

# A Liquid Membrane Mercury Selective Electrode Based on 2-(*N*-Pipyridino Methyl)-1-Cyano Cyclohexanol as a Novel Neutral Carrier

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**Abstract**—2-(*N*-pipyridino methyl)-1-cyano cyclohexanol was synthesized, characterized and used as an ionophore in construction of polyvinyl chloride (PVC) potentiometric sensor for Hg<sup>2+</sup> determination. The best result was obtained with membrane composition of PVC (29%), sodium tetraphenylborate as ionic additive (1%), 2-(*N*-pipyridino methyl)-1-cyano cyclohexanol (12%) and dibutylphthalate (58%). The designed electrode showed an acceptable Nernstian slope (29.1 mV/decade) for Hg<sup>2+</sup> over a wide concentration range from  $5 \times 10^{-7}$  to  $1 \times 10^{-2}$  M with a detection limit of  $2.5 \times 10^{-7}$  M. The potential response was independent from pH in the range of 6.0–9.0 and the sensor response time was relatively short (~25 s). The sensor performance was invariable for at least 6 weeks. Electrode selectivity was evaluated by matched potential method. Finally, the proposed sensor was used as an indicator electrode in potentiometric titration of Hg<sup>2+</sup> with ethylenediaminetetraacetic acid and in direct determination of mercury(II) in aqueous samples with admissible accuracy and high reproducibility.

**Keywords:** mercury selective electrode, liquid membrane, 2-(*N*-pipyridino methyl)-1-cyano cyclohexanol, potentiometry

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Mercury is a silvery-white liquid heavy metal that is known as the 80th element of the periodic table with Hg symbol and its most common oxidation state is +2. This perilous element occurs in three forms in nature (metallic, organic and inorganic) which originate from both natural sources such as volcanic eruptions and geothermal phenomena as well as human activities including mining, burning garbage and excessive use of fossil fuels [1, 2]. Mercury can have more toxic and destructive effects than other heavy metals such as lead and cadmium, due to its high volatility and long life time in atmosphere, so that, the United States Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) classified mercury and its related compounds as the third most poisonous chemicals in Priority List of Hazardous Substances [3]. Even trace amounts of this toxic metal can cause numerous diseases such as Alzheimer, autism, insomnia, anxiety, attention deficit, hyperactivity disorder, hearing loss, autoimmune disorders, respiratory diseases and depression [4–8]. Moreover, in higher doses, it can lead to mercurialism (mercury poisoning) that can be diagnosed by such symptoms as agita-

tion, ataxia, vomiting, acrodynia, anuria, muscular cramps, stomach pain, thirsty, shock, dysentery and finally can cause death [9]. Unfortunately, despite adverse effects of mercury on environment and all living organisms, it is widely used in manufacturing process of dental amalgams, fluorescent lamps, preservatives for vaccines, medicinal and ambient thermometers, sphygmomanometers, topical antiseptics, herbicides and fungicides [10, 11]. Therefore, due to the high utilization of this metal in the industry and possible resulting damages, it can be deduced that mercury determination is of an immense significance. So far, many methods for Hg<sup>2+</sup> ions determination have been reported, the most common are atomic absorption spectroscopy with both flame and graphite furnace atomizers, neutron analysis activation, atomic emission spectroscopy, gas chromatography, cold vapor atomic fluorescence spectrometry (CVAFS), inductively coupled plasma–mass spectrometry (ICP–MS) and complexometry [12, 13]. The referred techniques are not preferable due to their poor selectivity, expensive and intricate instrumentation, grueling and long-lasting sample treatment steps, the risk of expo-

sure to metallic free mercury especially in CVAFS and sample matrix destruction.

Fortunately, ion selective electrodes (ISEs) can be a prominent alternative for the mentioned complicated methods. This category of electrochemical sensors provides worthwhile privileges including noticeable selectivity, simple instrumentation, portability, wide working range, saving time, ability to be used in turbid and colorful samples, economy, high reproducibility and no need for sample pretreatment steps. Although several potentiometric polyvinyl chloride (PVC) based electrodes have been reported for the determination of  $\text{Hg}^{2+}$  ions and other transition, alkali and alkaline earth metals, but a large part of them have some defects such as long response time, short life span, narrow working pH range and serious interference from other cations [14–25]. Hence, research in this field ought to be continued in order to attain more useful sensors with better characteristics and promote ISEs position in routine analysis.

