielded copper wire (0.5 mm diameter and 15 cm length) was soaked into the mixture, after being polished. The coated wire was further left to dry for 12 hours and the resulting assembly was used as the ASS element, which was then dipped in a cocktail of the PVC membrane three or four times. This way the ASS element was covered with a layer of the ISE and the device was rested for one day to completely dry and be ready for use [26-29].

The optimal composition of the ion selective membrane (ISM) was determined to be 9% wt. of the ionophore L, 57% wt. of the plasticizer (the optimal plasticizer was found to be NB), 32% wt. of PVC, and 2% wt. of the ionic additive (i.e. NaTPB). The mixture of the membrane ingredients was prepared by admixing various amounts of the ligand L with proper amounts of PVC, the plasticizer and ionic additive in THF followed by thoroughly mixing the ingredients. Once the ingredients were completely dissolved in the solvent and a uniform solution was attained, the mixture was transferred into a glass dish (2 cm i.d.) and aged in air to reach to an acceptable level of viscosity. This cocktail was then used for coating an ISE membrane on the ASS element through dipping the ASS into the viscose mixture, as described above. The resulting ASS-ISEs were eventually left to dry and then conditioned in a 10^{-3} M solution of Cu^{2+} ion.

To evaluate their properties these ASS-ISEs were applied as the indicator electrodes, in potentiometric cells further including an Ag/AgCl double junction reference electrodes (Azar-Electrode Co., Iran) as the external reference electrode. The cell used for the analyses can be illustrated as:



The indicator and reference electrodes were externally in contact through an ion analyzer 250 pH/mV meter with a precision of ± 0.1 mV.

3. RESULTS AND DISCUSSION

A review of the previous reports on copper selective ISEs, reveals that most of these devices have been symmetrical electrodes (i.e. in their structure the polymeric ion selective membrane is located between the internal standard and the external sample solutions [32]. As briefly described earlier asymmetrical ISEs like ASS-ISEs do not require the presence of internal solutions and hence only the exterior surface of the ion selective membrane becomes in contact with the test solution, while its inner surface attached to the solid-state contact [26-32]. With symmetrical devices, the inner solution is necessary for developing a potential gradient between the two sides of the membrane. The presence of this solution, however, leads to limitation as addressed above particularly in terms of robustness and miniaturization capability of the device. The elimination of the inner solution in asymmetrical devices, provided these devices with the qualities required for many medical, biological, environmental and in-vivo applications. Combination of the qualities of a solid contact composed of a conductive epoxy support composite with the flexibility of ion selective membranes (ISMs) in terms of modifiable compositions turns ASS-ISEs into very powerful analytical tools. The fact that the nature and amount of the components of the PVC

membranes can be exploited in favor of constructing ISMs with optimal selectivity and response behaviors.

Given the role of the ISM composition, the composition of the polymeric membrane based on the L was optimized and a summary of the important information acquired during the course of optimization is presented in Table 1.

Many reports have established that a plasticizer/PVC ratio of about 2.0, generally tends to lead to optimal responses on the part of the PVC membranes. In this light, this has addressed in all compositions in Table 1. Consequently the amount of PVC which is 32% wt. in all cases is not mentioned in the table for the sake of simplicity.

Table 1. Compositions of the membranes used in preparation of GST sensor

No	Composition of the membrane			Characterization of AAS-PME		
	Plasticizer	Ionophore	Ionic Additive	Slope mV/decade	DL (M)	Response time
1	NB,63	5	-	12.5±0.2*	1.0×10 ⁻⁷	35 s
2	NB,61	7	-	14.7±0.3	9.0×10 ⁻⁸	32 s
3	NB,59	9	-	16.9±0.4	7.0×10 ⁻⁸	30 s
4	NB,57	11	-	16.9±0.5	6.0×10 ⁻⁸	30 s
5	NB,58	9	1 NaTPB	24.3±0.2	9.0×10 ⁻⁹	12 s
6	NB,57	9	2 NaTPB	29.3±0.3	4.0×10 ⁻⁹	9 s
7	NB,61	9	3 NaTPB	29.3±0.4	4.0×10 ⁻⁹	9 s
8	NB,61	9	2 KpCITPB	29.2±0.3	4.0×10 ⁻⁹	9 s
9	NPOE,59	9	2 NaTPB	29.0±0.2	5.0×10 ⁻⁹	10 s
10	DBP,59	9	2 NaTPB	25.7±0.3	7.0×10 ⁻⁹	15 s
11	BA,60	9	2 NaTPB	26.8±0.2	7.0×10 ⁻⁹	15 s
12	NB,60	-	2 NaTPB	6.1±0.3	3.0×10 ⁻⁵	30 s

