

## Preparation of a New selective PVC Membrane Electrode for Copper(II) Ion Based on Complex of 1,3-diphenyl-5-(P-nitrophenyl) Formazan as Ionophore with Copper(II).

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### □ ABSTRACT □

A new selective PVC (poly vinyl chloride) membrane electrode for Copper(II) ion was prepared depending on a complex of 1,3-diphenyl-5-(P-nitrophenyl) formazan (FM) as ionophore with copper(II). The best performance was obtained by a membrane electrode with the composition: PVC as matrix (32 %), (FM) as ionophore (3 %), DBP (Dibutyl phthalate) as plasticizer (64%), and NaTBP (Sodium tetraphenylborate) as anionic additive (1%). This electrode exhibited a linear potential response to copper(II) in the concentration 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, a response time of about 15 secs, and a life time which exceeded two months over a wide range of PH:3-6. The suggested PVC electrode had a high selectivity for copper over a large number of alkaline and alkaline earth ions and some heavy metals ions. Described membrane electrode could be successfully used in analytical measurements by direct potentiometry for the determination of  $\text{Cu}^{+2}$  in standard and real sample solutions.

**Keywords:** copper(II), ( ion selective electrode ISE) , formazan, polymer membrane electrodes, potentiometry

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## تحضير الكترود بغشاء PVC جديد انتقائي لأيون النحاس (II) يعتمد على معقد 1, 3- ثنائي فنيل- 5- (p- نترو فنيل) فورمازان كمادة فعالة الكتروكيميائيا مع أيون النحاس (II).

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### □ ملخص □

تم في هذا البحث تحضير الكترود غشاء بولي قثيل كلوريد (PVC) جديد انتقائي لأيون النحاس  $Cu^{2+}$  بالاعتماد على معقد النحاس (II) مع 1 - 3- ثنائي فنيل - 5- (p- نترو فنيل) فورمازان كمادة فعالة كهروكيميائيا ، وتبين من خلال الدراسة أن الغشاء ذو التركيب (32%) PVC ، 3% مادة فعالة كهروكيميائيا ، 64% مادة ملدنة DBP (ثنائي بوتيل فتالات)، 1% NaTPB (صوديوم رباعي فنيل بورات) كإضافة هو الأفضل، حيث يبدي استجابته جهدية (نيرنيستية) خطية تجاه أيون النحاس  $Cu^{2+}$  ضمن مجال خطي واسع ( $1.0 \times 10^{-6}$  -  $1.0 \times 10^{-1}$ ) مول/لتر وميل 28.23 mv/decade بحد كشف بحدود  $7 \times 10^{-7}$  M و زمن استجابة بحدود 15 sec. وزمن حياة طويل يتجاوز الشهرين ، كذلك ضمن مجال واسع pH بين 3 - 6 ، وتبين من خلال حساب معاملات الانتقائية باستخدام طريقة الكمون الموافق Matched Potential Method (MPM)، إن الكترود غشاء PVC المقترح يتمتع بانتقائية عالية لأيونات  $Cu^{2+}$  بوجود العديد من الايونات القلوية والقلوية الترابية وبعض أيونات المعادن الثقيلة الأخرى، واستخدم الكترود المقترح بنجاح في تحديد تركيز النحاس  $Cu^{2+}$  في عينات قياسية وأخرى واقعية من البيئة المائية .

الكلمات المفتاحية : ايون النحاس (II) ، ISE ، أصبغة الفورمازان ، الكترود غشاء PVC ، المعايير الكميونية.

