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A novel copper (II)-selective membrane potentiometric sensor based on new imine quinoline derivative ligand: (Z)-3-(((2-((2-Aminophenyl) Thio) phenyl) imino) methyl)-7-chloronaphthalen-2-ol

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Abstract
The imine-quinoline derivative ligand, *namely (Z)-3-(((2-((2-aminophenyl) thio) phenyl) imino) methyl)-7-chloronaphthalen-2-ol,* was synthesized and employed as an ionophore in the fabrication of poly (vinyl chloride) (PVC)-based membrane electrodes selective for Cu (II) ions. Optimal electrode performance was achieved with a membrane formulation consisting of (L): PVC: NaTPB: NPOE in the ratio 5:120:3: 150.The developed sensor exhibited excellent selectivity and sensitivity towards Cu (II) ions over a wide range of competing cations, including alkali, alkaline earth, transition, and heavy metal ions. The effects of membrane composition, solution pH, and the presence of anionic additives on the potentiometric response were systematically examined. The electrode demonstrated near-Nernstian behaviour with a slope of 29.6 mV decade^{-1} over a broad concentration range of 5.0×10^{-7} to 1.0×10^{-1} mol L^{-1}, with a detection limit of 3.0×10^{-7} mol L^{-1}. The sensor provided rapid response times (<15 s) throughout the tested concentration range and maintained stable performance for up to 12 weeks within a pH range of 2.8-5.8. The proposed electrode was successfully applied for the determination of Cu (II) in various water samples and served effectively as an indicator electrode in the potentiometric titration of Cu (II) ions with EDTA.

Keywords: Copper ion-selective electrode, Potentiometry, Imine Quinoline Derivative Ligand, EDTA

1. Introduction

The determination of copper is of considerable significance due to its widespread presence in various environmental matrices. Although humans can generally tolerate moderate levels of copper, excessive intake or prolonged exposure may lead to adverse health effects, including irritation of the nasal, oral, and ocular tissues, as well as neurological and gastrointestinal symptoms such as headache, abdominal pain, dizziness, nausea, vomiting, and diarrhea. Conversely, copper deficiency can result in haematological disorders such as anemia, while excessive accumulation in the body is associated with pathological conditions, notably Wilson's disease [1].

Numerous advanced analytical techniques have been employed for the trace-level quantification of copper ions, including ion chromatography [2,3], spectrophotometric approaches [4-10], atomic absorption spectrometry (AAS) [11-15], cold vapour AAS, flame AAS coupled with electrothermal atomization (AAS-ETA) [16, 17], inductively coupled plasma emission spectrometry (ICP-ES) [18, 19], gravimetric analysis [20, 21], anodic stripping voltammetry [22, 23], and neutron activation analysis [24]. Although these methodologies offer excellent sensitivity, low detection limits, and high selectivity, they typically demand sophisticated and costly instrumentation, precise sample handling, and specialized expertise. Furthermore, several of these methods are hindered by limitations such as high operational costs, requirement for expensive reagents, extended analysis time, and complex procedural steps. Consequently, their applicability is restricted for straightforward, economical, and on-site determination of copper, particularly in field-based or domestic settings.

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The selective interaction between metal ions and ligands constitutes a fundamental recognition mechanism in the design of potentiometric sensors [25]. Given the critical demand for highly selective potentiometric detection of trace-level copper ions particularly in food and water matrices numerous ionophores have been explored as potential ion carriers in the fabrication of Copper (II) ion-selective electrodes (ISEs) [26-31]. In the present communication New Imine Quinoline Ligand (IQL) *viz* (Z)-3-(((2-((2-Aminophenyl) Thio) phenyl) imino) methyl)-7-chloronaphthalen-2-ol has been synthesized and explored for the preparation of Cu^{2+} sensors and results are presented in the present paper.

