

Preparation of Cu-PVC membrane electrochemical membrane sensor based on β -Cyclodextrin

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The assembly and characteristics of a copper(II) electrochemical sensor (CuES) based on β -cyclodextrin (β CD) doped into PVC was reported in this paper. The CuES was prepared by combining Ag/AgCl reference electrode plus the polyvinyl chloride (PVC) membrane electrochemical sensor. The CuES reveals a Nernstian behavior over a wide copper ion concentration range (1.0×10^{-2} to 5.0×10^{-6} mol L⁻¹) and a relatively low detection limit (0.32 ppm). The potentiometric response was independent of the pH of the solution above 3.9 whatever the used concentration. The CuES showed a very short response time (5 s for 10^{-3} and 10^{-2} M) and (15 s for 10^{-4} M) for all compositions. It exhibited very good selectivity relative to a wide variety of metal cations. The proposed CuES was used for the analysis of copper in Haematon-containing samples. This method was compared with traditional spectrophotometric techniques.

Keywords: copper determination, copper electrochemical sensor, β -cyclodextrin, Cu analysis.

1. INTRODUCTION

Although several techniques [1,2] are designed for the Cu-assessment, electrochemical sensors is considered as a fast, simple and sensitive method of analysis. Isa et al. [3] determined copper in vegetable samples. Samples were digested using concentrated HNO₃ and sodium acetate was employed as the supporting electrolyte at pH 2.5 and a scan rate of 500 mV s⁻¹. The Cu(II) concentrations were found in the range of 0.04–6.88 μ g g⁻¹. Janegitz et al. [4] developed an anodic stripping voltammetric method to determine Cu²⁺ in aqueous samples using nanotubes carbon paste electrode modified with chitosan. The voltammetric response was linearly dependent on the Cu(II) concentration in the range from 7.90×10^{-8} to 1.60×10^{-5} mol L⁻¹ with a detection limit of 1.00×10^{-8} mol L⁻¹.

Guo et al [5] constructed nanopore sensor for copper ion detection using a polyamine decorated β -cyclodextrin as the recognition element. The linearity for concentrations of Cu(II) in the range 0.08–20

μM . The detection limit is as low as 12 nM.

Valilue et al [6] designed a PVC-ISE for Cu based on a Schiff base-ionophore 2-(5-bromo-2-hydroxy benzylideneamino)pyridine 3-ol in presence of Na TPB-additive. Marcinek et al [7] determined free Cu in sea-water by using a new meta-calibration approach. They applied jalpaite membrane. Faridbod and Bahman [8] applied selectophore for copper determination in blood plasma.

Wang et al [9] developed an all-solid electrode for determination of Cu ions. It was based on phytic acid on nano-silver. Nasser et al [10] prepared PVC Cu-ISE based on 3-(4-nitrophenylazo)pentane-2,4-dione-Cu complex/NaTPB/DBP. Zaho et al [11] applied a sensor based on coating by poly(3,4-ethylenedioxythiophene)-poly(sodium 4-styrene sulfonate) on gold wire. Heydari et al [12] introduced Cu-ISE based on synthesized ion carrier 2-(4-methyl piperazine-1-yl methyl)-1-cyano cyclohexanone.

Kumawat et al. [13] developed an optical Cu-sensor based on a ligand of phthalocyanine tetrasulfonic acid. The DL was 5.53×10^{-7} M. Aksunera et al. [14] prepared an optical sensor based on a Schiff base rooted in plastic layer for copper-assessment in green and black tea. The sensor displayed a calibration response for Cu(II) over a wide concentration range of 5.0×10^{-8} to 1.0×10^{-4} M. Yari and Afshari [15] used 1-hydroxy-3,4-dimethylthioxanthone as an ionophore for an optical copper(II)-selective sensor. The sensor worked between 1.6×10^{-7} and 1.3×10^{-2} M with a limit of detection of 4.0×10^{-7} M (25.1 ppb). The sensor showed a response time (<1 min), and the membrane can be used for more than six months.