Thereby, in this study, 2-(N-piperidino methyl)-1-cyano cyclohexanol was synthesized and, for the first time, its application as an exquisite ionophore in fabrication of a liquid membrane ion selective electrode for  $\text{Hg}^{2+}$  determination was investigated.

## EXPERIMENTAL

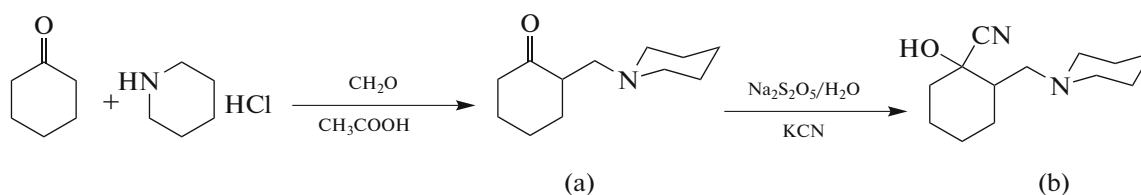
**Apparatus.** Fourier transform infrared spectra were recorded on a Bruker Tensor 27 instrument using KBr disks.  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were recorded with a Bransetead Bruker Avance BRX-250 MHz instrument using  $(\text{CD}_3)_2\text{SO}$  as the deuterated solvent containing tetramethylsilane as an internal standard. Mass spectra were obtained with a Finnigan-MAT-8430 electron ionization mass spectrometer (MS) (70 eV). UV-visible spectra were recorded on a Varian Cary100-Bio UV-visible spectrophotometer. The melting point was determined by

a Bransetead Electro Thermal B1 instrument. A corning ion analyzer 250 pH/mV meter was used for potential measurements at  $25.0(\pm 0.1)^\circ\text{C}$ . Two Ag/AgCl reference electrodes (Azar-Electrode, Iran) were used as the internal and external reference electrodes.

**Reagents and materials.** Reagent grade dibutyl phthalate (DBP), sodium tetraphenylborate (NaTPB) high relative molecular weight polyvinyl chloride and tetrahydrofuran were purchased from Merck and used as received. Cyclohexanone, piperidinium hydrochloride, paraformaldehyde, acetic acid, potassium cyanide and sodium metabisulfite, *n*-hexane and dichloromethane were purchased from Merck and Aldrich. 2-(N-piperidino methyl) cyclohexanone was synthesized according to Mannich reaction [26–28]. Nitrate salts of the cations used (from Merck and Aldrich) were of the highest purity available and were used without any further purification except for vacuum drying over  $\text{P}_2\text{O}_5$ . Double distilled deionized water was used throughout the experiment. In thin layer chromatography, iodine vapor was used for detection.

**Synthesis of 2-(N-piperidino methyl)-1-cyano cyclohexanol.** 2-(N-piperidino methyl)-1-cyano cyclohexanol was synthesized in two steps as follows.

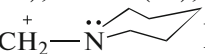
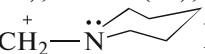
*Step 1. Synthesis of 2-(N-piperidino methyl) cyclohexanone.* This compound was prepared by Mannich reaction [26–28]. In a 250 mL two-necked flask, 17.68 g (180 mmol) of cyclohexanone, 10.94 g (90 mmol) of piperidinium hydrochloride, 2.7 g (90 mmol) of paraformaldehyde and 20 mL of acetic acid were added. The reaction mixture was stirred at  $90^\circ\text{C}$ . Then, the liquid of mixture was separated by evaporator and the solid was formed. The precipitate was dissolved in distilled water and pH was adjusted to 12 with NaOH (30%). After extraction by ether and drying over dehydrated sodium sulfate, the solvent was evaporated, and 22.57 g of viscous compound was obtained (64% yield) (Scheme 1).



**Scheme 1.** The structures of 2-(N-piperidino methyl) cyclohexanone (a) and 2-(N-piperidino methyl)-1-cyano cyclohexanol (b).

