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The use of different ionophores for the determination of Zn^{2+} ions

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ABSTRACT

In this study, poly(vinly chloride) (PVC) membrane ion–selective electrodes for the determination of zinc(II) ions were prepared using potassium hydrotris(*N*-tert-butyl-2-thioimidazolyl)borate (**L1**), 1-[Bis(dimethylamino)methylen]-5-chlorobenzotriazolium-3-oxide hexafluorophosphate (**L2**), 1,4,8,12-tetraazacyclopentadecane (**L3**) and tetrabutylthiuram disulphide (**L4**) ionophores. Based on potentiometric performance properties, the optimum membrane composition was determined as 8.0% tetrabutylthiuram disulphide (**L4**), 58.0% *o*–nitrophenyloctylether (*o*–NPOE), 33.5% PVC and 0.5% potassium tetrakis (*p*–chlorophenyl) borate (KT*p*ClPB). The electrode exhibits a wide concentration range from 1.0×10^{-5} to 1.0×10^{-1} M, and has a detection limit of 6.50×10^{-6} M. The proposed electrode has a very quickly response time of 5s, good repeatability and selectivity. In addition, the electrode works in the wide pH range of 5.0–10.0 without being affected by pH changes. Finally, the developed zinc(II)–selective electrode was successfully used for the determination of zinc(II) in a drug sample.

1. Introduction

Zinc is the second most abundant trace element essential for human body [1]. Zinc contributes to many metabolic processes including DNA synthesis, neurotransmission, gene expression, enzymatic catalysis, apoptosis, hormonal storage and release in the human body [2]. High doses of zinc can cause nausea, vomiting, fever, chills, stomach ache, renal and internal organs failures [3]. Zinc is widely used in the electroplating, chemical, pharmaceutical and paint industries, and its excess can be toxic and pollute the environment [4–6]. Thus, the determination of zinc in biological, environmental and industrial samples is of high importance. Several analytical techniques such as inductively coupled plasma atomic emission spectrometry (ICP–AES) [7], inductively coupled plasma mass spectrometry (ICP–MS) [8], ultraviolet–visible (UV–Vis) spectroscopy [9] and flame atomic absorption spectrometry (FAAS) [10] are available for the determination of zinc(II) ions. Generally, these methods involve complex analysis procedures and are more expensive and time consuming compared to potentiometry–based methods [11–16].

Potentiometric ion–selective electrodes (ISEs) were first described by Cremer in 1906 [17]. ISEs have advantages such as wide linear range, low detection limit, rapid determination, high sensitivity and selectivity, low cost, simplicity and high precision [18–23]. In this study, we prepared zinc(II)–selective ISEs using four different ionophore molecules (Fig. 1). We identified the ionophore (tetrabutylthiuram disulphide) with the best selectivity against zinc(II) ions. We propose that this novel ISE that can be used for the determination of zinc(II) ions using this ionophore.

2. Experimental

2.1. Chemicals and reagents

Potassium hydrotris(*N*-tert-butyl-2-thioimidazolyl)borate, 1-[Bis(dimethylamino)methylen]-5-chlorobenzotriazolium-3-oxide hexafluoro phosphate, 1,4,8,12-tetraazacyclopentadecane and tetrabutylthiuram disulphide were purchased from the Fluka. High molecular weight PVC, *o*–NPOE, KT*p*ClPB, tetrahydrofuran (THF), hydrochloric acid (HCl), sodium hydroxide (NaOH), and metal nitrate salts were purchased from

