

Copper Selective Electrode Based on 1,8-bis(2-Hydroxynaphthaldiminato)3,6-Dioxaoctane

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Abstract

A coated-wire ion selective electrode, which was selective and sensitive to Cu (II) ions, was developed using 1, 8-Bis(2-hydroxynaphthaldiminato)3, 6-dioxaoctane as carrier. The electrode exhibits a good potentiometric response for Cu (II) over a wide concentration range (3.3×10^{-6} -1.0 M) with a slope 29.0 ± 0.5 mV/decade. The proposed electrode has a response time between 10-15 s. The electrode is suitable for use in aqueous solutions in a wide pH range of 4.0 to 8.0. Applications of the proposed electrode to the determination of copper in real samples and as an indicator electrode for potentiometric titration of Cu²⁺ ion with EDTA are reported.

Keywords: Coated wire copper-selective electrode, 1,8-Bis(2-hydroxynaphthaldiminato)3,6- Dioxaoctaneas, Potentiometry

Introduction

The ion-selective electrode (ISE) approach to trace analysis is advantageous because of the speed and ease of ISE procedures in which little is required. Further, ISEs possess wide dynamic ranges, and are relatively low in cost. Ion-selective electrodes based on neutral carrier ligands are well established for alkali and alkaline-earth metal cations.¹⁻⁴ A significant number of macrocyclic compounds including crown ethers, cryptands, aza-crowns and thiocrowns, which have been synthesized in various cavity sizes and shapes, have already been exploited for the fabrication of poly(vinyl chloride) (PVC) membrane electrodes for transition and heavy metal ions.⁵⁻¹² Essentially, the neutral carriers have the characteristics of being uncharged, lipophilic, and undergoing reversible complexation with selected cations and hence of promoting cation transfer between the aqueous phase and the organic membrane phase by means of carrier translocation.

Copper ion generally exists as Cu (II) oxidation state, and, less often as Cu (I). Cu (II) forms amino, tartrate and EDTA complexes. The determination of copper is important due to its widespread use in industries and catalytic processes and its occurrence in various effluents. The demand for trace analysis for copper arises primarily in environmental and biological sciences since copper, although essential to life, is toxic at higher concentrations.¹³ Copper is one of the most widely distributed elements in the environment of industrialized countries. It is present in all organisms,

land and marine. It has been shown that copper is an essential element for many biological processes such as blood formation and function of many important enzymes.¹⁴⁻¹⁸ This element plays a vital role as a catalytic cofactor for several enzymes including cytochrom oxidase, superoxide-dismutase and other multi copper oxidations.¹⁹

In this paper, we report the use of 1,8-bis(2-hydroxynaphthaldiminato)3, 6-dioxaoctane as a neutral carrier in the construction of a new PVC membrane electrode selective to Cu (II) ions.

Experimental

Reagents

1,8-bis(2-hydroxynaphthaldiminato)3,6-dioxaoctane as neutral carrier (Fig.1) was prepared according to following method.

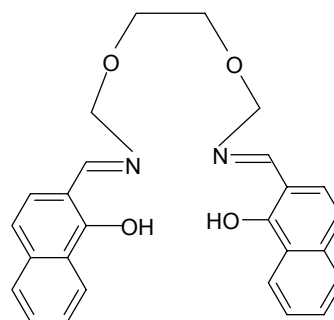


Figure 1. Structure of 1,8-bis(2-hydroxynaphthaldiminato)3, 6-dioxaoctane used as carrier in the Cu²⁺-CWSE.

Sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF), ethylenediaminetetraacetic acid (EDTA), hydrochloric acid, sodium hydroxide and nitrate or chloride salts of all cations, investigated as interferences, were of analytical reagent grade from Merck and were used as received, except THF, which was distilled before use. PVC of high relative molecular weight and dibutylphthalate (DBP) of high purity available from Aldrich were used without further purification. All metal ion solutions were prepared in doubly distilled water and solutions of different concentrations were made by serial dilution of 1.0 M stock solutions. The pH response profile for electrode was examined by the use of different concentrations of copper (II) ions.

