

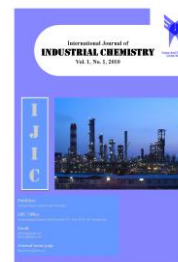


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Carbon Paste Electrode Modified with 2-Carboxythiophene Benzoylhydrazone as a Potentiometric Sensor for Cu(II)

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Abstract

A new modified carbon paste electrode (CPE) based on a recently synthesized ligand, 2-carboxythiophene benzoyl hydrazone (SHBHy), as a suitable carrier for copper(II) ion was described. The electrode exhibits a Nernstian slope of 28.3 mV per decade for Cu (II) ion over a wide concentration range from 3.9×10^{-6} - 1.0×10^{-3} mol/L. The lower detection limit is 2.5×10^{-6} mol/L Cu(II). The electrode has a fast response time (ca. 5-10 s). The proposed sensor shows a fairly good selectivity toward copper(II) ion in comparison to other common cations. The potentiometric responses are independent of the pH of the test solution in the pH range 3.8-5.8. Finally, it was satisfactorily used as an indicator electrode in complexometric titration with EDTA and determination of copper(II) in tap and well water samples.

Keywords: Cu(II); Ion selective electrode; Modified carbon paste electrode; Potentiometry.

1. Introduction

Copper is an important metal pollutant due to its widespread use and subsequent distribution into the environment, coupled with its toxicity at excess levels. The toxicity is generally attributed to the aquo-complexed "free" cupric ion (Cu^{2+}) rather than the inorganic or organic complexes [1]. Therefore, measurement of free Cu(II) is extremely important in assessing copper toxicity and environmental monitoring.

A number of methods used for determination of copper ions such as atomic absorption spectroscopy (AAS), cold vapor,

flam atomic absorption spectroscopy-electrothermal atomization (AAS-ETA) [2]. Spectrophotometry [3], anodic stripping voltammetry [4] and Chromatography [5].

However, these methods comprise sample manipulations, extraction steps, derivatization reactions that are liable to various interferences as well as being not applicable to colored and turbid solutions. These methods are expensive for they require large infrastructure backup and qualified personnel.

Thus, there is critical need for the development of a selective, inexpensive,

diagnostic tool for the determination of this analyte. Analytical methods based on potentiometric detection with ion-selective electrodes (ISEs) can be considered a good alternative for the attractable characteristics mentioned above. Many sensors for potentiometric determination of copper(II) have been reported [6-10].

In this work, the SNO-tridentate ligand, 2-thiophenecarboxaldehyde benzoylhydrazone (2-carboxythiophene benzoylhydrazone), was found sensitive for Cu(II). Therefore a Cu(II) sensitive electrode utilizing this ligand was designed, fully characterized in terms of its concentration range 3.9×10^{-6} - 1.0×10^{-3} mol/L and detection limit of 2.5×10^{-6} mol/L. It was used successfully for determination of Cu(II) in tap and well water samples through the pH range 3.8-5.8 in a short response time (ca. 5-10 s).

2. Experimental

2.1. Reagents

The ionophore (2-thiophenecarboxaldehyde benzoylhydrazone), was prepared as reported [11]. Freshly distilled water was used in preparing all solutions. Reagents grade pure graphite powder as well as the plasticizers, dioctyl phthalate (DOP), dibutyl phthalate (DBP), tris(2-ethylhexyl) phosphate (DOPh), dioctyl sebacate (DOS), as well as all metal salts such as chlorides, nitrates and sulphates were purchased from Aldrich. Diethyl ether and methanol, (spectroscopic grade) were commercially available. All reagents and solvents were used as received.

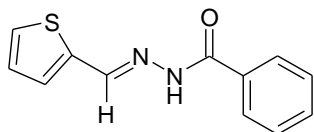


Fig. 1. The chemical structure of 2-carboxythiophene benzoyl hydrazone (SHBHy)

2.2. Apparatus

Potentiometric and pH measurements were made with a Pocket pH/mV Meters, pH315i (Wissenschaftlich-Technische Werkstätten GmbH (WTW)-Germany), under stirring conditions at room temperature (25.0 ± 1.0 °C). Potential readings were recorded when stable values had been obtained after each addition and these values were plotted against the logarithm of Cu(II) activities. The electrochemical system is represented as follows: Hg, Hg₂Cl₂(s), KCl(sat.)|| sample solution |carbon paste electrode

2.3. Preparation of the Electrode

The modified carbon paste electrode was made according to a general procedure as described elsewhere [12]. High purity graphite, ionophore and different types of plasticizers were intimately hand mixed in a Petri dish to obtain a very fine paste. A portion of the composite mixture was packed firmly into the end of a disposable polypropylene syringe (ca. 3 mm i.d. and 6 cm long) where electrical contact was established with a copper wire screw. To obtain stable electrochemical response, the outer layer of the carbon paste is renewed before each set of measurements by polishing the surface of the electrode. The sensor was used directly for potentiometric measurements without pre-conditioning.