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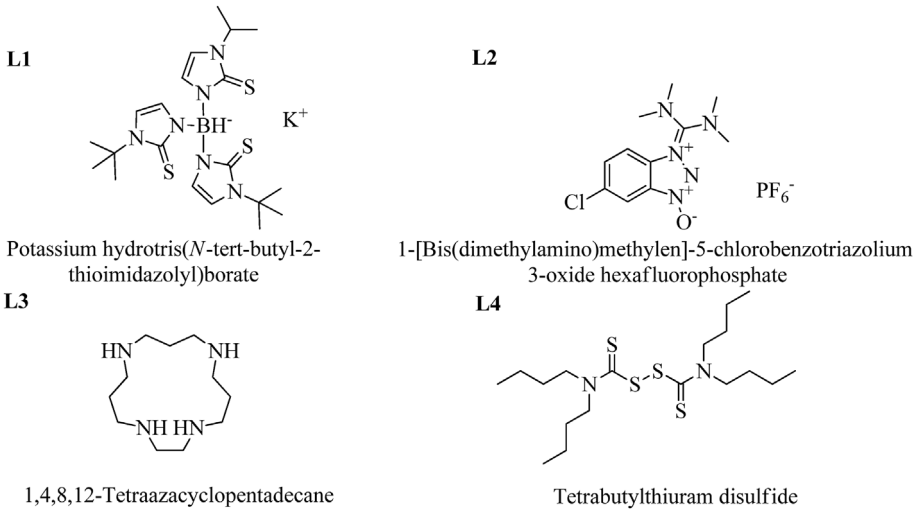

Fig. 1. The chemical structures of ionophores used.

Merck and Sigma Aldrich. Graphite, epoxy (Macroplast Su 2227) and hardener (Desmodur RFE), used to prepare conductive solid state, were obtained from Sigma Aldrich, Henkel (Istanbul, Turkey) and Bayer AG (Darmstadt, Germany), respectively.

2.2. Apparatus

Potential data were collected by using a laboratory–made, computer–controlled, multi–channel potentiometric measurement system. Throughout the potentiometric measurements, Ag/AgCl electrode (Thermo–Orion) was used as a reference electrode.

2.3. Method

The preparation of conductive all–solid–state contact ion–selective electrodes, which can be selective to Zn^{2+} ions, was carried out in two stages [24–26]. First, all–solid–state contact electrodes were prepared. Then, PVC membrane ion–selective electrodes with different components were prepared. All–solid–state contact electrodes were prepared by homogeneously mixing 35% (w/w) epoxy, 50% (w/w) graphite and 15% (w/w) hardener in approximately 3 mL THF. After obtaining a suitable viscosity, a copper wire (approximately 1 mm thick and 5–15 cm long) was coated by dipping it into this mixture 5–6 times and it was then left to dry overnight at room temperature. Then, the polymer membranes containing plasticizer (*o*–NPOE), anion excluder (KT*p*ClPB), PVC and ionophore at different ratios were formed by dissolution in approximately 3 mL THF. The membrane cocktail, which was mixed until a suitable viscosity was achieved, was coated on the all–solid–state contact electrodes surface at a certain thickness. The prepared electrodes were left to dry for about 4 h at room temperature. The electrodes were used after conditioning them in 1.0×10^{-2} M Zn^{2+} solution for 24 h.

2.4. Potential measurements

All potentiometric measurements were made at room temperature by using the following cell assembly:

Ag/AgCl; KCl (saturated) $\|Zn^{2+}$ sample solution$\,|\,$PVC–membrane$\,|\,$conductive solid contact$\,|\,$Cu wire.

3. Results and discussion

3.1. Membrane optimization

All–solid–state contact PVC–membrane zinc(II)–selective electrodes were prepared and their potentiometric performance characteristics such as linear working range, response time, selectivity, repeatability and detection limit were investigated. The optimal potentiometric behaviour of the prepared ion–selective electrodes was determined by using the ionophore, plasticizer, PVC and conductivity enhancer at different proportions in the membrane composition. The compositions and potentiometric performance properties of the prepared PVC membrane electrodes are given in Table 1. According to Table 1, the Electrode 12 exhibited the most ideal potentiometric behaviour in terms of linear working range and detection limit. Therefore, electrodes with this composition were prepared and their potentiometric properties were investigated.

Table 1
Membrane composition and potentiometric performance of the zinc(II)–selective electrode.

