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Thiosemicarbazone–based highly selective potentiometric sensor for the determination of copper(II) ions

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ABSTRACT

Thiosemicarbazone derivatives are widely used as ionophores in potentiometric ion selective sensors. In this study, a thiosemicarbazone derivative molecule was synthesized and its ionophore properties were investigated. Polymer membrane sensors using the synthesized molecule as ionophore were prepared with different plasticizers. The sensors exhibited very high selectivity towards copper(II) ions over different cationic species. The newly developed copper(II)–selective sensor had a Nernstian response of 27.8 ± 2.9 mV/decade in a wide concentration range of 1.0×10^{-1}–1.0×10^{-5} M and a low detection limit of 8.23×10^{-6} M. The proposed sensor had a fast response time (<5s), a wide pH working range (5.0–10.0) and good reproducibility. The prepared sensor was applied in various water samples and was able to determine copper(II) ions with very high recoveries.

1. Introduction

Thiosemicarbazone derivatives are compounds obtained from the reaction of thiosemicarbazide with aldehydes and ketones, and they are widely used as sensor materials in various analytical techniques (Özbek and Berkel, 2023). It is known that thiosemicarbazone derivatives exhibit strong coordination affinity, good selectivity and stability especially towards metals (Prajapati and Patel, 2019). Considering these properties, thiosemicarbazone derivatives can be considered as unique ionophores for potentiometric ion–selective sensors. There are many studies in the literature which report the use of thiosemicarbazone derivatives as ionophores, namely, thiophenealdehydethiosemicarbazone–zinc(II) complex (Mohan et al., 2017), 1*H*-pyrrole-2-carboxaldehyde thiosemicarbazone (Özbek, 2022a), salicylaldehyde thiosemicarbazone (Mahajan et al., 2003), benzylbis(thiosemicarbazone) (Ganjali et al., 2002), 2-acetylfurane thiosemicarbazone (Zamani et al., 2013), 2,4-dihydroxybenzaldehyde thiosemicarbazone (Özbek, 2022b), 2–furaldehyde thiosemicarbazone (Özbek et al., 2024), 2-hydroxy-1,4-naphthalenedione-1-thiosemicarbazone (Cakmak et al., 2025) and 3-deoxy-d-erythro-hexos-2-ulose bis(thiosemicarbazone) (Zamani et al., 2010) were used as ionophores.

Today's rapid industrialization leads to increases in the concentration of heavy metals in diverse environmental samples. Although copper, a heavy metal, is essential for the human body, its high amounts can also cause serious health problems in humans (Ulusoy et al., 2011; Behbahani et al., 2014). Therefore, the determination of copper is very important for both human and environmental health. Potentiometric devices, which have a very important place in electroanalytical chemistry, possess important advantages such as wide working range, low detection limit, good selectivity, good reproducibility, ease of preparation, fast response time, low cost, long life and stability (Özbek and Altunoluk, 2024; Cetin et al., 2023; Altunoluk et al., 2024; Topcu, 2016). Compared to other analytical methods, on-site analysis, absence of a requirement for an experienced personnel and for harmful solvents, and low energy consumption can be considered as important advantages (Abu Shawish et al., 2016, 2020; Vilasó-Cadre et al., 2024). Therefore, potentiometric ion selective sensors are important alternatives in the routine analysis of various ions (Wardak et al., 2023a, 2023b, 2023c; Morawska and Wardak, 2024).

In this study, a thiosemicarbazone derivative molecule (Fig. 1) was used as an ionophore, and a new sensor selective for copper(II) ions was developed using this molecule. In the study, techniques known in the literature were applied in the production of conductive solid contact electrodes. However, the thiosemicarbazone derivative molecule used as an ionophore in its composition is presented as a new sensor material. The potentiometric performance properties of the developed sensor were tested under laboratory conditions.

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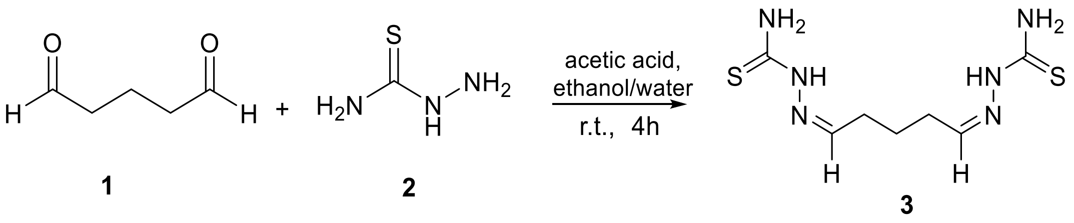

Fig. 1. Synthesis schema of (2Z,2′Z)-2,2'-(pentane-1,5-diylidene)bis(hydrazine-1-carbothioamide).

2. Experimental

2.1. Chemicals

All chemicals and solvents used in the ionophore synthesis in the present study were obtained commercially (Sigma–Aldrich and Merck), and were used without any further purification. High molecular weight poly(vinyl chloride) (PVC), plasticizers, anion excluder, and tetrahydrofuran (THF) were purchased from Sigma–Aldrich. Nitrate salts of the ions which were used in selectivity studies were obtained from Sigma–Aldrich and Merck. Nitric acid (HNO_3) and sodium hydroxide (NaOH) used in pH adjustments were obtained from Merck.

