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Research Article

Potentiometric Determination of Lead(II) Ions Based on 1,4–Naphthaquinone Derivative Molecule

Abdulkadir Akyasan[1], Mehmet Emin Cakmak[1], Kiymet Berkil Akar[2,*]

[1]Tokat Gaziosmanpaşa University, Faculty of Science and Letters, Department of Molecular Biology and Genetics, Tokat, Türkiye
[2]Tokat Gaziosmanpaşa University, Faculty of Science and Letters, Department of Chemistry, Tokat, Türkiye
***Corresponding Author: kiymet.berkilakar@gop.edu.tr**

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Abstract — Herein, the ionophore properties of a 1,4–naphthoquinone derivative molecule was investigated. For this purpose, polymer membrane ion selective sensors were prepared and their potentiometric performance characteristics were studied. The prepared sensors exhibited a very high selectivity against Pb(II) ions. The novel Pb(II)–selective potentiometric sensors had a low detection limit of 8.38×10^{-7}M and Nernstian response of 25.6±1.25 mV/decade in a wide concentration range of 1.0×10^{-6}–1.0×10^{-1} M. The newly developed sensors had a wide pH working range of 4.0–10.0 and a fast response time of 5 seconds. Finally, the newly developed Pb(II)–selective potentiometric sensor was shown to be able to determine Pb(II) ions in various samples with very high recoveries.

1. Introduction

Lead is one of the most critical environmental pollutants among the toxic heavy metals globally. Due to the rapid development of modern industries and their widespread presence, it is now highly ubiquitous in the environment, also based on its non-biodegradability and the accumulation in the organisms [1–3]. The common sources of lead exposure are the use of certain products including paints, cables, solders, cosmetic products, lead acid batteries, alloys, pigments, ammunitions, high quality glasses, and rust inhibitors, in addition to environmental emissions containing lead [4–7]. Lead has no known biological function without any benefit to human health and wildlife/environmental health. World Health Organization (WHO) has advised a limit of 10 µg/L (4.80×10^{-8} M) of lead ions in drinkable water [8]. Gradual accumulation of lead in human blood and other tissues induces abdominal cramps, learning disability, reproductive toxicity, attention deflect disorder, brain damage and is also associated with problems in lungs, kidneys, gastrointestinal tract, reproductive organs, nervous and hematopoietic systems, cardiovascular system and even in skin, in addition to its association with acute encephalopathy, headache, insomnia, fatigue, foot drop, wrist drop, muscle weakness, seizures, anemia, coma, pregnancy hypertension and preeclampsia [9–15]. Due to high environmental and biological toxicity of lead and also due to its association with many adverse health conditions reported in humans, the detection of lead at low concentrations (particularly in drinking water) has been the focus of extensive research in analytical chemistry. The most frequently used analytical methods in the determination of lead concentration in different samples are currently atomic absorption spectrophotometry (AAS), inductively coupled plasma mass spectroscopy (ICP-MS) and atomic fluorescence spectroscopy. Although these techniques show high selectivity and low limit of detection against lead ions, they are expensive to use (due to the high cost of the required equipment) and complicated to perform (thus, requiring a professional user) for the determination of lead present in drinking water [16–19]. In contrast, electrochemical techniques are relatively low-cost, portable, robust, and easier to handle. They are also characterized by non-toxic operation, quick response, and being suitable for online monitoring and outdoor / on-site applications [20, 21]. These techniques provide an essential analytical tool for the selective detection of different metal ions, drugs, and biomolecules in diverse sample types [22–26].

Potentiometric ion–selective electrodes (ISEs), as one of the most essential devices in the field of electrochemistry, are able to measure the difference in potential between a reference and an indicator electrode, under conditions with no current flow [27]. ISEs offer certain advantages such as wide linear concentration range, low limit of detection (LOD), good selectivity, ease of manufacturing and use/handling, low cost, short response time and long lifetime, making them superior to their alternatives with respect to these parameters [28–30]. They are commonly used in various areas such as industrial, clinical, food, environmental, pharmaceutical and agricultural analyses based on these advantages [31].