2.4. Selectivity coefficient determination

The separate solution method (SSM) and the Matched Potential Method (MPM) [13] were employed to determine the selectivity coefficients, $\log K_{Cu^{2+}, J^{z+}}^{pot}$, of the potentiometric sensors towards different species.

In the SSM, the potential of a cell comprising a working electrode and a reference electrode is measured in two separate solutions, one containing the copper ions, E_1 , and the

other containing the interferent ions (J), E_2 , and S is the slope of the calibration graph.

These values were used to calculate the selectivity coefficient, $\log K_{Cu^{2+}, J^{z+}}^{pot}$ from the following equation:

$$\log K_{Cu^{2+}, J^{z+}}^{pot} = \frac{E_2 - E_1}{S} + \log[Cu^{2+}] - \log[J^{z+}]$$

In MPM, specified amounts of $CuCl_2$ in the range of 2×10^{-4} to 2×10^{-5} mol/L were added to a reference solution of $CuCl_2$, and the corresponding potential change (ΔE) was measured. In a separate experiment, the interfering ion (J) (in the range of 1.0×10^{-1} – 1.0×10^{-2} mol/L) was successively added to an identical reference solution until the change in potential matched the ΔE value. The values of $\log K_{Cu^{2+}, J^{z+}}^{pot}$ were then calculated using the following equation:

$$\log K_{Cu^{2+}, J^{z+}}^{pot} = \frac{a_{Cu^{2+}}}{a_J}$$

Where the a_J is the activity of the added interferent.

2.5. Sample preparation

The analysis of water samples does not require pretreatment before potentiometric determination using the present sensor. Analyses were performed using the standard addition method on 100 mL of water samples followed by spiking with either 1.0×10^{-3} or 1.0×10^{-2} mol/L $CuCl_2$.

3. Results and discussion

3.1. Response of the electrode based (SHBHy) to Cu(II) ions

Potentiometric response of the (SHBHy) modified electrode was tested for different cations such as Na(I), K(I), NH_4 (I), Li(I), Ca(II), Zn(II), Mg(II), Cd(II), Ba(II), Cu(II), Co(II), Ce(III) and Al(III) ions. As can be seen from Fig. 2, the slopes of the linear parts of the

potential responses of the sensor for most of the tested cations are much lower than those expected by the Nernst equation. However, Cu(II) has the closest Nernstian response over a wide concentration range with low detection limit.

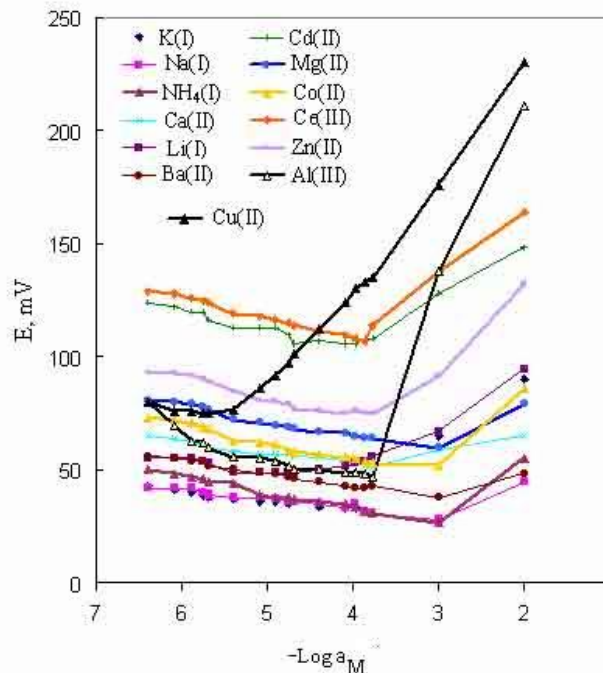


Fig. 2. Potential response of sensor for various metal ions.

