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Research Article

Electrochemical determination of copper(II) ions based on a semicarbazone derivative molecule

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Abstract — In this study, a new potentiometric sensor selective for copper(II) ions was developed. A semicarbazone derivative molecule synthesized as an ionophore was used in the composition of the new sensor. The proposed polymer membrane sensor had a wide linear operating range of 1.0×10^{-5}–1.0×10^{-1} M, a low detection limit of 4.2×10^{-6} M, and a near-Nernstian response. The new copper(II)-selective sensor had a wide pH range, fast response time, good selectivity and good reproducibility. The sensor, whose potentiometric performance characteristics were successfully completed, was able to determine copper(II) ions in water samples with very high recoveries.

1. Introduction

Today, the negative effects of heavy metals on the economy, environment and public health are a cause for concern [1]. Copper, a heavy metal, is an important molecule for organisms at low concentrations and is an essential trace metal element absorbed in the stomach and small intestine in the human body [2]. Copper cannot be produced or synthesized in the body; therefore, it must be obtained from food sources. The World Health Organization (WHO) recommends a copper intake of 2–3 mg per day for adults [3]. High concentrations of copper are toxic to human cells and can lead to various diseases [4–6]. Therefore, the determination of copper in environmental and clinical samples is especially important.

Potentiometry is an electroanalytical method in which the potential of an electrode system consisting of reference and working electrodes is measured as a function of time [7]. Potentiometric ion selective electrodes (ISEs) have significant advantages such as simple use, fast response time, low detection limit, wide concentration range, low cost, reduced energy consumption, high selectivity and good reproducibility [8–10]. Potentiometric sensors have an important place in the determination of heavy metals in various samples due to the advantages they provide [11, 12].

Semicarbazones are bioactive organic compounds obtained by the condensation of semicarbazide with an aldehyde or ketone. Semicarbazones have a wide biological spectrum including antioxidant, anti-inflammatory, anticancer, antifungal, analgesic, anticonvulsant and antibacterial functions [13, 14]. At the same time, metal complexes have excellent ligand properties due to the presence of oxygen and nitrogen atoms. Transition metal complexes of semicarbazone have a wide range of uses due to their coordination abilities in different analytical applications [15].

In this study, a new potentiometric sensor selective for copper(II) ions was developed using a semicarbazone derivative molecule as an ionophore. The potentiometric performance characteristics of the proposed sensor were investigated under laboratory conditions.

2. Experimental

2.1. Chemicals and Apparatus

All chemicals and solvents used in the study were obtained from Sigma-Aldrich and Merck, and were of high purity. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance DPX–400 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C). Potential measurements were made on a multi-channel potentiometer (Medisen Medical Ltd. Sti., Türkiye) consisting of a reference electrode (Ag/AgCl; Thermo Scientific) and prepared sensors.

2.2. Synthesis of ionophore

(*E*)-2-((3-methylthiophen-2-yl)methylene)hydrazine-1-carboxamide was synthesized as previously reported in the literature [16, 17]. Briefly, 3-Methylthiophene-2-carbaldehyde (1 mmol) was dissolved in ethanol (15 mL). Semicarbazide (1 mmol) was dissolved in warm water (15 mL), and then added to this solution. 5 drops of acetic acid were subsequently added to this mixture. The reaction was stirred magnetically for 3h at room conditions. The precipitate formed at the end of the reaction was filtered off. After washing with ethanol several times, ionophore was ultimately synthesized.

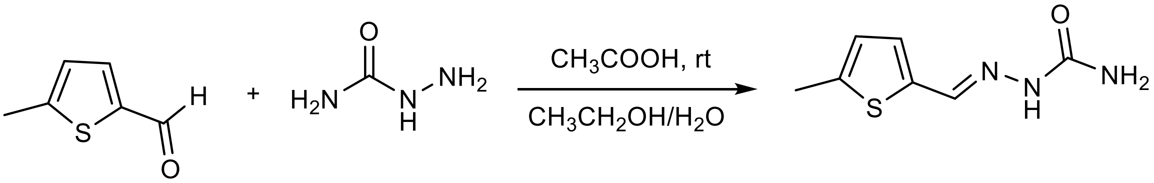

Figure 1. Synthesis schema of (*E*)-2-((3-methylthiophen-2-yl)methylene)hydrazine-1-carboxamide.