Different ionophores were used for preparing copper ion-selective electrodes. Topcu et al. [16] introduced graphite oxide-imprinted ionic sensor on for the assessment of copper(II) in water samples. The electrode showed a concentration range of 1.0×10^{-6} to 1.0×10^{-1} M with a sensitivity of 26 mV decade⁻¹. The detection limit of the fabricated electrode was 4.0×10^{-7} M. The electrode worked well in the pH-range of 4.0–8.0. The electrode had a potentiometric response (3 s). Also, the electrode had a lifetime of more than one year. Pouya [17] used 2-(benzyliminomethyl)-6-methoxy-4-(4-methoxyphenyl-azo)phenol in the construction of the ion-selective PVC membrane electrode for the determination of copper (II) in mineral water. The electrode had a response time (7s) and a Nernstian slope (29 mV/decade) to Cu²⁺ over a concentration range (2.0×10^{-6} to 5.0×10^{-2} M) with a detection limit of 5.9×10^{-7} M. Polymer composites were used by Ganjali et al. [18] to develop the all-solid-state electrode (ASSE) for the determination of Cu²⁺ ions in complex matrices. This electrode had a Nernstian potential response of 29 mV/decade over a dynamic linear range from 1.0×10^{-8} M to 1.0×10^{-3} M of Cu²⁺, and the detection limit of the sensing device was 2.4×10^{-9} mol L⁻¹. Anastasin et al. [19] developed solid-state sensors using PVC-based membranes with off-the-shelf N-hydroxysuccinimide and succinimide ionophores and used DOP (dioctyl phthalate) and NPOE (*o*-nitrophenyloctyl ether) as plasticizers. The potentiometric response of the electrode was independent of pH over the range 2–6. Wardak and Lenik [20] used alkylmethylimidazolium for all solid Cu-sensor. The electrode showed a Nernstian response for copper ions over a wide concentration range (1×10^{-7} to 1×10^{-1} mol L⁻¹) and a slope of 28.9 mV/decade. The limit of detection was 3.2×10^{-8} mol L⁻¹. It had a fast response time of 5–10 s. Etioporphyrin I dihydrobromide was used as ligand for preparing a modified CPE as Cu-sensor for the determination of copper in milk powder [21]. The sensor exhibited LOD value 5.7×10^{-2} ppm. Ghanei-Motlagh et al. [22] fabricated a copper ion-selective electrode using a polymer-based membrane with N,N'-(2,2-dimethylpropane-1,3-diyl) bis-(dihydroxyacetophenone) as an ionophore. The electrode

showed a good Nernstian slope of 30 mV/decade in a wide linear range activity of 3.0×10^{-7} to 1.0×10^{-2} mol dm⁻³ Cu(NO₃)₂ with a limit of detection of 2.5×10^{-7} . The sensor exhibited a fast response time ($t_{95\%} < 10$ s) and could be used for about four months in the pH range of 3.0–7.4. The proposed potentiometric sensor was found to work satisfactorily in partially non-aqueous media up to 30 (vol%) content of methanol, ethanol, and acetone. Mittal et al. [23] used 8-hydroxyquinoline-based neutral tripodal ionophore for a copper (II)-selective electrode. The electrode exhibited Nernstian response to Cu(II) ions in the range of 1.0×10^{-6} to 1×10^{-1} M and a reasonably fast response time of 15 s. The electrode was used as an indicator electrode in the potentiometric titration of Cu (II) ions with EDTA. Gupta et al. [24] developed Cu²⁺-selective electrode based on *bis*-(acetylaceton)propylenediimine. It showed linearity range 1.0×10^{-5} to 1.0×10^{-1} M and detection limit of 0.5 ppm. The operational pH range of the electrode was 3.3–7.0. Fakhari et al. [25] developed a copper-selective PVC membrane electrode based on Salens as carriers. The used ion-carrier was N,N'-ethylenebis(salicylimine). The membrane showed linear response in the concentration range of 1.0×10^{-5} M to 1.0×10^{-1} M with a Nernstian slope of 29.7 ± 0.3 mV/decade of Cu²⁺ and the limit of detection was 3.1×10^{-6} M. It had a response time of < 10 s, and was used for nine weeks. The electrode was used in the pH range of 3.5–6.5.

Ali et al [26] constructed a carbon paste electrode based on cyclodextrin as an ionophore. The electrode showed a slope value 29 mV/decade within a linear range 10^{-7} - 10^{-1} M Cu⁺⁺ and it was applied for analysis of Cu in polluted water.

Yoshimoto et al. [27] developed a copper(II)-selective membrane based on hydro-*tris*-(3-isopropylpyrazolyl) methane in a poly(vinyl chloride) matrix. This sensor showed linear response over a wide concentration range (10^{-6} to 10^{-2} M) with a near-Nernstian slope (29 mV) and a response time of 10 s. The selectivity for Cu²⁺ over metal ions in 10^{-2} M NaNO₃ ($\log K^{Pot}_{Cu^{+2}, X^{+z}} < -6.4$, and had a sufficiently long shelf life (4 months). Gholivand and Nozari [28] proposed copper(II)-selective electrode by using 2,2'-dithiodianiline as a neutral carrier. The electrode exhibited a good potentiometric response for Cu(II) in the concentration range of 5.0×10^{-2} to 7.0×10^{-7} mol L⁻¹ with a Nernstian slope of 30 mV per decade. The response time of the electrode was 10 s, and it was used for 1 month. Park et al. [29] introduced an electrode based on 2-picolyl armed 1,3-alternate calix [4]-azacrown ether that exhibited a Nernstian response toward copper (II) over a concentration range of $10^{-4.5}$ M to $10^{-2.5}$ M. Shamsipur et al. [30] determined copper ions in different types of black tea by using recently synthesized mixed aza-thioether crowns containing a 1,10-phenanthroline sub-unit. The electrode exhibited a Nernstian response for Cu²⁺ ions over a wide concentration range of 2×10^{-1} to 1×10^{-5} M with a limit of detection of 8.0×10^{-6} M (0.5 ppm.). The response time of the sensor was 15 s, and the membrane was used for more than three months. Ganjali et al. [31] determined copper in black tea using a PVC membrane electrode based on *bis*-2-thiophenal propane diamine coated directly on graphite. The electrode exhibited a Nernstian response for Cu²⁺ a concentration range of 63.5 g/L to 3.8×10^{-6} g/L and a LOD 1.9×10^{-3} ppm. It worked up for two months.