3.2. Influence of membrane composition

3.2.1. Ionophore selection

Ionophores used in ISEs should have rapid exchange kinetics and adequate formation constants in the paste. In addition, they should have good solubility in the paste matrix and sufficient lipophilicity to prevent leaching from the paste into the sample solution [14]. The ionophore 2-thiophenecarboxaldehyde benzolyhydrazone is nearly insoluble in water. It is a tridentate ligand with one nitrogen, one oxygen and one sulfur atoms. The O, N and S atoms in the ionophore play the role of an electron pair donor, and coordinate metals such as Cu(II) ions as electron acceptors. Thus it is possible to use this ligand as an ion-selective ionophore.

3.2.2. Optimization of the composition of the paste

It is well known that the sensitivity, linear dynamic range and selectivity obtained for a given electrode depend significantly on the

composition of the paste [15,16]. Several compositions for the studied electrode were tested. They are presented in Table 1, along with their other characteristics of the electrode.

Table 1. The paste compositions and the electrode characteristics of copper(II) sensor.

No.	Composition (wt%)				Electrode characteristics		
	I	G	P	S	D.R (mol/L)	LOD (mol/L)	R(s)
1	0.0	51.4	48.6	10.3	5.0×10^{-4} - 1.0×10^{-3}	1.0×10^{-4}	15-20
2	0.2	51.0	48.8	15.5	1.0×10^{-5} - 1.0×10^{-3}	5.5×10^{-4}	8-12
3	0.5	51.0	48.5	28.3	3.9×10^{-6} - 1.0×10^{-3}	2.5×10^{-6}	5-7
4	1.0	50.8	48.2	21.3	1.5×10^{-5} - 1.0×10^{-3}	8.9×10^{-6}	8-10
5	2.0	50.2	47.8	20.1	3.9×10^{-6} - 1.0×10^{-3}	3.0×10^{-6}	10-12
Effect of plasticizers							
6	0.5	51.0	48.5 DOPh	28.3	3.9×10^{-6} - 1.0×10^{-3}	2.5×10^{-6}	5-7
7	0.5	51.0	48.5 DOP	24.5	2.5×10^{-6} - 1.0×10^{-3}	2.1×10^{-6}	10-15
8	0.5	51.0	48.5 DBP	24.3	5.8×10^{-6} - 1.0×10^{-3}	4.8×10^{-6}	10-15
9	0.5	51.0	48.5 DOS	12.2	2.8×10^{-4} - 1.0×10^{-3}	1.2×10^{-4}	10-15
Effect of g/p ratio							
10	0.95 (g/p)	48.5	51.0	25.6	3.9×10^{-6} - 1.0×10^{-3}	3.0×10^{-6}	5-7
11	1.05 (g/p)	51.0	48.5	28.3	3.9×10^{-6} - 1.0×10^{-3}	2.5×10^{-6}	5-7
12	1.15 (g/p)	53.4	46.5	32.5	7.7×10^{-6} - 1.0×10^{-3}	7.5×10^{-6}	5-10
13	1.25 (g/p)	55.6	44.4	33.9	1.25×10^{-5} - 1.0×10^{-3}	8.1×10^{-6}	8-12

I, ionophore; G, Graphite; S, slope (mV/decade); D.R., Dynamic range (mol/L); LOD, low of detection (mol/L); R, response time (s)

3.2.3. Optimization of the amount of the modifier in the paste

For this purpose, electrodes with different percentages of the modifier were prepared namely 0.2%, 0.5%, 1.0% and 2.0% (w/w). The slopes, concentration range, detection limit and response time of the above electrodes are given in Table 1. The electrode without the modifier (sensor No. 1) showed poor sensitivity to copper cation, but in the presence of the modifier the electrode showed remarkable selectivity for Cu(II). The sensitivity of the electrode response increased with increasing modifier until the value of 0.5 wt% (electrode No. 3). However, further increase of the ionophore, (sensors No. 4 and 5), display somewhat smaller slopes and sensitivity, most probably due to some inhomogenities and possible saturation of the paste [17]. It is well known that the sensitivity and selectivity of the electrode depend on graphite/plasticizer ratio used [18]. The graphite/plasticizer ratios of

0.90–1.25 were examined. It is interesting to note that the ratio of ca. 1.05 showed the optimum physical properties and ensured high enough mobilities of their constituents [19].

Pastes with G/P more than 1.25 produced “crumbly” pastes and those with ratio smaller than 0.90 had a consistency resembling that of “peanut butter”, i.e., not workable.