Electrode Preparation

A mixture of PVC, plasticizer and the membrane additive, to give a total mass of 200 mg, was dissolved in about 5 mL of THF. To this mixture was added, ionophore [1,8-bis(2-hydroxynaphthaldiminato) 3,6-dioxaoctane] and the solution was mixed well. Membrane compositions are listed in Table 1. A platinum wire, about 1 mm diameter and 10 mm long, sealed into the end of a glass tube and soldered on to a shielded cable, was cleaned using nitric acid. The clean wire was then coated by repeated dipping (several times, a few minutes between dips) into the membrane solution in THF and allowed to dry each time. The electrodes were rinsed with water and conditioned in 0.1 M copper nitrate solution. Conditioning time was about 3 h for successive uses. The coating solutions are stable for several weeks if kept in refrigerator and can be used for the construction of new membranes.

Apparatus

Potentials were measured with a Metrohm model 691 pH / mV meter. A saturated calomel electrode (SCE, Metrohm) with a double junction was used as the reference electrode. The pH of the sample solutions was monitored simultaneously with a conventional glass pH electrode (Metrohm). Atomic absorption spectrometer (Perkin-Elmer, Model 2380) with an air-acetylene flame was used as a reference method for determination of copper in rock samples. Measurements were performed according to the manufacturer's directions.

Potential measurements and calibration

The coated-wire electrode containing 1,8-Bis(2-hydroxynaphthaldiminato) 3,6-dioxaoctane carrier was used as the measuring electrode in junction with a double junction saturated calomel electrode (SCE, Metrohm). All measurements were performed at ambient temperature (25 ± 1 °C) using the galvanic cell of the following type:

– Hg, Hg₂Cl₂, KCl (saturated) || sample solution | PVC membrane | Pt electrode

The performance of each electrode was investigated by measuring its potential in copper nitrate solutions prepared in the concentration range of 1.0×10^{-7} –1.0 M by serial dilution at constant pH with buffer solutions. Activities were calculated according to the Debye-Hückle procedure.²⁰ Concentration was used instead of activity for construction of the calibration curve. The pH of the sample solutions were monitored simultaneously with a conventional glass pH electrode (Metrohm).

Before starting the measurements, the electrode was preconditioned in stirred water until a steady potential was obtained. The solutions were stirred and potential readings recorded when they became stable. The data were plotted as observed potential vs. the logarithm on the copper concentration.

Preparation of 1,8-Bis(2-hydroxynaphthaldiminato) 3,6-dioxaoctane

The Schiff base ligand was prepared according to literature through a well-known procedure as follows: 2-hydroxy-1-naphthaldehyde (0.008 mol, 1.376 g), was dissolved in 30 mL ethanol and transferred into a 250 mL three-neck flask. 0.016 mol, (2.37 g) 1,8-diamino-3,6-dioxaoctane in 30 mL of ethanol was added drop wise to the flask at room temperature under stirring. The stirred mixture was kept reacting for 1 h, under reflux, and then cooled to room temperature. The solid product was filtered and then recrystallized from chloroform and vacuum dried for 12 h. Yield ~80%, anal.calcd. for C₂₆H₂₄O₄N₂: C, 73.66; H, 6.18; N, 6.14; Found: C, 73.83; H, 6.31; N, 6.29. IR (wave number, cm⁻¹): 3450 (-OH), 1640 (C=N); ¹H NMR / CDCl₃ / δ (ppm): 13.4 (OH, s, br), 7.81 (N=CH, s), 6.81-7.29 (C₁₀H₆, m), 3.51(CH₂, t), 2.81 (CH₂, t).

Results and Discussion

The 1,8-Bis(2-hydroxynaphthaldiminato)3,6-dioxaoctane as a carrier was found to be highly responsive to Cu (II) with respect to several other metal ions. Therefore, we studied in detail the performance of the plasticized PVC membrane containing this ionophore for Cu (II) in aqueous solutions.

In order to test the performance of the membrane characteristics, various operation parameters including selectivity, response time, sensitivity, lifetime, linear range, the influence of pH and the membrane composition on the response of the electrode were investigated.