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## Introduction:

Copper is an essential element and is also toxic at high concentration, the maximum tolerable level for copper is  $2.0 \text{ mg.L}^{-1}$  [1]. Determination of copper assumes importance in view of its widespread occurrence in environmental samples. As such large concentrations of copper can be tolerated by human beings, however, excessive dosage and long term exposure may cause irritation of the nose, mouth and eyes, as well as headache and stomach ache [2]. 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 with high selectivity and sensitivity. In spite of availability of a number of Cu(II) sensors, their use for Cu(II) estimation is limited, because they have shown interference by  $\text{K}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  [7-16] ions, and working over a 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 applications, 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 determined metal ion and give poor response for all others. Continuing efforts in this direction was achieved in this study using several compositions based on 1,3-diphenyl-5-(P-nitrophenyl) formazan (FM) as an ionophore for Cu(II). This work describes the preparation, characterization and analytical applications of new Cu(II) ion-selective membrane electrode using complex of 1,3-diphenyl-5-(P-nitrophenyl) formazan (FM) and  $\text{Cu}^{+2}$  ion as an 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 electroactive species, fast, accurate, compact, portable, and inexpensive. Several electrochemical devices, such as oxygen or pH electrodes, have been widely used for many years in the 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 display and describe 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:

- 1- Preparation of a new selective PVC membrane electrode for Copper(II) ion.
- 2- Investigate the electrochemical performance characteristics of these electrodes according to the IUPAC recommendations.
- 3- Use of the proposed electrodes for potentiometric determination of Copper in pure solutions and in real samples by applying standard addition method.

## 2. Experimental

### 2.1. Reagents and materials

1,3-diphenyl-5-(P-nitrophenyl) formazan, have been synthesized Sodium tetratphenylborate  $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$  (NaTPB), dioctyl phthalate  $\text{C}_{26}\text{H}_{38}\text{O}_4$  (DOP), dibutyl-butyl phthalate  $\text{C}_{16}\text{H}_{22}\text{O}_4$  (DBP), and dioctyl sebacate  $\text{C}_{26}\text{H}_{50}\text{O}_4$  (DOS), Copper nitrate trihydrate  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , were purchased from merck company.

## 2.2. Solutions

Deionized water was used for all preparations and throughout all experiments. Stock solution of Copper nitrate trihydrate ( $0.1 \text{ mol.L}^{-1}$ ) (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 to prevent hydrolysis and finally kept in a glass bottle in refrigerator (at  $10^0$ ).

## 2.3. 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 sulation/membrane/sample solution /salt bridge KCl  $1 \text{ mol.L}^{-1}$  / Ag/AgCl**

## 2.4. Synthesis of 1,3-diphenyl-5-(p-nitrophenyl)Formazan

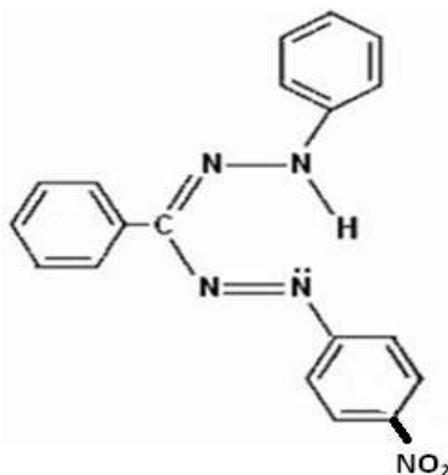
For the synthesis of 1,3-diphenyl-5-(P-nitrophenyl) formazan, Figure 1. Solution of benzaldehyde (0.02 mol , 2.12g , 2.04 ml ) in 12.5 mL methanol was gradually added to phenylhydrazine (0.02 mol , 2.16 g , 1.96 ml ) with constant stirring at pH 5-6. The reaction was completed in 45 min. The resulting yellow hydrazone was left on the bench over night, then filtered and recrystallized from methanol. The benzaldehyde phenylhydrazine (0.01 mol) was dissolved in methanol (50 mL). In another flask, p-nitrobenzediazonium chloride solution was prepared using p-nitroaniline (0.01 mol), concentrated HCl (2.5 mL) and sodium nitrite (0.75 g) at  $0-5^\circ\text{C}$ . This solution was added to the benzaldehyde phenylhydrazine solutions drop wisely with constant stirring to form compound. The solution was stirred for 2 h at the same temperature and kept in a refrigerator for 2 days. Dye was filtered and then washed with water and methanol. The compound was recrystallised from dichloromethane. Red colored crystal; m.p  $183^0-189^0$ ; yield 74%. IR spectra for  $\text{C}_{19}\text{H}_{15}\text{O}_2\text{N}_5$  , shown in table (1) , The C = N bands observed at  $1592 \text{ cm}^{-1}$  , The N–H band observed at  $3448 \text{ cm}^{-1}$  , N = N band observed at  $1492 - 1564 \text{ cm}^{-1}$  , C = C observed at  $1517-1637 \text{ cm}^{-1}$  and CNNC skeleton stretching peaks were observed at  $691-846 \text{ cm}^{-1}$ .