3.2.4. Plasticizer selection

Two parameters are of importance when manufacturing a carbon paste: (1) its mechanical stability and (2) its active surface area. Mechanical stability can be interpreted as the ability of the carbon paste to avoid erosion in solution. The use of plasticizers will give some permeable properties to the paste and will improve its mechanical stability by promoting binding between grains [20]. In addition, the solvent mediator, in particular, has a dual function: it acts as a liquifying agent, enabling homogenous solubilization and modifying the

distribution constant of the ionophore used. The proportion of solvent mediator must be optimized in order to minimize the electrical asymmetry of the paste, to keep the sensor as clean as possible, and to stop leaching to the aqueous phase [21]. For a plasticizer to be adequate for use in sensors, it should gather certain properties and characteristics such as having high lipophilicity, high molecular weight, low tendency for exudation from the paste matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the paste [22]. In exploration for a suitable plasticizer for constructing this electrode, we used four plasticizers, with the values of dielectric constants, lipophilicity and molecular weight respectively listed in parantheses, namely, DOS ($\epsilon_r = 4.2$, $P_{TLC} = 10.1$, M.wt. = 426), DOP ($\epsilon_r = 5.1$, $P_{TLC} = 7.1$, M.wt. = 390), DBP ($\epsilon_r = 6.4$, $P_{TLC} = 4.5$, M.wt. = 278), and DOPh ($\epsilon_r = 4.8$, $P_{TLC} = 10.2$, M.wt. = 435). The CPE with DOPh as a solvent mediator produced the best response, as shown in Fig. 2. It is likely due to high lipophilicity, relatively high molecular weight and low dielectric constant as well as two ester groups that, in principle, are capable of interacting with cationic species; hence this plasticizer may solvate and adjust the mobility of ionophore.

The results, given in Table 1, indicate that sensor no. 3, composed of 0.5% ionophore, 48.5% graphite and 51.0% plasticizer, gives the best sensitivity, with a Nernstian slope of 28.3 ± 0.5 mV/decade and detection limit of 3.0×10^{-6} mol/L over a relatively wide dynamic range (3.4×10^{-6} - 1×10^{-2} mol/L) of Cu^{2+} ions. Therefore, this composition was used to study the various operation parameters of the electrode. The electrochemical performance characteristics of this electrode were systematically evaluated according to the IUPAC recommendations [23].

3.3. Homogeneity, surface-renewal and reproducibility of the electrode

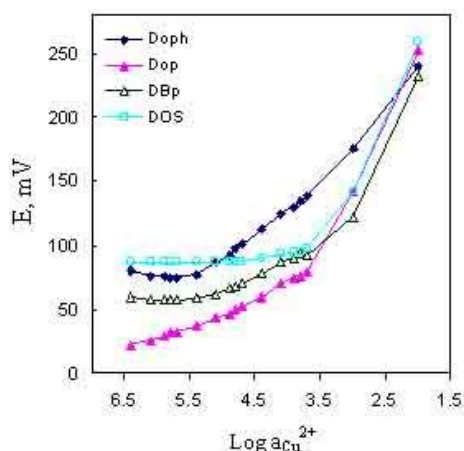
The main attraction of using the modified electrode is that the electrode surface can be renewed after every use. The bulk modified electrode can be renewed by squeezing a little carbon paste out of the tube and a fresh surface is smoothed on a piece of weighing paper whenever needed [24]. Accordingly, a paste of optimum composition and suitable weight (~1.5 g) can be used for several months without any deterioration or change in the response of the electrode. To test paste homogeneity, the proposed electrode was applied for copper measurement in a 1.0×10^{-5} mol/L copper(II) solution. The measurement was repeated five times and after each measurement the electrode surface was renewed as explained above. The average potential was 92 mV and the relative standard deviation (R.S.D.) 0.81, which are reasonable values. The slope of the calibration curve was found to decrease slightly from 28.3 to 20.5 mV/decade after five times of use. This decrease may be attributed to surface contamination and memory effect. Every use of the electrode results in coordination of copper ions to some of the functional groups on the surface. Repeated use of the electrode results in a drop of the measured potential as the number of coordination sites at the surface is limited. Precision in potential measurements of a certain solution requires removal of the coordinated sites. Therefore, the electrode surface should be polished to expose a fresh layer for use. The sensor reproducibility was evaluated on the same surface by three successive measurements and resulted in a relative standard deviation of 4.1% and 1.9% for 1.0×10^{-3} and 1.0×10^{-4} mol/L of Cu(II), respectively.