*standard deviation of five repeated measurements

The plasticizer or membrane solvent, on the other hand, is incorporated for enhancing the mobility free and complexed ionophores across the ISM. Commonly, non-volatile liquids which are capable of dissolving and not reacting with PVC and the other membrane ingredients are used as the plasticizers. These solvents should not have chemically active functional groups, and their polarities should be compatible with the nature of the analyte. The membrane solvents with a characteristic dielectric constant that were used in the composition of the ISM include dibutyl phthalate (DBP), *o*-nitrophenyloctylether (NPOE), nitrobenzene (NB) and benzylacetate (BA), and the experimental results proved NB to lead to better response behavior. The good behavior of ISMs based on NB arise from its compatibility with the rather highly polar Cu²⁺ ion, which tend to prefer high polarity media .

Another common ingredient of ISMs is the ionic additive. The appropriate polarity of the membrane plasticizer alone, has proven to be inadequate to facilitate an acceptable level of

extraction and exchange of the analyte into the membrane and hence experiments have shown that the presence of small amounts of ionic additives improves the exchange mechanism, and also decreases the Ohmic resistance polymeric ISMs .

The effect of incorporating various amounts of the ionophore on the response of ASS-ISE was also evaluated and the results are given in Table 1, which shows a 9% amount of L (membrane no. 3) to lead to the optimal response. To prove the role of the ionophore in determining the selectivity of the sensor, a blank membrane lacking the ionophore was also constructed (membrane no. 12). Not surprisingly the ASS-ISE based on this ISM was found to produce poor results. An overview of the results in Table 1, reveals that the best results were produced by membrane no. 6, with a Nernstian slope of 29.3 ± 0.3 mV/decade. Accordingly this membrane was used for further evaluations .

Initially the potential response of the ASS-ISE was studied at various Cu^{2+} ion concentration in the range of 1.0×10^{-9} to 1.0×10^{-1} M and a potential vs. $-\log [\text{Cu}^{2+}]$ curve was plotted (Figure 1). The figure revealed the linear segment of the plot to extend from 1.0×10^{-8} - 1.0×10^{-3} M which represents the linear range of the ASS-ISE.