2. Experimental Section
2.1 Reagents and Materials
High-molecular weight polyvinyl chloride (PVC) was obtained from Aldrich (USA). 2-Nitrophenyl octyl ether (NPOE) was procured from ACROS Organics (New Jersey, USA), dioctyl phthalate (DOP) from Reidel (India), chloronaphthalene (CN) from Merck (Germany), and tri-n-butyl phosphate (TBP) from BDH (England). Sodium tetraphenyl borate (NaTPB) was supplied by BDH (UK). All reagents were used without further purification. Stock solutions of 0.1 M concentration were prepared by dissolving analytical reagent (AR) grade metal nitrates in double-distilled water and were standardized when required. Working solutions of desired concentrations were subsequently obtained by appropriate dilution of the stock solutions. Solvents and reagents were purified and dried by distillation

2.2 Synthesis of the Imine Quinoline Derivative Ligand (IQL):(Z)-3-(((2-((2-Aminophenyl) Thio) phenyl) imino) methyl)-7-chloronaphthalen-2-ol
The ligand, (Z)-3-(((2-((2-aminophenyl) thio) phenyl) imino) methyl)-7-chloronaphthalen-2-ol [L], was synthesized [32] as outlined in Scheme 1, via the condensation reaction of 7-chloro-2-hydroxyquinoline-3-carbaldehyde with 2,2′-thiodianiline in an equimolar ratio (1:1). Specifically, a solution of 7-chloro-2-hydroxyquinoline-3-carbaldehyde (10 mmol, 1.5 g) was prepared in 15 mL of ethanol, to which a solution of 2,2′-thiodianiline (10 mmol, 2.2 g) in 15 mL ethanol was added gradually under continuous stirring. The reaction mixture was stirred for 1-2 h at ambient temperature, resulting in the formation of a yellow solution. Subsequently, 5-10 drops of glacial acetic acid were introduced into the mixture while stirring. The progress of the reaction was monitored by thin-layer chromatography (TLC). Upon completion, a yellow precipitate was obtained, which was collected by filtration, washed thoroughly with 20 mL ethanol, and dried to constant weight. The product was isolated as a yellow crystalline solid with a yield of 89.2%, melting point 145-150 °C, and molecular weight 405.9 g/mol. The infrared spectral analysis exhibited characteristic absorption bands at 3854 cm^{-1} and 1734 cm^{-1} (v-NH), 3742 cm^{-1} (v-OH), and 1601, 1560 cm^{-1} (v-C=N).
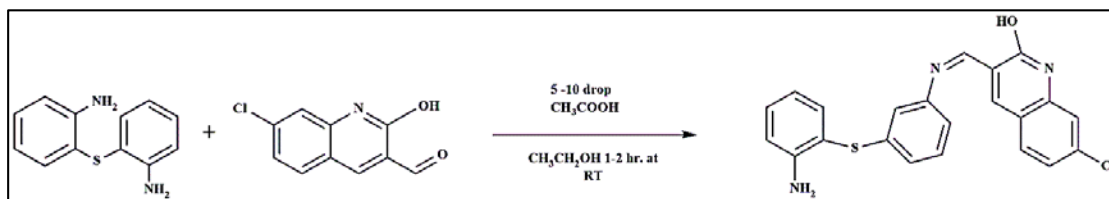
Scheme 1: Synthesis of IQL, (Z)-3-(((2-((2-Aminophenyl) Thio) phenyl) imino) methyl)-7-chloronaphthalen-2-ol.

2.3. Preparation of Membrane Electrodes
The PVC membranes were prepared according to the following general procedure. The required amounts of membrane ingredients: 30 mg PVC, 50 mg NPOE, 15 mg OA and 5 mg DIBAE was mixed and dissolved completely in 5 mL THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm in top) was dipped into the oily mixture for about 10s, so that a nontrans parent film of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature about 2 h. The tube was then filled with internal filling solution (1.0 x 10^{-3} M copper nitrate). The electrode was finally conditioned for 24 h by soaking in a 1.0 x 10^{-2} M solution of Cu (NO$_3$)$_2$. A silver-silver chloride electrode was used as an internal reference electrode.