Although the aforementioned sensors had almost similar linear range, most of them were the conventional type of electrodes which need special cell and reference electrode. The present Cu-ES is one unit and easy to use. In addition, the measurements were applied at room temperature and dose not needs the expensive precautions for measurements. Here, the preparation of Cu-ES using PVC

membrane is of interest. Teflon was used to construct the sensor body. The PVC membrane was fixed to the end of the Teflon tube. The Cu-ES in this study were constructed using β -cyclodextrin as an ionophoric compound (Figure 1). Unlike other methods (HPLC, AAS, and spectrophotometry), which need well-equipped instruments and training. This Cu-ES is sensitive, low cost, and easy to use. Also, it does not need any organic solvents or sample pretreatment.

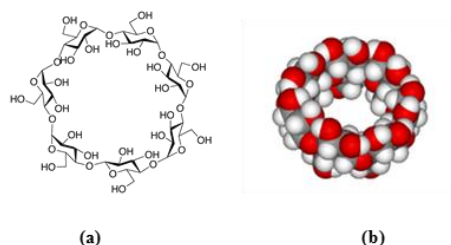


Figure 1. Structures formula (a) and space filling (b) of typical β -cyclodextrin (7-membered sugar ring molecule).

2. EXPERIMENTAL

2. 1. Preparation of membranes and Cu-ES:

The membrane was prepared as previously described by Zareh et al. [32]. β -Cyclodextrin was used as an ionophore for the preparation of copper-PVC membranes. Polyvinyl chloride (PVC) was the membrane matrix, and diethyl phthalate (DEP), 1-(2-nitrophenoxy)octane (NPO), or bis-(2-ethylhexyl)phthalate (DEHP) were the plasticizers used in types A-C (Table 1) Each of the mixtures was unthawed in 1.5 mL of dried tetrahydrofuran by vigorous shaking. The cocktail was then transferred to a glass-circle (resting on a glass plate), then let to solidify overnight. The Cu-ES was designed as previously described [32].

The electrodes were prepared by attaching the membrane disks to the ends of Teflon-tubes. The Cu-ES was immersed in fresh 6.35 g/L Cu^{2+} aqueous solution for one day before use.

Table 1. Composition of the three membranes used for Cu-ES.

Electrode type	β -cyclodextrin, (mg)	Plasticizer, (mg)			PVC, (mg)
		NPOE	DEP	DOP	
A	5.3	-	65.5	-	30.6
B	5.3	65.5	-	-	30.6
C	5.3	-	-	65.5	30.6

2.2. Apparatus

The potentiometric/pH-measurements were carried out using a digital multimeter (Jenway, UK) coupled with a channel selector.

2.3. Cu-ES calibration

All the electrochemical potential measurements were performed by using Cu-ES-arrangement:

Silver-silver Chloride/IFS/Membrane/Sample//potassium chloride/ Silver-silver Chloride

The potential was measured at room temperature. The sample was agitated at a constant rate. Cu-ES execution was examined in a series of solutions containing Cu-range between 6.4×10^{-5} g/L and 0.635 g/L of Cu^{2+} . After Cu-ES was immersed into aliquots of 25 mL of these solutions, the cell emf was plotted against $p[\text{Cu}^{2+}]$.

2.4. Effect of membrane composition

In this study, 25 mL aliquots of Cu^{2+} amounts between 6.4×10^{-5} g/L and 0.635 g/L were transferred to 50 mL beakers. After the Cu-ES set was dipped into the examined and the potential vs. $p[\text{Cu}^{2+}]$ were plotted. This step was repeated for the Cu-ES (A, B, and C) and subsequently, their corresponding calibration graphs were constructed.

2.5. pH-influence

The effect of pH of the test solution on the Cu-ES potential was examined for 0.635, 0.0635 and 0.00635 g/L of Cu^{2+} solutions. The pH of the test solution was adjusted by the addition of either HCl (0.1 M) or NaOH (0.1 M). Here, 25 mL of dissolved copper were transported into the potentiometric cell. The Cu-ES, along with the pH-measurement system, were submerged into Cu^{2+} solutions. The cell potential (mV) was charted alongside $(-\log[\text{H}^+])$ for each Cu-ES -type (A, B, and C) for 0.635, 0.0635 and 0.00635 g/L of Cu^{2+} solutions.

