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## Preparing a Copper(II) Ion Selective PVC Membrane Electrode based on Complex of 3-(4-Nitrophenylazo)-pentane-2,4-dione (LP) with Copper(II) as Ionophore

Dr. Hajar Naser Nasser<sup>1</sup>, Dr. Elham Munir Baddour<sup>2</sup>, Dr. Mossab Brakat Khalel<sup>3</sup>

<sup>1</sup>Professor, Dep. of Chemistry – Faculty of Sciences – Tishreen University. (hajar.nasser@tishreen.edu.sy)

<sup>2</sup>Associate professor, Dep. of Environmental Engineering – Faculty of technical engineering- Aleppo University- Aleppo- Syria. (dr\_elham\_bador@hotmail.com)

<sup>3</sup>Lecturer, National Center for Excellence– Tishreen University, Latakia, Syria

**Abstract** 3-(4-nitrophenylazo)-pentane-2,4-dione as ionophore was synthesized and used as ion carrier to prepare copper(II) ion selective PVC membrane electrodes. The best performance was obtained by a membrane electrode with the composition: PVC as matrix (32%), (LP) as ionophore (3%), *DBP* as plasticizer (64%) and NaTBP as anionic additive (1%). This electrode showed a linear potential response to copper(II) was within this range  $1.0 \times 10^{-6}$ – $1.0 \times 10^{-1}$ M, with Nernstian slope of 28.23 mV/decade and detection limit down to  $7 \times 10^{-7}$ M. It is suitable for copper(II) determination within pH between 3 and 6, and performs well over a period of 2 months. The electrode is selective for copper for a large number of metal ions. Described membrane electrode can be used in analytical measurements by direct potentiometry to determine  $\text{Cu}^{+2}$  in standard and real sample solutions.

**Keywords** copper(II), ISE, LP, polymer membrane electrodes, potentiometry

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### 1. Introduction

Copper is an essential and toxic element at high concentration, the maximum tolerable level for copper is  $2.0 \text{ mg.L}^{-1}$  [1]. Copper deficiency causes Anemia while its accumulation causes Wilson disease (WD) [2]. Potentiometric determination of copper assumes high importance because of its widespread occurrence in the environment but the techniques which are used to determine Reactivity and biological uptake of copper are expensive and strongly influenced by its free ion concentration. Potentiometric measurements with a copper selective electrode allow direct determination of free copper ion concentration in water samples [3–6]. For this reason researchers attempted to develop sensors for its determination at high selectivity and sensitivity. In spite of the availability of a number of Cu(II) sensors, their use for Cu(II) estimation is limited, because they have shown interference by  $\text{K}^+$  [7],  $\text{Pb}^{2+}$  [8–12],  $\text{Fe}^{3+}$  [13],  $\text{Ni}^{2+}$  [14,15] and  $\text{Co}^{2+}$  [16] ions, working over narrow concentration range [8,17–19], and show non-Nernstian response [8,9,18], limited pH range [20] and high response time [18]. In order to achieve wider applicability, these limitations need to be removed or neutralized. Efforts in this direction are exerted to use different materials for preparing  $\text{Cu}^{2+}$  sensors. The essential requirements to impart selectivity to the ion sensor are to use specific ion-recognition elements which show strong affinity for the assayed metal ion and give poor response for all others [45]. Continuing efforts in this direction, we tested several compositions based on 3-(4-nitro phenyl azo)-pentane-2,4-dionas an ionophore for Cu(II). This work studies the preparation, characterization and analytical



applications of new Cu(II) ion-selective membrane electrode using complex of 3-(4-nitro phenyl azo)-pentane-2,4-dion and  $\text{Cu}^{+2}$  ion as electro active material in the membrane.

### Aim of the Present Work

Electrochemical sensors and detectors are very attractive devices for on-site and in-site monitoring of priority pollutants. Such devices are highly sensitive, selective toward electro active species, fast, accurate, compact, portable, and inexpensive. Several electrochemical devices, such as oxygen or pH electrodes, have been widely used for years for environmental analysis. Recent advances in electrochemical sensor technology have expanded the scope of electrochemical devices toward a wide range of organic and inorganic contaminants. The present work aims to present and characterize a new ion-selective electrodes for copper ions. The performance characteristics of these electrodes were fully characterized according to the International Union of Pure and Applied Chemistry (IUPAC) recommendations. The present work has focused on the following:

- Preparing Copper(II) ion selective PVC membrane electrode.
- Investigating the electrochemical performance characteristics of these electrodes according to the IUPAC recommendations.
- Using proposed electrodes for potentiometric determination of Copper in pure solutions and in real samples by applying standard additions method.