2.4 Equilibration of Membranes and Potential Measurements
The membranes were equilibrated for 4 days in 1.0×10^{-1} mol L^{-1} Cu(NO$_3$)$_2$ solution. The potentials were measured by varying the concentration of Cu(NO$_3$)$_2$ in test solution in the range 1.0×10^{-8}-1.0×10^{-1} mol L^{-1}. Each solution was stirred and the potential reading was recorded when it became stable, and then plotted as logarithmic function of Cu^{2+} cation activity. The activities of metal ions were calculated using the following modified form of the Debye-Huckel equation:

$$\log \gamma = -0.511 Z^2 [\mu^{1/2}/(1+1.5\mu^{1/2}) - 0.2\mu] \qquad (1)$$

Where μ is the ionic strength and Z the valency, The potential were measured at 25±0.1 °C using silver electrodes as reference electrodes with the following cell assembly:

Ag/AgCl| KCl (satd.) |0.1 M Cu (NO$_3$)$_2$ ||PVC membrane||test solution |Ag/AgCl| KCl
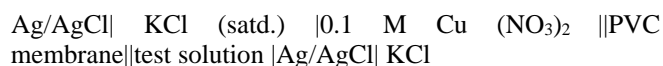
3. Results and Discussion
3.1 Potential Response of the membranes
The electrochemical response of the fabricated sensors was evaluated as a function of Cu^{2+} ion concentration (Figure 1). From these calibration plots, the linear working concentration ranges and slopes were determined, and the corresponding data including membrane composition and response times are summarized in Table 1. As evident from Figure 1, the sensor designated as No 1, consisting of the Imine Quinoline Derivative Ligand (I) incorporated into a

PVC matrix without any plasticizer, exhibited a linear response within the concentration range of 7.0×10^{-6} to 1.0×10^{-1} M. The electrode displayed a near-Nernstian slope of 27.3 ± 0.1 mV per decade of activity with a response time of 23 s. However, the relatively narrow linear range necessitated further optimization.

To enhance the electro analytical performance, plasticizers were introduced into the membrane composition. Incorporation of plasticizers not only facilitated improved mechanical flexibility and durability of the membranes but also broadened the concentration range, enhanced stability,

and extended the operational lifetime of the sensors [33, 34]. Nevertheless, the selectivity characteristics remained predominantly governed by the specific metal-ionophore interactions. An ideal plasticizer for membrane preparation should possess high lipophilicity, elevated molecular weight, negligible exudation tendency from the polymer matrix, low vapor pressure, and sufficient solvating capacity for the ionophore and additives. Furthermore, appropriate viscosity and dielectric constant values are essential to ensure optimal membrane performance [35].

Table 1: Composition of PVC membranes of (L) and performance characteristics of Cu^{2+} selective sensors based on them

Sr. No.	L	PVC	NaTPB	CN	TBP	DOP	NPOE	Working Concentration range M	Slope (mV/decade of activity)	Response Time (s)
1.	5	120	3	-	-	-	-	7.0×10^{-6} to 1.0×10^{-1}	27.3	23
2.	5	120	3	150	-	-	-	6.3×10^{-6} to 1.0×10^{-1}	31.4	19
3.	5	120	3	-	150	-	-	6.1×10^{-6} to 1.0×10^{-1}	28.1	20
4.	5	120	3	-	-	150	-	5.5×10^{-6} to 1.0×10^{-1}	30.6	18
5.	5	120	3	-	-	-	150	5.0×10^{-7} to 1.0×10^{-1}	29.6	15

In this context, four plasticizers dioctyl phthalate (DOP), chloronaphthalene (CN), tris(2-ethylhexyl) phosphate (TPB), and o-nitrophenyl octyl ether (NPOE) were incorporated into the membranes containing the Imine Quinoline Derivative Ligand (I) (Sensors NOS 2-5). As illustrated in Figure 1 and summarized in Table 1, the incorporation of plasticizers resulted in substantial improvements in both the linear response range and slope values. Among them, the membrane plasticized with NPOE (sensor No. 5) exhibited superior performance, demonstrating a broad dynamic concentration range of $5.0 \times$

10^{-7} to 1.0×10^{-1} M, an almost ideal Nernstian slope of 29.6 ± 0.1 mV per decade of activity, and a rapid response time of 12 s.

