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A Novel Potentiometric Sensor for the Determination of Pb(II) Ions Based on a Carbothioamide Derivative in PVC Matrix

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Abstract: In this research, a carbotioamide derivative molecule was synthesized to be used as an electroactive material, and poly (vinyl chloride) (PVC) membrane lead(II)–selective potentiometric sensors with different components were prepared. Among various compositions, the best potentiometric performance was exhibited by the membrane having the electroactive material, bis(2–ethylhexyl)sebacate (BEHS), PVC, and potassium tetrakis(*p*–chlorophenyl)borate (KT*p*ClPB) in the ratio of 4.0:63.0:32.0:1.0 (*w/w*). The proposed sensor exhibited a Nernstian response in the concentration range of 1.0×10^{-5}–1.0×10^{-1} mol L^{-1} with a slope of 29.5±1.6 mV/decade. The detection limit of the sensor was 3.96×10^{-6} mol L^{-1}. The potentiometric response of the lead(II)–selective sensor was independent of pH of test solution in the pH range of 5.0–9.0. The developed sensor had very good repeatability, stability, and selectivity, as well as a response time of 5s. These novel lead(II)–selective sensors, produced cost–efficiently, have been successfully used as an indicator electrode for the potentiometric titration of Pb(II) against EDTA and for the determination of Pb(II) ions in different water samples.

Keywords: Lead, potentiometry, sensors, PVC membrane.

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INTRODUCTION

The determination of heavy metal ions in various environmental samples has become very important due to the increasing interest in monitoring environmental pollution (1). Lead, one of the toxic heavy metal ions, can be found in various sources such as industrial emissions, car exhaust, drinking water, soil, contaminated food and beverages (2). These and similar sources can lead to an accumulation of lead in the body, and excessive lead can cause certain health problems, including those in synthesis of hemoglobin, in digestive, reproductive, and nervous systems, joints, and kidneys (3). Therefore, it is highly important to determine its concentration in various environmental and biological samples. Lead concentration is commonly determined using various analytical methods such as inductively coupled plasma mass spectroscopy (ICP–MS) (4), liquid chromatography (5), and atomic absorption spectrometry (AAS) (6). However, these methods are expensive, involve complex procedures, require experienced personnel, are time consuming and often require pre–treatment.

The ion–selective electrodes (ISEs) developed using the potentiometry technique have very important advantages, such as the ease of preparation and use, short response time, low cost, wide linear concentration range, high selectivity, and low detection limit (7–10). These electrodes are widely

used in areas such as environmental, food, drug, clinical, and industrial analyses (11, 12).
The molecular structure of ionophores, which are in the composition of ion–selective electrodes and interact directly with the analyte, is very important in the design of potentiometric sensors. Ionophores, which contain various functional groups in their structure, are important components due to their interaction with ions. The use of non–commercial ionophores is an important factor that makes the sensors produced very cost–effective. In this study, a carbothioamide derivative molecule was synthesized, and lead(II)–selective sensors were prepared. The potentiometric performance characteristics and applications of these sensors were investigated.

EXPERIMENTAL

Reagents and chemicals

All reagents used in the ionophore synthesis were obtained from Sigma Aldrich. All reagents used were of analytical grade. High molecular weight PVC, BEHS, KT*p*ClPB, bis(2–ethylhexyl)adipate (DEHA), *o*–nitrophenyloctyl ether (*o*–NPOE), tetrahydrofuran (THF), graphite and ethylenediaminetetraacetic acid (EDTA) were purchased from Sigma Aldrich. Sodium hydroxide (NaOH) and nitric acid (HNO_3) used for pH adjustment were obtained from Merck. Nitrate salts of the cations used in selectivity studies were obtained from Sigma Aldrich and Merck. Epoxy (Macroplast Su 2227) and hardener (Desmodur RFE) were obtained from Henkel (Istanbul, Turkey) and Bayer AG (Darmstadt, Germany), respectively.

Apparatus

Potentiometric measurement were obtained by using a computer–controlled multichannel potentiometric system (Medisen Medical Ltd. Sti., Turkey). In this system, a laboratory–made software was used. Ag/AgCl electrode used as reference electrode was purchased from Thermo–Orion. ^1H– and ^{13}C– NMR spectra were recorded on a Bruker Advance DPX–400 instrument. Melting points were measured on an Electrothermal 9100.