2.3. Preparation of sensors

In this study, the method frequently used in the literature was followed to prepare ion selective electrodes [18, 19]. 3 mL of tetrahydrofuran was added to the mixture containing 50.0% (*w/w*) graphite, 35.0% (*w/w*) epoxy and 15.0% (*w/w*) hardener and mixed until it becomes homogeneous. 20 cm copper wires with one end open were immersed in the mixture and dried for 24 hours in a dark medium. Then, poly(vinyl chloride) (PVC) membrane sensors were prepared. For this purpose, a mixture containing 3.0% synthesized ionophore, 64.0% bis(2-ethylhexyl)adipate (DEHA), 32.0% PVC and 1.0% potassium tetrakis(*p*-chlorophenyl)borate (KT*p*ClPB) was dissolved in 3 mL of THF. Previously prepared solid contact electrodes were dipped into this mixture several times in order to coat their surfaces. The prepared PVC membrane sensors were dried and later included in the potentiometric measurement system to perform potential measurements.

3. Results and Discussion

^{1}H and ^{13}C–NMR spectra of the synthesized semicarbazone derivative molecule are given in Figures 2 and 3. Based on these figures, spectroscopic data are compatible with the structure of the synthesized molecule. Yield:

89%. Melting point 185–187 ^{0}C. **^{1}H NMR** (400 MHz, DMSO–d_6): δ 10.17 (s, 1H, NH), 7.93 (s, 1H, CH=N), 7.10 (d, *J* = 4.8 Hz, 1H), 6.76 (d, *J* = 4.8 Hz, 1H), 6.21 (bs, 2H, NH_2), 2.43 (s, 3H, CH_3); **^{13}C NMR** (100 MHz, DMSO-d_6): 156.7, 141.4, 137.5, 135.7, 129.3, 126.4, 15.5. Anal. calc. for $C_7H_9N_3OS$: C, 45.89; H, 4.95; N, 22.93. Found: C, 45.79; H, 4.91; N, 22.89.