In this study, we used a 1,4-naphthoquinone derivative molecule as an ionophore and prepared a new sensor. The potentiometric performance properties of the newly developed lead(II)-selective sensor were tested under laboratory conditions and applied to various real samples.

2. Experimental

2.1. Chemicals and Apparatus

Graphite, epoxy and hardener used to prepare solid-contact electrodes were purchased from Sigma-Aldrich, Henkel and Bayer AG, respectively. Other chemicals used in the study were of analytical grade and were obtained from Sigma-Aldrich, Merck and Fluka. Ag/AgCl reference electrode (Thermo Scientific) and prepared sensor were connected to a multichannel potentiometer (Medisen Medical Ltd. Sti., Turkey). Ultrapure water (18.2 MΩ cm^{-1}) was used in all stages of the study (Zeneer Power I).

2.2. Method

2.2.1. Synthesis of 2-(benzylamino)-5,8-dibromonaphthalene-1,4-dione (ionophore)

2-(benzylamino)-5,8-dibromonaphthalene-1,4-dione was synthesized according to the literature procedure (Figure 1) [32].

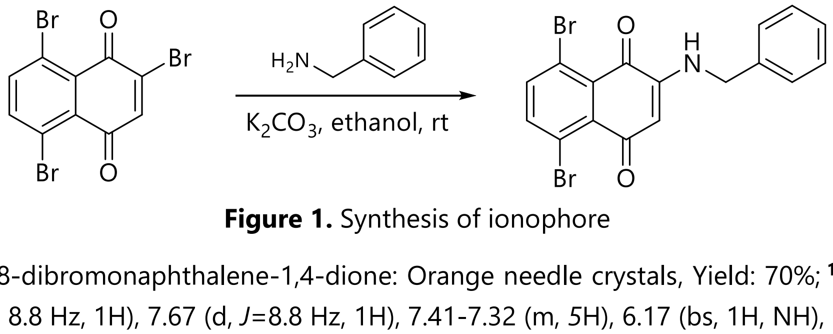

Figure 1. Synthesis of ionophore

2-(benzylamino)-5,8-dibromonaphthalene-1,4-dione: Orange needle crystals, Yield: 70%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J*= 8.8 Hz, 1H), 7.67 (d, *J*=8.8 Hz, 1H), 7.41-7.32 (m, 5H), 6.17 (bs, 1H, NH), 5.82 (s, 1H), 4.38 (d, *J*= 5.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.8, 179.4, 146.6, 141.2, 138.7, 135.4, 132.4, 130.0, 128.7 (2C), 127.9, 127.3 (2C), 121.8, 120.8, 102.1, 46.6.

2.2.2. Preparation of polymer membrane sensors

In this study, 1,4-naphthoquinone derivative molecule was used as ionophore and poly(vinyl chloride) (PVC) membrane ion–selective sensors were prepared. The sensors were prepared in two steps as reported in the literature [33–35]. First, solid contact electrodes and then PVC-membrane sensors were prepared. Solid contact electrodes were prepared by dipping 20 cm copper wires with one end open into a homogeneous mixture containing 50% (w/w) graphite, 35% (w/w) epoxy and 15% (w/w) hardener which is dissolved in around 3 mL tetrahydrofuran (THF) and then by drying in the dark for 24 h. PVC membrane sensors were prepared by dissolving PVC, ionophore, plasticizer [(bis(2-ethylhexyl)sebacate (BEHS) and bis(2-ethylhexyl)adipate (DEHA)] and potassium tetrakis (*p*-chlorophenyl)borate (KT*p*ClPB) in approximately 3 mL of THF at the ratios given in Table 1. The surfaces of the solid contact electrodes previously prepared were coated by dipping into the PVC membrane mixtures several times and left to dry for 12 h. After the prepared PVC membrane sensors were dried, they were included in the potentiometric measurement system, and potential measurements were taken.