Method

Synthesis of (E)-2-((1H-pyrrol-2-yl)methylene) hydrazinecarbothioamide

(*E*)-2-((1*H*-pyrrol-2-yl)methylene)hydrazine carbothioamide was synthesized as previously reported in the literature (13). The 1*H*-pyrrole-2-carbaldehyde **(1)** (1 mmol) was dissolved in warm ethanol (15 mL). Thiosemicarbazide **(2)** (1 mmol) was dissolved in warm water (15 mL) and then added to this solution. Five drops of acetic acid were subsequently added to the mixture. The reaction was stirred magnetically for 4 hours at room conditions. The precipitate formed at the end of the reaction was filtered off. After washing with ethanol several times, (*E*)-2-((1*H*-pyrrol-2-yl)methylene) hydrazine-carbothioamide **(3)** was synthesized (Figure 1).

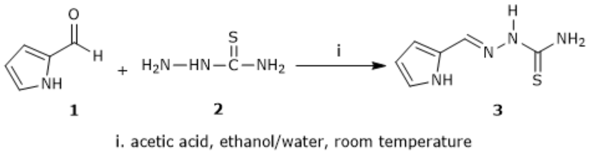

Figure 1: Synthesis schema of ionophore **(3).**

Preparation of PVC membrane lead(II)–selective sensors

Lead(II)–selective PVC membrane sensors based on the synthesized carbothioamide derivative molecule (ionophore) were prepared by the method we previously reported (14–17). First, all solid state contact consisting of graphite, epoxy and hardener was taken at 50% (*w/w*), 35% (*w/w*) and 15% (*w/w*) ratios, respectively, and completely dissolved in approximately 3 mL of THF. After obtaining the appropriate viscosity, the ends of the copper wires were coated by dipping them into this mixture several times, and were kept in the dark at room temperature for about 24 hours. Then, different ratios of ionophore, plasticizer, PVC and KT*p*ClPB were dissolved in THF and mixed homogeneously. Finally, the surface of the conductive solid contact was covered with PVC membrane by dipping it several times into the prepared membrane mixture. The coated electrodes were left to dry in the dark at room temperature. The prepared sensors and their potentiometric properties are given in Table 1.

Potential measurements

Potentials were measured using an Ag/AgCl reference electrode. All potential studies were carried out at 25 ± 1.0 °C temperature by using the following cell assembly:

Ag/AgCl; KCl (saturated) ‖ Pb^{2+} sample solution│lead(II)–selective sensor │conductive solid contact│Cu wire

The schema of the potentiometric measurement system is given in Figure 2.

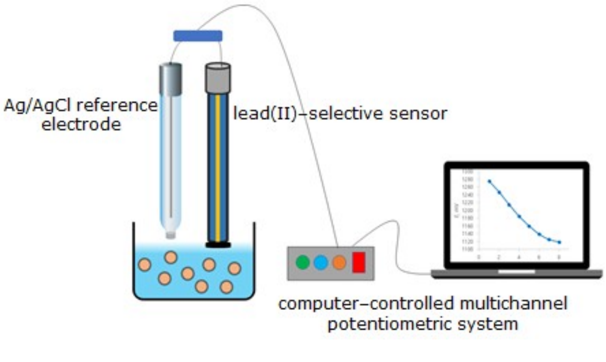

Figure 2: Potentiometric measurement system.

RESULTS AND DISCUSSION

The synthesis of the ionophore used in this study was carried out in the laboratory. The synthesized molecule was characterized by ^{1}H– and ^{13}C– NMR (Figures 3 and 4). After the molecular structure was verified, PVC membrane sensors were prepared directly, and potentiometric measurements were taken.

(*E*)-2-((1*H*-pyrrol-2-yl)methylene)hydrazinecarbothioamide: Yellow solid. Yield 93%. M.p. 158–160 °C.^{1}H NMR (400 MHz, δ, ppm, DMSO-*d6*): δ 11.36 (s, 1H), 11.26 (s, 1H), 8.05 (s, 1H), 7.95 (s, 1H), 7.83 (s, 1H), 6.98 (s, 1H), 6.40 (s, 1H), 6.11–6.09 (m, 1H); ^{13}C NMR (101 MHz, δ, ppm, DMSO–*d6*): 177.74, 134.17, 128.09, 122.23, 113.28, 109.66. The peaks of the protons in the structure are shown in Figure 3.