2.2. Apparatus

^{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). IR spectra was recorded on a Jasco FT/IR 430 instrument. Elemental analysis was performed using the LECO CHNS 932 instrument. Melting points was determined with an Electrothermal–9100 apparatus. Potentiometric measurements were taken using a laboratory designed multi–channel potentiometric measurement system (Medisen Medical Ltd. Şti., Türkiye), controllable via lab–made software. Ag/AgCl electrode was used as a reference electrode (Thermo Scientific Orion 900100). All solutions were prepared using ultrapure water (MP Minipure water system, Dest up, 0513957).

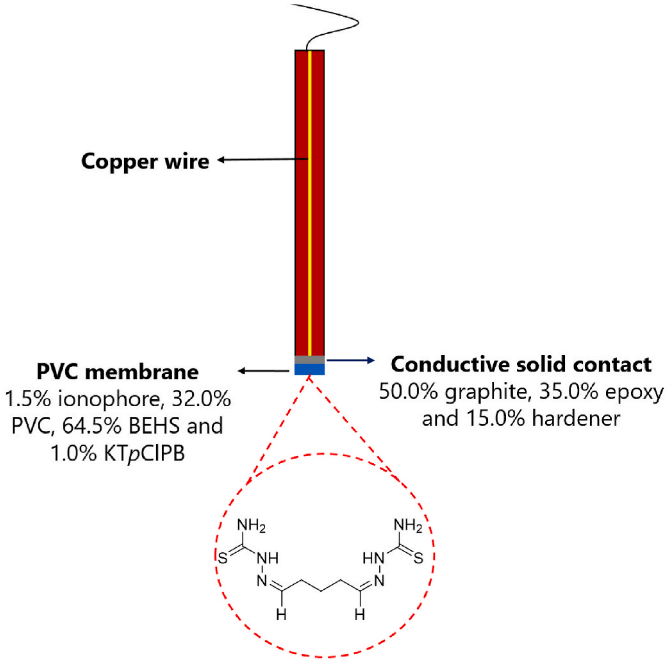

Fig. 2. The schematic representation of the prepared sensor.

2.3. Method

2.3.1. Synthesis of (2Z,2′Z)-2,2'-(pentane-1,5-diylidene)bis(hydrazine-1-carbothioamide)

(2Z,2′Z)-2,2'-(pentane-1,5-diylidene)bis(hydrazine-1-carbothioamide) was synthesized using the method reported in our previous studies (Özbek et al., 2023; Doğan et al., 2022). The glutaraldehyde **(1)** (1 mmol) was dissolved in warm ethanol (20 mL). Thiosemicarbazide **(2)** (2 mmol) was dissolved in warm water (20 mL) and then added to this solution. Acetic acid (5 drops) was added to this mixture and stirred overnight at room temperature. The precipitate formed at the end of the reaction was filtered and washed several times with ethanol. The synthesis scheme of (2Z,2′Z)-2,2'-(pentane-1,5-diylidene)bis(hydrazine-1-carbothioamide) **(3)** is given in Fig. 1.

(2Z,2′Z)-2,2'-(pentane-1,5-diylidene)bis(hydrazine-1-carbothioamide): White solid, Yield: 96% M.p. 163–165 °C. **^{1}H–NMR** (400 MHz, *d*–DMSO, ppm): $\delta = 11.06$ (s, 2H, –NH), 7.96 (s, 2H, $-NH_2$), 7.49 (s, 2H, $-NH_2$), 7.39 (s, 2H, –CH), 2.23–2.18 (m, 4H), 1.67 (t, $J = 6.8$ Hz, 2H). **^{13}C–NMR** (100 MHz, *d*–DMSO, ppm): $\delta = 177.80$ (2C), 147.52 (2C), 31.60 (2C), 22.72. **FT–IR** (ATR, cm^{-1}): 3400 ($-NH_2$), 3166 (–NH), 2948, 2887 (aliphatic –C–H), 1598 (–C=N), 1538 (–C=S). **Anal. calc. for $C_7H_{11}N_3O_2S$:** C, 34.13; H, 5.73; N, 34.11. Found: C, 33.98; H, 5.67; N, 34.01.

2.3.2. Preparation of potentiometric sensors

In this study, PVC membrane copper(II)–selective sensors were

Table 1
The prepared thiosemicarbazone–based sensors and their potentiometric performances.

No	Membrane composition (*w/w*)							Potentiometric Performance			
	PVC	Ionophore	Plasticizers				KT*p*ClPB				
			DEHA	BEHS	DBP	DOPP		Linear range (M)	Detection limit (M)	Slope (mV decade^{-1})	R^2
1	32.0	3.0		64.0			1.0	1.0×10^{-2}–1.0×10^{-4}	1.0×10^{-4}	40.0 ± 3.0	0.9647
2	32.0	3.0	64.0				1.0	1.0×10^{-1}–1.0×10^{-4}	5.29×10^{-5}	46.0 ± 5.4	0.9769
3	32.0	4.0	63.0				1.0	1.0×10^{-1}–1.0×10^{-4}	2.12×10^{-5}	35.7 ± 3.0	0.9853
4	32.0	2.0	65.0				1.0	1.0×10^{-1}–1.0×10^{-4}	8.26×10^{-4}	44.7 ± 7.8	0.9507
5	32.0	3.0			64.0		1.0	1.0×10^{-1}–1.0×10^{-4}	3.97×10^{-5}	16.7 ± 0.5	0.9835
6	32.0	3.0				64.0	1.0	1.0×10^{-1}–1.0×10^{-3}	1.51×10^{-4}	27.5 ± 1.5	0.9533
7	32.0	1.5		65.5			1.0	1.0×10^{-1}–1.0×10^{-5}	8.23×10^{-6}	27.8 ± 2.9	0.9984
8	32.0			65.5			1.0	1.0×10^{-2}–1.0×10^{-4}	9.36×10^{-6}	16.0 ± 3.7	0.9176

KT*p*ClPB: potassium tetrakis(*p*–chlorophenyl)borate, **DEHA:** [bis(2–ethylhexyl)adipate, **DBP:** dibutyl phthalate, **DOPP:** Dioctyl phenylphosphonate.