## 2. Materials and Methods

### Reagents and Materials

3-(4-nitrophenylazo)-pentane-2,4-dion, Sodium tetratphenylborate (NaTPB), dioctyl phthalate (DOP), dibutyl-butyl phthalate (DBP), and dioctyl sebacate (DOS) were purchased from Merck company. Copper nitrate trihydrate was purchased from Merck.

### Solutions

Deionized water was used for all preparations and throughout all experiments. Stock solution of Copper nitrate trihydrate solution ( $0.1 \text{ mol.L}^{-1}$ ) (merck) was prepared by dissolving 2.415 g  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in 100 ml deionized water, and nitric acid was added for reservation to prevent hydrolysis. It was also kept in glass bottles in refrigerator.

### Apparatus

For potential measurements DT9205A – DIGITAL MULTIMETER /mV meter was used. (Part No: E21M003,) TYPE: REF361 Ag/AgCl electrode was used as the outer reference electrode. EMF measurements were carried out using the following assembly: Ag/AgCl/ internal solution/membrane/sample /salt bredg KCl 1 M/Ag/AgCl.

### Synthesis of 3-(4-nitro phenyl azo)-pentane-2,4-dion

Aniline (0.91 ml , 10 mmol) or any of its derivatives for example: Para nitro aniline (1.38g , 10 mmol ) or Orto nitro aniline (1.38g , 10 mmol ) is dissolved in a mixture of distilled water and concentrated Chlorine water (5 ml HCl + 5 ml  $\text{H}_2\text{O}$ ) 1:1 with temperature within range (0-5) °C using ice bath , Sodium Nitrite solution is added to the previous solution by dissolving (0.69mmol, 10 mmol) in 2 ml of distilled water to make diazotizing process by adding Sodium Nitrite carefully within 30 minutes to have Diazonium salt solution which is added to Acetylacetone solution (1.02 ml , 10 mmol) in 7 ml of Ethanol , after that a precipitate is resulted which presents the aim dyer which is leached and dried to be used as organic bond to form complexities.

The melting point of the compound which is resulted from the use of Aniline was found to be 75 °C, and its color was light red (orange color agrees with the references). The melting point of the compound which is resulted from the use of Para nitro aniline was 180 °C and the color of the compound was brown.



### Preparation of complex

The aim ion solution (1 mmol) in 10ml of Ethanol is added to the solution of the organic bond which is the dyer (2 mmol) in 20 ml of Ethanol and Chloroform with a ratio 1:1, after that the mixture is heated by condensation for at least 3 hours to have a precipitate that presents a metal compound with the aim dyer which can be used as an electrolytic material to the sensitive membrane.

The melting point of the formed compound was found to be 82 °C, in the case of using Aniline in the manufacturing process was 80 °C and in the case of mutual using with Aniline (Para nitro aniline) was 182 °C.

The color of dyer became greenish with the existence of Cu ion compound and became brown colored with the existence of Pb ion compound.

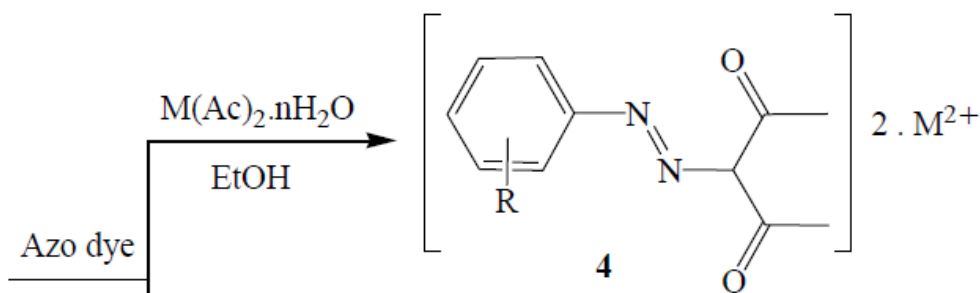


Figure 1: Complex between LP compound and metal ion (II)

Table 1: IR spectra for 3-(4-nitro phenyl azo)-pentane-2,4-dion

N=N	C=O	O-H	Bond type
1525	1670 - 1680	3440- 3450	cm <sup>-1</sup>
1523	1675	3447	cm <sup>-1</sup> reference