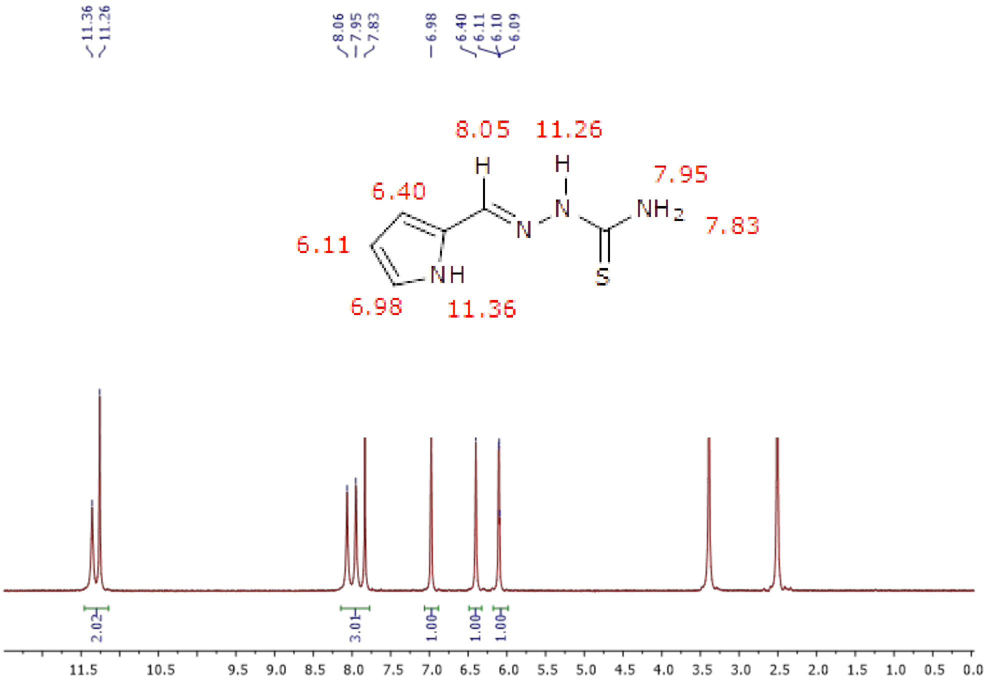

Figure 3: ^{1}H NMR of the synthesized carbothioamide derivative molecule.

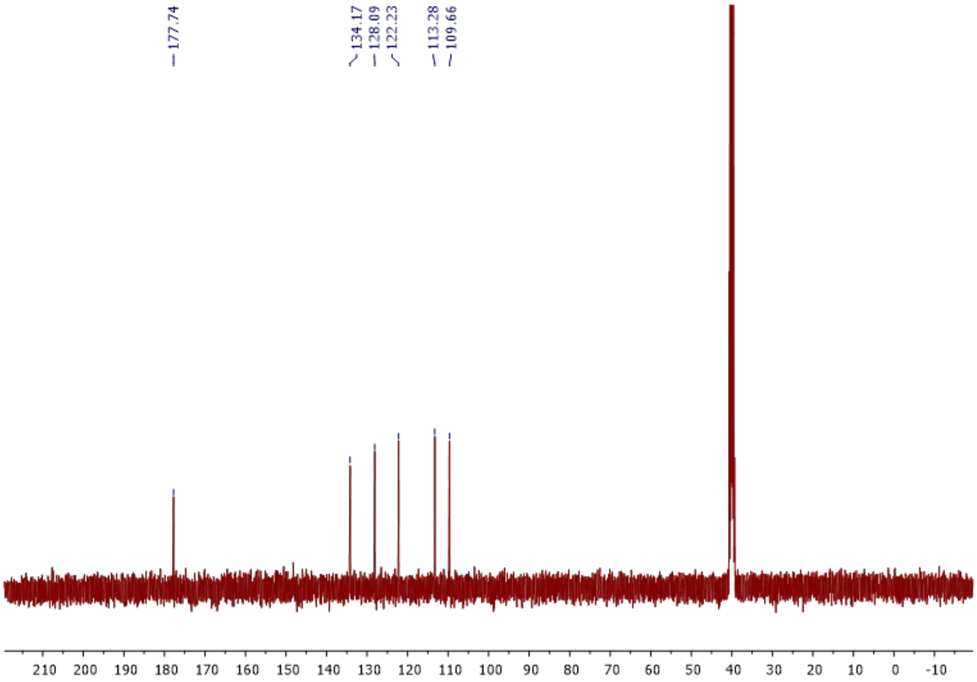

Figure 4: ^{13}C NMR of the synthesized carbothioamide derivative molecule.