## 2.5. Preparation of the copper complex

The 1,3-diphenyl-5-(p-nitrophenyl) formazan (0.002 mol) was dissolved in boiling acetone solution (50 mL) and Copper nitrate trihydrate (0.002 mol) was dissolved in a mixture of water and ethanol (1:1), and added slowly with stirring to Cu(II) solution. The precipitated complex was collected, washed with a mixture of water and ethanol (1:1) , then dried, and recrystallised from ethanol.

**Table(1) :IR spectra for 1,3-diphenyl-5-(p-nitrophenyl) formazan  $\text{C}_{19}\text{H}_{15}\text{O}_2\text{N}_5$  (in KBr,  $\text{cm}^{-1}$ ).**

group	N-H	CNNC structural vibration	Aromatic C=C	N=N	C=N
$\text{cm}^{-1}$	3448	691-846	1517-1637	1492-1564	1592



Figure(1): structure of ionophor 1,3-diphenyl-5-p-nitro phenyl formazan

### 2.6. Electrode preparation

112 mg PVC powder, 224 mg plasticizer dibutyl phthalate (DBP), 0.35 mg anionic additives sodium tetraphenylborate (NaTPB) and 0.35 mg ionophore (complex of 1,3-diphenyl-5-(P-nitrophenyl) formazan with Copper(II) ) 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 for (24 h), the formed transparent membrane of 0.3 mm thickness was removed carefully from the glass plate, then a 5 mm diameter piece was cut out and glued with commercial liquid PVC to one end of a PVC tube with the same diameter. After 24 h the tube was filled with an internal filling solution [ $1.00 \times 10^{-3} \text{ mol L}^{-1} \text{ Cu}(\text{NO}_3)_2 \cdot 3 \text{ H}_2\text{O} + 0.1 \text{ mol L}^{-1} \text{ KCl}$ ], The electrode was finally conditioned for 48 hours by soaking in  $1 \times 10^{-2} \text{ M}$  copper(II) solution and stored in the same solution when it is not in use.

### 2.7. Effect of interfering ions

The selectivity coefficient values were determined by applying the matched potential method [21,22] that depends neither on the Nicolsky–Eisenman equation nor on any of its modifications. This method was recommended in 2002 by IUPAC [23] as a method that gives analytically relevant practical selectivity coefficient values.

### 2.8. Potentiometric determination

The standard addition method was applied, in which a known incremental change is achieved through the addition of standard solution to the sample. This was achieved by adding known volumes of a standard copper (II) solution 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,  $\Delta E$  is the change in potential after the

addition of a certain volume of the standard solution, and S is the slope of the calibration curve fig (2).

### 3. Results and discussion

1,3-diphenyl-5-p-nitrophenyl formazan Fig.(1) is one of the formazan dyes which are promising to be used in molecular electronics due to their rich electronic components/photonic properties. Based on the unique configuration of formazan and the extremely high stability of its metal-complexes, the compound is considered as a highly attractive material for developing potentiometric metal ion sensor. Incorporating formazan 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 a low detection limit and high selectivity over wide variety of cations.