2.6. Response time

The relationship between the time and potential of the Cu-ES was determined. Here, 25 mL aliquots of 0.635, 0.0635 and 0.00635 g/L of Cu^{2+} were added to the potentiometric cell. Then, the Cu-ES was directly immersed in the solution and the potential values against time (in seconds) were recorded until the potential reached a steady state.

The time dependence of the Cu-ES potential is represented by the equation according to Lindner et al. [33]:

$$E_t = E_{st} + (E_i - E_{st}) \exp(-t/\tau)$$

where E_i : the initial potential of the cell,

E_{st} : the final steady state cell potential,

τ : the relaxation time, which is identified with its response time.

t : the time at any instance.

2.7. Effect of soaking on the Cu-ES potential

The three types of Cu-ES forms (A, B, and C) were soaked in 0.635g/L of Cu^{2+} solution at room temperature. A calibration graph was constructed for each cell at different time ranges of 1 h, 24 h, 7 d, 14 d, 21 d, 28 d, and 35 d.

2.8. Selectivity coefficient

The selectivity coefficient $K^{\text{Pot}}_{\text{Cu}^{2+}, X^{z+}}$ was calculated by the IUPAC-recommended separate solution method of Buck and Linder [34] as below:

$$\log K^{\text{Pot}}_{\text{Cu}^{2+}, X^{z+}} = (E_2 - E_1)/S + \log(\text{Cu}^{2+}) - \log(X^{z+})^{1/z}$$

where E_1 : represents cell mV for 0.001 M of Cu^{2+} , E_2 : represents cell mV for 0.001M of the interferent cation X^{z+} , S : the slope of the calibration curve, and Z : the charge of the interfering ion.

In this method, the measuring of the cell selectivity depends on measuring the potential of 10^{-3} M solution of both the interfering and Cu^{2+} ions.

2.9. Determination of copper in its formulation

Five capsules of the Haematon drug (GlaxoSmithKline, New Cairo, Egypt) was dissolved in 20 mL of ethyl alcohol. Each capsule contains 350 mg ferrous sulfate, 75 mg B_{12} -vitamin, 2 mg folic acid, 150 mg ascorbic acid, 2.5 mg manganese sulfate, and 2.5 mg copper sulfate. The solution was filtered, the residue was washed with ethyl alcohol and dried. Then, 100 mL solution was prepared containing 50 mg of the residue and was adjusted to pH 5.5. Then, 50 mL aliquots of the solution were transferred to 100 mL beakers. The proposed Cu-ES type-I was immersed into the solution, and potential values were recorded. The EMF values were plotted on a calibration graph that was previously constructed under the same experimental conditions. From the calibration graph, the concentration of the sample solution was calculated.

3. RESULTS AND DISCUSSION

3.1. Effect of composition on Cu-ES

Three membrane compositions (I, II, and III) were studied. Each membrane type had a different plasticizer (DEP, NPOE and DOP), respectively. Table 2 shows the composition of each type of membrane. β -cyclodextrin (βCD) was used as the main ionophore for preparing Cu-ES. The inclusion ability of β -cyclodextrin helped the formation of the metal cation complex.

The Cu-ES types A, B, and C were showed linear graph with slopes 26, 24, and 32 mV/decade, respectively. Cu-ES type-III showed the best slope value for the divalent cation. This is because of the higher lipophobicity of DOP when compared with that of NPOE and DEP. Fig. 2 shows the results obtained for the calibration graphs for each of the cell types I–III.

The mechanism of the cell response comprising only the βCD -ionophore can be represented as follows:

$$[Cu^{2+}(H_2O)_4]^{2+}_s = [Cu^{2+}]_m + 4 H_2O$$

$$[Cu^{2+}]_m + [\beta CX]_m = [Cu^{2+}-\beta CX]^{2+}_m$$

$$\Delta E = E_m - E_s = (RT/2F) \ln \{k_i a_{Cu^{2+}} [1 + K_f(carrier)] / (sites)\}$$

s : refers to the solution site, and m : refers to the membrane site. E_m : is the cell potential at membrane site, E_s : is the cell potential at the solution site. K_f : complex formation constant, k_i : the ionization constant, and $a_{Cu^{2+}}$: is the copper activity.

Table 2. Effect of composition of membrane comprising different plasticizers.

Electrode type	Slope, mV/decade	LR, M	DL, M	R ²
A, (DEP)	26	$1 \times 10^{-5} - 10^{-2}$	5×10^{-5}	0.9715
B, (NPOE)	24	$5 \times 10^{-5} - 10^{-2}$	5×10^{-6}	0.9839
C, (DOP)	32	$5 \times 10^{-6} - 10^{-2}$	5×10^{-6}	0.9615

The response times for Cu-ES (A, B, and C) were tested by recording potential (mV) vs. time (s) for each electrode type. Table (3) summarizes the obtained results.