Membrane components and their ratios are the most important factors that determine the potentiometric performance. In this study, PVC membranes with six different compositions were prepared using three different plasticizers (BEHS, DEHA, *o*–NPOE), and their potentiometric performance properties such as linear operating range, limit of detection, and slope were evaluated. The prepared membranes and their potentiometric properties are given in Table 1. As can be seen, sensor no 2 has the lowest detection limit (3.96×10^{-6} mol L^{-1}) over a wide linear working range. In addition, this sensor exhibited the most ideal Nernstian behavior in the concentration range of 1.0×10^{-1} – 1.0×10^{-5} mol L^{-1}. While the sensor prepared with *o*–NPOE does not exhibit Nernstian behavior, the sensors prepared with DEHA have a lower R^2 value. Therefore, sensor no 2 exhibited the best potentiometric performance, and sensors with these components were used in the later stages of the study.

In this study, the potentiometric behavior of the proposed novel lead(II)–selective sensor aganist lead(II) ions was investigated in a concentration range of 1.0×10^{-1} – 1.0×10^{-7} mol L^{-1}. In this range, the sensor exhibited linear behavior in the concentration range of 1.0×10^{-1} – 1.0×10^{-5} mol L^{-1}. The potentiometric behavior of the developed sensor is given in Figure 5. The detection limit was calculated by substituting the potential value (916.0 mV) corresponding to the intersection point of the extrapolations of the two linear regions on the calibration curve (Figure 6) in the linear equation ($E = -29.487\ (-\log[Pb^{2+}]) + 1075.3$). Thus, the detection limit of the sensor was calculated as 3.96×10^{-6} mol L^{-1}.

Table 1: The prepared PVC membrane components and its potentiometric characteristics.

No	Composition (% *w*/*w*)							Linear working concentration (mol L^{-1})	Limit of detection (mol L^{-1})	Slope (mV dec^{-1})
	Ionophore	PVC	KT*p*ClPB	BEHS	DEHA	*o*–NPOE	R^2			
1	3.0	30.0	1.0	66.0			0.9767	1.0×10^{-1} – 1.0×10^{-5}	5.2×10^{-6}	20.5±3.7
2	4.0	32.0	1.0	63.0			0.9949	1.0×10^{-1} – 1.0×10^{-5}	3.9×10^{-6}	29.5±1.6
3	5.0	30.0	1.0	64.0			0.9624	1.0×10^{-2} – 1.0×10^{-5}	7.9×10^{-6}	23.6±2.5
4	4.0	32.0	1.0		63.0		0.9901	1.0×10^{-1} – 1.0×10^{-5}	7.8×10^{-6}	27.5±2.2
5	5.0	32.0	1.0		62.0		0.9816	1.0×10^{-1} – 1.0×10^{-5}	1.3×10^{-5}	31.5±3.0
6	4.0	32.0	1.0			63.0	0.9912	1.0×10^{-2} – 1.0×10^{-5}	9.1×10^{-6}	14.5±1.2

The response time of the developed lead(II)–selective sensor was determined according to IUPAC recommendations (18). The time it takes the sensor to reach equilibrium at each 10–fold concentration change was examined. The developed sensor has a very fast response time of 5 seconds.

The repeatability study was performed with repeated measurements in three different concentration ranges (1.0×10^{-2}, 1.0×10^{-3} and 1.0×10^{-4} mol L^{-1}). The repeatability of the measurements can also give information about the stability of the sensor. The return of signals for the 1.0×10^{-3} mol L^{-1} is more unstable than for the 1.0×10^{-2} mol L^{-1} and 1.0×10^{-4} mol L^{-1}. This may be due to the late arrival of the electrode to equilibrium. The experimental measurements in Figure 7 and Table 2 clearly show that the proposed sensor gives reproducible results.