Thin layer chromatography on aluminum oxide showed  $R_f$  of 0.19 (solvent: diethyl ether-*n*-hexane, 30 : 70). IR (KBr,  $\text{cm}^{-1}$ ): 2933.17; 2848.85; 1707.98; 1445.80; 1373.63; 1271.86; 1058.17; 998.85; 859.76; 775.14.  $^1\text{H}$  NMR: ( $\text{CDCl}_3$ )  $\delta$ , ppm, 1.29–1.31 (3H, m); 1.43–1.45 (6H, m), 2.09–2.28 (1H, m), 2.64–

2.68 (1H, m).  $^{13}\text{C}$  NMR: ( $\text{CDCl}_3$ )  $\delta$ , ppm, 24.69; 24.97; 26.30; 28.42; 33.31; 42.32; 48.97; 55.23; 58.59; 212.92. MS:  $m/z$  (relative intensity, %): 55 (38); 70 (26); 84 (33); [98 (100)  $\text{CH}_2=\text{N}^+$ ]; 99 (33); 111 (23); 142 (23); 153 (17); 165 (20); 181 (15); [195 (29),  $\text{M}^+$ ].

**Step 2. Synthesis of 2-(N-piperidino methyl)-1-cyano cyclohexanol.** 0.94 g (7.7 mmol) of piperidinium chloride salt was poured in a 250 mL flask. Then, 10 mL of distilled water was added. 9.32 g (42 mmol) of 2-(N-piperidino methyl) cyclohexanone and 3.99 g (21 mmol) of sodium metabisulfite were dissolved in 4 mL of distilled water under rapid stirring. Then, 2.73 g (42 mmol) of potassium cyanide powder dissolved in 3.5 mL of distilled water was added in a drop-wise manner under rapid stirring at 0°C. The reaction mixture was stirred for 24 h at 0°C. Then, 40 mL of distilled water was added. The white precipitate was filtered and dried in the oven under suitable vacuum. Pure 2-(N-piperidino methyl)-1-cyano cyclohexanol (Scheme 1) was obtained by recrystallization from the *n*-hexane–dichloromethane mixture. Thin layer chromatography on aluminum oxide showed  $R_f$  of 0.21 (solvent: diethyl ether and petroleum ether, 30 : 70). The schematic representation of reaction is shown in Scheme 1 (m.p. 65–67°C). IR (KBr,  $\text{cm}^{-1}$ ): 3000.6; 2939.70; 2853.23; 2803.95; 2221.62; 1473.51; 1445.63; 1362.16; 1305.12; 1129.16; 1075.63; 796.91.  $^1\text{H}$  NMR: ( $\text{CDCl}_3$ )  $\delta$ , ppm, 1.43–1.53 (12H, m); 1.67–1.78 (4H, m); 2.10–2.15 (2H, m); 2.29–2.34 (2H, dd); 2.62–2.70 (2H, m).  $^{13}\text{C}$  NMR: ( $\text{CDCl}_3$ )  $\delta$ , ppm, 22.81; 24.18; 25.15; 26.30; 27.37; 33.40; 37.98; 41.98; 63.68; 76.38; 121.59. MS:  $m/z$  (relative intensity, %): 39 (55); 41 (63); 42 (58); [98 (100) $\text{CH}_2=\overset{+}{\text{N}}\text{---}$    $\longleftrightarrow$   $\text{CH}_2-\overset{+}{\text{N}}\text{---}$   ]; 126 (40); 137 (43); 196 (20); [222 (23),  $\text{M}^+$ ].

**Selectivity of the ionophore.** The interaction of 2-(N-piperidino methyl)-1-cyano cyclohexanol and some other cations was investigated by UV-visible spectrophotometry as follows: 300  $\mu\text{L}$  aliquots of different cations solutions (1 mM) were added to a solution of ligand at a concentration of  $5 \times 10^{-5}$  M and spectral changes in the ligand spectrum were surveyed.

**Electrode preparation.** The general procedure of the PVC membrane preparation was as follows: different amounts of 2-(N-piperidino methyl)-1-cyano cyclohexanol along with appropriate amounts of additive (NaTPB) were weighed. Afterward, known amounts of plasticizer and PVC were added to the mixture. The mixture was dissolved in 3 mL of tetrahydrofuran, and the solution was well blended. The resulting mixture was transferred to a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A sampler tip (3–5 mm o.d.) was dipped into the mixture for about 5 s so that a transparent membrane with about 0.3 mm thickness was formed. The sampler tip was then pulled out from the mixture and kept at room temperature for about 24 h. Afterward, the sampler tip was filled with an internal filling solution (1.0 mM  $\text{Hg}(\text{NO}_3)_2$ ). The electrode was finally conditioned for 24 h by soaking in 1.0 mM  $\text{Hg}(\text{NO}_3)_2$  solution.