The calculation of the response times was based on the IUPAC method [39]. The response time is the time from the instant when the cell comes into contact with the sample solution until the limiting potential value is reached.

The results indicate a fast response for all the studied Cu-ES types. The response time was 5 s for all the electrodes when 10^{-2} and 10^{-3} M Cu^{2+} solutions were used for the measurements. For 10^{-4} M Cu^{2+} solution, longer response times were observed (table 3). This was expected because the lower the concentration, the slower is the equilibrium between the exchanged ions. Fig. 3 shows representative curves for the dynamic response of Cu-ES type-II for the three concentrations of 10^{-2} , 10^{-3} , and 10^{-4} M Cu^{2+} solution.

Table 4 represents the comparison between the present Cu-ES and previously recorded Cu-electrodes. The presented Cu-ES was based only on β CD as an ionophoric matter compared to previously recorded sensors [5 and 26] where β CD-derivatives were used. This make the preparation of the membrane is easier. In addition, all previous sensors should prepare Cu- β CD complex to be applied for the membrane sensor, which is not required in our sensor. Here, only β CD compound was dopped into the membrane. The proposed Cu-ES showed perfect Nernstiaian slope as well as all the recorded sensors. The detection limit of the proposed sensor was 3.2×10^{-1} ppm which is comparable to some old sensors [25, 29, 19]. The working pH-range of the present Cu-ES was starting from 3.5 and it showed stable potential value to the highest possible pH value, compared to other sensors the pH ranges were between 2-8.5. The Cu-ES age was 1.25 months, which was practically sufficient. In addition, the easy preparation of the membrane of the proposed Cu-ES was advantageous since no IP was prepared.

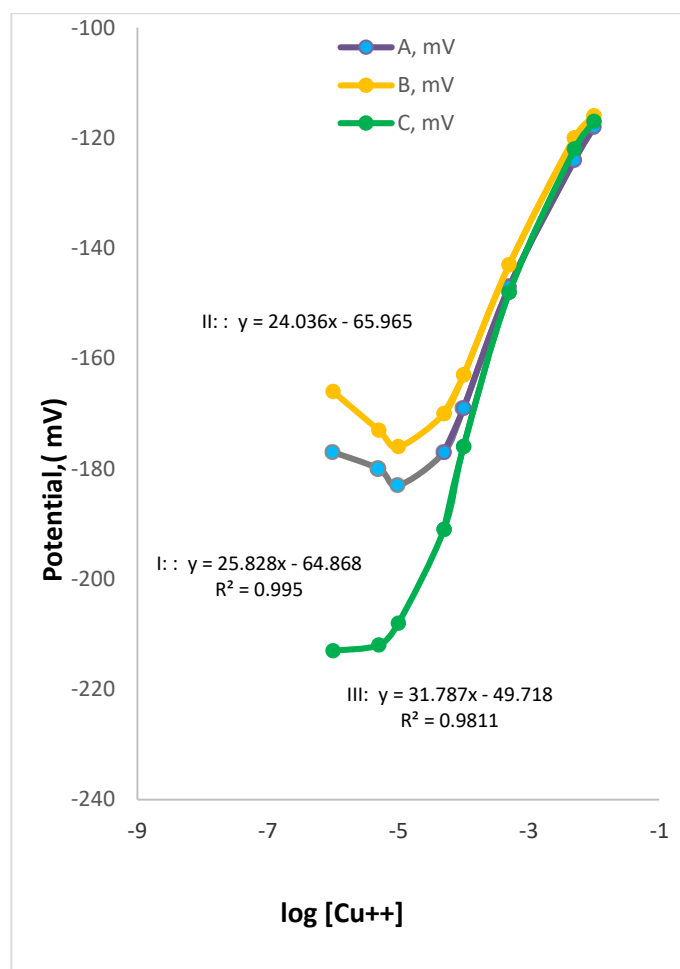


Figure 2. Standardization curves of Cu-ES -A, B and C.

Table 3. Response time for the three types (A-C) of Cu-ES

Electrode type	Response time, s		
	10^{-4} M	10^{-3} M	10^{-2} M
A, DDP	10	5	5
B, NPOE	15	5	5
C, DOP	10	5	5

Table 4. Comparison between the proposed Cu-ES and previous Cu-selective electrodes.