#### 3.1. Composition of the PVC Membrane

##### 3.1.1. 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 be significantly influence the sensitivity and the selectivity of the sensor. The influence of the complex amount of FM and Cu<sup>2+</sup> 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 1,3-diphenyl-5-p-nitrophenyl formazan 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 mv/decade, respectively. The optimization of the selectivity of sensors is known to be highly dependent on the incorporation of additional membrane compounds [26–28]. The data 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 electrodes (No. 8,10,11,14,17) increased 27 -30 mV/decade for the same amount of ionophore with a wider linear range, against detection limit which decreased to  $7 \times 10^{-6} \text{ mol L}^{-1}$  Fig. (3).

Table (2) Compositions of Copper (II)-membrane electrodes.

No	Composition %				Slope mv	Concentration range mol.l <sup>-1</sup>
	Ionophor	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	$1 \times 10^{-4} - 10^{-1}$

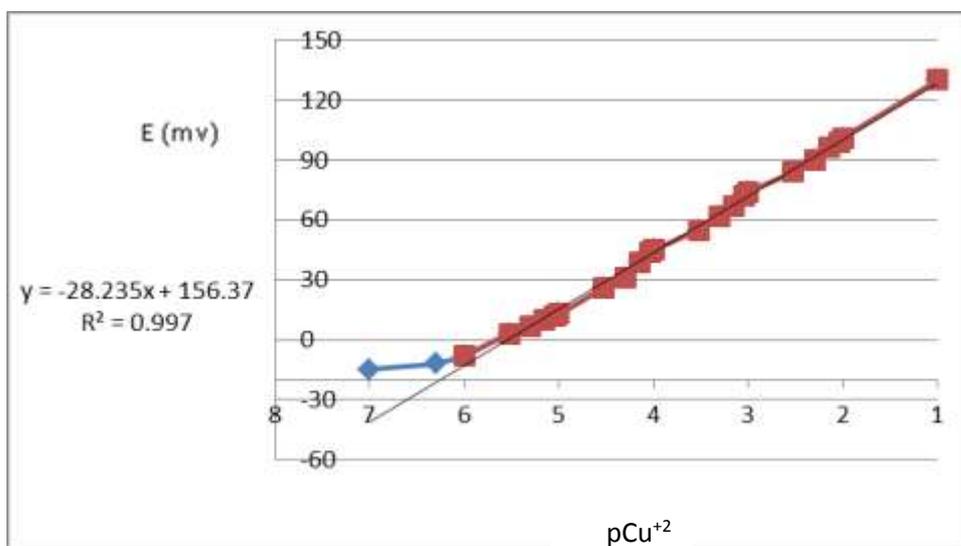


Fig. (2): calibration curve of Cu(II)-membrane electrode (No 14) .