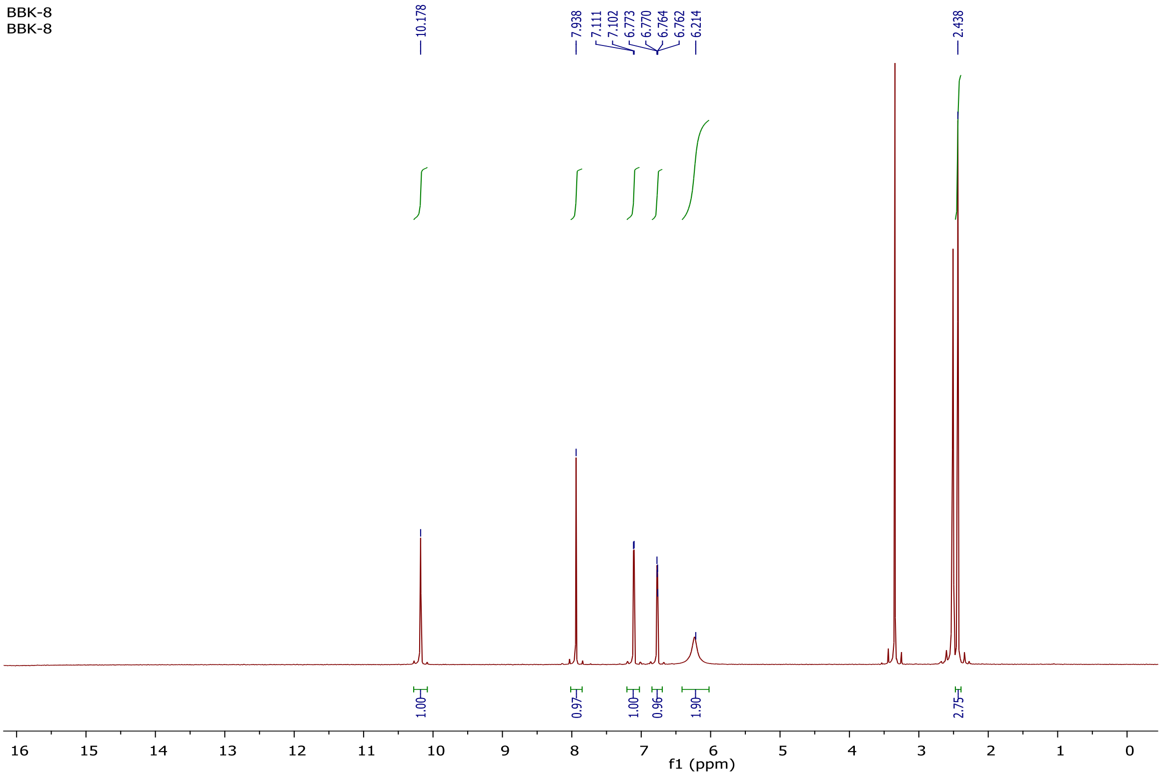

Figure 2. ^{1}H NMR spectrum of synthesized semicarbazone derivative molecule

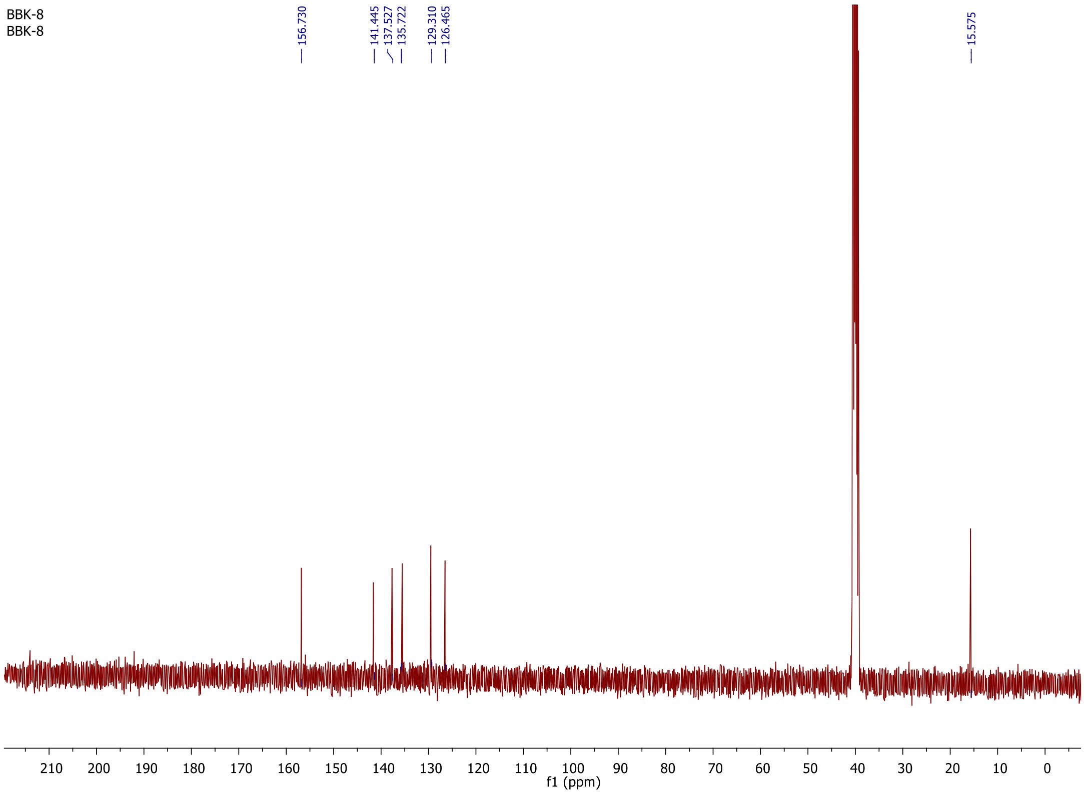

Figure 3. ^{13}C NMR spectrum of synthesized semicarbazone derivative molecule

The potentiometric response, calibration curve, reproducibility and response time of the developed copper(II)–selective sensor are given in Figure 4 which shows that the developed copper(II)–selective sensor exhibited a near–Nernstian (32.7±3.0 mV/decade) response to copper(II) ions in a wide concentration range of 1.0×10^{-1}–1.0×10^{-5} M. The limit of detection (LOD) of the developed novel copper(II)–selective sensor was calculated by substituting the potential value corresponding to the intersection of the extrapolations of the horizontal and vertical linear regions in Figure 3b into the linear equation [20]. Thus, the limit of detection of the proposed copper(II)–selective sensor was found as 4.2×10^{-6} M. The repeatability of the copper(II)–selective sensor was determined based on its potentiometric response at three different concentration values (10^{-1}, 10^{-2} and 10^{-3} M). According to data presented in Figure 4c, the proposed new sensor was found to have a repeatable and stable behavior. The response time of the copper(II)-selective sensor was examined according to the rules recommended by IUPAC [20]. Thus, the time for the sensor to reach the equilibrium at each 10–fold concentration change was determined (Figure 4d). As a result, it was found that the copper(II)–selective sensor has a fast response time of less than 10 s.