Considering its excellent analytical features namely, a wide working concentration range, near-Nernstian response, and short response time sensor no 5 was selected for subsequent investigations. The electrode retained consistent performance for more than six months under proper storage conditions, with the membranes stored in 0.5 M Cu^{2+} solution when not in use.
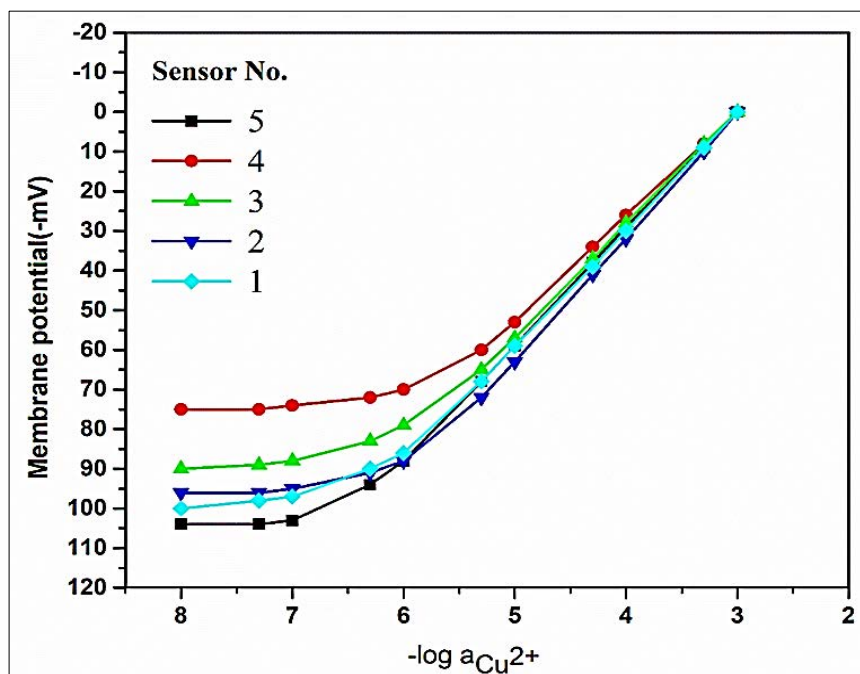

Fig 1: Variation of membrane potential with Cu^{2+} ions concentration; PVC based membranes of (L) (IQL) without solvent mediator (1), with solvent mediators, CN (2), TBP (3), DOP (4), and NPOE (5).

3.2 pH and solvent effect

The pH response characteristics of the membrane sensor (No. 5) were examined at two Cu^{2+} concentrations, namely 1.0×10^{-3} M and 1.0×10^{-4} M. The corresponding results are presented in Figure 2. As observed, the electrode

potential remains stable within the pH range of 3.5-7.5. A pronounced deviation in potential below pH 3.5 is attributed to the co-transport of protons (H^+) along with Cu^{2+} ions, whereas the decrease in stability above pH 7.5 may result from hydrolysis of Cu^{2+} species.
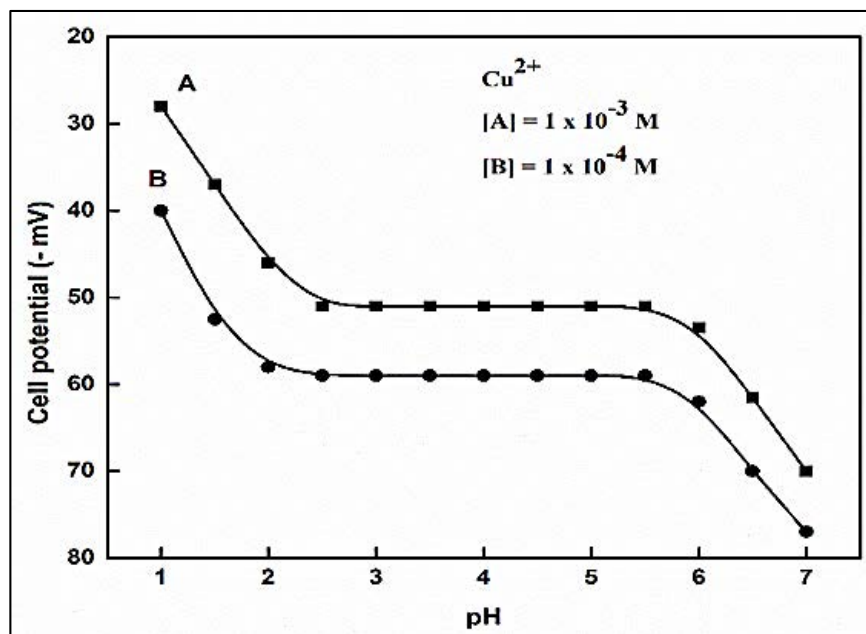
Fig 2: Effect of pH on cell potential; $[Cu^{2+}] = 1.0 \times 10^{-3}$ M (A) and 1.0×10^{-4} M (B)