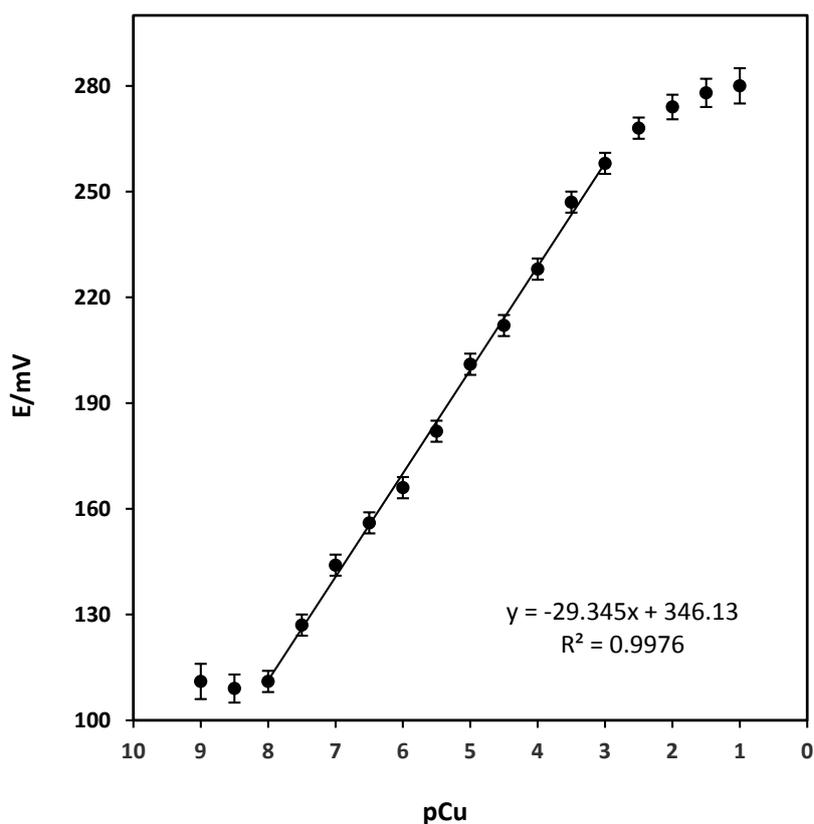


Fig. 1. Calibration curve of the Cu^{2+} -ASS-ISE

The response of conventional symmetric PVC membranes sensors is known to range from 0.1 to 10^{-5} or even 10^{-6} M. Yet asymmetric devices like ASS-ISE provide far lower detection

limits in sub 10^{-8} M range [26-30]. Accordingly, in this case the lower detection limit was estimated to be 4.0×10^{-9} M, based on the extrapolation of the linear segments at the lower part of the calibration curves. The upper detection limit of the ASS-ISE was found to be 10^{-3} M. This is due to the saturation of the active sites present in the ISM over this concentration. This value is less than those of symmetrical sensors, which have larger surface areas due to their larger dimensions, and enjoy better upper detection limits.

Additional assessments were made on the dynamic response time (DRT) of the device. DRT is defined as the time need to reach responses within ± 1 mV of the equilibrium potential, after inducing a 10 fold concentration increase in to the test solution [20-25]. This is usually determined through it's the successive immersion of the sensor into sample solutions with 10 fold concentration differences. In this case this was done in the range of 1.0×10^{-8} to 1.0×10^{-3} M and the results showed that the sensor reached its equilibrium response very quickly (after about 9 s) over the whole concentration range.

The influence of the pH of the sample solution on the response of ion-selective devices is also important. Such studies are usually carried out through evaluating the response of a sensor to a constant and known concentration of the analyte (in this case a 1.0×10^{-5} M solution of Cu^{2+}) while changing the pH through adding concentrated acid or base solutions, to avoid considerable volume/concentration changes. In this case the study was conducted in the pH range of 2.0 to 10.0 (using concentrated NaOH or HCl solutions), and the results as illustrated in Fig. 2, showed the response of the device to be pH-independent in the pH range of 4.0 to 8.5.

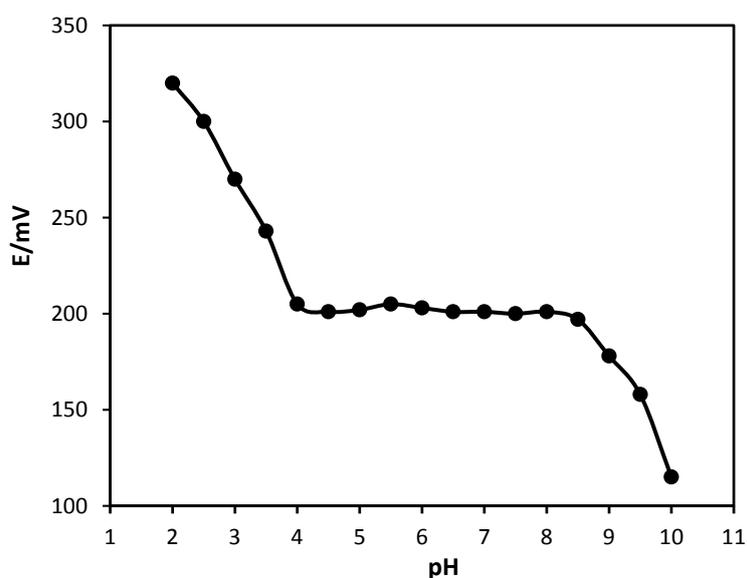


Fig. 2. pH effect on the potential response of the Cu^{2+} -ASS-ISE

The potential drifts beyond the range reveal that the device cannot be used below a pH value of 4.0 and above 8.5. At pH values more alkaline than 8.5 the formation of solvated

$\text{Cu}(\text{OH})^+$ or $\text{Cu}(\text{OH})_2$ most probably lowers the concentration of the free Cu^{2+} ion and hence the sensor response. Below 4.0, on the other hand, the acidic media protonates the nitrogen atoms of L, and hence causes drifts in the response.