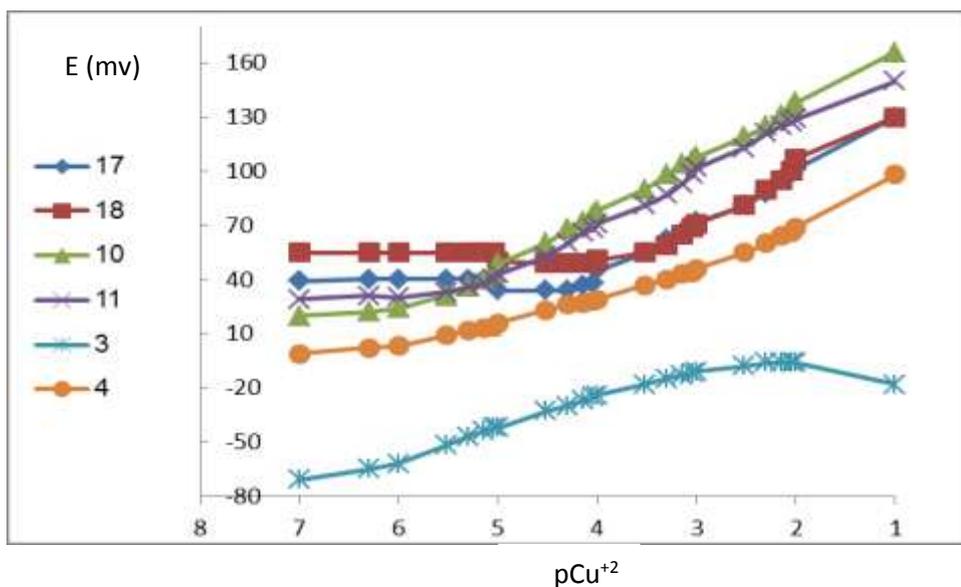


Fig. (3): Potential response of Cu(II)-membrane electrodes (3,4,10,11,17,18) of different composition.

### 3.1.2. Effect of plasticizer

The influence of solvent mediator (plasticizer) type on the characteristics of the Cu(II)-membrane electrode was investigated using three solvents with different polarities DBP, DOP, DOS, Fig. (4). The presence of plasticizers dose not only improve the workability of the sensor, but also contribute significantly to the improvement of the working concentration range, stability and life span of the electrode. The data given in Table (2) and fig (4) showed that the membranes incorporating DOP, DBP, DOS (No.10, 14,17) as solvent mediator has the best response towards copper producing Nernstian responses over the concentration range  $1 \times 10^{-4} - 1 \times 10^{-1}$ ,  $1 \times 10^{-6} - 1 \times 10^{-1}$ ,  $1 \times 10^{-4} - 1 \times 10^{-1}$  mol.L<sup>-1</sup>, respectively. The membranes incorporating DOP, (No.8,9) as plasticizer have the best response towards copper giving Nernstian responses over the concentration range  $3 \times 10^{-6} - 1 \times 10^{-1}$  mol.L<sup>-1</sup>, compared 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 lipophilic 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 solvation of ions and mobility of ionophore through the membrane.

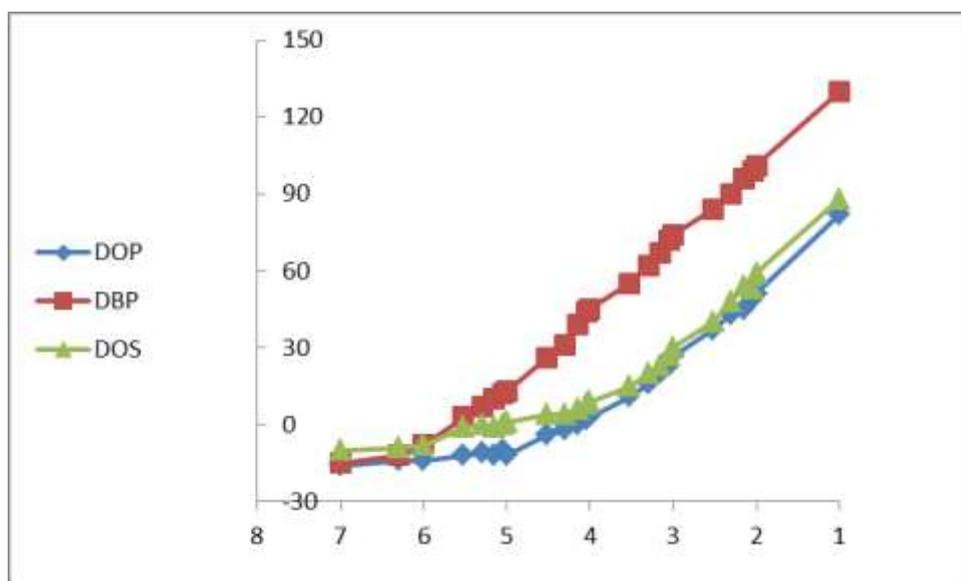


Fig. 4. Effect of plasticizers on the response of Cu(II)-membran electrode (32% PVC , 64%plasticizer , 3% complex as ionophor, 3% NaTPB as addative ).