The operational characteristics of the sensor were additionally evaluated in partially non-aqueous environments, specifically in methanol-water, ethanol-water, and acetone-water binary mixtures. The experimental data are presented in Table 2. It was observed that an increase in the proportion of the aqueous phase led to a slight enhancement in the slope of the calibration curve; however, this was accompanied by a reduction in the linear dynamic concentration range. The electrode exhibited reliable performance in media containing up to 20% (v/v) methanol, ethanol, or acetone. Beyond this threshold, a pronounced decrease in the effective working concentration range was recorded, indicating limitations of the sensor at higher non-aqueous solvent content.

Table 2: Performance of Cu^{2+} selective electrode in partially non-aqueous media

Non-aqueous content (%v/v)	Slope (mV/decade)	Working Concentration range (M)
0	29.6	5.0×10^{-7}-1.0×10^{-1}
Methanol		
10	29.4	5.0×10^{-7}-1.0×10^{-1}
20	29.6	5.2×10^{-7}-1.0×10^{-1}
30	24.6	4.7×10^{-6}-1.0×10^{-1}
Ethanol		
10	29.5	$5.1x10^{-7}$-$1.0 x10^{-1}$
20	27.6	$5.2x10^{-7}$-$1.0 x10^{-1}$
30	23.5	$5.7x10^{-6}$-$1.0 x10^{-1}$
Acetone		
10	29.6	$5.2x10^{-7}$-$1.0 x10^{-1}$
20	29.7	$5.3x10^{-7}$-$1.0 x10^{-1}$
30	28.4	$1.2x10^{-6}$-$1.0 x10^{-1}$

Table 3: Selectivity coefficients of sensors no 5 on the membrane of (L) by fixed interference method

Caption	Selectivity coefficients ($K_{Cu^{2+},B}^{Pot.}$)
Ag^+	3.2×10^{-5}
Pb^{2+}	3.2×10^{-3}
Mg^{2+}	3.3×10^{-4}
Na^+	2.6×10^{-5}
Zn^{2+}	5.7×10^{-2}
K^+	4.2×10^{-5}
Bi^{3+}	3.6×10^{-3}
Hg^{2+}	4.8×10^{-2}
Co^{2+}	5.2×10^{-2}
Cd^{2+}	6.1×10^{-2}
Al^{3+}	2.5×10^{-3}
Ca^{2+}	2.0×10^{-4}
Cr^{3+}	3.4×10^{-3}
Ni^{2+}	5.2×10^{-3}
Mn^{2+}	6.2×10^{-3}

3.3 Potentiometric Selectivity

The selectivity of membrane sensors is one of the most important parameters that determines the utility of the sensor. Thus, selectivity studies were carried out only for sensor no 5, which exhibited the best performance characteristics. The selectivity coefficients ($K_{Cu^{2+},B}^{Pot.}$) were determined by the modified form of Fixed Interference Method as suggested by Sae's de Viteri and Diamond [36] and are given in Table 3.

A selectivity coefficient of 1.0 signifies an identical response towards both the primary ion and the interfering ion. As presented in Table 3, the obtained selectivity coefficients are considerably lower than 1.0, indicating that the sensor exhibits high selectivity for Cu^{2+} in comparison to the examined mono-, di-, and trivalent cations. Therefore,

this sensor is suitable for the determination of Cu^{2+} in the presence of these metal ions, provided their concentrations are equal to or lower than that of Cu^{2+}.