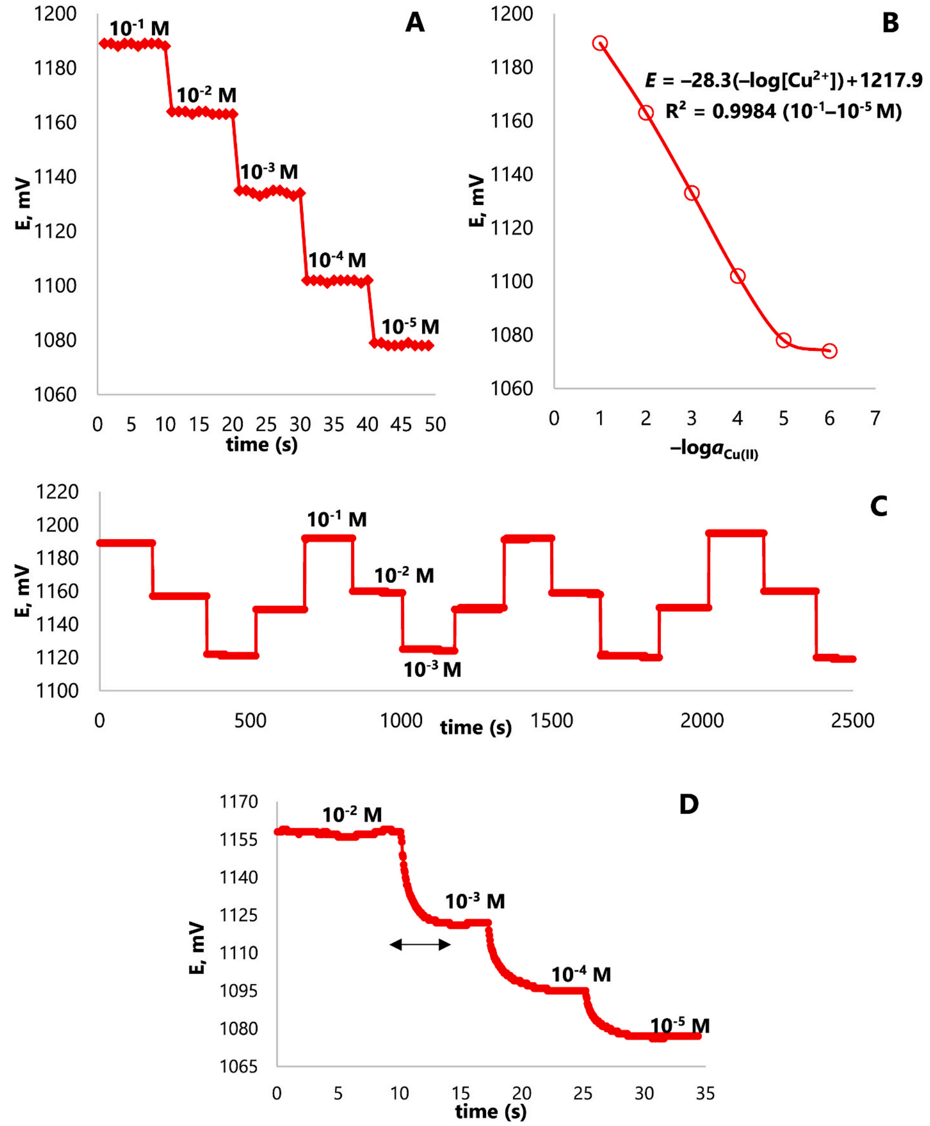

Fig. 3. a. Potentiometric response, b. calibration curve, c. repeatability and d. dynamic response time of newly developed sensor.

prepared, and later their potentiometric properties were tested. For this purpose, firstly, all solid contact electrodes containing graphite (50.0% *w/w*), epoxy (35.0% *w/w*) and hardener (15.0% *w/w*) were prepared (Özbek and Ölcenoglu, 2023; Özbek, 2023; Kalay et al., 2025). These components were dissolved in approximately 3 mL of THF and subsequently mixed until it becomes homogeneous. Then, approximately 15 cm long copper wires with one end open were dipped into this mixture several times and left to dry in the dark overnight. Then, polymer membrane sensors were prepared. PVC, plasticizer, anion excluder (KT*p*ClPB) and synthesized ionophore were taken in the ratios given in Table 1, and dissolved in approximately 3 mL of THF. Previously prepared solid contact electrodes were immersed in the mixtures that reached a homogeneous and certain viscosity, and their surfaces were coated with the PVC membrane mixture. The PVC membrane electrodes were left to dry in the dark for approximately 12 h. The schematic representation of the prepared sensor is given in Fig. 2. The prepared PVC membrane copper(II)–selective sensors were directly included in the potentiometric measurement system without any conditioning. In addition, the prepared sensors were kept in a dark environment at room conditions between measurements. Potential measurements were performed within a controlled room temperature utilizing the following electrochemical cell configuration:

Ag/AgCl reference electrode (3 M KCl) || Cu^{2+} solution | Cu^{2+}–selective membrane|solid contact|Cu wire.