### 3.1.3. Effect of additives

The effect of anionic additives was studied since it shows that 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 ionophor 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 shows that the composition of 3.0% ionophor, 32.0% PVC, 64.0% DBP and 1.0% NaTPB improved the slope of the electrode as mentioned before No.(14) with the best sensitivity of a Nernstian slope of 28.23 mV/decade concentration of Cu(II) ions over a wide dynamic concentration range  $1 \times 10^{-6} - 1 \times 10^{-1}$  mol.L<sup>-1</sup>. Therefore, this composition

was selected to be the optimum one in order to study the various operation parameters of the electrode.

### 3.2. Effect of pH

The effect of pH on the response of membrane electrode was examined by use of  $1.0 \times 10^{-3} - 1.0 \times 10^{-1} \text{ mol L}^{-1} \text{ Cu}^{2+}$  solution over a pH range of 2.0–9.0. The pH was adjusted by dropping nitric acid ( $0.1 \text{ mol L}^{-1}$ ) or sodium hydroxide ( $0.1 \text{ mol L}^{-1}$ ) to the medium. The results are shown in Fig.(5), which indicates that the potential remained constant over a range of pH: 3–6, beyond which the potential changed considerably, Fig. 5. The observed drift at higher pH values could be due to the formation of some hydroxyl complexes of  $\text{Cu}^{2+}$  ion in solution [32,33,34,35,36]. At low pH, the  $\text{H}^+$  ions interference and membrane sensor responds to the hydrogen ions.

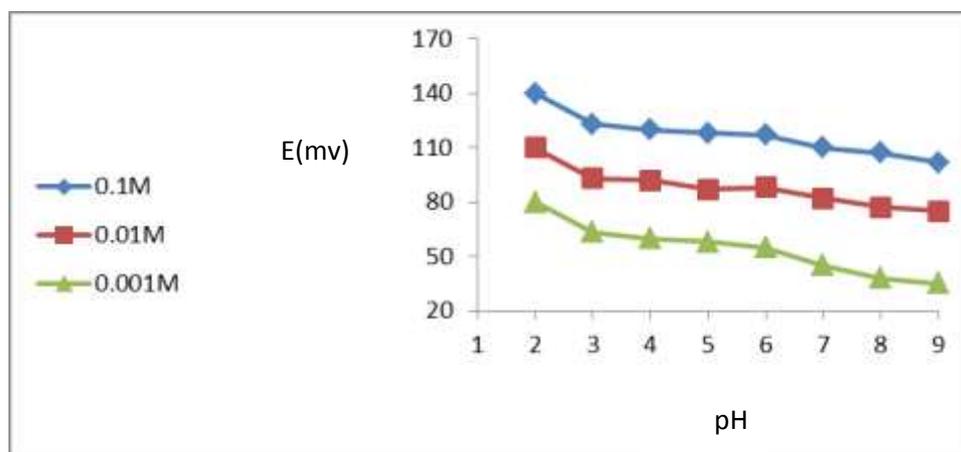


Fig. 5. Effect of pH of test  $\text{Cu}(\text{NO}_3)_2$  solution on Cu(II)-membrane electrode (32% PVC, 64%DBP, 3% complex as ionophore, 3% NaTPB as additive).

### 3.4. 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  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ . The actual potential versus time Fig.(6) 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 FM ionophore on the tested solution–membrane interface [33]. The tests show that the membrane electrode with the best characteristics (No 14 in Table 2) 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 of the sensors' lifetime [37–42]; therefore, we can suppose that these factors also influence the decay of our electrode.