### Electrode Preparation

112 mg PVC powder, 224 mg plasticize dibutyl phthalate DBP 0.35 mg anionic additives sodium tetraphenylborate (NaTPB) and 0.35 mg complex were dissolved in 5 mL tetrahydrofuran (THF), and stirred vigorously for 20 min. The resulting mixture was transferred into a glass dish of 7 cm diameter. After evaporation of solvent (24 h), the formed transparent membrane of 0.3 mm thickness and 0.35 gram was removed carefully from the glass plate, then a 5mm diameter piece was cutout and glued with commercial liquid PVC to one end of a PVC tube with the same diameter. After 24 h the electrode was filled with an internal filling solution [ $1.00 \times 10^{-3} \text{M Cu(NO}_3)_2 \times 3\text{H}_2\text{O} + 0.1 \text{M KCl}$ ], preconditioned for 48 h in a  $1.00 \times 10^{-2} \text{M}$  solution of  $\text{Cu(NO}_3)_2 \times 3\text{H}_2\text{O}$  before use and stored in the same solution when not in use.

### Effect of Interfering Ions

The selectivity coefficient values were determined by applying the matched potential method [21, 22] that depends on the Nicolsky–Eisenman equation. This method was recommended in 2002 by IUPAC [23] as a method that gives analytically relevant practical selectivity coefficient values.

### Potentiometric Determination

The standard addition method was applied, by adding standard solution with known volumes of copper(II) to 50 ml water containing different amounts of the copper(II) samples and different wastewater samples. The change in mV reading was recorded for each increment and used to calculate the concentration of the copper(II) in sample solution using the following equation [24]:

$$C_x = C_s \left( \frac{V_s}{V_x + V_s} \right) \left( 10^{(\Delta E/S)} - \frac{V_x}{V_s + V_x} \right)^{-1}$$



where  $C_x$  is the concentration to be determined,  $V_x$  is the volume of the original sample solution,  $V_s$  and  $C_s$  are the volume and concentration of the standard solution added to the sample to be analyzed, respectively,  $\Delta E$  is the change in potential after addition of certain volume of standard solution, and  $S$  is the slope of the calibration graph.

### 3. Results and Discussion

3-(4-nitro phenyl azo)-pentane-2,4-dione Fig( 1) is one of the LPs dye kinds which can be used in molecular electronics due to their rich electronic components/photonic properties. Based on the unique configuration of LP and the extremely high stability of its metal-complexes, the compound is considered highly attractive material and used to develop potentiometric metal ion sensor. Incorporating LP in PVC plasticized with a solvent such as DBP resulted in a novel sensitive sensor to Cu(II) ions. The sensor exhibits relatively fast and stable Nernstian response over a wide concentration range with low limit of detection and high selectivity over wide variety of cations.

#### Composition of the PVC Membrane

##### Effect of the amount of ionophore

It is well known that the electrode response for specific metal ions depends on the amount and the nature of the electrode components [25]. The general characteristics of sensor are outlined by determining its sensitivity, detection limit, linear range and selectivity coefficients. Some important features of PVC electrode, such as the properties of the plasticizer, the PVC/ plasticizer ratio, the nature and amount of the ionophore, are reported to significantly influence the sensitivity and selectivity of the sensor. The influence of amount of complex of LP and  $Cu^{+2}$  as an ionophore on the potential response of the electrode was studied and the corresponding results are summarized in Table 2. Electrodes based on complex of 3-(4-nitro phenyl azo)-pentane-2,4-dione only and containing no additive exhibited non-Nernstian response towards Cu(II) and relatively high detection limits. The data in Table 2 clearly indicate that the membranes containing only complex, PVC, and DOP (Nos. 3 and 4) has shown response towards copper more than other membranes (1,2,5,6,7) but of narrow linear range,  $1 \times 10^{-6} - 10^{-3} \text{ mol.L}^{-1}$  and detection limit of about  $1 \times 10^{-4} - 10^{-1} \text{ mol L}^{-1}$ , and slope  $16.4 - 21.82 \text{ mv/decade}$ , respectively. The optimization of perm-selectivity of sensors is known to be highly dependent on the incorporation of additional membrane compounds [26–28]. The data which are given in Table (2) revealed that incorporating NaTPB in the membrane improves the performance characteristics of the electrode in terms of slope, detection limit and linear range. Thus, the slope of the electrode (No. 8,10,11,14) increased 27 -30 mv/decade for the same amount of ionophore with a wider linear range, and the detection limit decreased to  $7 \times 10^{-6} \text{ mol L}^{-1}$  fig (2).