Table 1. Prepared solid contact polymer membrane sensors and their certain potentiometric properties

No	Sensor composition (*w/w*)					Potentiometric performance			
	PVC	Ionophore	Plasticizers		KT*p*ClPB	Linear Range, M	Detection Limit, M	Slope (mV/decade)	R^2
			DEHA	BEHS					
1	32.0	4.0	63.0		1.0	1.0×10^{-5}–1.0×10^{-1}	9.72×10^{-6}	24.4 (±2.25)	0.9959
2	32.0	4.0		63.0	1.0	1.0×10^{-6}–1.0×10^{-1}	8.38×10^{-7}	25.6 (±1.25)	0.9970

2. Results and Discussion

The potentiometric response and calibration curve of the newly developed lead(II)–selective sensor was given in Figures 2 and 3. As shown in Figure 2, the developed lead(II)–selective sensor exhibited a Nernstian (25.6±1.25 mV/decade) response to lead(II) ions in a wide concentration range from 1.0×10^{-1} to 1.0×10^{-6} M. The limit of detection of this lead(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 3 into the linear equation. Thus, the limit of detection of the proposed lead(II)–selective sensor was calculated as 8.38×10^{-7} M. The response time of the lead(II)–selective sensor was studied according to the rules recommended by IUPAC [36]. Thus, the time it took for the electrode to reach equilibrium point for each 10-fold change in concentration was determined. Subsequently, it was calculated that the lead(II)-selective sensor had a fast response time of about 5 s.