Table 2. Selectivity coefficients of various interfering ions for sensor

Interfering ions	SSM	MPM
NH ₄ ⁺	1.41×10 ⁻⁵	6.41×10 ⁻⁵
Na ⁺	3.51×10 ⁻⁶	3.15×10 ⁻⁶
K ⁺	2.01×10 ⁻⁶	2.26×10 ⁻⁶
Li ⁺	4.94×10 ⁻⁵	5.66×10 ⁻⁵
Cd ²⁺	5.09×10 ⁻⁴	8.31×10 ⁻⁴
Mg ²⁺	3.24×10 ⁻⁶	2.81×10 ⁻⁶
Ca ²⁺	3.13×10 ⁻⁵	4.10×10 ⁻⁵
Ba ²⁺	3.52×10 ⁻⁶	4.02×10 ⁻⁶
Zn ²⁺	4.73×10 ⁻⁵	5.11×10 ⁻⁵
Co ²⁺	3.31×10 ⁻⁵	4.26×10 ⁻⁵
Al ³⁺	1.98×10 ⁻²	3.73×10 ⁻²
Ce ³⁺	8.86×10 ⁻²	9.30×10 ⁻²

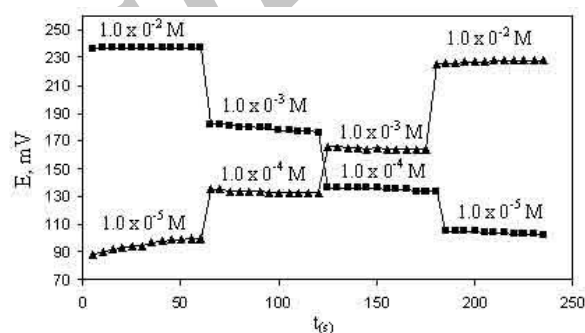
3.4. Effect of acidity

The influence of the acidity of the solution on the electrode potential of the Cu-CMCPE was studied for 1.0×10^{-5} and 1.0×10^{-4} mol/L CuCl₂ solutions. The acidity was adjusted by adding small volumes of (1 mol/L) HCl or NaOH to the test solutions and the variation in potential was followed. The results, shown in Fig. 3, indicate that the variation in potential due to pH change is considered acceptable in the pH range 3.8–5.8. However, there is a slight deviation at pH values lower than 3.8 which may be due to H⁺ interference. On the other hand, the potential decreases gradually at pH values higher than 5.8. This drop may be attributed to formation of free copper hydroxide in the test solution.

**Fig. 3.** Variation of electrode potentials with different plasticizers

3.5. Dynamic Response Time of Cu-CMCPE

It is well known that the dynamic response time of the modified electrode is one of the most important factors in its evaluation. The response time of the electrode is defined as the time between the addition of analyte to the sample solution and the time when a limiting potential has been reached [23]. In practice, the response time was recorded by increasing the Cu(II) ion concentration in solution from 1.0×10^{-5} to 1.0×10^{-2} mol/L and the result, depicted in Fig. 3, clearly indicates that the measured response time is 5-10 s.

**Fig. 4.** Dynamic response of Cu-CMCPE for step changes in concentration of Cu(II) (from low to high and vice versa)

3.6. Interference studies

The potentiometric selectivity coefficient of an electrode, one of its most important characteristics, is defined by its relative response for the primary ion over the other ions present in the solution [24]. The separate solution method (SSM) is recommended by IUPAC to determine the selectivity coefficient of the ISE [13]. SSM is based on Nernst–Eisenman equation. However, it has been shown that this method suffers some limitations in terms of the values for ions of unequal charges, a non-Nernstian behavior of interfering ions [25]. Therefore another method named the “matched potential method (MPM)” was recommended especially when the primary ion and/or the interfering ion dissatisfy the Nernst response or when the involved ions are

unequal in charge [26]. The resulting values, presented in Table 3, show that these sensors display significantly high selectivity for Cu(II) over many common inorganic ions. Comparing the selectivity coefficient values obtained for the investigated electrodes in both SSM and

MPM methods collected in Table 3, makes obvious that there is a measurable difference between the values for each interfering ion obtained in both cases. The values of selectivity coefficients obtained using MPM method are more reliable.