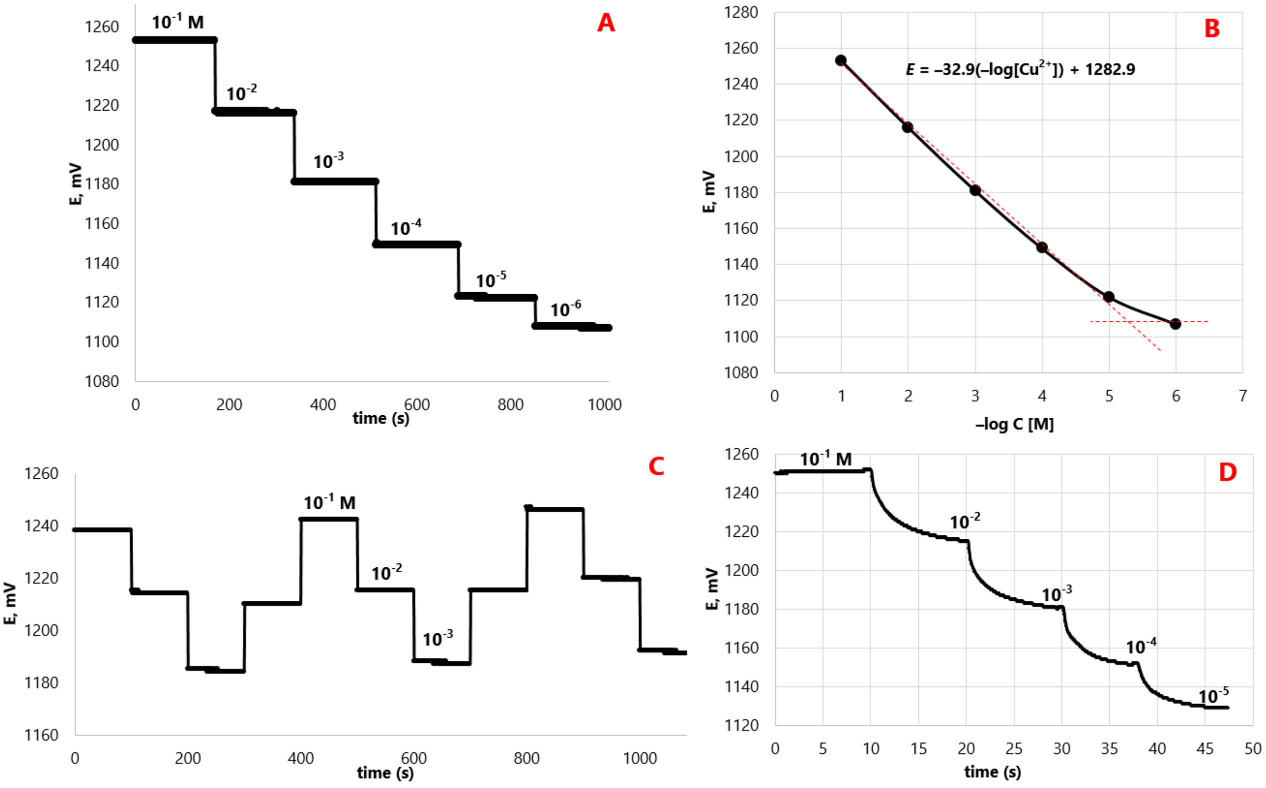

Figure 4. a) Potentiometric response, **b)** calibration curve, **c)** repeatability and **d)** response time of copper(II)–selective sensor

Nitric acid and sodium hydroxide solutions were used to determine the pH working range of the developed ion selective sensor. 10^{-2} M Cu(II) was added to the prepared pH solutions, and subsequently potentiometric measurements were taken with the developed sensor. The potential-pH graph was drawn with the obtained data. The pH working range of the copper(II)-selective potentiometric sensor is given in Figure 5. Data in this figure showed that the potential remains constant in the pH range of 4.0–11.0, and the proposed sensor has a very wide pH range.

In this study, the selectivity of the proposed sensor was determined according to the separate solution method (SSM) recommended by IUPAC [21], and the selectivity coefficients were calculated. For this purpose, the potential values of the ions given in Table 1 at a concentration of 1.0×10^{-2} M were calculated by using the data obtained from the potentiometric measurements and written in the equation recommended by IUPAC. Consequently, it was observed that the proposed new sensor is more selective towards copper(II) ions than other ionic species.

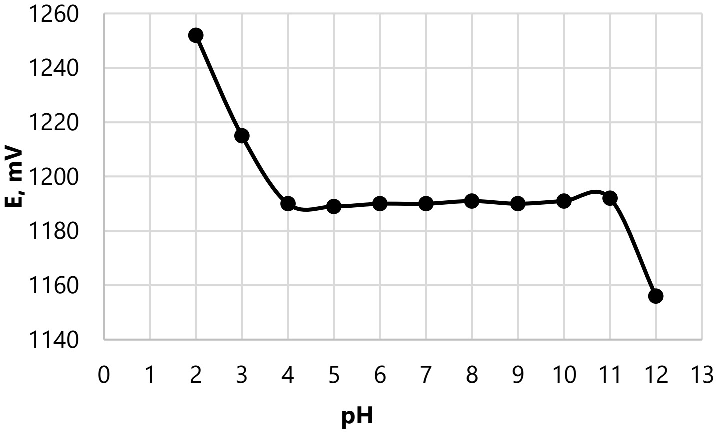

Figure 5. pH working range of sensor.

Table 1. Selectivity coefficients of the proposed sensor

Interfering ions	$logK^{pot}_{Cu(II),M^{n+}}$	$K^{pot}_{Cu(II),M^{n+}}$	**Interfering ions**	$logK^{pot}_{Cu(II),M^{n+}}$	$K^{pot}_{Cu(II),M^{n+}}$
Pb^{2+}	−0.55	0.281	Sr^{2+}	−2.20	6.3×10^{-3}
Cr^{3+}	−1.0	0.100	Ca^{2+}	−2.27	5.4×10^{-3}
Na^{+}	−1.69	0.204	Ce^{3+}	−2.41	3.9×10^{-3}
Ni^{2+}	−1.93	0.012	Cd^{2+}	−2.90	1.3×10^{-3}
Co^{2+}	−2.06	8.7×10^{-3}	Mn^{2+}	−3.20	6.3×10^{-4}
Mg^{2+}	−2.10	7.9×10^{-3}	Zn^{2+}	−3.31	4.9×10^{-4}
Ba^{2+}	−2.16	6.9×10^{-3}	Li^{+}	−4.12	7.6×10^{-5}

Analytical applications of the newly prepared copper(II)-selective potentiometric sensor were carried out using water samples. Cu(II) was added to these water samples in the amounts given in Table 2, and the potential values were then measured using the newly developed sensor. According to Table 2, the developed sensor was found to be able to detect Cu(II) ions in water samples with high recoveries.