3. Results and discussion

3.1. Membrane composition

In this study, a total of eight different sensors with different compositions were prepared at the ratios given in Table 1, and the potentiometric performance properties of the prepared sensors were tested using Cu^{2+} solutions. The composition of PVC and KT*p*ClPB was kept constant, and the optimum sensor composition was determined by varying the ratio of plasticizers and ionophore. Among the prepared sensors, sensor VII exhibited the lowest detection limit (8.23×10^{-6} M) and Nernstian behavior (27.8 ± 2.9 mV/decade) in a wider concentration range (1.0×10^{-1}–1.0×10^{-5} M). As a result of this screening, it was determined that the most suitable plasticizer was bis(2-ethylhexyl) sebacate (BEHS). Thus, the most suitable sensor composition was determined to contain 1.5% ionophore, 32.0% PVC, 64.5% BEHS and 1.0% KT*p*ClPB (Table 1).

Table 2
Repeatability data of copper(II)–selective sensor.

Concentration (M)	Potentials (mV)			
	I	II	III	Average (±SD)
1.0×10^{-1}	1189.0	1192.0	1192.0	1191.0 (±1.41)
1.0×10^{-2}	1159.0	1160.0	1160.0	1159.7 (±0.47)
1.0×10^{-3}	1122.0	1125.0	1122.0	1123.0 (±1.41)

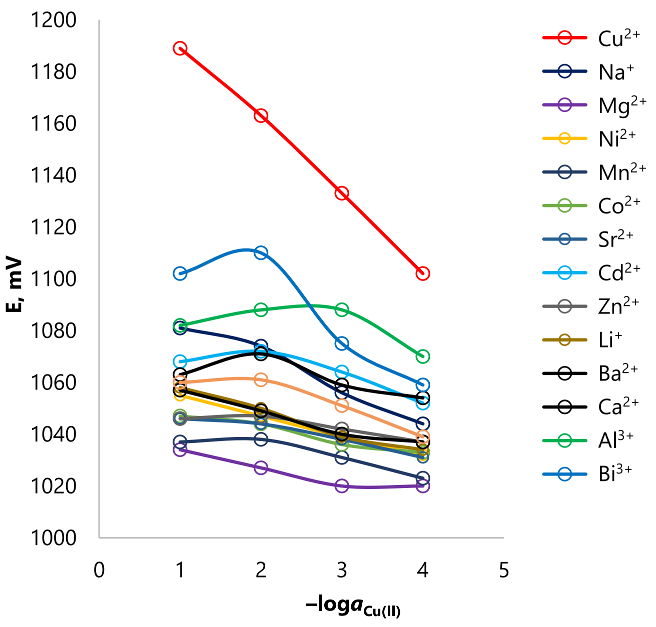

Fig. 4. Potentiometric selectivity of newly developed sensor.

3.2. Potentiometric response

The potentiometric response of the developed sensor to copper(II) ions is given in Fig. 3a which shows that the developed sensor had Nernstian behaviour (27.8 ± 2.9 mV/decade) in the concentration range of 1.0×10^{-1}–1.0×10^{-5} M. The calibration graph was drawn with the data obtained from the potentiometric response of the proposed sensor. Fig. 3b shows the calibration graph of the sensor, indicating that the sensor had a high correlation coefficient in the concentration range of 1.0×10^{-1}–1.0×10^{-5} M. The detection limits of the sensors given in Table 1 were calculated according to the rules specified by IUPAC (Buck and Lindner, 1994). For this purpose, the calibration graph of each sensor was drawn, and the potential values corresponding to the point where the horizontal and vertical axes of the graphs intersect were written in the linear equation, and the detection limits were calculated accordingly. Based on Fig. 3b, the linear equation of the sensor with the suggested optimum components was: $E = -28.3\ (-\log[Cu^{2+}]) + 1217.9$, and the detection limit was calculated as 8.23×10^{-6} M. The repeatability of the prepared sensor was determined using copper(II) solutions of different concentrations. Repeated measurements were taken with the developed sensor using three different concentrations of Cu^{2+} solutions (10^{-1}, 10^{-2} and 10^{-3} M). The repeatability data are given in Table 2. The standard deviation (±SD) values calculated for the three concentrations are ±1.41, ±0.47 and ± 1.41, respectively. Based on the data presented in Fig. 3c and Table 2, the proposed sensor exhibited repeatable results at different concentrations. The response time of the newly prepared sensor was investigated according to the rules reported by IUPAC (Buck and Lindner, 1994), and was determined to be < 5s (Fig. 3d). The lifetime of the proposed newly developed sensor was examined in weekly periods. After a period of four weeks, a decrease in the slope (mV/decade) of the sensor was observed. The lifetime of the sensor was determined as 1 months.

Table 3
The selectivity coefficient of newly developed sensor for different ions.

