Cu(II)-All Solid State Ion Selective Electrode (ASS-ISE) with a Nano-molar Detection Limit and its Use for the Analysis of Waste Water Samples

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Abstract- An all-solid-state ion selective electrode (ASS-ISE) has been developed and used for the selective determination of Cu(II) in the presence of interfering species in complex samples. The device is composed of a conductive graphite-epoxy resin composite coated on a copper wire to act as the ASS, which is further coated with a Cu(II) selective PVC membrane, containing 30% PVC, 60% 0-nitrophenyloctyl ether (NPOE), 3% of sodium tetr phenyl borate, and 7% of 2-(1’-(4’-(1’’-Hydroxy-2’’-naphthyl)methyleneamino)butyl iminomethyl)-1-naphthol as the selective ion-carrier (L). The behavior of the device revealed that it has a Nernstian response of 29.7±0.2 mV/decade over a rather wide concentration range from 1.0×10^{-8} M to 1.0×10^{-3} M and the ASS-ISE could be used down to detection limits as low as 5.5×10^{-9} M. Further evaluations of the electrode proved it to have a good selectivity for Cu(II) as opposed to different commonly occurring interfering ions. The applicability of the ASS-ISE to the analysis Cu(II) concentration in copper electroplating waste water samples with complex matrices was also evaluated and found to be viable.

Keywords- All solid state, Potentiometry, Copper, Sensor, Waste water
1. INTRODUCTION

Cu(II) species, that have been proven to influence the lifetime of phytoplanktons, are present in sea water, in rather high amounts [1,2] and the ion further has a wide range of applications in animal husbandry and human health. Given the reports on the fact that even trace amounts of Cu(II) can leave toxicological effects on different organisms [3,4], determination of the concentration of this ion is a critical need, which is further highlighted by the increased emission and higher concentrations of Cu(II) in the environment. This is in part due to various industrial applications [5], and naturally increases the significance of the analysis of the species even at trace amounts [6].

The monitoring of Cu(II) species is further important due to the role of the ion in the absorption and function of iron in biological systems, especially in the course of production of hemoglobin, and the role Cu(II) in the function of enzymes which play a fundamental role in the production and preventing the oxidation of collagen, as well as generating energy [7].

Development of sensitive methods with reproducible and accurate results has always been welcomed in analytical circle. Analysis of Cu(II) ions is no exception [8], and a series of conventional routines based on spectrophotometry [9,10] dispersive liquid–liquid microextraction [11,12], adsorptive stripping voltammetry [13], sequential injection analysis [14], high performance liquid chromatography [15], and anodic stripping voltammetry [16,17] have already been developed for this purpose. On the other hand, the merits of ion selective electrodes (ISEs) which range from accuracy and portability, to sensitivity, selectivity, low cost and facility of use have made these devices an attractive choice for various analytical applications, including the monitoring of Cu(II) ions [18-25].

All solid-state ion-selective electrodes (ASS-ISEs), that are a sub-category of ISEs, enjoy the advantages of being free form the limitations of the presence of internal solutions, that are inherent with symmetrical devices leading to limitations in the limit of detection, life time and applications position of the devices, in addition to the possibility of using different intermediary materials in the construction of the devices have attracted an increasing interest to these devices, in recent years [26-31]. Further advantages of ASS-ISEs include improved detection limits due to the elimination of the inner filling solution, reducing the chances of leaking, [32–34], as well as enhanced mechanical stability, which makes it possible to use flexible mechanical designs for the electrodes, and also makes it possible to produce disposable devices.

In the light of the advantages of ASS-ISEs and the need for precise, accurate and selective devices for the analysis of traces of Cu(II) in aqueous samples, various ligands have been tested and used for the construction of polymeric copper-selective electrodes. So, given the fact that development of a portable device with a low detection limit and facile application method for on- and off-line monitoring of Cu(II) concentration in different samples is an desirable goal, and that the ASS-ISE configuration can be used to this end the present work
has been directed towards the design and construction of a novel copper selective ASS-ISE. The ASS element of the device was based on a conductive polymeric composite (CPC) of multi-walled carbon nanotubes (MWCNTs) and an epoxy resin and the CPC was coated on a copper wire. This whole ASS was then coated with a selective PVC membrane to yield a copper selective ASS-ISE.

2. MATERIALS

Tetrahydrofuran (THF), dibutyl phthalate (DBP), benzyl acetate (BA), o-nitrophenyloctylether (NPOE), potassium tetrakis (p-chlorophenyl) borate (KpClTPB) and sodium tetrapenyl borate (NaTPB), graphite powder (1–2 μm particle size), the MWCNTs and all salts (nitrate or chloride form) were of analytical reagent grade and were obtained from Merck Co., high-molecular weight polyvinylchloride (PVC) was from Fluka Co. and the ion-carrier L, 2-(1’-(4’-(1”-(1”-Hydroxy-2”-naphthyl)methyleneamino)butyliminomethyl)-1-naphthol, (Scheme 1) was synthesized as described earlier [35]. Macroplast Su 2227 epoxy was from Henkel Co. and the desmodur RFE hardener was obtained from Bayer Ag.