Table 2. Determination of Cu^{2+} ions in different water samples with the novel sensor

Real Samples	**Cu^{2+} quantity, (M)**		
	Added Cu^{2+}	**Found (± SD) with sensor***	**% Recovery**
Bottled water	1.0×10^{-3}	$9.33 (\pm0.3) \times10^{-4}$	93.3
Purification drinking water		$9.55 (\pm0.2) \times10^{-4}$	95.5
Tap water (Tokat, Turkey)		$9.02 (\pm0.4) \times10^{-4}$	90.2

*Average value (*n* = 3).

In this study, the proposed copper(II)-selective potentiometric sensor was compared with the sensors previously reported in the literature using the parameters of concentration range, detection limit, slope, pH working range and response time. As seen in Table 3, the proposed new sensor was found to be superior or have some similar values with its counterparts in the literature in terms of certain parameters such as concentration range, detection limit and response time. On the other hand, when the pH working ranges are evaluated, the new sensor was shown to be able to work at pH 11.0.

Table 3. Comparison of the proposed sensor with its counterparts previously reported in the literature

Ionophore	Linear range, M	LOD, M	pH range	Response time (s)	Slope (mV/decade)	Ref.
1-(3-carboxyphenyl)-2-thiourea	1.0×10^{-5} – 1.0×10^{-1}	8.56×10^{-6}	5.0–10.0	<10	29.3±0.5	[22]
1-(2-hydroxybenzylidene) thiosemicarbazide	1.0×10^{-5} – 1.0×10^{-1}	5.4×10^{-6}	3.5–7.5	25	28.6±0.4	[23]
2-furaldehyde thiosemicarbazone	1.0×10^{-5} – 1.0×10^{-1}	6.89×10^{-6}	5.0–9.0	5	28.5±1.5	[19]
25,27-dihydroxy-26,28-bis(ethoxycarbonylbutyoxy)-5,11,17,23-p-tert-butylcalix[4]arene	1.0×10^{-5} – 1.0×10^{-1}	7.67×10^{-6}	5.0–8.0	<15	31.3±2.1	[24]
N,N′-bis(salicylidene)-1,3-diaminopropane Schiff base	1.0×10^{-5} – 1.0×10^{-2}	6.31×10^{-6}	2.0–8.0	5–10	30.4±0.5	[25]
5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrin	1.0×10^{-5} – 1.0×10^{-1}	1.88×10^{-6}	4.4–10.6	10	27.0±2.5	[26]
(*E*)-2-((5-methylthiophen-2-yl)methylene)hydrazine-1-carboxamide	1.0×10^{-5} – 1.0×10^{-1}	4.2×10^{-6}	4.0–11.0	5	32.7±3.0	This work

4. Conclusion

Ion selective electrodes are preferred as alternatives to other analytical methods in routine analysis of anionic and cationic species in various samples due to their particular advantages. In this study, a new copper(II)-selective polymer membrane potentiometric sensor was prepared using a semicarbazone derivative molecule as an ionophore and its certain potentiometric parameters were then studied in detail. The proposed sensor exhibited a low detection limit in a wide concentration range. On the other hand, the developed new sensor was reported to offer significant advantages such as fast response time, wide pH operating range and low cost. Finally, we showed that the new sensor is able to determine copper(II) ions in different water samples (bottled water, purified drinking water and tap water) with very high recoveries.

Conflicts of Interest

The authors declare that there is no conflict of interest for this article.

Authors' Contributions

Muhammed Elik: Investigation, Analysis, **Abdulkadir Akyasan:** Investigation, Analysis, **Aysegul Nazli Ozcan:** Investigation, Analysis**; Meliha Burcu Gürdere:** Investigation, Analysis, Writing - Review&Editing.

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