Type/Active ionophore	LR, M	Slope, mV/decade	DL, M	Working pH	Response time, s	Age*	Other properties	Ref. no.
1. Polyamine β CD	0.08-20 μ M 8×10^{-8} - 2×10^{-5} M	-	7.6×10^{-5} ppm	-	-	-	-	5, 2017
2. 2-(4-bromo-2-hydroxy benzylidene amino) pyridine 3-ol/NaTPB/NPOE/PVC	10^{-7} - 10^{-2} M	30	4.7×10^{-3} ppm	4-7	10	8w	Cu-EDTA Pot. Tit.	6, 2016
3. Selectophore/NaTPB/nitrobenzene/ PVC	10^{-6} - 10^{-2} M	28	-	3.5-7	20	-	Cu in blood plasma	7, 2020
4. 3-(4-nitrophenylazo) pentane-2,4-dione-Cu/DBP/NaTPB	10^{-6} - 10^{-1} M	28	4.4×10^{-3} ppm	3-6	-	2m	-	10, 2019

5.	Poly(3,4-ethylenedioxythiophene)-poly(sodium 4-styrene sulfonate on gold wire	2.5×10^{-7} - 2.5×10^{-4} M in NaCl 0.5 M	-	2.5×10^{-3} ppm	-	-	-	-	11, 2019
6.	2-(4-methyl piperazine-1-yl methyl)-1-cyano cyclohexanone.	10^{-6} - 10^{-2} M	31	6.4×10^{-2} ppm	3.5-8.5	10	-	Cu-EDTA Pot. Tit.	12, 2019
7.	GO imprinted	10^{-6} - 10^{-1} M	26	2.5×10^{-2} ppm	4-8	3	-	-	16, 2018
8.	(benzyliminethyl)-6-methoxyazophenol-PVC	2×10^{-6} - 5×10^{-2} M	29	3.2×10^{-2} ppm	-	7	-	Mineral water	17, 2018
9.	Solid state ASSE Cu-complex matrix	10^{-8} - 10^{-3}	29	1.5×10^{-4} ppm					18, 2015
10.	Solid PVC-N-hydroxy succinimide, DOP, NPOE	-	38	2.7×10^{-1} ppm	2-6	-	-	-	19, 2013
11.	Alkyl methyl imidazolium chloride	10^{-7} - 10^{-1}	-	2.0×10^{-3} ppm	-	5-10		-	20, 2013
12.	CPE/etioporphyrin dihydrobromide	1.3×10^{-6} - 1.3×10^{-2}	30	5.7×10^{-2} ppm	4.5-8.5	5		Cu in milk powder	21, 2012
13.	CPE/ β CD, bromohydroxybenzene	10^{-7} - 10^{-2}	29	-	7-3.5	-		Polluted water	26, 2003
14.	Polymer N,N-(2,2-dimethylpropane-1,3 diyl) bis-(dihydroxy acetophenone)	3×10^{-7} - 10^{-2}	30	1.6×10^{-2} ppm	3-7.4	<10		Non-aq-30%, methanol-ethanol, acetone	22, 2011
15.	8-hydroxyquinoline	10^{-6} - 10^{-1}	-	-	-	15	-	Pot.tit. against EDTA	23, 2007
16.	Acetylacetone-propylene diimine	10^{-5} - 10^{-1}	30	0.5 ppm	3.3-7	-	-	-	24, 2005
17.	p-cresol derivative	10^{-5} - 10^{-1}	30	1.9×10^{-1} ppm	3.6-6.5	<10	9 w	-	25, 2005
18.	Isopropyl-pyrazole-methane/PVC	10^{-6} - 10^{-2}	29	-	-	10	4 m	-	27 2003
19.	Dithiodianiline	7×10^{-7} - 5×10^{-2}	30	-	-	10	1m	-	28, 2001
20.	2-picolyly calix-4-arene-azacrown	$10^{-4.5}$ - $10^{-2.5}$	Nernstian	6.4×10^{-1} ppm	7	-	-	-	29, 2001
21.	Aza-crown thio 1,10, phenanthroline	10^{-5} - 2×10^{-1}	-	0.5 ppm	-	15	>3m	Black tea	30, 2001
22.	PVC-thiophenol propane diamine/on graphite	6×10^{-8} - 10^{-1}	-	1.9×10^{-3} ppm		5	2m	Black tea	31, 2001
23.	PVC/ β CD/dopped, DOP	5×10^{-6} - 10^{-2}	31	5×10^{-6} - 3.2×10^{-1} ppm	>3.5	<10	5w	Heamaton, pharmaceutical formulation.	Present work

*)w: week, m:month

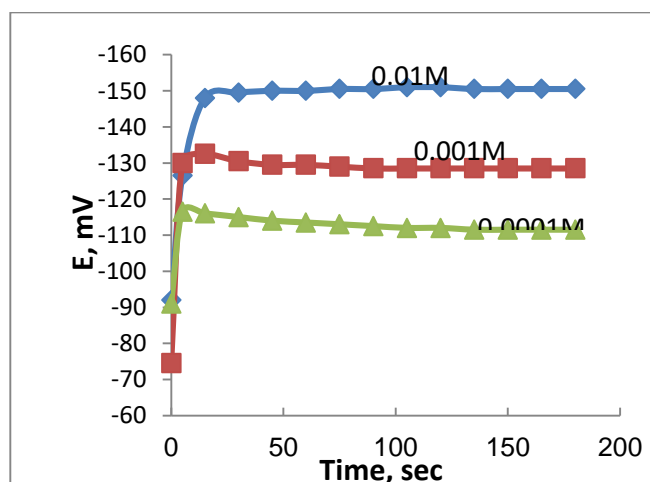


Figure 3. Dynamic response for Cu-ES type-B when measuring 10^{-2} , 10^{-3} and 10^{-4} M Cu^{+2} concentrations.