**Electromotive force measurements.** The following cell was assembled for the conduction of the electromotive force measurements:

$\text{Ag}-\text{AgCl}, \text{KCl} (\text{sat.}) \mid \text{internal solution}, 1.0 \text{ mM } \text{Hg}(\text{NO}_3)_2 \mid \text{PVC membrane} \mid \text{sample solution} \mid \text{Ag}-\text{AgCl}, \text{KCl} (\text{sat.}).$

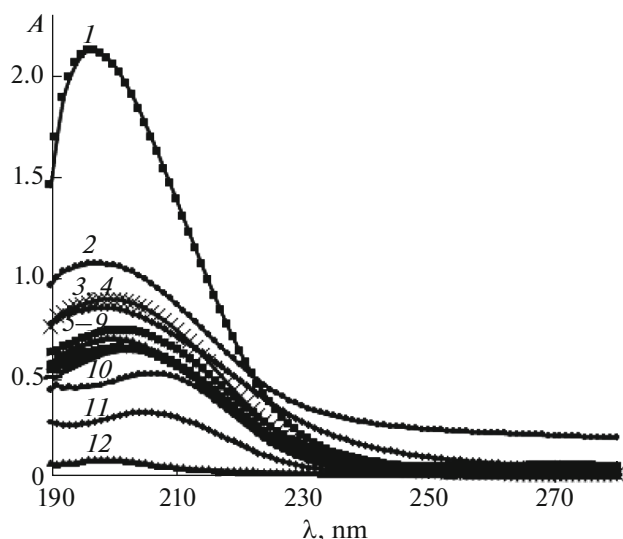
## RESULTS AND DISCUSSION

### Evaluation of the ligand tendency to various metals.

Owing to the presence of two nitrogen and one oxygen electron donating atoms in the structure of 2-(N-piperidino methyl)-1-cyano cyclohexanol, its complexation with transition and soft metals is predictable. However, to achieve high selectivity and sensitivity of the potentiometric sensor, finding the appropriate cation that forms the most stable and strong complex with the sensing material plays a decisive role. In the same vein, before initiating the construction and development process of the liquid membrane electrochemical sensor, the ionophore affinity to several metals was scrutinized by UV-visible spectrophotometry. Hence, equal amounts of various ions and mercury were added to 2-(N-piperidino methyl)-1-cyano cyclohexanol solutions one by one. The UV-Vis spectra were recorded (Fig. 1) and changes in absorption were investigated. The spectra showed a large change in the absorption of ligand after  $\text{Hg}^{2+}$  addition which could be pertinent to the strong affinity for complexing between the ionophore and  $\text{Hg}^{2+}$  in comparison to other ions [29]. Hence, ligand has the ability to be utilized as a neutral ion carrier in fabrication of PVC membrane  $\text{Hg}^{2+}$  selective electrode.

**Membrane composition influence on sensor development.** Although the used ionophore plays a crucial role in the electrode performance, the influence of other variables such as nature and amount of ionic additive, quality of solvent mediator and its ratio to polymeric matrix cannot be refuted [30, 31]. For this reason, in order to achieve the widest linear range and highest sensitivity, optimization of membrane composition is essential. To examine this subject, 10 different compositions were made as exhibited in Table 1, and their potential responses were investigated. As can be seen, the best Nernstian slope ( $29.1 \pm 0.3$ ) has been observed by the membrane with the composition of 29% of PVC, 12% of ionophore, 1% of NaTPB and 58% of DBP, therefore, this composition is the most promising one in the sensor development.

The extraction of  $\text{Hg}^{2+}$  ion into PVC membrane has a clear relationship to ligand adequate concentration in the membrane. From Table 1, it is clear that the designed electrode function is too poor in ionophore absence (no. 9, 10) and low non-Nernstian slopes are a reliable evidence for it (slopes of  $10.0 \pm 0.5$  and  $11.0 \pm 0.4$ ). The sensor sensitivity is promoted by adding ion carrier until a value of 12% is attained. Adding more ionophore leads to weakening the sensor perfor-



**Fig. 1.** UV-visible spectrum variations of  $5 \times 10^{-5}$  M ligand solution after adding 300  $\mu\text{L}$  of 1 mM solutions of different ions: (1)  $\text{Hg}^{2+}$ , (2)  $\text{Ag}^{+}$ , (3)  $\text{Cr}^{3+}$ , (4)  $\text{Pb}^{2+}$ , (5)  $\text{Cu}^{2+}$ , (6)  $\text{Zn}^{2+}$ , (7)  $\text{Cd}^{2+}$ , (8)  $\text{Co}^{2+}$ , (9)  $\text{Mn}^{2+}$ , (10)  $\text{Ni}^{2+}$ , (11)  $\text{Fe}^{2+}$ , (12) ligand.

mance, most likely owing to some inhomogeneities and possible saturation of the membrane [14].