**Table 2:** Compositions, concentrations and slope of Copper(II)-membrane electrodes

No	Composition %				Slope mv	Concentration range M
	Ionophore	PVC	Plasticizer	Additive		
1	1	33	66.0 DOP	--	9.89	$1 \times 10^{-7} - 10^{-4}$
2	2	33	65.0 DOP	--	--	--
3	3	33	64.0 DOP	--	16.4	$1 \times 10^{-6} - 10^{-3}$
4	4	32	64.0 DOP	--	21.82	$1 \times 10^{-4} - 10^{-1}$
5	5	32	63.0 DOP	--	11.89	$5 \times 10^{-7} - 10^{-3}$
6	6	32	62.0 DOP	--	13.33	$1 \times 10^{-6} - 10^{-1}$
7	7	31	62.0 DOP	--	11.62	$5 \times 10^{-7} - 10^{-3}$
8	3	32.4	64.0 DOP	0.6 NaTPB	30.03	$3 \times 10^{-6} - 10^{-1}$
9	4	31.4	64.0 DOP	0.6 NaTPB	27.93	$3 \times 10^{-6} - 10^{-1}$
10	3	32	64.0 DOP	1 NaTPB	29.02	$1 \times 10^{-4} - 10^{-1}$
11	4	31	64.0 DOP	1 NaTPB	28.86	$1 \times 10^{-4} - 10^{-1}$
12	3	32.4	64.0 DBP	0.6 NaTPB	26.6	$1 \times 10^{-5} - 10^{-1}$
13	4	31.4	64.0 DBP	0.6 NaTPB	26.1	$1 \times 10^{-4} - 10^{-1}$
14	3	32	64.0 DBP	1 NaTPB	28.23	$1 \times 10^{-6} - 10^{-1}$
15	3	32.4	64.0 DOS	0.6 NaTPB	20.9	$1 \times 10^{-5} - 10^{-1}$



16	4	31.4	64.0 DOS	0.6 NaTPB	23.4	$1 \times 10^{-5} - 10^{-1}$
17	3	32	64.0 DOS	1 NaTPB	27.28	$1 \times 10^{-4} - 10^{-1}$

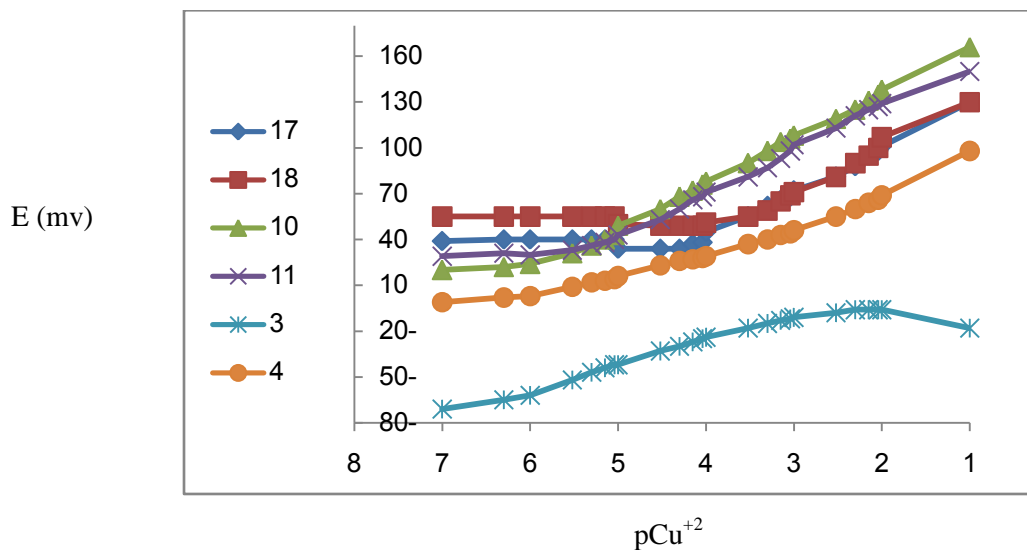


Figure 2: Potential response of Cu(II)-membranes electrodes (3,4,10,11,17,18) of different composition

### Effect of plasticizer

The influence of solvent mediator (plasticizer) type and concentration on the characteristics of the Cu(II)- membrane electrode was investigated using three solvents with different polarities DBP, DOP, DOS, fig (3). The presence of plasticizers does not only improve the workability of the sensor, but also contributes significantly to the improvement of the working concentration range, stability and life span of the electrode. The data which are given in Table (2) showed that the membranes incorporating DOP, DBP, DOS (No.10,14,17) fig(3) as solvent mediator had the best response towards copper gave Nernstian responses over the concentration range  $1 \times 10^{-6} - 1 \times 10^{-1} \text{ mol.L}^{-1}$ ,  $1 \times 10^{-4} - 1 \times 10^{-1}$ ,  $1 \times 10^{-4} - 10^{-1}$ , respectively, the membranes incorporating DOP, (No.8,9) as solvent mediator had the best response towards copper gave Nernstian responses over the concentration range  $3 \times 10^{-6} - 1 \times 10^{-1} \text{ mol.L}^{-1}$ , comparing with DBP, DOS at the same additive (No.12,13,15,16). The Cu(II)-membrane electrode with DBP as solvent mediator and 1% NaTPB as additive produced the best response, this is likely due to high lipophilicity, relatively high molecular weight and low dielectric constant of this plasticizer which enables salvation and mobility of ionophore through the membrane.