![Scheme 1](image)

**Scheme 1.** Chemical structure of the used selectophore

2.1. Preparing the ASS-ISE

To prepare ASS initially the CPC was made by mixing different amounts of graphite powder, MWCNTs, the epoxy resin and the hardener in a THF. The mixture was then left to age in the air, and lose some of its THF content. a shielded copper wire (0.5 mm diameter and 15 cm length) was polished and dipped into the viscose mixture to be coated with a layer of the CPC, and the resulting assembly was left to dry in air for 12 h. The so prepared ASS element was next dipped into a mixture of the selective PVC membrane cocktail three or four times. This way a polymeric membrane was formed on the surface of the ASS element, which was allowed to dry in air for one day.
The experimental results showed that the best responses could be achieved with a PVC membrane containing 7% wt. of L, 60% wt. of NPOE, 30% wt. of PVC, and 3% wt. of NaTPB. The PVC membrane mixture was prepared by mixing the various ingredients in a small volume of THF through thorough mixing, and giving the resulting homogenous mixture some time to viscosify through the evaporation of its THF content in a glass dish of 2 cm diameter.

The so-prepared ASS-ISEs device was eventually conditioned in a $10^{-3}$ M Cu(II) solution before being used as the indicating electrode in a cell assembly as below, further containing an Ag/AgCl double junction reference electrode (Azar-Electrode Co., Iran):

\[
\text{Cu wire/ASS layer/ion selective PVC membrane | sample solution || Ag-AgCl, KCl (satd.)}
\]

The two electrodes were externally linked by an ion analyzer with a 250 pH/mV $\pm$0.1 mV and the measurements were performed using the calibration method.

3. RESULTS AND DISCUSSION

A review of the literature reveals that most of the reported ISEs have been symmetrical devices in which the polymeric ISE acts as the interface of an internal standard and the external test solutions as opposed to asymmetrical devices like ASS-ISEs [43-46], in which only the external surface of the ISE membrane comes in contact with the test solution and the inner layer of the membrane is in close contact with the solid-state contact. Although the presence of the inner standard solution can help develop a potential gradient through the ISE membrane, it has been found to lead to certain limitations especially in terms of robustness and miniaturization of the devices and hence the elimination of this solution in asymmetrical devices helps avoid such limitations. Consequently the asymmetrical devices enjoy the advantages required for medicinal, biological, environmental and even in vivo applications.

In the case of ASS-ISEs, the application of the CPC allows for using combining the advantages of PVC membranes, which arise from their variable and adjustable compositions, with those of solid state devices. It is evident that the nature and amount of each of the components of PVC membranes, has critical effects on the response and behavior of the resulting sensor [36-45]. Consequently, the effect of the member ingredients on the membrane response were evaluated through preparing and testing various PVC membrane compositions and the results are summarized in Table 1. Previous experiments have revealed that a plasticizer/PVC ratio of around 2.0 generally leads to optimal responses, and hence in all compositions tested (Table 1) this ratio was maintained. Further, for the simplicity of calculations in all compositions the amount of PVC was kept at 30%wt and hence this value is bot mentioned in the Table.
A plasticizing agent is also used in PVC membranes to enhance the mobility of the free and complexed species throughout this phase. Plasticizers are inert and generally non-volatile compounds that can dissolve PVC, and have various polarity values based on their nature. Some typically used plasticizers, including dibutyl phthalate (DBP), o-nitrophenyloctylether (NPOE) and benzylacetate (BA) were evaluated in this study and the experiments revealed NPOE to lead to the best responses. This was ascribed to the rather high polarity of the target Cu(II) ions, which tend to prefer a high polarity media.

Another conventional, yet critical ingredient of PVC membranes is the ionic additive, the presence of small amounts of which has been found to enhance the exchange mechanism of the target species and also to lessen the Ohmic resistance of the membrane.

The studies on the optimization of the PVC membrane composition, the results of which are summarized in Table 1, revealed that increasing the amount of the ligand up to 7% wt. led to increased sensor response while above this value the response did not change and hence this value was chosen as the optimal value for the concentration of the ligand. Evaluations of the response of a membrane lacking the ion carrier (membrane no.10), showed that such a blank membrane leads to very poor sensing behaviors. Further investigations, revealed that a membrane with the composition of no. 6 led to the best Nernstian slope (29.7±0.2 mV/decade), and hence this composition was selected for further evaluations.