The next matter strongly influencing the electrode response is type of plasticizer and its proportion to PVC. Dielectric constant value of plasticizer is one of most important parameters that should be considered in membrane construction. Solvent mediators with great dielectric constant value can have a harmful influence on the sensor selectivity due to their high tendency to extract polar ions that can compete with the complexation of primary ion with ionophore, moreover an ideal plasticizer should be immiscible with water, have low volatility and without any functional groups that may participate in protonation reactions [32–35]. In this research, DBP (with dielectric

constant of 6.4) was selected to be used in membrane fabrication since it had all the referred qualities.

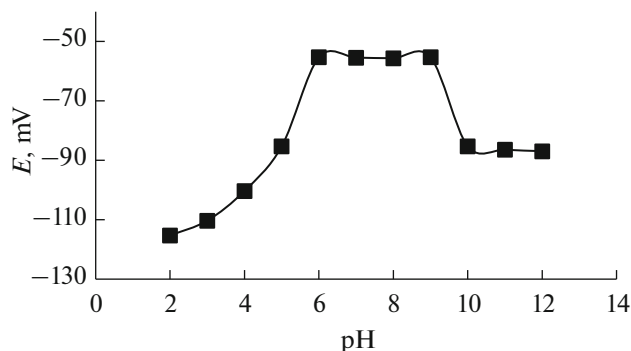
The effect of lipophilic anions on membrane performance was also studied. Ionic additives have been completely proved not only diminish Ohmic resistance, but also to ameliorate the selectivity, linear range and Nernstian slope of neutral carrier based ISEs. In this case, adding 1% NaTPB as an ionic additive resulted in a significant increase in the slope (nos. 3, 4, Table 1) from sub-Nernstian value of 19.2 mV/decade to an admissible-Nernstian value of 29.1 mV/decade. In fact, this category of anions catalyzes the analyte exchange procedure on the membrane surface.

**Internal solution.** To evaluate the effect of inner solution, the electrode potential response was recorded after altering the internal solution concentration ( $\text{Hg}(\text{NO}_3)_2$ ) from  $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-4}$  M. The results have shown that there is no considerable difference in the linearity and slope of Nernstian plots, except for an anticipated variation in the intercept of the diagrams. Thus, it seems that 1.0 mM concentration of  $\text{Hg}(\text{NO}_3)_2$  is entirely adequate for correct performance of the electrode system.

**pH effect on the electrode response.** In order to observe the performance of proposed electrode at different pH values, firstly, 0.1 mM  $\text{Hg}(\text{NO}_3)_2$  was prepared and its pH was regulated by concentrated NaOH and  $\text{HNO}_3$  solutions in the range from 2.0 to 12.0. Afterward, the potential response of test solutions was obtained and depicted in Fig. 2. As is obvious from the diagram, the potential remained constant in the pH range of 6.0–9.0, representing the usage of this sensor in this particular pH range. However, in the referred range, a striking diminution in potential response was accomplished. In detail, it seems that the swings upper the pH value of 9.0 result in the  $\text{Hg}^{2+}$ -hydroxy complex formation in solution. On the other hand, when pH decreases from 6.0,  $\text{H}^{+}$  can compete with primary ion ( $\text{Hg}^{2+}$ ) for making complex with the utilized iono-

**Table 1.** The optimization of the membrane ingredients

Membrane number	Ionophore, wt %	NaTPB, wt %	DBP, wt %	PVC, wt %	Slope, mV/decade
1	10	2	58	30	19.1
2	10	3	58	29	23.1
3	12	0	57	31	19.2
<b>4</b>	<b>12</b>	<b>1</b>	<b>58</b>	<b>29</b>	<b>29.1</b>
5	12	3	57	28	23.9
6	13	2	58	27	21.6
7	13	3	57	27	26.2
8	14	3	56	27	25.2
9	0	0	58	42	10.0
10	0	1	58	42	11.0