No	Molecule	Membrane composition (*w/w*)				Potentiometric performance		
		Ionophore	PVC	*o*–NPOE	KT*p*ClPB	Linear working range (M)	Limit of detection	R^2 (10^{-1} – 10^{-5} M)
1	L1	3.0	33.5	63.0	0.5	1.0×10^{-2}–1.0×10^{-5}	6.92×10^{-5}	0.9506
2	L1	4.0	32.5	63.0	0.5	1.0×10^{-2}–1.0×10^{-4}	2.51×10^{-4}	0.8379
3	L1	6.0	30.5	63.0	0.5	1.0×10^{-1}–1.0×10^{-5}	1.29×10^{-5}	0.9765
4	L2	2.5	33.0	64.0	0.5	1.0×10^{-2}–1.0×10^{-5}	4.63×10^{-5}	0.9430
5	L2	4.0	32.0	64.0	0.5	1.0×10^{-2}–1.0×10^{-4}	9.74×10^{-5}	0.9551
6	L2	7.0	30.5	62.0	0.5	1.0×10^{-1}–1.0×10^{-5}	1.37×10^{-5}	0.9828
7	L3	3.0	33.5	63.0	0.5	1.0×10^{-1}–1.0×10^{-3}	5.66×10^{-4}	0.8260
8	L3	5.0	31.5	63.0	0.5	1.0×10^{-2}–1.0×10^{-5}	8.29×10^{-5}	0.8595
9	L3	6.0	30.5	63.0	0.5	1.0×10^{-1}–1.0×10^{-5}	1.79×10^{-5}	0.9733
10	L4	3.0	33.5	63.0	0.5	1.0×10^{-1}–1.0×10^{-5}	1.42×10^{-5}	0.9826
11	L4	6.0	31.5	62.0	0.5	1.0×10^{-2}–1.0×10^{-5}	2.07×10^{-5}	0.9586
12	L4	8.0	33.5	58.0	0.5	1.0×10^{-1}–1.0×10^{-5}	6.50×10^{-6}	0.9992

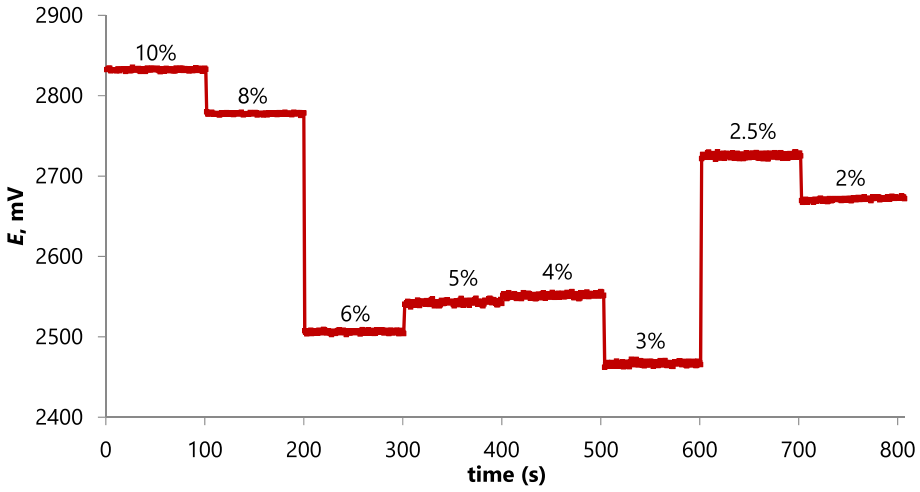

Fig. 2. Potential responses of electrodes with different ratios of ionophores.