Influence of membrane composition

It is well known that the sensitivity, linear dynamic range and selectivity of the ion selective electrodes

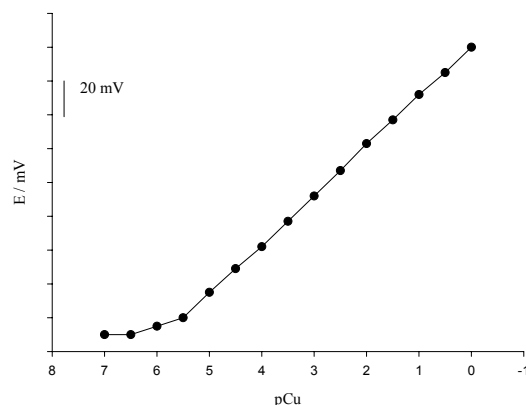
Table 1. Composition of several typical membranes together with some of their response characteristics.

No.	%PVC	%DBP	%Ionophor	%NaTPB	Slope mV/decade	Linear range / M
1	31	61	4	4	26.0	3.3×10^{-5} –1.0
2	32	61	4	3	22.0	1.0×10^{-5} – 1.0×10^{-1}
3	31	60	4	5	28.0	3.3×10^{-6} –1.0
4	31	61	3	5	23.0	1.0×10^{-5} –1.0
5	30	60	5	5	29.0	3.3×10^{-6} –1.0
6	30	59	6	5	27.0	3.3×10^{-6} –1.0
7	29	60	5	6	28.0	3.3×10^{-6} –1.0
8	31	60	5	4	26.5	1.0×10^{-5} –1.0

depend not only on the nature of the carrier used, but also significantly on the membrane composition and the properties of the additives employed. Thus, the influence of the membrane composition, nature and amount of plasticizer, and lipophilic additives on the potential response of the membranes were investigated. Several membrane compositions were investigated by varying the ratio of PVC, DBP and ionophore as the membrane active material. Table 1 presents the compositions of several typical membranes, along with their other characteristics. The potential response of all the electrodes was studied in the concentration range 1.0×10^{-7} –1.0 M Cu^{2+} . As can be seen in Table 1, increase in the concentration of the membrane active phase up to 5% (by weight) seems to be beneficial for obtaining any electrode slope closer to the theoretical value. Among the different compositions studied, membrane 5 incorporating 30% PVC, 60% DBP, 5% ionophore and 5% NaTPB shows the best sensitivity. The potential response of the optimized coated-wire electrode to varying concentrations of Cu (II) ions was examined. The calibration plot is shown in Fig. 2, which indicates a linear range from 3.3×10^{-6} –1.0 M Cu^{2+} with a Nernstian slope of 29.0 ± 0.5 mV per decade of Cu^{2+} concentration.

It was observed that the potentiometric response of the electrode toward Cu (II) is dependent on the concentration of the ionophore incorporated within the membrane. Maximum sensitivity was observed for the membrane containing 5% weight of the ionophore. The characteristic parameters of the optimized membrane are summarized in Table 2.

It is known that lipophilic salts not only reduce the membrane resistance, but also enhance the response behavior and selectivity, and reduce interferences from sample anions.^{21,22} The presence of lipophilic ionic sites is beneficial for both neutral carrier and charged carrier based ion-selective electrodes.^{23,24} Neutral carrier based cation-selective electrodes require lipophilic ionic sites with a charge sign opposite to that of the primary ion for obtaining a Nernstian response.^{25,26}

**Figure 2.** Calibration plot of the Cu^{2+} -CWISE based on 1,8-bis(2-hydroxynaphthaldimino)3,6-dioxaoctane.**Table 2.** Specifications of the Cu^{2+} -CWISE based on 1,8-bis(2-hydroxy naphthaldimino)3,6-dioxaoctane

Properties	Values/range
Optimized membrane composition	PVC(30%), DBP(60%), Ionophor(5%), NaTPB(5%)
Electrode type	Coated-wire (Pt) electrode
pH range	4.0–8.0
Linear range / M	3.3×10^{-6} –1.0
Detection limit / M	1.0×10^{-6}
Slope / mVdecade ⁻¹	29.0 ± 0.5
Standard deviation	± 0.9 for 1.0×10^{-4} and ± 0.6 for 1.0×10^{-3} M
Response time / s	10–15 (for 1.0×10^{-1} – 1.0×10^{-5} M)

However, for the charged carrier based ion-selective electrodes, the charge sign of the ionic sites that gives the highest potentiometric selectivity's depends on the charge of the ionophore, charge of the primary and interfering ions as well as on the stoichiometry of their complexes with the ionophore.²⁷ Therefore, from the different effect the charge of the added ionic sites has on neutral and charged carrier based ion-selective electrodes, the carrier mechanism

may be evaluated by investigating membranes that contain ionic sites of opposing charges.^{28,29} On the basis of the above discussions, enhancement of the electrode response in the presence of NaTPB, i.e., higher sensitivity and wider linear range, it appears that 1,8-Bis(2-hydroxynaphthalidinato)3,6-dioxaoctane acts as a neutral carrier in the membranes.