Interfering ions	$\log K^{pot}_{Cu(II),M^{n+}}$	$K^{pot}_{Cu(II),M^{n+}}$
Bi^{3+}	−1.79	1.62×10^{-2}
Al^{3+}	−2.54	2.88×10^{-3}
Na^{+}	−3.0	1.0×10^{-3}
Cd^{2+}	−3.07	8.51×10^{-4}
Ca^{2+}	−3.11	7.76×10^{-4}
Li^{+}	−3.82	1.51×10^{-4}
Ba^{2+}	−3.86	1.38×10^{-4}
Zn^{2+}	−3.92	1.20×10^{-4}
Ni^{2+}	−3.95	1.12×10^{-4}
Co^{2+}	−4.02	9.55×10^{-5}
Sr^{2+}	−4.16	6.92×10^{-5}
Mn^{2+}	−4.23	5.89×10^{-5}
Mg^{2+}	−4.60	2.51×10^{-5}

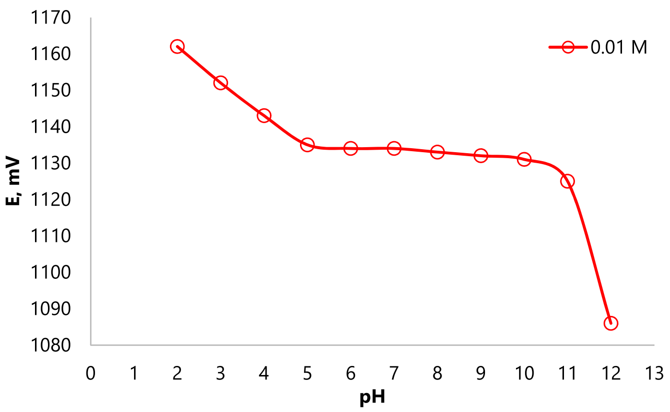

Fig. 5. pH working range of newly developed sensor.

3.3. Selectivity

As the name suggests, the most important feature of ion selective sensors is their selectivity. Potentiometric ion selective sensors exhibit selectivity for only one species while responding to multiple species. Selectivity screening of the prepared sensors against fourteen different cationic species (Cu^{2+}, Mg^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Sr^{2+}, Cd^{2+} Zn^{2+}, Ba^{2+}, Ca^{2+}, Na^{+}, Li^{+}, Al^{3+} and Bi^{3+}) was performed in the present study. According to the scans, the prepared sensors exhibited the highest potential against Cu^{2+} ions among other ions. The potentiometric behavior of the developed copper(II)–selective sensor against different cationic species is given in Fig. 4 which shows that the sensor exhibited the highest potential values against Cu^{2+} ions. The selectivity coefficients of the developed sensor were calculated using the values in Fig. 4 according to the separate solution method recommended by IUPAC (Umezawa et al., 2000). The selectivity coefficients of the developed sensor were calculated using the potential values corresponding to 1.0×10^{-2} M concentration of each species and are presented in Table 3.

3.4. pH effect

In this study, the pH working range of the new copper(II)–selective sensor was determined using nitric acid and sodium hydroxide solutions. Nitric acid solutions were prepared for the pH range of 2.0–7.0, sodium hydroxide solutions were prepared for the pH range of 8.0–12.0, and 1.0×10^{-2} M Cu^{2+} solution was added to these solutions at different pHs. Then, potential measurements were taken in the pH range of 2.0–12.0 with the developed sensor. The pH working range of the newly developed sensor is given in Fig. 5. Based on the data given in this figure, the newly developed sensor was shown to be able to work in the pH range of

Table 4
Applications of the newly developed sensor in water samples.

Water Samples	Cu^{2+} quantity, (M)		
	Added Cu^{2+}	Found (± SD) with sensor[a]	% Recovery
Bottled water	1.0×10^{-3}	$9.82\ (\pm 0.3) \times 10^{-4}$	98.2
Purification drinking water	1.0×10^{-3}	$9.72\ (\pm 0.2) \times 10^{-4}$	97.2
Tap water	1.0×10^{-3}	$9.33\ (\pm 0.3) \times 10^{-4}$	93.3

[a] Average value ($n = 3$).

5.0–10.0 without being affected by pH changes. While the high potentials at $pH < 5.0$ was due to hydronium ion concentration, the low potentials at $pH > 10.0$ might be due to $Cu(OH)_2$ formation. As a result, it can be stated that the proposed new sensor has a wide pH working range and can work without being affected by pH changes in this range.

3.5. Analytical applications

After the determination of the working parameters of the new copper (II)–selective sensors, their analytical applications were investigated. The usability of the prepared sensors in real samples was studied. For this purpose, Cu^{2+} was added to various water samples at the rates given in Table 4, and Cu^{2+} analysis was performed with the developed sensor in this mixtures. The concentrations obtained with the sensor were calculated by writing the potential value into the linear equation obtained from the calibration curve. According to the results obtained in these measurements, the developed sensor was found to be able to determine copper(II) ions with very high recoveries. Therefore, it was shown that copper(II) ions in water samples can be determined selectively, rapidly and economically by the newly developed sensor.

3.6. Comparison study

In this study, the newly developed copper(II)–selective sensor was compared with other potentiometric ion-selective sensors in the literature in terms of concentration range, detection limit, slope, response time and pH working range parameters (Table 5). The proposed new copper(II)–selective sensor has a faster response time and a wider pH working range than its counterparts. On the other hand, the developed sensor exhibited relatively similar results with the majority of its counterparts in terms of concentration range (Table 5).