Study of the lifetime of sensors is also very important. The life time of the ASS-ISE was evaluated through using it for 1 hour a day for a 12 week period and recording its potential response behavior. The study revealed the average lifetime of the ASS-ISEs to be between 4–10 weeks, which is typical [17-25]. As it can be seen from Table 2. After 7 weeks, under the mentioned conditions the slope of the calibration curve gradually decreased and the lower detection limit increased, which was attributed to the loss of the plasticizer, the ligand and the ionic additive from the ISM due to prolonged use.

Table 2. Lifetime of Cu^{2+} -ASS-ISE

Week	ASS-ISE Performance	
	Slope (mV per decade)	DL (M)
First	29.3±0.3	4.0×10 ⁻⁹
Second	29.2±0.4	4.5×10 ⁻⁹
Third	29.0±0.2	5.5×10 ⁻⁹
Fourth	29.1±0.3	5.0×10 ⁻⁹
Fifth	29.2±0.3	6.0×10 ⁻⁹
Sixth	29.1±0.4	6.0×10 ⁻⁹
Seventh	29.0±0.3	6.5×10 ⁻⁹
Eighth	25.7±0.4	3.5×10 ⁻⁸
Ninth	22.1±0.3	7.5×10 ⁻⁸
Tenth	20.4±0.2	1.0×10 ⁻⁷
Eleventh	17.9±0.3	2.0×10 ⁻⁷
Twelfth	15.9±0.4	3.0×10 ⁻⁷

Eventually the selectivity behavior of the ASS-ISEs was also evaluated. The selectivity of an ISE is generally defined as its response to the target ion, in the presence of other interfering ions. The selectivity evaluations in this work were conducted according to the so-called matched potential method (MPM) [34-38] and the results are presented in Table 3. Reviewing the results proves that none of the interfering ions, considerably influenced the response of the ASS-ISE.

After all of the evaluations, to prove the applicability of the ASS-ISE to real samples, it was used for the analysis of Cu^{2+} ion content of industrial wastewater samples. The samples were simply acidified with HNO_3 prior to the analyses and then adjust the pH to 5. Next, each sample was subjected to three analyses through the calibration method. The obtained results

were compared with those obtained from inductively coupled plasma optical emission spectrometry (ICP-OES) and were found to be in good agreement with them (Table 4), proving the ASS-ISE results to be valid.

Table 3. Selectivity coefficients obtained for the sensor

Interfering species	Log (K_{MPM})
Na ⁺	-7.5
K ⁺	-7.2
NH ₄ ⁺	-7.4
Ca ²⁺	-5.9
Mg ²⁺	-6.9
Co ²⁺	-5.5
Ni ²⁺	-5.6
Zn ²⁺	-6.1
Cd ²⁺	-5.8

Table 4. Results of the copper content analysis of waste water samples

Sample	Found by Cu ²⁺ -ASS-ISE (ppm)	Found by ICP-OES (ppm)
1	2.6±0.3	2.7±0.2
2	3.7±0.2	3.6±0.2
3	3.1±0.3	3.3±0.1

4. CONCLUSIONS

A potentiometric all-solid-state ion selective electrode (ASS-ISE) was constructed and evaluated for the determination of Cu²⁺ in waste water samples. The ASS was composed of a solid conductive polymeric composite (CPC), which was composed of graphite powder, MWCNTs, and epoxy resin. The CPC was coated on a copper wire to form the ASS element, which was next covered with a thin PVC-ISM containing of 32% wt. of PVC, 57% wt. of NB, 2% wt. of an ionic additive, and 9% of the ionophore L. The resulting ASS-ISE showed a dynamic linear range from 1.0×10^{-8} to 1.0×10^{-3} M of Cu²⁺ ion and reached a detection limit

as low as 4.0×10^{-9} M. The device was successfully applied to the determination of Cu^{2+} ion concentration in electroplating waste water samples.

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