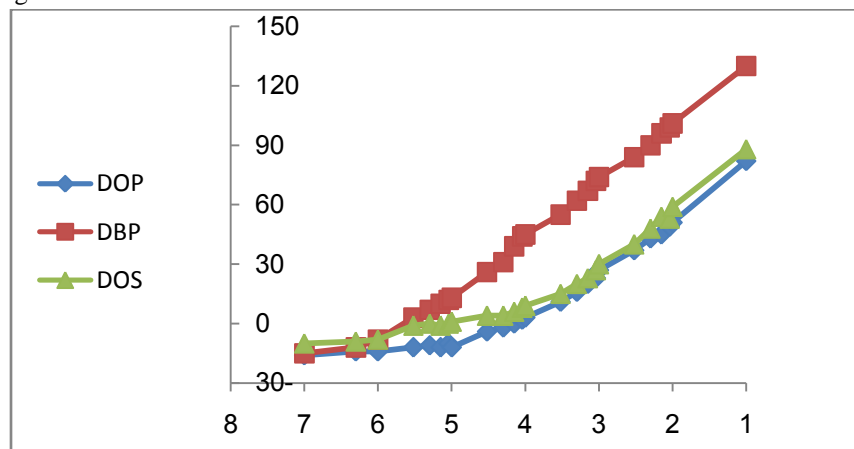


Figure 3: Effect of plasticizers on the response of Cu(II)-membrane electrode (32% PVC, 64% plasticizer, 3% complex as ionophore, 3% NaTPB as additive)

### Effect of Additives

The effect of anionic additives have been studied since the lipophilic negatively charged additives improve the potentiometric behavior of certain cation-selective electrodes, not only by reducing the ohmic resistance and improving the response behavior and selectivity [29,30] but also in cases, where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the electrode [28,31]. For this purpose, NaTPB were examined as anionic additives in the copper selective electrodes. The data in Table 2 revealed that the presence of NaTPB in the membrane containing 3.0% ionophore (complex) and DBP plasticizer improved the slope of the electrode as mentioned before the membrane No.( 14) with composition of 3.0% ionophore, 32.0% PVC, 64.0% DBP and 1.0% NaTPB which happens in the best sensitivity with a Nernstian slope of 28.23 mV/decade concentration of Cu(II) ions over a wide dynamic concentration range  $1 \times 10^{-6} - 1 \times 10^{-1} \text{ mol.L}^{-1}$ . Therefore, this composition was selected as the optimum one to study various operation parameters of the electrode.

### Effect of pH

The effect of pH on the response of membrane electrode was examined by use of  $1.0 \times 10^{-3} - 1.0 \times 10^{-1} \text{ M Cu}^{2+}$  solution over a pH range of 2.0–9.0. The pH was adjusted by introducing small drops of nitric acid (0.1 M) or sodium hydroxide (0.1 M). The results are shown in Fig (3), which indicates that potential remained constant over a pH range of 3–6, beyond which the potential changed considerably Fig (4). The observed drift at higher pH values could be due to the formation of some hydroxyl complexes of  $\text{Cu}^{2+}$  ion in solution [32-36]. At low pH, the  $\text{H}^+$  ions interference and membrane sensor responds to the hydrogen ions.