4. Conclusion

In this study, a new thiosemicarbazone–based copper(II)–selective sensor was developed. The advantages of the developed sensor can be listed as follows:

- The ionophore was synthesized in the laboratory. Thus, a more economical sensor was prepared. The results obtained in this study once again proved the usability of thiosemicarbazone derivative molecules as ionophore.
- The proposed sensor had a wide concentration range, low detection limit and Nernstian behavior.
- The developed sensor exhibited high selectivity against Cu^{2+} ions among fourteen different ions.
- The developed sensor had a wide pH working range, good reproducibility and fast response time.
- Finally, the proposed sensor was able to determine Cu^{2+} ions in various samples with very high recoveries, and in this respect, it can be a new alternative to other analytical techniques used in heavy metal analysis.

CRediT authorship contribution statement

Muhammed Elik: Investigation, Formal analysis. **Ali Aydin Kogu:** Investigation, Formal analysis. **Oguz Özbek:** Writing – original draft, Investigation, Formal analysis. **Meliha Burcu Gürdere:** Investigation, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 5
Comparison of the new copper(II)–selective sensor with its counterparts reported in the literature.

Ionophore	Slope mV dec^{-1}	Concentration range, M	Limit of detection, M	pH working range	Response time (s)	Ref.
(2*Z*,2′*Z*)-2,2’-(pentane-1,5-diylidene)bis(hydrazine-1-carbothioamide)	27.8 ± 2.9	1.0×10^{-5} –1.0×10^{-1}	8.23×10^{-6}	5.0–10.0	<5	This work
2-Furaldehyde thiosemicarbazone	28.5 ± 1.5	1.0×10^{-5} –1.0×10^{-1}	6.89×10^{-6}	5.0–9.0	5	Özbek et al. (2024)
5,5′-(1,4-phenylene)bis-(1,3,4-oxadiazol-2-amine)	42.2 ± 3.5	1.0×10^{-5} –1.0×10^{-1}	4.64×10^{-6}	4.0–8.0	10	Özbek and Ölcenoglu (2023)
2-[(*E*)-1-(2-hydroxy phenyl)ethylidene]-1-hydrazine carbothioamide	29.2	1.0×10^{-5} –1.0×10^{-1}	3.0×10^{-6}	4.0–7.5	10–50	Ardakani et al. (2004)
Copper-carboxybenzotriazole complex	28.1	1.0×10^{-5} –2.0×10^{-1}	2.0×10^{-6}	3.0–8.0	22	Abu-Dalo et al. (2015)
N-hydroxysuccinimide	37.5	1.0×10^{-4} –1.0×10^{-2}	4.4×10^{-6}	2.0–6.0	0.25	Tutulea-Anastasiu et al. (2013)
Dimethyl 4, 4′-(o-phenylene)bis(3-thioallophanate)	30.3	9.8×10^{-6} –1.0×10^{-1}	–	3.1–7.6	20	Gupta et al. (2012)
8-Aminoquinoline-functionalized bentonite	28.2	1.0×10^{-5} –1.0×10^{-2}	5.0×10^{-6}	4.2–7.7	<20	Dogan et al. (2023)
N,N,N′,N′-tetracyclohexyl-2,2′-thiodiacetamide	28.9	1.0×10^{-7} –1.0×10^{-2}	3.2×10^{-8}	2.5–6.0	5–10	Wardak and Lenik (2013)
N,N′-bis(5-bromo-2-hydroxy-3-methoxybenzylidene) 2-hydroxypropylene1,3-diamine	29.7	1.0×10^{-6} –1.0×10^{-1}	6.2×10^{-7}	2.4–5.5	<10	Pietrzak et al. (2022)
(1E,3E)-1,3-bis(5-bromo-2-hydroxybenzylidene) thioure	31.1	5.0×10^{-6}–1.0×10^{-1}	5.0×10^{-7}	2.0–6.5	<10	Yildirim et al. (2024)
2-(3-Phenoxy phenyl) propanoic acid (fenoprofen (FP))	29.9	1.0×10^{-6} –1.0×10^{-2}	8.0×10^{-7}	3.0–5.0	6	Mohamed et al. (2021)

Data availability

The authors do not have permission to share data.

References

Abu Shawish, H.M., Abed Almonem, K.I., Saadeh, S.M., Al-lham, W.S., 2016. Determination of haloperidol drug in ampoules and in urine samples using a potentiometric modified carbon paste electrode. Measurement 78, 180–186. https://doi.org/10.1016/j.measurement.2015.10.008.

Abu Shawish, H.M., Ghalwa, N.A., Al-Kashef, I.D., Saadeh, S.M., Abed Almonem, K.I., 2020. Extraordinary enhancement of a 5-fluorouracil electrode by praepagen HY micellar solutions. Microchem. J. 152, 104316. https://doi.org/10.1016/j.microc.2019.104316.

Abu-Dalo, M.A., Salam, A.A., Nassory, N.S., 2015. Ion imprinted polymer based electrochemical sensor for environmental monitoring of copper (II). Int. J. Electrochem. Sci. 10, 6780–6793.

Altunoluk, O.C., Özbek, O., Kalay, E., Tokali, F.S., Aslan, O.N., 2024. Surface characterization of barium(II)-selective potentiometric sensor based on a newly synthesized thiosemicarbazone derivative molecule. Electroanalysis 36, e20230. https://doi.org/10.1002/elan.202300407.