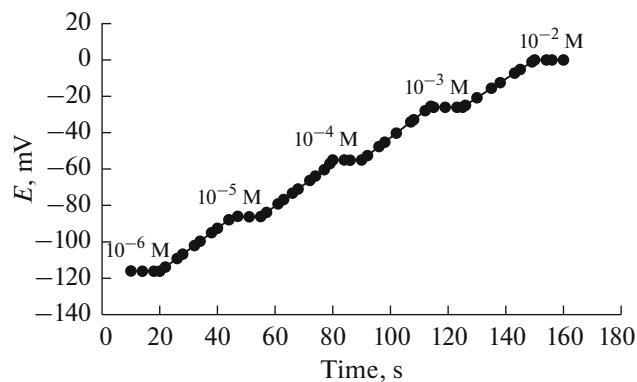
**Fig. 2.** The pH effect on the potential response of mercury sensor.

phore and partially protonate the ligand due to its high concentration, which leads to oscillations in potential response. In the pH range between 6.0 and 9.0, proton concentration is not sufficient for competing with metal ions, therefore, the sensor function could be stable only in this pH range.

**Response time.** Response time is one of the most important characteristics for ISEs that is defined from the moment when both reference and indicator electrodes are inserted in test solution until the system reaches a constant value or 90% of the endpoint or equilibrium potential. This parameter can be influenced by experimental conditions including the stirring or flow rate, ionic strength and matrix of the test solution, previous applications or preconditioning of the electrode and testing temperature [36]. Here, dynamic response time was measured by dipping the electrodes in a series of solutions with a 10-fold difference in concentration in the range from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-2}$  M. The factual potential vs. time plot is represented in Fig. 3. As can be seen, the electrode attains its equilibrium response in a relatively short time ( $\sim 25$  s) in the whole concentration range. This phenomenon can be originated by prompt exchange kinetics of complexation–decomplexation of  $\text{Hg}^{2+}$  ion with the ionophore at the test solution–membrane interface.

**Measuring range and detection limit.** A series of solutions with different activities were prepared and analyzed, and the plot of membrane potential response vs. the activity of  $\text{Hg}^{2+}$  was obtained. The regression equation is  $y = -29.181x + 58.258$  ( $R^2 = 0.9975$ ), where  $y$  is the electromotive force (mV) and  $x$  is the negative logarithm of the  $\text{Hg}^{2+}$  activity in solution. The proposed sensor response is linear with an appropriate Nernstian slope (29.1 mV/decade) in a broad range from  $5 \times 10^{-7}$  to  $1 \times 10^{-2}$  M with a detection limit of  $2.5 \times 10^{-7}$  M that was obtained by extrapolating the two segments of the calibration plot.

**Selectivity.** Selectivity is one of the most important traits in every type of sensors. And the more an elec-



**Fig. 3.** Dynamic response time of mercury electrode for step changes in  $\text{Hg}^{2+}$  concentration over a concentration range from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-2}$  M.

trode can discriminate between primary ion and interfering ones, its response will be more accurate and precise, and it can be utilized in a greater scope of specimens without any need for extraction and sample pretreatment steps. Thus, in this study, the interference of other cations was evaluated by matched potential method (MPM) and the calculated selectivity coefficient ( $K_{\text{MPM}}$ ) values are presented in Table 2. This parameter can be varied between 0 to 1, and when the coefficient value gets closer to 1, it indicates that the observed interference is more serious and electrode reaction bears a lot of resemblance between the analyte and interfering ion, but when  $K_{\text{MPM}}$  takes distance from 1 and gets closer to 0, it can be deduced that the interfering ion has a negligible effect on electrode potential behavior and the sensor has more affinity to primary ion in comparison to interfering ones [37, 38]. It is seen from the Table 2 that the selectivity coefficient values are significantly smaller than 1 indicating that they exhibit sufficient selectivity toward  $\text{Hg}^{2+}$  over all the interfering ions studied. Of course, it should be mentioned that the only cation that is competitive with the analyte is  $\text{Ag}^+$  which can be removed by masking or using a sequestering agent if it exists in a sample with mercury. This issue can be ascribed to the softness of silver. This ionophore has N atoms which are intermediate donor atoms and relatively soft. Therefore, charge-dipole interaction between soft ions (such as  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ ) and nitrogen atoms of ionophore is stronger than interaction between nitrogen atom and other ions.