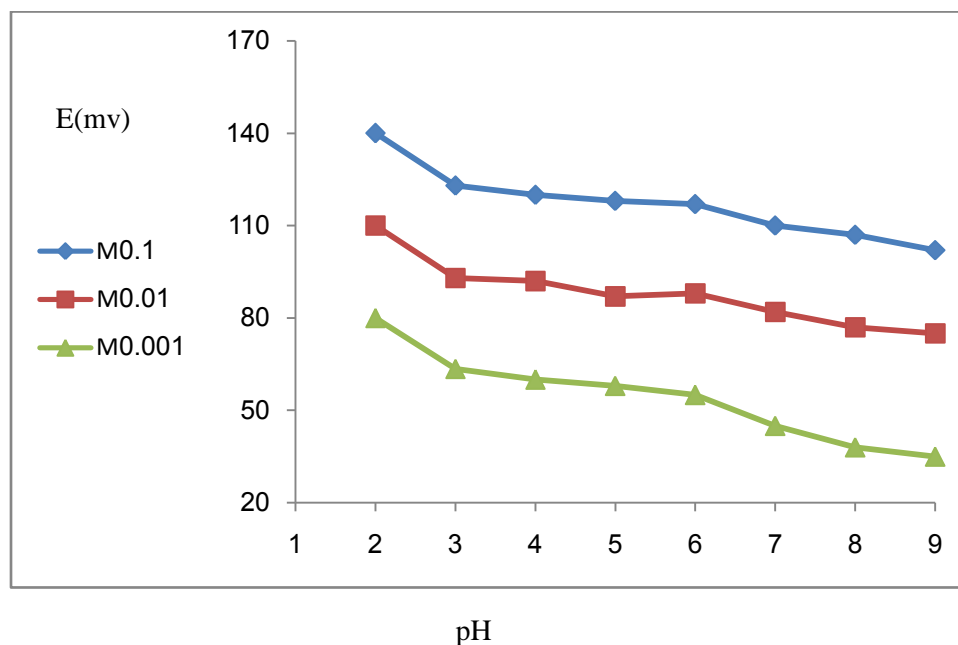


Figure 4: Effect of pH of test  $\text{Cu}(\text{NO}_3)_2$  solution on Cu(II)-membrane electrode (32% PVC, 64%DBP, 3% complex as ionophore, 3% NaTPB as additive)

### Dynamic response and life time

For analytical applications, the dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded by fast stepwise changing of the  $\text{Cu}^{2+}$  concentration from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-3} \text{ M}$ . The actual potential versus time Fig.(5) shows that the dynamic response time was 15 s. This short response time is most probably due to the fast exchange kinetics of complexation decomplexation of  $\text{Cu}^{2+}$  ion with



the LP ionophore on the tested solution–membrane interface [33]. The tests show that the membrane electrode with the best characteristics (No 14 from Table 1) can be used for at least 2 months without any measurable response decay. After this time the Nernstian slope and detection limit of the sensor decrease and increase, respectively. It was established that the leaching of plasticizer, carrier, or ionic site from the polymeric membrane is the primary reason for the limit in the sensors' lifetime [37–42]; therefore, we can suppose that these factors also influence the decay of our electrode.

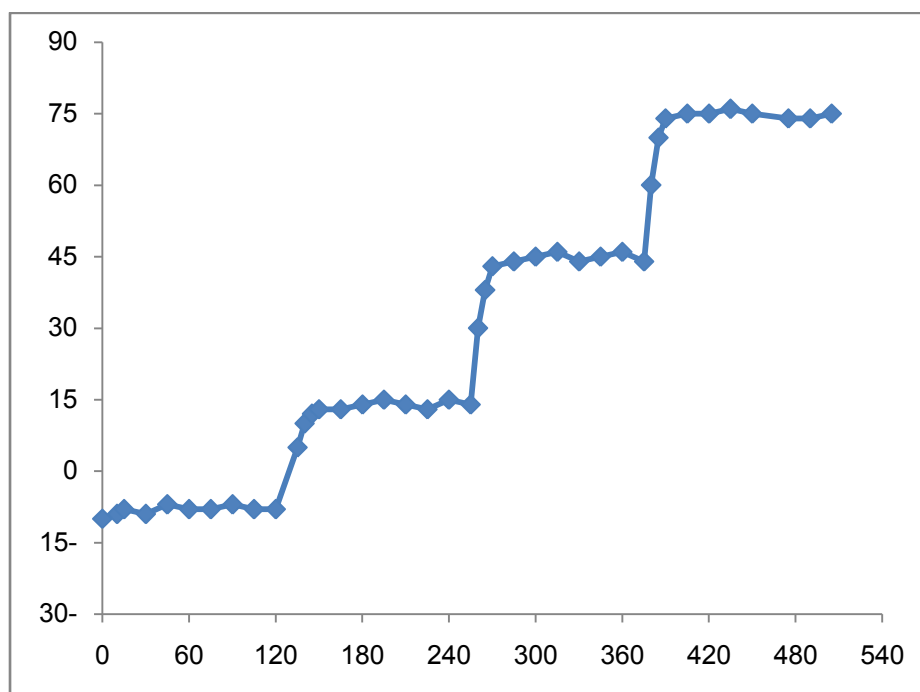


Figure 5: Potential–time plot for the response of Cu(II)-membrane electrode (32% PVC, 64%DBP, 3% complex as ionophore, 3% NaTPB as additive) for step changes in concentration of Cu(II): (A)  $1.0 \times 10^{-6}$  M, (B)  $1.0 \times 10^{-5}$  M, (C)  $1.0 \times 10^{-4}$  M, (D)  $1.0 \times 10^{-3}$  M