Table 3. Recovery of copper ions from different water samples

Sample	Cu ²⁺ added (mol/L)	Cu ²⁺ found (mol/L)	X	RSD%
Tap water				
Direct method	5.00 x 10 ⁻⁶	5.02 x 10 ⁻⁶	100.4	0.98
	5.00 x 10 ⁻⁵	4.96 x 10 ⁻⁵	99.2	1.03
Standard additions method	5.00 x 10 ⁻⁶	4.91 x 10 ⁻⁶	98.2	0.77
	5.00 x 10 ⁻⁵	4.85 x 10 ⁻⁵	97.0	0.85
Well water				
Direct method	5.0 x 10 ⁻⁶	5.11 x 10 ⁻⁶	102.2	1.46
	5.0 x 10 ⁻⁵	4.88 x 10 ⁻⁵	97.6	0.67
Standard additions method	5.0 x 10 ⁻⁶	4.89 x 10 ⁻⁶	97.8	1.21
	5.0 x 10 ⁻⁵	4.97 x 10 ⁻⁵	99.4	0.87

X: recovery; RSD: relative standard deviation.

3.7. Analytical performance

In order to test the analytical applicability of the proposed sensor, it has been applied for determination of copper ions in environmental samples using the standard additions method and the calibration curve method.

3.7.1. Titration of copper solution with a standard EDTA solution

The proposed electrode was successfully applied as an indicator in titration of 5.0 mL Cu²⁺ (1.0×10⁻³ mol/L) with a standard EDTA solution (1.0×10⁻² mol/L). The resulting titration curve is shown in Fig. 5. The amount of Cu²⁺ ions in solution could be accurately determined with the electrode.

3.7.2. Determination of copper ions in various water samples

In an analogous way, copper(II) was determined in tap water and well water using this electrode and the results, presented in Table 3, are reasonable as the recovery ranges are 97.8–100.4 % and R.S.D. ranges are 0.87–1.21.

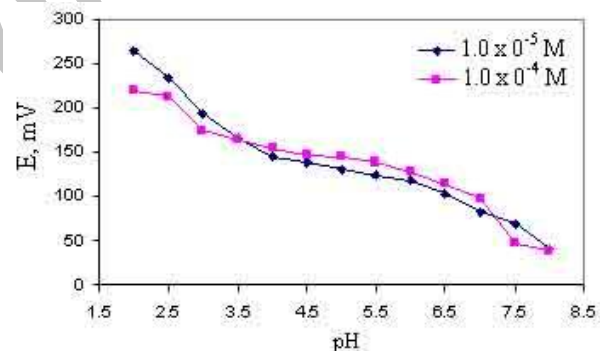


Fig. 5. Influence of pH on the response of the Cu-CMCPE at 1.0 x 10⁻⁴ and 1.0 x 10⁻⁵ mol/L

4. Conclusion

In this study, a new chemically modified carbon paste electrode based (CTBH) as ionophore was used for Cu(II) determination. The electrode shows high sensitivity (2.5×10⁻⁶), reasonable selectivity, fast static response, long term stability and applicability over a wide concentration range (3.5×10⁻⁶ to 1.0 ×10⁻³). The modified electrode was applied as indicator electrode in potentiometric titration and successfully used to determine mercury(II) in water samples with satisfactory results.

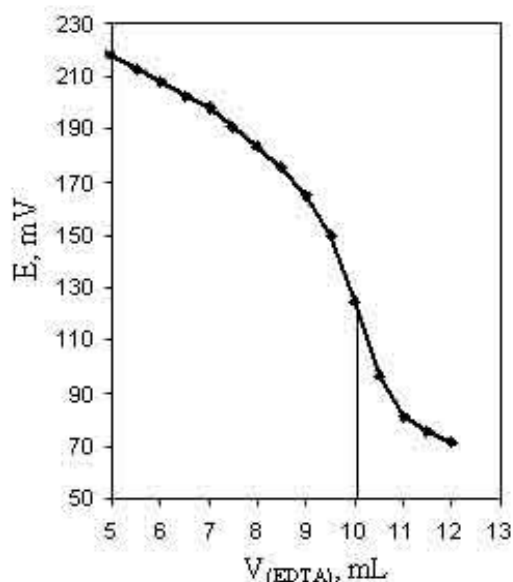


Fig. 6. Potentiometric titration curve of 10.0 mL of 1.0×10^{-3} mol/L solution of Cu(II) with 1.0×10^{-3} mol/L EDTA

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