3.4 Potentiometric Titration

The applicability of the sensor was further evaluated by employing it as an indicator electrode in the potentiometric titration of Cu^{2+} ions. For this purpose, 10 mL of 1.0×10^{-3} M $Cu(NO_3)_2$ solution was titrated against 1.0×10^{-2} M EDTA. The pH of the medium was adjusted and maintained at 4.0 using dilute HCl and NaOH. The resulting titration curve (Figure 4) exhibited a typical sigmoidal profile, and the equivalence point confirmed the 1:1 stoichiometric formation of the Cu-EDTA complex.
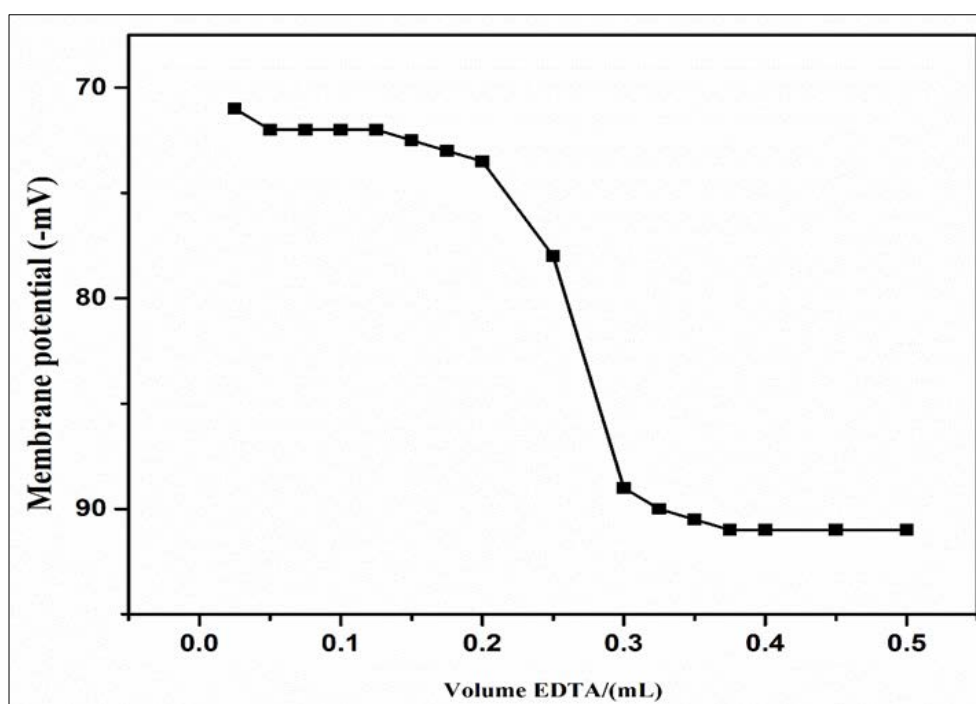

Fig 4: Potentiometric titration plot of 1.0×10^{-3} M Cu^{2+} solution (10 mL) with EDTA (1.0×10^{-2} M).

4. Analytical Application

The sensor was also used to determine the concentration of Copper in waste water. The result obtained by the proposed sensor is in good agreement with AAS (Table 4).

Table 4: Quantification of Copper in waste water using AAS and Cu^{2+} sensor (No 5)

Name of Samples	Proposed Sensor (mg L⁻¹)	Determination by AAS (mg L⁻¹)
Wastewater 1	1.64±0.02	1.59±0.05
Wastewater 2	2.43±0.05	2.39±0.03
Wastewater 3	0.26±0.03	0.24±0.04

5. Conclusion

The present study highlights the effectiveness of the membrane sensor containing the imine-quinoline derivative ligand, (Z)-3-(((2-((2 aminophenyl)thio) phenyl)imino) methyl)-7-chloronaphthalen-2-ol (IQL), as the electroactive component for the selective detection of Cu^{2+} ions. The sensor exhibits a wide linear response over the concentration range of 5.0×10^{-7} to 1.0×10^{-1} mol L⁻¹ with an optimal working pH window of 2.8-5.8. Interfering ions commonly coexisting with Cu^{2+} in real samples show negligible effect on its performance. The electrode has also been successfully applied as an indicator in the potentiometric titration of Cu(II) with EDTA, demonstrating its analytical applicability. The sensor offers rapid response, high

reproducibility, and prolonged operational stability exceeding six months in both aqueous and mixed solvent systems. Compared with previously reported copper-selective electrodes, the proposed sensor displays either equivalent or superior performance in terms of detection limit, concentration range, pH tolerance, and response time. Thus, this electrode represents a valuable contribution to the development of reliable Cu^{2+} ion-selective sensors for routine analytical applications.

6. Acknowledgements

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