The selectivity coefficients measured by mercury-selective electrode and the results of UV-Vis spectrophotometry are in satisfactory agreement. The results of two methods indicate that ionophore has more affinity to  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  comparing to other ions.

**Lifetime.** ISEs mostly lose their sensitivity after a while, since membrane ingredients such as ionophore, plasticizer and ionic additive leak to the sample solu-

**Table 2.** Selectivity coefficients of various interfering cations for the membrane

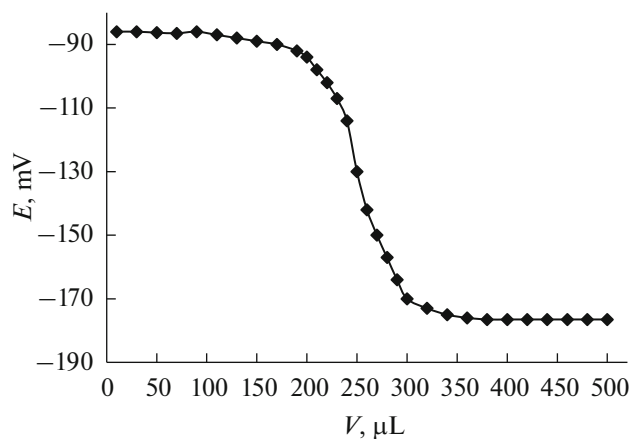
Ion	$K_{\text{MPM}}$
Cu <sup>2+</sup>	0.046
Cr <sup>3+</sup>	0.066
Cd <sup>2+</sup>	0.011
Co <sup>2+</sup>	0.012
Ag <sup>+</sup>	0.39
Fe <sup>3+</sup>	$6.6 \times 10^{-3}$
Pb <sup>2+</sup>	$4.3 \times 10^{-2}$
Ni <sup>2+</sup>	$6.5 \times 10^{-3}$
Mn <sup>2+</sup>	$8.8 \times 10^{-3}$
Zn <sup>2+</sup>	0.044

**Table 3.** Determination of Hg<sup>2+</sup> in various samples

Sample	Added amount, mg/L	Measured with proposed sensor, mg/L
Drinking water	0	<LOD
	0.5	$0.50 \pm 0.02^a$
	1.0	$1.1 \pm 0.1$
Sewerage	0	$0.4 \pm 0.1$
	1.0	$1.4 \pm 0.1$

<sup>a</sup> SD based on three replicate analyses.

tion gradually over time, and this phenomenon leads to a slump in calibration curve slope and rising detection limit. Here, for evaluating electrode lifetime, after conditioning step the potentiometric response of electrode toward Hg<sup>2+</sup> ion was measured by calibrating

**Fig. 4.** Potentiometric titration curve of 25 mL  $1.0 \times 10^{-5}$  M Hg<sup>2+</sup> with 1.0 mM EDTA using the proposed sensor as an indicator electrode.

three times a day (the sensor was used 1 h each day) and the slope of Nernstian plot and linearity were recorded regularly. Mercury selective electrode function was reproducible and highly sensitive for at least 6 weeks, but after this period, Nernstian slope fell substantially from 29.1 to 27.5 mV/decade and working range got narrower step by step.

**Analytical application.** Ion selective electrodes are economical, time saving, selective and facile devices that are able to be utilized for small sample volumes. These traits boost their position among other analytical techniques. This type of sensors is used in two different fields for analyte determination: indirect potentiometry (that is also known as potentiometric titration) and direct potentiometry (based on calibration curve). Hence, firstly, in order to examine the usability of the designed membrane sensor in indirect potentiometry as an indicator electrode, 25.0 mL of  $1.0 \times 10^{-5}$  M of Hg<sup>2+</sup> solution was titrated with 1.0 mM ethylenediaminetetraacetic acid (EDTA). The resulting titration curve is demonstrated in Fig. 4. As can be observed, the equivalent point is extremely recognizable and the amount of Hg<sup>2+</sup> ions in solution can be accurately determined by the electrode with high precision.

In the next step, the capability of proposed sensor was assessed in the quantification of Hg<sup>2+</sup> in two sewerage and drinking water specimens as real samples by direct potentiometry. In this experiment, at first, hovering particulate matters of samples were eliminated by filtering them with a 0.45- $\mu$ m pore size membrane filter. Then, 0.05 and 0.1 mg of Hg<sup>2+</sup> ions were added to 0.1 L of some sample solutions, while nothing was added to some of other solutions and pH values of the samples were regulated between 6.0–7.0. Afterward, their potential responses were measured and Hg<sup>2+</sup> concentration was obtained from the calibration curve and the results given in Table 3 obviously indicate that the constructed membrane sensor is able to quantify this toxic cation with high accuracy in real samples.