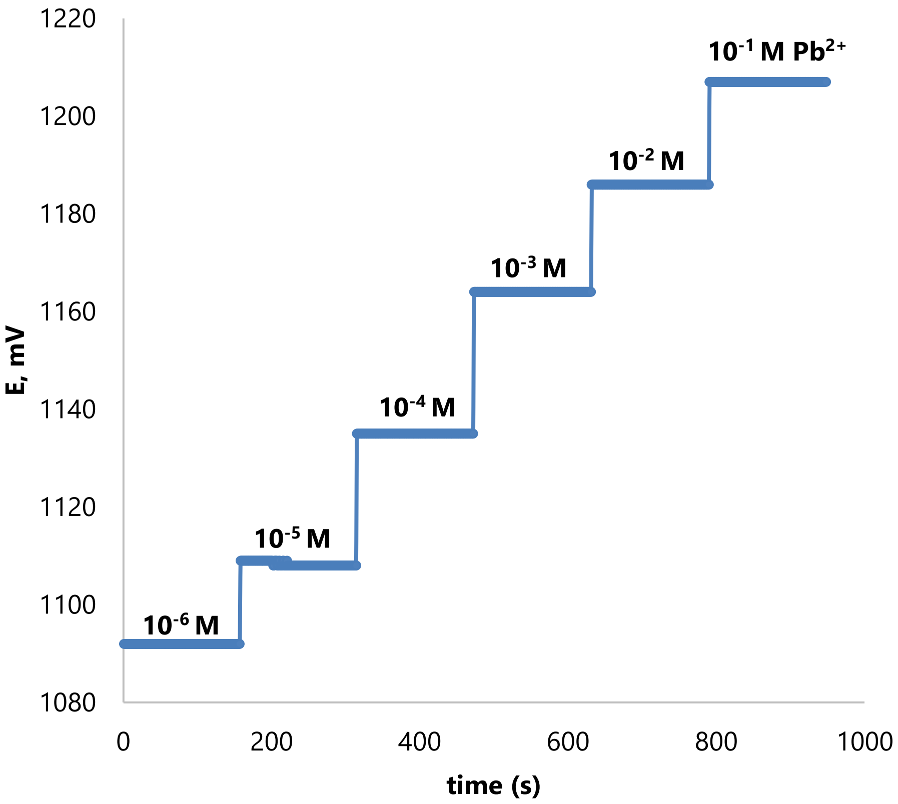

Figure 2. Potentiometric behavior of newly developed sensor

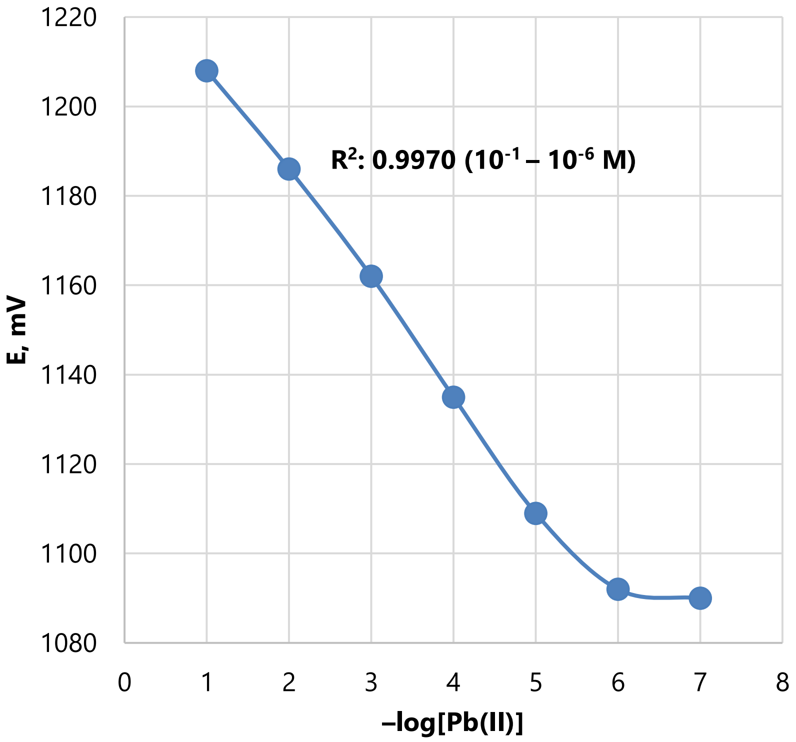

Figure 3. The calibration curve of newly developed sensor

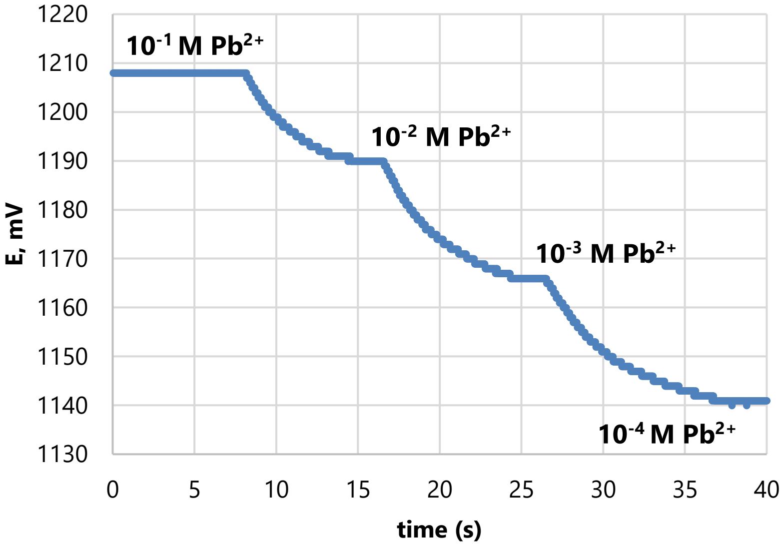

Figure 4. Response time of newly developed sensor

One of the most critical characterization parameters of ion-selective electrodes is their selectivity. Selectivity is the behavior of a proposed ion-selective electrode specific to a single species without being influenced by other species present in the medium. In the present study, the selectivity of the proposed electrode was determined according to the separate solution method (SSM) as recommended by IUPAC [37], and selectivity coefficients were then calculated. For this purpose, the potential values of the ions given in Table 2 at a concentration of 1.0×10^{-2} M were calculated by using the data obtained from potentiometric measurements and written in the equation recommended by IUPAC [37].