3.2. pH-Effect

The working pH-range for the three Cu-ES types was studied by recording the potential against different pH values. The break at pH value is the point at which the potential value suddenly changes. It was found that the break-in acidic part changes with changing the concentration of copper. This point is considered the lower limit of the working pH. The pH-value at that point increased a little when the Cu^{2+} concentration was increased (Table 4). This is because more OH^- ions are required with increasing Cu^{2+} concentrations. The plateau potential occurred at the point where the K_{sp} for $\text{Cu}(\text{OH})_2$ was achieved (at pH 6). Fig. 4 shows the obtained results. The potential value were stable whatever the pH up to 11.

Table 5. The working pH range for the three Cu-ES types A-C.

Electrode type	Working pH range		
	10^{-4}M	10^{-3}M	10^{-2}M
A, DDP	>3.5	>3.6	>3.9
B, NPOE	>3.7	>3.1	>3.8
C, DOP	>3.2	>3.4	>3.5

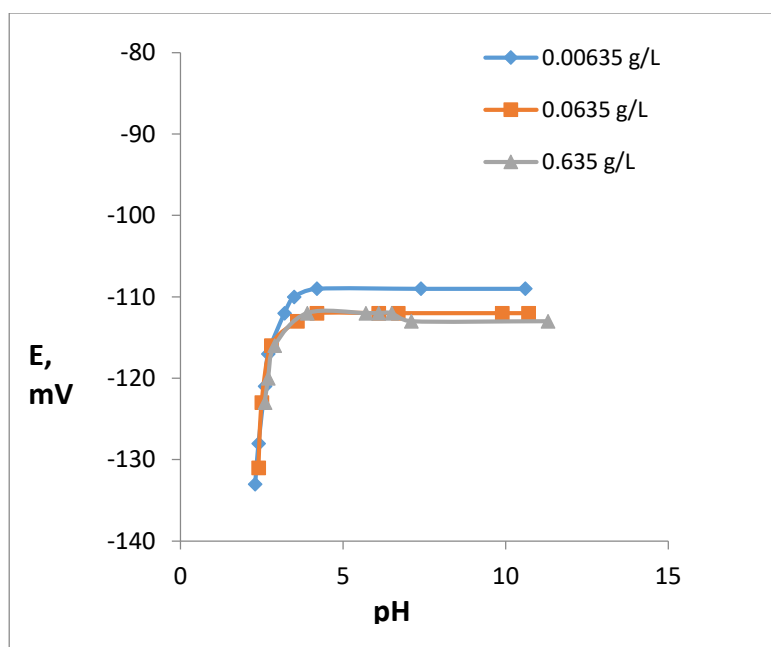


Figure 4. Potential-pH representative graphs for Cu-ES type-I for three Cu^{2+} -concentrations 0.635, 0.0635 and 0.00635 g/L Cu^{2+} .

3.3. Effect of immersion time

The Cu-ES age is important for the evaluation of its performance. The three Cu-ES types A, B, and C were soaked into the 10^{-2}M Cu^{2+} -solution for different time intervals. The calibration graph for each Cu-ES was recorded. Table (6) shows the recorded results for the time range between 1 h and 5 weeks.

When Cu-ES type-I was used, the slope changed after two weeks by -0.8 mV/decade and reached -1.7 mV/decade after 5 weeks from the first Cu-ES slope value. This means that the slope was mostly stable throughout the soaking period. The working linear range (10^{-2} to 5×10^{-5} M) of the cell was not changed throughout the study period (5 weeks).

The Cu-ES type-II had a stable slope value ($\sim 26 \pm 1$ mV/decade) until 4 weeks. Then, it decreased to the lowest value (20 mV/decade) after 5 weeks of continuous soaking. The working linear range was 10^{-2} to 5.0×10^{-6} M throughout the soaking period (5 weeks).

The cell type-III showed slope values that varied between 26 and 31 mV/decade. The lowest slope value was recorded after 5 weeks. The linear range was similar to that of cell type-II (10^{-2} to 5.01×10^{-6} M).

The decrease in the slope value recorded for all electrode types after 5 weeks of soaking can be attributed escape of the ionophore from the membrane.