Response characteristics of the electrodes

The effect of pH of the test solution on the response of the membrane electrodes was examined at two copper concentrations. As illustrated in Figure 3 for 1.0×10^{-2} M Cu (II), the potentials remain constant from pH of about 4.0 to 8.0. Variation of the potential at $\text{pH} < 4.0$ could be related to protonation of the ligand in the membrane phase, which results in a loss of its ability to complex with Cu^{2+} ions. The working pH range is slightly reduced at lower Cu^{2+} concentrations, and therefore, all of the measurements were performed at pH 6.0. At higher pH (> 8.0), the potential drop may be due to the hydrolysis of the Cu^{2+} ions.

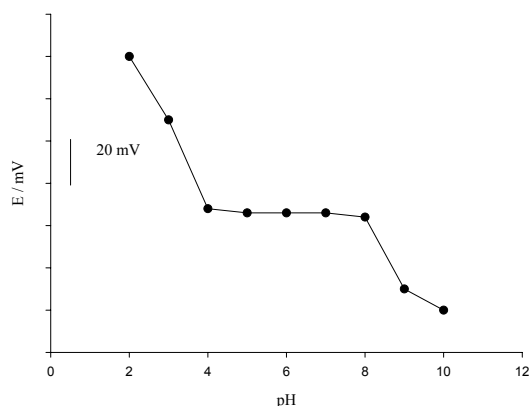


Figure 3. The pH response of the Cu^{2+} -CWISE based on 1,8-bis(2-hydroxynaphthalidinato)3,6-dioxaoctane at 1.0×10^{-2} M Cu^{2+} concentration.

The stability and reproducibility of the electrodes were also tested. The standard deviations of 20 replicate measurements for PVC sensor at 1.0×10^{-3} and 1.0×10^{-4} M copper were ± 0.6 and ± 0.9 mV, respectively. The long-term stability of the electrode was studied by periodically recalibrating in standard solutions and calculating the response slope over the range of 1.0×10^{-7} – 1.0 M. The slopes of the electrode response were reproducible to within 2.5 mV/decade over a period of two months (Table 3).

The IUPAC preferred manner of reporting response times is now a defined rate ($\Delta E/\Delta t$) instead of the previously used $t_{0.95}$.³⁰ Accordingly, the response time is defined herein as the time between addition of analyte to the sample solution and the time when a steady-state potential with less than 0.1 mV/min change has been achieved.

Table 3. Stability and reproducibility of the Cu^{2+} -CWISE ($n=5$).

Time (day)	Slope (mV/decade)	Linear range (M)
1	29.0 ± 0.5	$3.3 \times 10^{-6} - 1.0$ M
7	29.0 ± 0.5	$3.3 \times 10^{-6} - 1.0$ M
14	29.0 ± 0.5	$3.3 \times 10^{-6} - 1.0$ M
21	29.0 ± 0.5	$3.3 \times 10^{-6} - 1.0$ M
35	28.5 ± 0.6	$8.0 \times 10^{-6} - 1.0$ M
49	28.1 ± 0.6	$8.0 \times 10^{-6} - 1.0$ M
60	27.8 ± 0.7	$1.0 \times 10^{-5} - 1.0$ M
70	27.8 ± 0.8	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$ M

The response time of the electrode was measured after successive immersion of the electrode in a series of copper solutions, in each of which the copper concentration was increased tenfold, from 1.0×10^{-6} to 1.0 M. The static response time thus obtained was 10 s for 1.0×10^{-1} M copper concentration. At lower concentrations, however, the response time was longer and reached 15 s for a copper concentration of 1.0×10^{-5} M. The actual potential versus time traces is shown in Figure 4. The potentials remained constant for approximately 5 min, after which a very slow change within the resolution of the meter was recorded. The sensing behavior of the membrane electrode did not depend on whether the potentials were recorded from low to high concentrations or vice versa.