Next the response of the ASS-ISEs at different Cu(II) concentration ranging from 1.0×10⁻⁹ to 1.0×10⁻¹ M was recorded and the potential vs. –log [Cu(II)] curve was plotted (Figure...

Table 1. Various membrane ingredients used in making ASS-PVC membrane sensor

<table>
<thead>
<tr>
<th>No.</th>
<th>Composition (%)</th>
<th>PVC</th>
<th>Plasticizer</th>
<th>Ion-carrier</th>
<th>Additive</th>
<th>Slope* (mV/decade)</th>
<th>DL (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>30</td>
<td>67 NPOE</td>
<td>3</td>
<td>-</td>
<td>14.4±0.3</td>
<td>3.7×10⁻⁶</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>30</td>
<td>65 NPOE</td>
<td>5</td>
<td>-</td>
<td>16.2±0.3</td>
<td>2.4×10⁻⁶</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>30</td>
<td>63 NPOE</td>
<td>7</td>
<td>-</td>
<td>18.9±0.2</td>
<td>1.1×10⁻⁶</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>30</td>
<td>62 NPOE</td>
<td>8</td>
<td>-</td>
<td>18.9±0.3</td>
<td>1.1×10⁻⁶</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>30</td>
<td>61 NPOE</td>
<td>7</td>
<td>2 NaTPB</td>
<td>28.8±0.2</td>
<td>8.5×10⁻⁹</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>30</td>
<td>60 NPOE</td>
<td>7</td>
<td>3 NaTPB</td>
<td>29.7±0.2</td>
<td>5.5×10⁻⁹</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>30</td>
<td>60 NPOE</td>
<td>7</td>
<td>3 KpClTPB</td>
<td>29.6±0.3</td>
<td>6.5×10⁻⁹</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>30</td>
<td>60 DBP</td>
<td>7</td>
<td>3 KpClTPB</td>
<td>25.8±0.2</td>
<td>9.5×10⁻⁹</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>30</td>
<td>60 BA</td>
<td>7</td>
<td>3 KpClTPB</td>
<td>26.2±0.4</td>
<td>9.0×10⁻⁹</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>30</td>
<td>67 NPOE</td>
<td>-</td>
<td>3 NaTPB</td>
<td>5.5±0.3</td>
<td>4.4×10⁻⁴</td>
</tr>
</tbody>
</table>
1), which revealed the response of the device to be linear in the range of $1.0 \times 10^{-8} - 1.0 \times 10^{-3}$ M, which is much improved as compared to that of symmetrical devices which usually show a linear response in the range of $0.1$ to $10^{-5}$ or even $10^{-6}$ M. The detection limit of the ASS-ISE was further calculated to be $5.5 \times 10^{-9}$ M, through extrapolating the two linear parts at the lower concentrations of the calibration curve. The upper detection limit of device was $10^{-3}$ M, which can be attributed to the saturation of the active sites of the membrane at this concentration and above.

![Calibration curve of Cu ASS PVC membrane sensor](image)

**Fig. 1.** Calibration curve of Cu ASS PVC membrane sensor; the results are based on 5 replicate measurements.

Next the dynamic response time of the device, which is defined as the period of time needed for the response to reach ±1 mV of the equilibrium value upon a 10 fold increase in the concentration of the test solution [46-51], was assessed through the successive immersion of the ASS-ISE into different sample solutions from $1.0 \times 10^{-8}$ to $1.0 \times 10^{-3}$ M. The result revealed that the response time of the sensor to be only around 8 s.

The potential-pH behavior of the ASS-ISE, which is a critical parameter for any ISE, was also evaluated by recording the response behavior of the device in a fixed and known concentration of Cu(II) ($1.0 \times 10^{-5}$ M), while varying the pH of the solution in the range of 2.0 to 10.0. The changes in the pH were introduced through adding small volumes of concentrated NaOH or HCl solutions. This way, only negligible changes occurred in the concentration of the test solution, allowing to assume this value constant. The recorded data was plotted (Figure
2) and showed that the potential response of the sensor was independent from pH in the range of 4.0 to 9.0, while it considerably changed beyond these limits. The considerable potential drift at pH values above 9.0, were attributed to the formation of Cu(OH)$^+$ or Cu(OH)$_2$ species, in the solution which in turn lower the activity of the free Cu(II) ion Below 4.0, the rather acidic media leads to the protonation of the nitrogen atoms in the structure of L, and hence due to the interference of protons in the solution the potential drift towards more positive values.