Table 6. Influence of soaking Cu-ES types I, II and III, into 10^{-2} M Cu^{+2} solution

Soaking Time	I, DEP			II, NPOE			III, DOP		
	Slope mV/d	LR, M	R ²	Slope	LR, M	R ²	Slope	Linear Range	R ²
1 hr.	26	10^{-2} - 5×10^{-5}	0.9813	26	10^{-2} - 5×10^{-6}	0.9768	30	10^{-2} - 5×10^{-6}	0.9577
1 day	27	10^{-2} - 5×10^{-5}	0.9888	26	10^{-2} - 5×10^{-6}	0.9767	26	10^{-2} - 5×10^{-6}	0.9784
1 week	26	10^{-2} - 5×10^{-5}	0.9922	27	10^{-2} - 5×10^{-6}	0.9739	26	10^{-2} - 5×10^{-6}	0.9823
2 week	25	10^{-2} - 5×10^{-5}	0.9895	26	10^{-2} - 5×10^{-6}	0.9637	31	10^{-2} - 5×10^{-6}	0.9642
3 week	27	10^{-2} - 5×10^{-5}	0.9871	27	10^{-2} - 5×10^{-6}	0.9775	27	10^{-2} - 5×10^{-6}	0.9772
4 week	25	10^{-2} - 5×10^{-5}	0.9841	27	10^{-2} - 5×10^{-6}	0.9799	27	10^{-2} - 5×10^{-6}	0.9799
5 week	25	10^{-2} - 5×10^{-5}	0.9873	20	10^{-2} - 5×10^{-6}	0.9295	26	10^{-2} - 5×10^{-6}	0.9399

3.4. Selectivity of Cu-ES:

The selectivity of the three types of Cu-ES was calculated using the separate solution method (SSM) by Buck and Linder [40], Table (7). The logarithm $K^{\text{Pot}}_{\text{Cu}^{+2}, \text{X}^{+z}}$ of Cu-ES types A, B, and C were close to each other. Most of the recorded values were of the order of 10^{-1} . For Cu-ES type-I, all of the tested divalent cations showed selectivity coefficient values between 0.071 for Hg^{2+} and 0.694 for Ni^{2+} . In the case of Cu-ES type-III, the selectivity coefficient values changed slightly between 0.045 for Hg^{2+} and 0.761 for Ni^{2+} . These values are close to each other as both DEP and DOP plasticizers have similar active groups.

When the Cu-ES type-II was studied, the selectivity behavior was different and showed some interference from Co^{2+} , Cd^{2+} , Ni^{2+} , Ba^{2+} , and Mn^{2+} cations. The other cations tested (Zn^{2+} , Mg^{2+} , Pb^{2+} and Hg^{2+}) exhibited selectivity values between 0.141 and 0.80. This interference effect of the electrode type can be attributed to the active ether group of NPOE, which facilitated the attachment with different cations.

In the case of the trivalent cation (Fe^{3+}) tested, $\log K^{\text{Pot}}_{\text{Cu}^{+2}, \text{X}^{+z}}$ were between 0.272- 0.617 for A-C Cu-ES. Monovalent cations greatly interfered with the measurements; hence measurements are not recommended in their presence.

Table 7. Selectivity coefficient of Cu-ES with membrane types I-III

Interferent	$\log K^{\text{Pot}}_{\text{Cu}^{+2}, \text{X}^{+z}}$		
	I, DEP	II, NPOE	III, DOP
Fe^{3+}	0.272	0.425	0.617
Zn^{2+}	0.335	0.696	0.367
Co^{2+}	0.579	1.0	0.579
Ni^{2+}	0.694	1.242	0.761
Ba^{2+}	0.482	1.242	0.482
Mg^{2+}	0.402	0.521	0.233
Cd^{2+}	0.440	1.335	0.634
Hg^{2+}	0.071	0.141	0.045
Mn^{2+}	0.579	1.0	0.528
Pb^{2+}	0.402	0.804	0.528

3.5. Determination of copper in Haematon

The three Cu-ES types were used for actual sample analysis. Haematon drug (GlaxoSmithKline, New Cairo, Egypt) is used for the treatment of anemia. It contains 2.50 mg CuSO_4 . Calibration graphs for each cell type were constructed with all of the inactive ingredients present in the background. The recovery of the analysis of Haematon showed suitable values (95.2–97.8%), with relative standard deviations (1.9–2.5). Table (8) shows the obtained results.

Table 8. Determination of copper in Haematon by using three Cu-ES-types I, II, and III in Haematon drug

Electrode Type	Found as CuSO_4 , (mg)	Recovery, (%)	RSD, %
I	2.38	95.2	2.2
II	2.44	97.8	2.5
III	2.44	97.8	1.9

4. CONCLUSION

The use of β -cyclodextrin as an ionophoric compound was successfully applied for introducing a Cu-ES. Here, the Cu-ES was easily prepared by the doping method. Unlike other methods (HPLC, AAS, and spectrophotometry), which need well-equipped instruments and training, this electrochemical sensor is sensitive, low cost, and easy to use. Also, it does not need any organic solvents or sample pretreatment.

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