Ardakani, M.M., Salavati-Niasari, M., Khayat Kashani, M., Ghoreishi, S.M., 2004. A copper ion-selective electrode with high selectivity prepared by sol-gel and coated wire techniques. Anal. Bioanal. Chem. 378, 1659–1665. https://doi.org/10.1007/s00216-003-2462-4.

Behbahani, M., Bide, Y., Salarian, M., Niknezhad, M., Bagheri, S., Bagheri, A., Nabid, M. R., 2014. The use of tetragonal star-like polyaniline nanostructures for efficient solid phase extraction and trace detection of Pb (II) and Cu (II) in agricultural products, sea foods, and water samples. Food Chem. 158, 14–19. https://doi.org/10.1016/j.foodchem.2014.02.110.

Buck, R.P., Lindner, E., 1994. Recommendations for nomenclature of ion-selective electrodes. Pure Appl. Chem. 66, 2527–2536. https://doi.org/10.1351/pac199466122527.

Cakmak, M.E., Özbek, O., Berkil Akar, K., Gürdere, M.B., 2025. Selective and fast potentiometric sensors based on thiosemicarbazone with low detection limit for the determination of Cu^{2+} ions. Microchem. J. 209, 112894. https://doi.org/10.1016/j.microc.2025.112894.

Cetin, A., Özbek, O., Erol, A., 2023. Development of a potentiometric sensor for the determination of carbamazepine and its application in pharmaceutical formulation. J. Chem. Technol. Biotechnol. 98, 890–897. https://doi.org/10.1002/jctb.7292.

Doğan, M., Koçyiğit, Ü.M., Gürdere, M.B., Ceylan, M., Budak, Y., 2022. Synthesis and biological evaluation of thiosemicarbazone derivatives. Med. Oncol. 39, 157. https://doi.org/10.1007/s12032-022-01784-y.

Dogan, B., Coldur, F., Caglar, B., Ozdemir, A.O., Guner, E.K., Ozdokur, K.V., 2023. Construction of a novel Cu(II)-selective electrode with long life span based on 8-aminoquinoline functionalized bentonite. Monatsh. Chem. 154, 53–64. https://doi.org/10.1007/s00706-022-03008-5.

Ganjali, M.R., Hosseini, M., Salavati Niasari, M., Poursaberi, T., Shamsipur, M., Javanbakht, M., Hashemi, O.R., 2002. Nickel ion-selective coated graphite PVC-membrane electrode based on benzylbis (thiosemicarbazone). Electroanalysis 14, 526–531. https://doi.org/10.1002/1521-4109(200204)14:7/83.0.CO;2-O.

Gupta, V.K., Singh, L.P., Singh, R., Upadhyay, N., Kaur, S.P., Sethi, B., 2012. A novel copper (II) selective sensor based on Dimethyl 4, 4′(o-phenylene) bis(3-thioallophanate) in PVC matrix. J. Mol. Liq. 174, 11–16. https://doi.org/10.1016/j.molliq.2012.07.016.

Kalay, E., Özbek, O., Elik, M., Berkel, C., Aslan, O.N., 2025. The synthesis, sensor and biological properties of two novel rhodanine derivative molecules. J. Indian Chem. Soc. 102, 101591. https://doi.org/10.1016/j.jics.2025.101591.

Mahajan, R.K., Kaur, I., Lobana, T.S., 2003. A mercury (II) ion-selective electrode based on neutral salicylaldehyde thiosemicarbazone. Talanta 59, 101–105. https://doi.org/10.1016/S0039-9140(02)00473-3.

Mohamed, M.E.B., Frag, E.Y.Z., El Brawy, M.H., 2021. Rapid potentiometric sensor for determination of Cu(II) ions in food samples. Microchem. J. 164, 106065. https://doi.org/10.1016/J.MICROC.2021.106065.

Mohan, C., Sharma, K., Chandra, S., 2017. Aluminium (III) selective PVC membrane sensor based on zinc complex of thiophenealdehyde thiosemicarbazone as an ionophore. Pharma Chem. 9, 133–139.

Morawska, K., Wardak, C., 2024. Application of ionic liquids in ion-selective electrodes and reference electrodes: a review. ChemPhysChem 25, e202300818. https://doi.org/10.1002/cphc.202300818.

Özbek, O., 2022a. A novel potentiometric sensor for the determination of Pb (II) ions based on a carbothioamide derivative in PVC matrix. J. Turk. Chem. Soc. A: Chem 9, 651–662. https://doi.org/10.18596/jotcsa.1060973.

Özbek, O., 2022b. Potentiometric PVC membrane ion–selective electrode for the determination of Sr (II) ions. Sensors Int. 3, 100185. https://doi.org/10.1016/j.sintl.2022.100185.

Özbek, O., 2023. A potentiometric sensor for the determination of potassium in different baby follow–on milk, water, juice and pharmaceutical samples. J. Food Compos. Anal. 115, 104937. https://doi.org/10.1016/j.jfca.2022.104937.

Özbek, O., Altunoluk, O.C., 2024. Potentiometric determination of the local anesthetic procaine in pharmaceutical samples. Anal. Biochem. 695, 115657. https://doi.org/10.1016/j.ab.2024.115657.