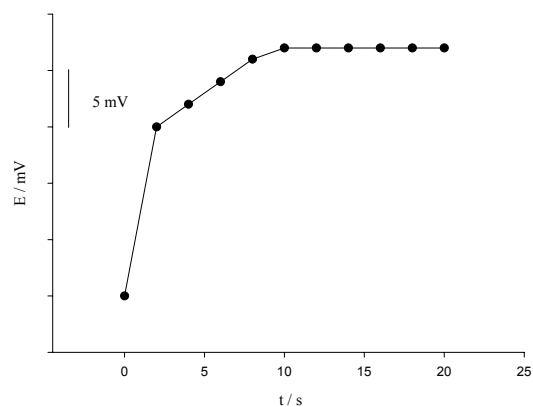


Figure 4. The response time of the Cu^{2+} -CWISE based on 1,8-bis(2-hydroxy-naphthalidinato)3,6-dioxaoctane for changing the concentration from 1.0×10^{-4} to 1.0×10^{-3} M Cu^{2+} .

Using the optimized membrane composition and conditions described above the potentiometer response of the sensor systems was studied in Cu^{2+} concentration range of 1.0×10^{-7} – 1.0 M at constant pH of 5.5. The calibration plot of this electrode is shown in Fig 2, which indicates a linear range from 3.3×10^{-6} to 1.0 M Cu^{2+} with a Nernstian slope of 29.0 ± 0.5 mV/decade of Cu^{2+} concentration. The limit of detection defined

as the concentration of copper ion obtained when extrapolating the linear region of the calibration plot to the base-line potential was 1.0×10^{-6} M.

Selectivity of the electrodes

The selectivity is clearly one of the most important characteristics of any ion-sensitive sensor. It is response to the primary ion in the presence of other ions present in solution, which is expressed in terms of the potentiometric selectivity coefficients. The selectivity coefficient should preferably be evaluated by measuring the response of an ion selective electrode in solutions of the primary ion, Cu (II), and an interfering ion, M^{n+} (fixed interference method). The selectivity coefficients of the proposed electrode with respect to several cations are presented in Table 4.

Table 4. Selectivity coefficients of the Cu^{2+} -CWISE using the fixed interferences method.

Interferent species	$K_{\text{Cu},M}$	Interferent species	$K_{\text{Cu},M}$
Li^+	9×10^{-4}	Hg^{2+}	1×10^{-4}
Na^+	5×10^{-3}	Ba^{2+}	1×10^{-5}
Ag^+	7.5×10^{-2}	Cd^{2+}	6×10^{-4}
Mg^{2+}	3×10^{-4}	Ce^{4+}	1×10^{-4}
Ca^{2+}	5×10^{-3}	Sr^{2+}	2×10^{-5}
Ni^{2+}	2×10^{-4}	Al^{3+}	5×10^{-2}
Pb^{2+}	7.5×10^{-3}	Cr^{3+}	2×10^{-3}
Co^{2+}	4.5×10^{-3}	Fe^{3+}	3×10^{-2}
Na^+	5×10^{-2}	Mn^{2+}	2×10^{-4}
K^+	3.5×10^{-2}	Zn^{2+}	6×10^{-3}

The selectivity coefficient pattern clearly indicates that the electrode is highly selective to Cu (II) over alkali, alkaline earth, and several common transition and heavy metal ions. From the potentiometric

selectivity data in Table 4, it is obvious that 1,8-bis(2-hydroxynaphthaldiminato) 3,6-dioxaoctane interacts relatively strongly with Cu (II) ion and can be used successfully as a sensing agent in copper selective electrodes.

Table 5 compares the linear range, detection limit, slope, response time and selectivity coefficients of several reported copper-selective electrodes^{31–37} with those of the proposed electrode. It is noteworthy that the selectivity coefficients, linear range, slope and response time of the proposed electrode are considerably improved with respect to those the previously reported copper-selective electrodes.

Analytical Applications

The optimized coated-wire electrode was successfully applied as an indicator electrode in the potentiometric titration of Cu (II) solution with EDTA. Typical results for titration of a 20.0 mL 0.005 M Cu^{2+} solution with 0.01 M EDTA are shown in Fig. 5. A very good inflection point, showing perfect stoichiometry, was observed in the titration plot.