### Selectivity of Cu(II)-membrane electrode

The selectivity coefficient of an electrode, as one of the most important characteristics, is defined by its relative response to the primary ion over the other ions present in the solution [31]. The selectivity coefficients of the proposed electrode were evaluated by the matched potential method (MPM) [22, 43]. The results of selectivity coefficients were obtained for the Cu(II)-membrane electrode which are given in Table (3). The values of  $K_{A,B}^{MPM}$  are all in the order of  $10^{-2}$  which means that no interference occurred by any of the examined cations. According to this method, the activity of each analyte was increased from  $a_A$  (reference solution) to  $a'_A$ , and the change in potential ( $\Delta E$ ) corresponding to the increase of this activity which is measured. Next, a solution of an interfering ion of concentration  $a_B$  in the range of ( $1.0 \times 10^{-2}$ - $10^{-1}$  M) is added to a new analyte reference solution until the same potential change ( $\Delta E$ ) is recorded. The selectivity factor  $K_{A,B}^{MPM}$  for each interferent was calculated using the following equation:

$$K_{A,B}^{MPM} = (a'_A - a_A) / a_B$$





**Table 3:** Selectivity coefficients of various interfering ions for Cu(II)- membrane electrode (32% PVC , 64%DBP , 3% complex as ionophore, 3% NaTPB as additive)

Interfering ion	$K_{Cu(II),j}^{MPM}$	Interfering ion	$K_{Cu(II),j}^{MPM}$
Na <sup>+</sup>	$1.8 \times 10^{-4}$	Ni <sup>2+</sup>	$5.07 \times 10^{-3}$
K <sup>+</sup>	$1.75 \times 10^{-4}$	Cd <sup>2+</sup>	$7.00 \times 10^{-3}$
Ca <sup>2+</sup>	$1.6 \times 10^{-4}$	Zn <sup>2+</sup>	$8.43 \times 10^{-3}$
Mg <sup>2+</sup>	$1.52 \times 10^{-2}$	Pb <sup>2+</sup>	$5.07 \times 10^{-2}$
Ba <sup>2+</sup>	$3.43 \times 10^{-3}$	Hg <sup>+2</sup>	$1.34 \times 10^{-2}$
Co <sup>2+</sup>	$6.32 \times 10^{-2}$		

### Analytical Applications

The utility of the proposed electrode was further investigated to determine copper concentration in different samples. The Cu(II)-membrane electrode was used successfully to determine Cu(II) ions in different standard and environmental samples. Determination of Cu(II) in the previously mentioned samples was performed using the standard addition method. We had made experiment three times for the statistical treatment of the results. Different samples were analyzed namely standard samples and wastewater (Table 4, 5). The samples were acidified with HNO<sub>3</sub> acid to dissociate the metal-complexes then adjusted to pH 4.0–5.0 using acetate buffers. The amount of copper was measured by the proposed copper selective electrode and by atomic absorption spectrometry (AAS). The results which are given in Table 4 shows clearly that there is a good agreement between the results of the proposed sensor and those which are obtained from AAS method. The recovery ranges are between 99% and 105%.

**Table 4:** Determination of copper in pure solution using the standard addition method by proposed electrode

Taken, mol.l <sup>-1</sup>	Found, mol.l <sup>-1</sup>	RSD %	Recovery, %	Confidence limits CL
$1 \times 10^{-3}$	$0.99 \times 10^{-3}$	1.06	99	$0.99 \times 10^{-3} \pm 2.6 \times 10^{-5}$
$1 \times 10^{-4}$	$1.056 \times 10^{-4}$	1.972	105.6	$1.05 \times 10^{-4} \pm 5.16 \times 10^{-6}$
$1 \times 10^{-5}$	$1.033 \times 10^{-5}$	1.479	103.3	$1.033 \times 10^{-5} \pm 6.57 \times 10^{-7}$

**Table 5:** Determination of copper in waste water samples potentiometrically using the proposed Cu(II)- membrane electrode and by AAS

Sample	Found Potentiometrically	Found by AAS method
1	0.121	0.119
2	0.0816	0.080
3	0.1567	0.155

### Statistical Treatment of Data

The calculated F values [44] were less than the critical F value (19) where  $\nu_1 = 2$  at 95% confidence level. t-Test [44] was also performed at 95% confidence level (tabulated  $t = 4.303$ ) and the results are shown in Table 6. The method which applies the constructed electrode does not exhibit significant differences in comparison with the official method (AAS) which reflects the accuracy and precision of this method.