Özbek, O., Berkel, C., 2023. Sensor properties of thiosemicarbazones in different analytical methods. Polyhedron 238, 116426. https://doi.org/10.1016/j.poly.2023.116426.

Özbek, O., Ölcenoglu, A., 2023. The use of bis–thiadiazole and bis–oxadiazol derivatives as ionophores: a novel copper (II)–selective potentiometric electrodes. Microchem. J. 190, 108679. https://doi.org/10.1016/j.microc.2023.108679.

Özbek, O., Gürdere, M.B., Berkel, C., Isildak, Ö., 2023. Electroanalytical determination of copper(II) ions using a polymer membrane sensor. J. Electrochem. Sci. Technol. 14, 66–74. https://doi.org/10.33961/jecst.2022.00661.

Özbek, O., Ugur, Ö.B., Ören, S., Gürdere, M.B., Kocabas, S., 2024. New solid state contact potentiometric sensor based on a thiosemicarbazone derivative molecule for determination of copper(II) ions in environmental samples. Polyhedron 252, 116878. https://doi.org/10.1016/j.poly.2024.116878.

Pietrzak, K., Wardak, C., Cristóvão, B., 2022. Copper ion-selective electrodes based on newly synthesized salentype Schif bases and their complexes. Ionics 28, 2423–2435. https://doi.org/10.1007/s11581-022-04482-x.

Prajapati, N.P., Patel, H.D., 2019. Novel thiosemicarbazone derivatives and their metal complexes: recent development. Synth. Commun. 49, 2767–2804. https://doi.org/10.1080/00397911.2019.1649432.

Topcu, C., 2016. Highly selective direct determination of chlorate ions by using a newly developed potentiometric electrode based on modified smectite. Talanta 161, 623–631. https://doi.org/10.1016/j.talanta.2016.09.018.

Tutulea-Anastasiu, M.D., Wilson, D., Del Valle, M., Schreiner, C.M., Cretescu, I., 2013. A solid-contact ıon selective electrode for copper(II) using a succinimide derivative as ıonophore. Sensors 13, 4367. https://doi.org/10.3390/s130404367.

Ulusoy, H.I., Gürkan, R., Akcay, M., 2011. Kinetic spectrophotometric determination of trace copper (II) ions by their catalytic effect on the reduction of brilliant cresyl blue by ascorbic acid. Turk. J. Chem. 35, 599–612. https://doi.org/10.3906/kim-1101-968.

Umezawa, Y., Bühlmann, P., Umezawa, K., Tohda, K., Amemiya, A.S., 2000. Potentiometric selectivity coefficention of ion-selective electrodes, Part I. Inorganic Cations. Pure Appl. Chem. 72, 1851–2082. https://doi.org/10.1351/pac200072101851.

Vilasó-Cadre, J.E., Reyes-Domínguez, I.A., González-Fontanet, J.G., Hidalgo-Viteri, J., González-Fernández, L.A., Arada-Pérez, M.Á., Turdean, G.L., 2024. Voltammetry and related electrochemical methods based on low-cost instrumentation: a review from basic to advanced. J. Anal. Chem. 79, 520–539. https://doi.org/10.1134/S1061934824050150.

Wardak, C., Lenik, J., 2013. Application of ionic liquid to the construction of Cu(II) ion-selective electrode with solid contact. Sens. Actuators B Chem. 189, 52–59. https://doi.org/10.1016/j.snb.2012.12.065.

Wardak, C., Pietrzak, K., Morawska, K., Grabarczyk, M., 2023a. Ion-selective electrodes with solid contact based on composite materials: a review. Sensors 23, 5839. https://doi.org/10.3390/s23135839.

Wardak, C., Pietrzak, K., Morawska, K., 2023b. Nanocomposite of copper oxide nanoparticles and multi-walled carbon nanotubes as a solid contact of a copper-sensitive ion-selective electrode: intermediate layer or membrane component–comparative studies. Appl. Nanosci. 13, 7017–7028. https://doi.org/10.1007/s13204-023-02846-x.

Wardak, C., Morawska, K., Paczosa-Bator, B., Grabarczyk, M., 2023c. In: Materials, Improved Lead Sensing Using a Solid-Contact Ion-Selective Electrode with Polymeric Membrane Modified with Carbon Nanofibers and Ionic Liquid Nanocomposite, 16, p. 1003. https://doi.org/10.3390/ma16031003.

Yildirim, O., Coldur, F., Topcu, C., Caglar, B., 2024. Development of a composite Cu (II)-Selective potentiometric sensor based on a Thiourea derivative symmetric Schiff base. J. Mex. Chem. Soc. 68, 296–312. https://doi.org/10.29356/jmcs.v68i2.1884.

Zamani, H.A., Hamed-Mosavian, M.T., Aminzadeh, E., Ganjali, M.R., Ghaemy, M., Behmadi, H., Faridbod, F., 2010. Construction of barium (II) PVC membrane electrochemical sensor based on 3-deoxy-d-erythro-hexos-2-ulose bis (thiosemicarbazone) as a novel ionophore. Desalination 250, 56–61. https://doi.org/10.1016/j.desal.2009.09.014.

Zamani, H.A., Tadjarodi, A., Eslaminezhad, S., 2013. Ho3+-PVC membrane potentiometric electrochemical sensor based on 2-acetylfurane thiosemicarbazone as an ionophore. J. Indian Chem. Soc. 90, 1347–1352. https://doi.org/10.5281/zenodo.5788819.