**A comparison between the constructed Hg<sup>2+</sup> selective electrode and some of the previously reported electrodes.** Some of the most substantial characteristics of ISEs including limit of detection, linearity domain, Nernstian slope, working pH range and response time of the designed liquid membrane sensor with some of the most eminent previous reports have been compared in Table 4 [12, 14, 39–44]. The provided data evidently reveals that the suggested electrode is superior to other electrodes in terms of working range and detection limit, and its response time, slope of calibration curve and pH working range are close to the best prior reports.

## CONCLUSIONS

In recent years, contamination by heavy metals and its eventuated problems have been very controversial

**Table 4.** Comparison of the proposed Hg<sup>2+</sup> ion sensor and some previous reports

Ionophore	Detection limit, M	Linear range, M	Response time, s	pH	Slope, mV/decade	Reference
4-(Benzylidene amino)-3,4-dihydro-6-methyl-3-thioxo-1,2,4-triazin-5(2H)one	$6 \times 10^{-7}$	$1 \times 10^{-6}$ –0.01	10	3.5–6.5	29.06	[12]
Dibenzodiazathia-18-crown-6-dione	$1 \times 10^{-6}$	$8.0 \times 10^{-6}$ –0.01	10	0.5–2.5	29	[39]
Poly-o-toluidine Zr(IV) tungstate	–	$1 \times 10^{-7}$ –0.1	15	1.5–3.5	28.1	[40]
Oxime-2-(N-piperidino methyl) cyclohexanone	$6.3 \times 10^{-7}$	$1 \times 10^{-6}$ –0.01	5	4.0–7.5	29.4	[14]
Calix[2]thieno[2]pyrrole	$7 \times 10^{-6}$	$1 \times 10^{-6}$ –0.01	20	1.0–6.0	27.8	[41]
1,5-Diphenylthiocarbazon	$3 \times 10^{-6}$	$5 \times 10^{-6}$ –0.01	20	3.5–8.0	29.7	[42]
Bis-salicylaldehyde diamino dipropylamine	$7 \times 10^{-7}$	$9.5 \times 10^{-7}$ –0.064	10–25	1.5–3.5	30.5	[43]
Salicylaldehyde thiosemicarbazone	$1 \times 10^{-6}$	$1.8 \times 10^{-6}$ –0.1	30	3.0–6.0	29	[44]
2-(N-piperidino methyl)-1-cyano cyclohexanol	$2.5 \times 10^{-7}$	$5 \times 10^{-7}$ –0.01	25	6.0–9.0	29.1	This work

all over the world. In this category of hazardous metals, mercury gathered more attention due to its high volatility, widespread usage in numerous industries and adverse effects on the health of all living organisms. Therefore, its accurate determination and fast removal of this toxic chemical are of significant importance, therefore, a precise, selective, sensitive, simple, speedy and economical method for Hg<sup>2+</sup> determination is required. Hence, in this study, owing to the fact that ISEs meet all the referred conditions, 2-(N-piperidino methyl)-1-cyano cyclohexanol was utilized as an ionophore in fabrication of a PVC based potentiometric membrane electrode. The sensor reveals a remarkable Nernstian slope ( $29.1 \pm 0.4$  mV/decade) over a wide concentration range from  $5 \times 10^{-7}$  to  $1 \times 10^{-2}$  M with a detection limit of  $2.5 \times 10^{-7}$  M. Its performance was reproducible for at least 6 weeks without any divergence in potential response. The interference of other different, monovalent, bivalent and trivalent cations was also evaluated by matched potential method and Ag<sup>+</sup> was the only metal causing a serious interference in electrode function. The sensor exhibits a fast response time (~25 s) and can be applied in solutions with pH in the range of 6.0–9.0. At the end, it was used as an indicator electrode in potentiometric titration of Hg<sup>2+</sup> with EDTA and in direct determination in aqueous specimens including sewerage and drinking water. It can be deduced from the results that the proposed electrode is capable to determine mercury(II) ions with outstanding sensitivity and accuracy.

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#### CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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