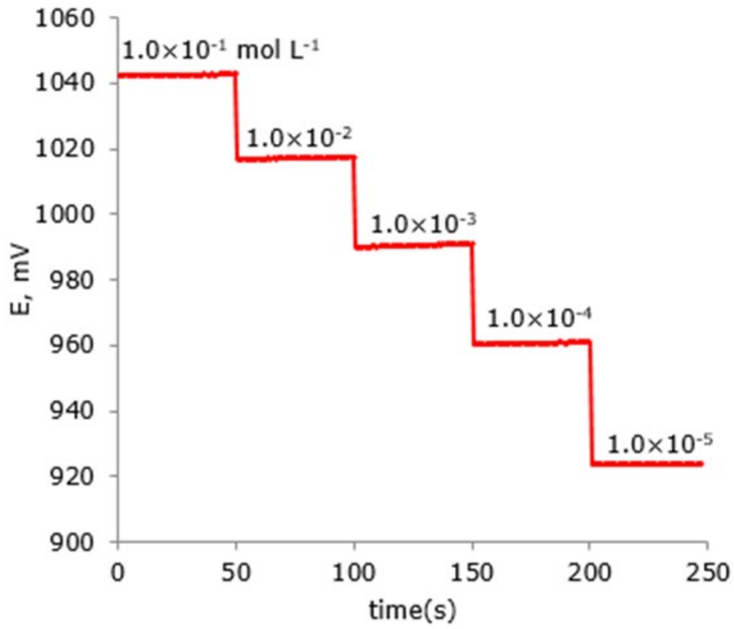

Figure 5: Potentiometric behavior of the developed lead(II)–selective sensor.

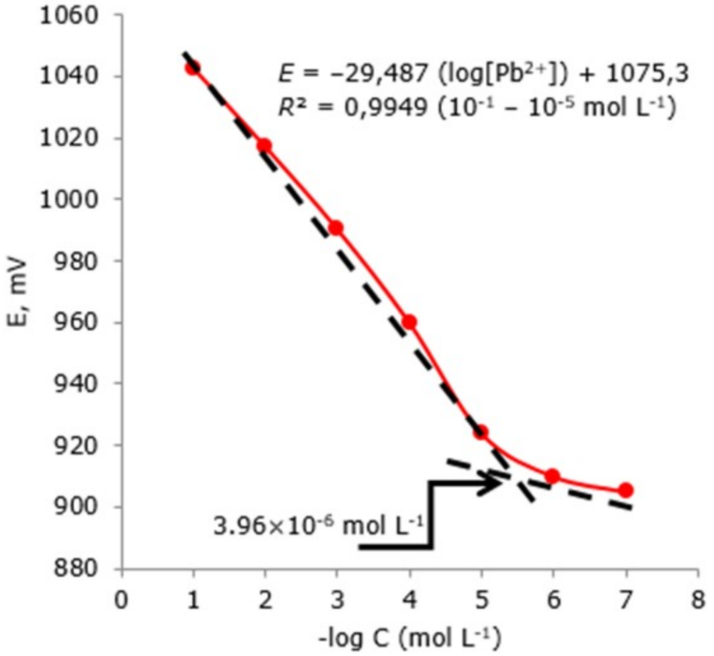

Figure 6: Calibration curve of the developed lead(II)–selective sensor.

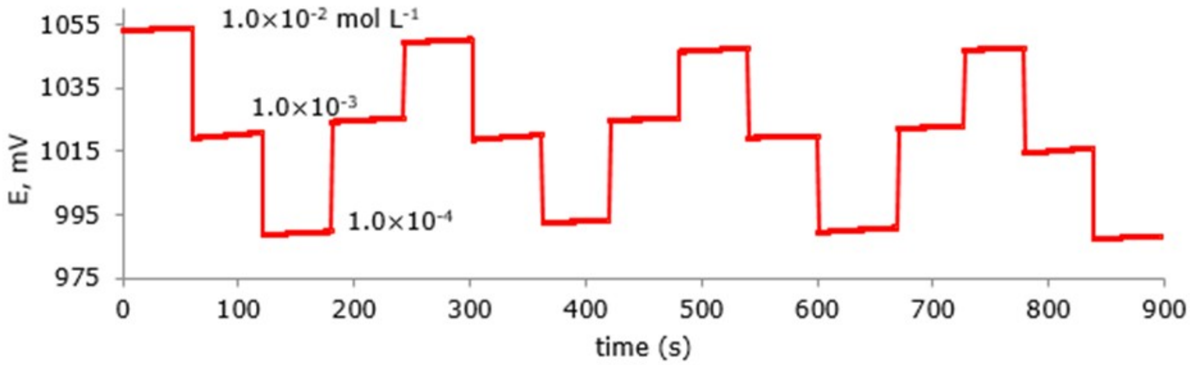

Figure 7: Repeatability of the developed lead(II)–selective sensor.

Table 2: The repeatability data of the lead(II)–selective sensor.