Table 2. The selectivity coefficients of newly developed sensor.

Interfering ions	$logK_{Pb(II),M^{+n}}$	$K_{Pb(II),M^{+n}}$	Interfering ions	$logK_{Pb(II),M^{+n}}$	$K_{Pb(II),M^{+n}}$
Cu^{2+}	−1.29	5.13×10^{-2}	Co^{2+}	−3.25	5.62×10^{-4}
Ce^{3+}	−1.62	2.40×10^{-2}	Ni^{2+}	−3.28	5.25×10^{-4}
Cr^{3+}	−1.79	1.62×10^{-2}	Na^{+}	−3.62	2.40×10^{-4}
Al^{3+}	−1.96	1.1×10^{-2}	Ca^{2+}	−3.65	2.24×10^{-4}
K^{+}	−2.40	3.98×10^{-3}	Zn^{2+}	−3.69	2.04×10^{-4}
Ba^{2+}	−2.47	3.38×10^{-3}	Mg^{2+}	−3.89	1.29×10^{-4}
Sr^{2+}	−2.57	2.69×10^{-3}	Li^{+}	−4.63	2.34×10^{-5}
Mn^{2+}	−3.15	7.08×10^{-4}			

According to the data in Table 2, the selectivity order of the examined cations changes as Cu^{2+}> Ce^{3+}> Cr^{3+} > Al^{3+} > K^{2+} > Ba^{2+}> Sr^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+} > Na^{+} > Ca^{2+} > Zn^{2+} > Mg^{2+}> Li^{+}.

As a result, the proposed new sensor can be proposed to eb highly selective against Pb^{2+} ions compared to other ionic species.

Nitric acid (HNO_3) and sodium hydroxide (NaOH) solutions were used to determine the pH working range of the developed ion-selective sensor. HNO_3 solutions was used for the pH range from 2.0 to 7.0, and NaOH solutions was used for the pH range of 8.0–12.0. 1.0×10^{-2} M Pb(II) was added to the prepared pH solutions. The pH working range of the novel lead(II)–selective potentiometric sensor was given in Figure 5. According to these data, the potential was shown to remain stable in the pH range of 4.0–10.0. The high potential values at pH<4.0 might be due to the presence of hydronium ions, and the low potential values at pH>10.0 might be due to the formation of $Pb(OH)_2$

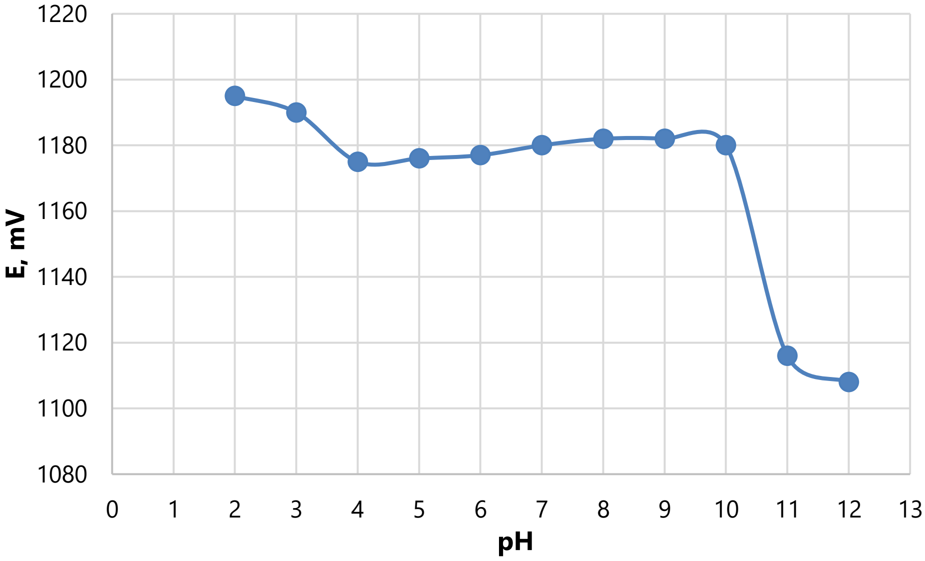

Figure 5. pH working range of newly developed sensor.