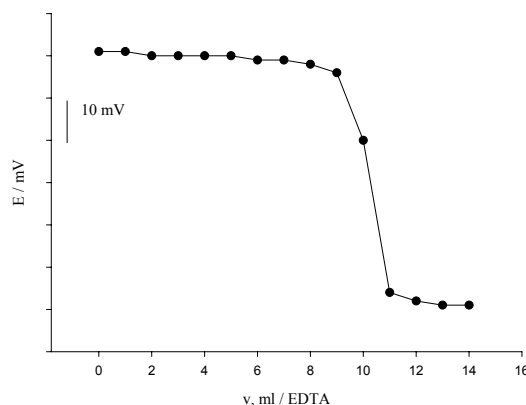


Figure 5. Potentiometric titration curve for 20 mL 0.005 M Cu (II) with 0.01 M EDTA, using the proposed Cu^{2+} -CWISE.

Table 5. Comparing some of the Cu^{2+} -CWISE characteristics with some of the previously reported Cu^{2+} -ISEs.

References	Slope (mV/decade)	Linear range (M)	DL (μM)	Interfering ions with $K^{\text{pot}} \geq 1 \times 10^{-1}$	Response time (s)
Proposed electrode	29.0 ± 0.5	$3.3 \times 10^{-6} - 1.0$	1.0	–	10–15
31	29.5 ± 1	$3.0 \times 10^{-6} - 5.0 \times 10^{-2}$	1.0	$\text{Hg}^{2+}, \text{Ag}^+$	5
32	30 ± 1	$7.0 \times 10^{-7} - 5.0 \times 10^{-2}$	0.6	Pd^{2+}	10
33	28.5	$1.0 \times 10^{-4.5} - 1.0 \times 10^{-2.5}$	10	–	–
34	28.5	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	10	Na^+, Ag^+	≤ 30
35	28.5	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	0.5	–	15
36	28.2	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	0.5	–	10–15
37	29.6	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$	4.7	$\text{Hg}^{2+}, \text{Ag}^+$	< 30

The electrode was also used for the potentiometric measurement of copper ion in real samples. A 1.0 g of coin was dissolved in nitric acid by heat and then diluted to a volume of 1.0 liter with distilled water. Rock and wastewater samples preparations were performed as instruction manual of factory. The copper content was determined potentiometrically by the standard addition method and also by atomic absorption spectrometry (AAS), as a reference method. The results, which are given in Table 6, show a satisfactory agreement between the two methods.

Table 6. Application of the Cu²⁺-CWISE for determination of copper content in real samples.

Real sample	Atomic absorption method (ppm)	Coated-wire copper-selective method (ppm)
Wastewater sample	2.3 ± 0.2	2.4 ± 0.3
Rock sample 1	79.0 ± 1.0	78.4 ± 1.0
Rock sample 1 + copper added (15ppm)	95.0 ± 0.5	95.5 ± 1.0
Coin, %w(Cu)	81.0 ± 0.2	79.5 ± 0.5

Conclusions

Taking all the discussed results into account, the proposed electrode is very easy to prepare and show high sensitivity and wide dynamic range. The high degree of copper selectivity by the electrode makes it potentially useful for monitoring concentration levels of copper in real samples, without the need for preconcentration or pretreatment steps and without significant interactions from other cationic species present in the samples. The proposed electrode has been shown to have good operating characteristics (sensitivity, stability, response time, detection limit and a wide linear range). The electrode was successfully applied for the determination of copper content in real samples.

Acknowledgements

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Povzetek

Za selektivno določanje Cu(II) ionov smo z uporabo 1,8-bis(2-hidroksinaftaldiminato)-3,6-dioksaoktana razvili ionoselektivno elektrodo na osnovi prevlečene žice. Elektroda ima dober potenciometrični odziv v širokem koncentracijskem intervalu ($3,3 \times 10^{-6}$ -1,0 M) z naklonom $29,0 \pm 0,5$ mV/dekado z odzivnim časom 10–15 s. Uporabna je v vodnih raztopinah s pH 4,0-8,0. Podajamo tudi primer uporabe razvite elektrode za določanje bakra v realnih vzorcih in kot indikatorsko elektrodo pri potenciometričnih titracijah Cu²⁺ionov z EDTA.