Pb(II) solution (mol L^{-1})	Potential (mV)				
	I	II	III	IV	Average (± SD)
1.0×10^{-2}	1053	1050	1047	1048	1049.5 (± 2.3)
1.0×10^{-3}	1021	1020	1019	1016	1019.0 (± 1.8)
1.0×10^{-4}	988	992	990	987	989.3 (± 1.92)

The selectivity of an ion–selective sensor is its specific behavior towards the main ion in the presence of different ionic species. The selectivity study of the sensor with optimum properties was performed using different cationic species. With the developed lead(II)–selective sensor, the potentiometric behavior of ions with different charges was investigated in the concentration range of 1.0×10^{-1} – 1.0×10^{-5} mol L^{-1}. Obtained test results are given in Figure 8. As can be seen here, there is a selectivity towards lead ions. On the other hand, the selectivity coefficients were determined by the separate solution method as suggested by IUPAC (19) and are given in Table 3. The values in Table 3 were calculated using the potential values of the ions at 1.0×10^{-1} mol L^{-1}.

Table 3: The calculated potentiometric selectivity coefficients of the lead(II)–selective sensor.

Interfering ions	Selectivity coefficient		Interfering ions	Selectivity coefficient	
	$\log K^{pot}_{\mathrm{Pb(2+),\ M(n+)}}$	$K^{pot}_{\mathrm{Pb(2+),\ M(n+)}}$		$\log K^{pot}_{\mathrm{Pb(2+),\ M(n+)}}$	$K^{pot}_{\mathrm{Pb(2+),\ M(n+)}}$
Cu^{2+}	−1.515	3.05×10^{-2}	Li^{+}	−3.644	2.27×10^{-4}
Cr^{3+}	−1.787	1.63×10^{-2}	Ni^{2+}	−4.999	1.00×10^{-5}
Al^{3+}	−2.598	2.52×10^{-3}	Zn^{2+}	−5.438	3.65×10^{-6}
Cd^{2+}	−2.936	1.16×10^{-3}	Ca^{2+}	−6.351	4.46×10^{-7}
Na^{+}	−2.968	1.08×10^{-3}	K^{+}	−6.620	2.40×10^{-7}

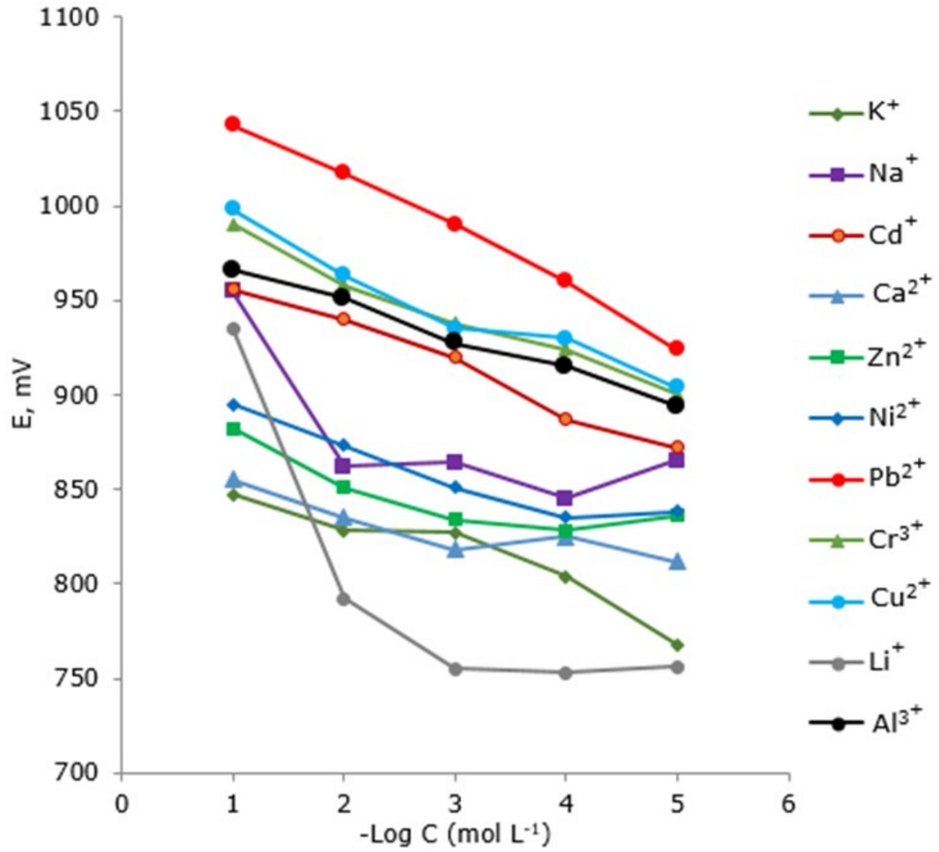

Figure 8: Potentiometric selectivity of the developed lead(II)–selective sensor.