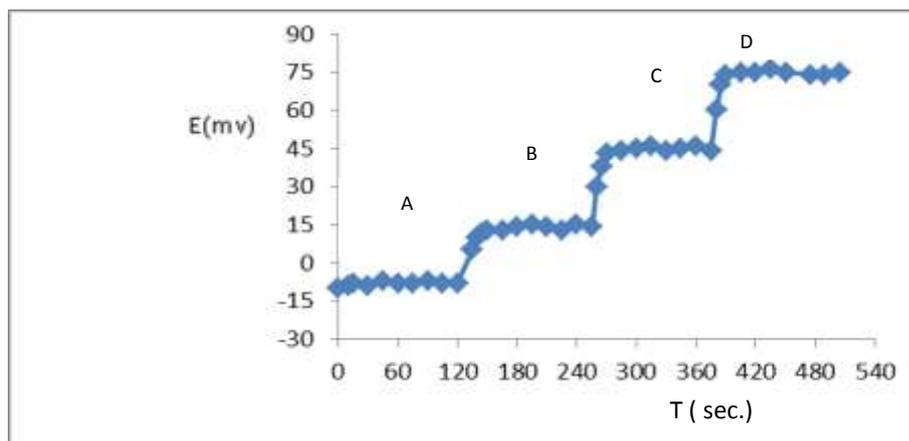


Fig.( 6). Potential–time plot for the response of Cu(II)-membrane electrode (32% PVC , 64%DBP , 3% complex as ionophor, 3% NaTPB as additive) for step changes in concentration of Cu(II): (A)  $1.0 \times 10^{-6}$  M, (B)  $1.0 \times 10^{-5}$  M, (C)  $1.0 \times 10^{-4}$  M, (D)  $1.0 \times 10^{-3}$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

### 3.5. Selectivity of Cu(II)-membran electrode

The selectivity coefficient of an electrode, as one of the most important characteristics, is defined by its relative response to the primary ion on 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 obtained for the Cu(II)-membrane electrode 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 this increase in activity is measured. Next, a solution of an interfering ion of concentration  $a_B$  in the range of ( $1.0 \times 10^{-2}$ - $10^{-1}$  mol L<sup>-1</sup>) 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)- membran electrode (32% PVC , 64%DBP , 3% complex as ionophor, 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>	$6.32 \times 10^{-2}$		

### 3.6. 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 for determination of Cu(II) ions in different standards and environmental samples. Determination of Cu(II) in the previously mentioned samples was performed using the standard addition method. Triplicate experiments were achieved for the statistical

treatment of the results. Different samples were analyzed namely standard samples and wastewater samples and summarized in Tables (4, and 5), The samples were acidified by nitric acid in order 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 graphite furnace atomic absorption spectrometry (GFAAS) at wavelength ( $\lambda = 324.8$  nm) and an ashing step with a temperature of  $800^{\circ}\text{C}$  and an atomization step with a temperature of  $2400^{\circ}\text{C}$ . The results, given in Tables (4 and 5) show that there is a good agreement between the results of the proposed sensor and those obtained from GFAAS 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 limit $CL = \pm \frac{t.S}{\sqrt{n}}$ at 95% confidence level
$1 \times 10^{-3}$	$0.99 \times 10^{-3}$	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 GFAAS at  $\lambda = 324.8$  and  $t = 2400^{\circ}\text{C}$ .**

Sample	Found Potentiometrically mg/l	Found by GFAAS technique mg/l
1	0.121	0.119
2	0.0816	0.080
3	0.1567	0.155

### 3.7. Statistical treatment of data

The calculated F values [44] were less than the tabulated F value (19) where  $f = 2$  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 results show that the constructed electrode does not exhibit significant differences in comparison with the routine method (AAS) technique 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 GFAAS technique**

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 1,3-diphenyl-5-p-nitrophenyl formazan as electroactive phase can be used in the development of copper ion-selective electrode. The electrode having the composition of 3.0% complex, 32.0% PVC, 64.0% DBP and 1.0% NaTPB responds to Cu(II) ions in a Nernstian behavior with a slope of 28.23 mV/decade

and a 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 previously prepared copper sensors. The interference study 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.**

Ionophor	Slope mv/decade	Working concentration range M	Detection limit M	Response time S	Interferig ions	Ref.
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
1,3-diphenyl-5-p-nitro phenyl formazan	28.23	$1 \times 10^{-6}$ – $1 \times 10^{-1}$	$7 \times 10^{-7}$	15	--	This work

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