![Graph showing pH effect on potential response of sensor in Cu(II) solution](image)

**Fig. 2.** pH effect on the potential response of the sensor in a solution of Cu(II) (1.0×10$^{-5}$ M)

Another evaluation was made on the lifetime of the sensor. The overall procedure for measuring the lifetime of the sensor included recording the calibration curve and potential response of a number of sensors on a daily basis for a long period of time. To this end 3 sensors were chosen and each was used for 1 hour/day for 10 weeks, and the results were recorded. The results life time of ASS-ISEs are expected to falls in the range of 4–10 weeks [45-50], and the experimental results showed that after a period of 9 weeks of use the potential slope and lower detection limit decreased and increased respectively, which was most probably due to the gradual leakage and loss of the membrane ingredients (i.e, plasticizer, the ion-carrier, or the ionic additive) into the solution, due to repeated use.

The selectivity coefficients of the device, which can be described as an ISE’s tendency to respond to a specific ion (target ion) in the presence of interfering ions and can be
considered as the most important characteristic of any ion selective electrode, was also evaluated through the well-established matched potential method (MPM) [52-58]. The results, given in Table 2, reveal that none of the tested interfering ions cause a significant error in the response of the sensor.

Eventually, to evaluate the applicability of the ASS-ISE to the analysis of real samples, the device was used in the determination of the amount of Cu(II) in industrial wastewater samples. The wastewater samples were only acidified with HNO₃ prior to analysis and each sample was analyzed 3 times using the calibration curve method and the results are summarized in Table 3. The validation of the results was carried out by comparing these results with those of analyzing the same samples by inductively coupled plasma optical emission spectrometry (Table 3). The comparisons showed the results of the ASS-ISE analysis to be consistent with those of the reference method.

**Table 2.** The selectivity coefficients of various interfering cations for Cu(II) ASS PVC membrane sensor

<table>
<thead>
<tr>
<th>Cation</th>
<th>Selectivity Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>&lt;10⁻⁶</td>
</tr>
<tr>
<td>K⁺</td>
<td>&lt;10⁻⁶</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>&lt;10⁻⁶</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>&lt;10⁻⁶</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>3.9×10⁻⁴</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>1.2×10⁻⁴</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>3.7×10⁻⁴</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>5.9×10⁻⁴</td>
</tr>
<tr>
<td>Pb⁴⁺</td>
<td>8.9×10⁻⁴</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>3.9×10⁻⁴</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>2.2×10⁻⁴</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>4.1×10⁻⁶</td>
</tr>
</tbody>
</table>
Table 3. Results of copper analysis in waste water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Found by the sensor* (ppm)</th>
<th>Found by ICP-OES (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>5.6±0.3</td>
<td>5.8±0.2</td>
</tr>
<tr>
<td>Sample 2</td>
<td>4.8±0.2</td>
<td>5.9±0.1</td>
</tr>
<tr>
<td>Sample 3</td>
<td>6.4±0.3</td>
<td>6.3±0.2</td>
</tr>
</tbody>
</table>

* The results are based on five replicate measurements

4. CONCLUSION

An All-solid-state ion selective electrode was designed and applied to the determination of Cu(II) in waste water samples. The ASS element was based on a conductive polymeric composite (CPC), composed of graphite powder, MWCNTs, and epoxy resin. The CPC was coated on a copper wire to form the ASS, which was next covered with a thin layer of a PVC-based ion selective membrane containing 30% wt. of PVC, 60% wt. of NPOE, 3% wt. of an ionic additive, and 7% wt. of the ion-carrier L. The resulting ASS-ISE proved to have a dynamic linear range of 1.0×10⁻⁸ to 1.0×10⁻³ M of Cu(II), and had a detection limit of as low as 5.5×10⁻⁹ M. The device was successfully used in the analysis of Cu(II) content of waste water samples.

Acknowledgements

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REFERENCES


Ion-selective electrodes (ISEs) have been a subject of major interest during the recent years within all the development of membrane selective electrode for chloride (PVC) membrane selective electrode for the determination of were the first class of atypical anti-psychotics to be successfully. 28 mm, height 30 mm) on a Fluka glass plate, and allowed to evaporate overnight. Cu(II)-All Solid State Sensor Ion Selective Electrode (ASS-ISE) with a Nano-molar Detection Limit and its Use for the Analysis of Waste Water Lithium Ion-Selective Electrode with Improved Lifetime. Keywords : Lithium ion-selective electrode, Potentiometric property, Lifetime of ISE, Polyurethane mixed matrix. Ion-selective electrodes (ISEs) are a class of electrochemical sensors with increasing importance for on-site analysis of environmentally relevant ions. Potentiometric ion detection with ion-selective all-solid-state (ASS) electrodes has been widely developed in recent years and will be broadly applicable due to their simplicity and fast analysis. Potentiometric detection requires minimum sample pretreatment and preparation and has great potential for field analysis. In literature, the use of different ion-complexing compounds like calixarenes, Schiff’s bases and thiocrown ethers is described.