When Table 3 is evaluated, it can be seen that Cu^{2+} has the highest selectivity coefficient. However, the developed sensor is approximately 100 times more selective for Pb^{2+} ions compared to Cu^{2+} ions.

The pH effect of the sensor was investigated at two concentrations of Pb^{2+} (1.0×10^{-2} and 1.0×10^{-3} mol L^{-1}). For this purpose, the solutions used in the pH working range of the sensor were prepared with HNO_3 for the pH range of 2.0–7.0, and NaOH for the pH range of 8.0–12.0. 1.0×10^{-2} mol L^{-1} Pb^{2+} solution was added to these solutions, and direct potentiometric measurements were taken. The potentiometric measurement results are shown in Figure 9. As can be seen in this figure, the developed sensor works independently of the pH of the test solution in the pH range of 5.0–9.0 at both concentrations. The high potential observed at low pH values (< 5.0) shows that the sensor can respond to hydrogen ions, while the low potential observed at high pH (>9.0) values may be due to the formation of $Pb(OH)_2$ in the solution.

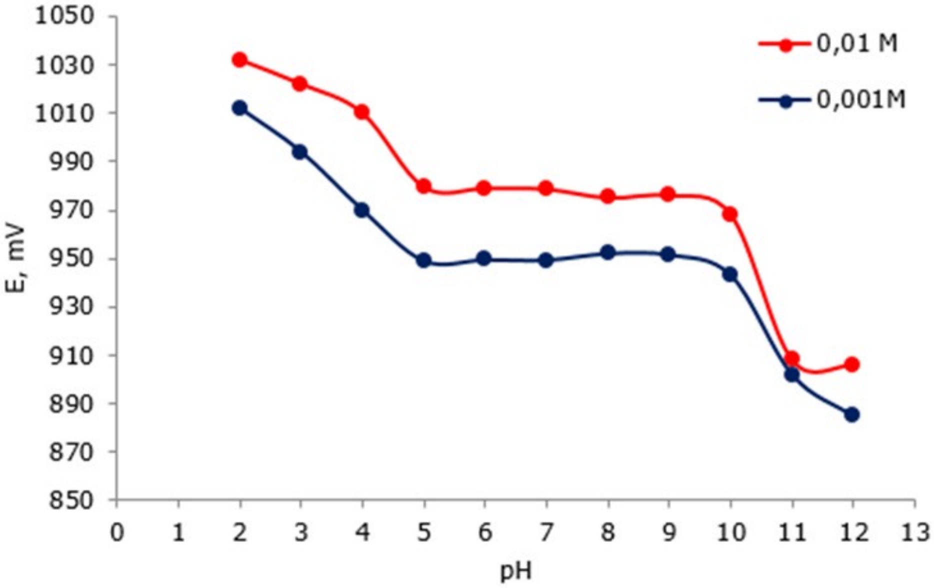

Figure 9: The effect of pH on the developed lead(II)–selective sensor.

Analytical applications of the sensor, whose potentiometric performance features were successfully completed, were carried out. The usability of the developed lead(II)–selective sensor as an indicator electrode by potentiometric titration was investigated. For this purpose, 1.0×10^{-2} mol L^{-1} EDTA solution was added to 10 mL of 1.0×10^{-3} mol L^{-1} Pb^{2+} solution and the potential obtained after each addition was recorded. A total of 2.0 mL of EDTA was added and, the titration end point was determined as 1.2. The potential (*E*)–added EDTA (mL) graph in Figure 10 was drawn with the obtained data. As a result, it is clear that the developed sensor can be used as an indicator electrode.