The analytical applications of the sensor, which exhibits a low detection limit in a wide concentration range, were carried out in water samples. Pb(II) ions were added to the water samples in the amounts given in Table 3. Pb(II) analysis was performed in water samples using the developed sensor. According to Table 3, the proposed sensor can determine Pb(II) ions at low concentrations in various water samples with very high recoveries.

Table 3. Determination of Pb^{2+} in different real samples by use of the proposed sensor.

Real Sample	Pb^{2+} quantity, (M)		
	Added Pb^{2+}	Mean (± SD) found with sensor*	% Recovery
Tap water (Tokat, Türkiye)	1.00×10^{-4}	$9.72\ (\pm\ 0.17)\times10^{-5}$	97.20
Commercial water	1.00×10^{-4}	$9.62\ (\pm\ 0.45)\times10^{-5}$	96.20

*Average value (n = 3)

In this study, the prepared lead(II)–selective potentiometric sensor was evaluated with its counterparts in the literature in terms of some potentiometric performance properties (Table 4). The proposed sensor had a wider concentration range and a lower detection limit than its counterparts in the literature. The new lead(II)-selective sensor had similar properties with its counterparts in the literature in terms of pH working range and response time. As a result, the proposed novel sensor can be stated to have advantages over the sensors proposed in recent years.

Table 4. The comparison of the newly developed sensor with other potentiometric ISE reported in literature.

Ionophore	concentration range (M)	limit of detection (M)	pH working range	response time (s)	Slope (mV/decade)	Ref.
$[Pb_2(maa)_4(vim)_2]$	1.0×10^{-6} – 1.0×10^{-2}	8.30×10^{-8}	3.0–7.0	15	29.4	[38]
(E)-2-(1-(4-(3-(4-chlorophenyl)ureido)phenyl)ethylidene)hydrazine carbothioamide	1.0×10^{-5} – 1.0×10^{-1}	1.65×10^{-6}	5.0–11.0	5	28.0±2.0	[5]
(E)-2-(2-((2-((4-methoxyphenyl)sulfonyl)hydrazineylidene)methyl)phenoxy) acetic acid	1.0×10^{-5} – 1.0×10^{-1}	2.89×10^{-6}	3.0–9.0	5	27.7±1.3	[19]
acridono-crown ether	1.0×10^{-4} – 1.0×10^{-2}	7.9×10^{-6}	4.0–7.0	5	26.9	[39]
(E)-2-((1H-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	[40]
2-(benzylamino)-5,8-dibromonaphthalene-1,4-dione	1.0×10^{-6} – 1.0×10^{-1}	8.38×10^{-7}	4.0–10.0	5	25.6±1.25	This work

3. Conclusion

In the present study, a novel 1,4–naphthoquinone derivative molecule was investigated in terms of its ionophore properties. Polymer membrane ion selective sensors were manufactured using this molecule, and then their potentiometric performance characteristics were studied with respect to different parameters. It was found that the prepared sensors display very high selectivity against Pb(II) ions. The novel Pb(II)–selective potentiometric sensors were also shown to have a low detection limit of 8.38×10^{-7} M in a wide concentration range of 1.0×10^{-6}–1.0×10^{-1} M. We also reported that the newly developed sensors have a wide pH working range of 4.0–10.0, and a short response time of 5 seconds. Lastly, the newly developed Pb(II)–selective potentiometric sensor was shown to be able to determine Pb(II) ions in various samples with very high recoveries.

Conflicts of Interest

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

Authors' Contributions

Authors have equal contributions.

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