**Table 6:** Statistical treatment of data obtained for the determination of copper using copper membrane electrode in real samples in comparison with the AAS methods

Sample	SD <sub>1</sub> (Cu-ISE)	SD <sub>2</sub> (AAS)	F-test	t-test
1	$1.41 \times 10^{-3}$	$2 \times 10^{-3}$	0.4970	2.456
2	$2.517 \times 10^{-3}$	$6 \times 10^{-3}$	0.1759	1.10
3	$0.377 \times 10^{-3}$	$1 \times 10^{-3}$	0.1421	0.0119





#### 4. Conclusion

The membrane electrode incorporating 3-(4-nitrophenylazo)-pentane-2,4-dione as electro active phase can be used to develop copper ion-selective electrode. The electrode has the composition of 3.0% complex, 32.0% PVC, 64.0% DBP and 1.0% NaTImB responds to Cu(II) ions in a Nernstian behavior with slope of 28.23 mV/decade with limit of detection of  $7 \times 10^{-7}$  mol L<sup>-1</sup>. The electrode is characterized by a relatively fast response, reasonable long-term stability and responsive potential stability. Most of metal ions do not affect the selectivity of the copper electrode. The electrode was applied to direct determination of Cu(II) ions in water samples. Table 7 shows the comparison of the performance characteristics of the proposed sensor with those of the best copper sensors which were previously prepared. From the interference study it is obvious that the proposed sensor has no interference from many ions which cause serious interference for other similar electrodes such as K<sup>+</sup> [7], Pb<sup>2+</sup> [8–12], Ni<sup>2+</sup> [14,15] and Co<sup>2+</sup> ions [16]. Wider working concentration range, and lower limit of detection were also offered by the proposed sensor compared to some of those previously suggested [8,14,15]. The response time of the present sensor is smaller than many of the reported electrodes [6].

**Table 7:** Comparison of the performance characteristics of the proposed sensor with those of the best previously prepared copper sensors

Ionophore	Slope mv/decade	Working concentration range M	Detectio n limit M	Respo nse time S	Interferi ng ions	Re
diaminopyridine and o-vanilin Schiff base	29.6	$5.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$	$4.7 \times 10^{-6}$	<30	Hg <sup>2+</sup> , Ag <sup>+</sup>	5
tetraphenyl-octaaza-cyclotetra-deca-dithizone-tetraene	26.2	$1.0 \times 10^{-5}$ - $1.0 \times 10^{-2}$	$2.5 \times 10^{-6}$	2–18	Hg <sup>2+</sup> , Cl <sup>-</sup>	17
2,2'-dithio-dianiline	30±1	$7.0 \times 10^{-7}$ - $5.0 \times 10^{-2}$	$6.0 \times 10^{-7}$	10	Pd <sup>2+</sup> at high conc.	18
dihydro-trimethyl--pyrimidine thione	30±2	$9.8 \times 10^{-7}$ - $7.6 \times 10^{-2}$	$7.0 \times 10^{-7}$	45	--	19
dithiane,2-(4-methoxyphenyl)	29.5±1	$3.0 \times 10^{-6}$ - $5.0 \times 10^{-2}$	$1.0 \times 10^{-6}$	5	--	16
ethandiyl-bis(nitrilomethylidene) cresole	29.2	$1.0 \times 10^{-5}$ - $1.0 \times 10^{-1}$	$3.9 \times 10^{-6}$	10	Ni <sup>2+</sup>	20
tetrakis-(diallyl methyl silyl)phenyl] porphyrin	29.3	$4.4 \times 10^{-6}$ - $1.0 \times 10^{-1}$	$4.2 \times 10^{-6}$	8	Ni <sup>2+</sup>	22
pyridinyl)-2H-pyridotriazine-dithione	29.5	$5.0 \times 10^{-8}$ - $1.0 \times 10^{-2}$	$4.0 \times 10^{-8}$	12	Co <sup>2+</sup> , Ag <sup>+</sup>	23
Cyclic tetrapeptide derivative	25.9-30.2	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-2}$	$7.6 \times 10^{-7}$	15	Pb <sup>2+</sup>	24
3-(4-nitro phenyl azo)-pentane-2,4-dion	<b>28.23</b>	$1 \times 10^{-6}$ – $1 \times 10^{-1}$	$7 \times 10^{-7}$	15	--	Thise work

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