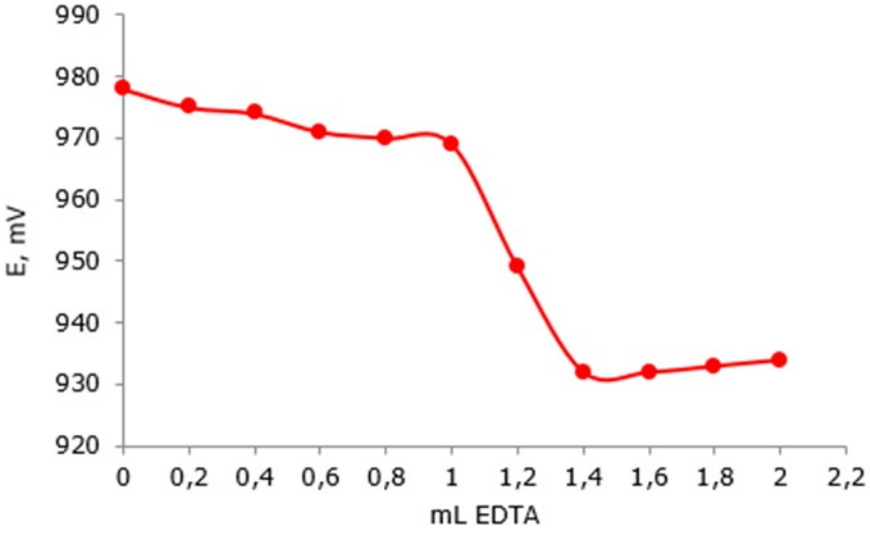

Figure 10: Potentiometric titration curve of Pb^{2+} ion with EDTA.

The standard addition method was used for the applications of the developed sensor in real samples. Herein, known concentrations of Pb(II) were added to different water samples. Then, direct potentiometric measurements were carried out with the developed sensor. The potential values thus obtained were substituted in the linear equation obtained from the calibration curve. Finally, the Pb^{2+} concentrations in the solution were determined by the sensor. The data of the measurements performed in triplicate are given in Table 4, which shows that the developed sensor can be used successfully for lead determination in real samples.

Table 4: Analysis of Pb(II) in different water samples by use of the proposed sensor.

Real Sample	Pb(II) quantity, (mol L^{-1})		
	Added Pb(II)	Mean (± SD) found with sensor (average=3)*	% Recovery
Purification drinking water	1.00×10^{-2}	$9.71(\pm 0.15)\times10^{-3}$	97.1
Tap water (Zonguldak, Turkey)	1.00×10^{-3}	$9.60(\pm 0.21)\times10^{-4}$	96.0
Commercial drinking water	1.00×10^{-4}	$9.56(\pm 0.19)\times10^{-5}$	95.6

Comparison of the developed sensor with other potentiometric lead(II)–selective sensors is given in Table 5. When compared to other potentiometry–based sensors in the literature, the developed lead(II)–selective sensor has a relatively better linear concentration range, pH working range, and low detection limit. This developed sensor has a faster response time than existing lead(II)–selective sensors.

Table 5: The comparison of the proposed sensor with other lead(II)-selective sensors.

Ionophore	concentration range (mol L^{-1})	limit of detection (mol L^{-1})	pH working range	response time (s)	Slope (mV dec^{-1})	Ref.
acridono-crown ether	1.0×10^{-4} – 8.0×10^{-2}	7.9×10^{-6}	4.0–7.0	5	26.9	(20)
1,4,8,11-tetrathia cyclotetradecane	1.0×10^{-5} – 1.0×10^{-2}	2.2×10^{-6}	3.0–6.5	15	29.9	(21)
PbS nanoparticles	1.0×10^{-5} – 1.0×10^{-2}	Not reported	3.0–7.0	10	Not reported	(22)
amide-linked diporphyrin xanthene	2.6×10^{-6} – 1.0×10^{-1}	Not reported	4.5–7.5	<30	28.2	(23)
poly(m-phenylene diamine) microparticles	3.16×10^{-6} – 3.16×10^{-1}	6.31×10^{-6}	3.0–5.0	14	29.8	(24)
Schiff base complex $[Co(L)_2](ClO_4)\cdot(C_3H_6O)\cdot(H_2O)$	1.0×10^{-5} – 1.0×10^{-2}	4.6×10^{-6}	4.0–13.0	10	23.9	(25)
(*E*)-2-((1*H*-pyrrol-2-yl)methylene)hydrazinecarbothioamide	1.0×10^{-5} – 1.0×10^{-1}	3.96×10^{-6}	5.0–9.0	5	29.5±1.6	This work

CONCLUSION

In this study, the usability of a carbothioamide derivative molecule as an ionophore was investigated. Using the synthesized molecule, PVC membrane sensors were prepared at different rates, and high selectivity against Pb^{2+} ions was obtained. The new lead(II)–selective sensors, which can be produced very economically, have Nernstian behavior over a wide concentration range. The developed sensor has a very fast response time compared to other potentiometric lead(II)–selective sensors in the literature. Besides having a fast response time, this developed sensor can operate in a wide pH range without being affected by the changes in pH. The sensor, which performs very well in analytical applications, could be a new alternative for the determination of lead(II) ions in various samples considering the advantages it provides.

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