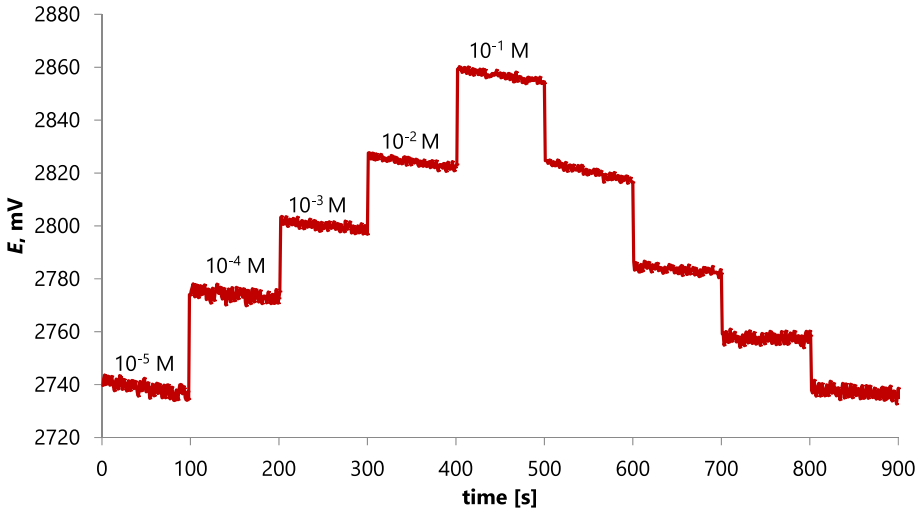

Fig. 3. Potentiometric response of zinc(II)–selective electrode.

3.2. *Effect of ionophore*

The performance of potentiometric ion–selective electrodes depends on the structure and ratio of the ionophore interacting directly with the analyte. In this study, four different ionophores, which can show selectivity to Zn^{2+} ions, were used. The molecular structures of the ionophores used are shown in Fig. 1. A total of twelve different PVC membrane electrodes were prepared using the ionophores in Fig. 1. The potentiometric behaviour of these prepared electrodes was then investigated. The obtained potentiometric performance characteristics are given in Table 1. When Table 1 is examined, the electrode that can operate in a wider concentration range and exhibit a lower detection limit was prepared using tetrabutylthiuram disulphide (**L4**). To determine the optimum ratio of tetrabutylthiuram disulfide ionophore, PVC membrane mixtures containing 2%–10% ionophore were prepared. In Fig. 2, the highest potential value belongs to the electrode containing 10% ionophore. Although this electrode showed high potential, it exhibited a rather unstable and non–linear potentiometric behaviour. As a result of the measurements, the highest potential value and stability against zinc(II) ions at every 10–fold concentration change were obtained with the electrode containing 8% ionophore.

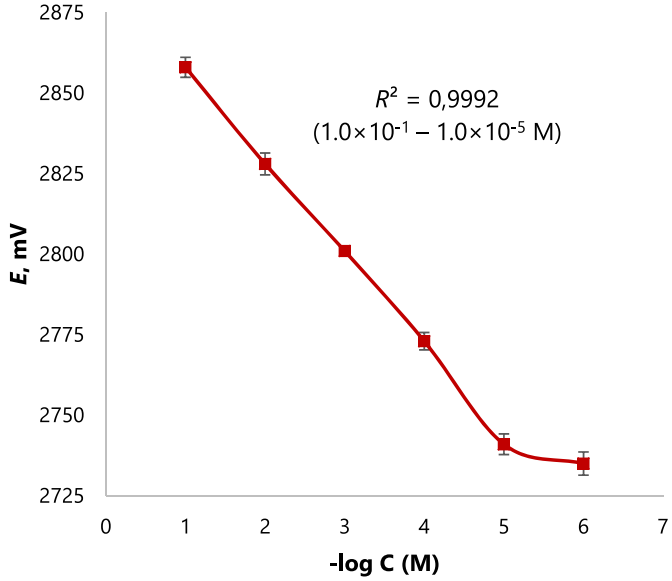

Fig. 4. The calibration curve of the zinc(II)–selective electrode.

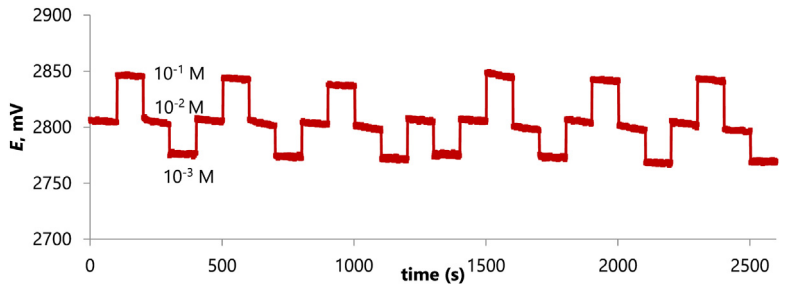

Fig. 5. The repeatability of the zinc(II)–selective electrode.

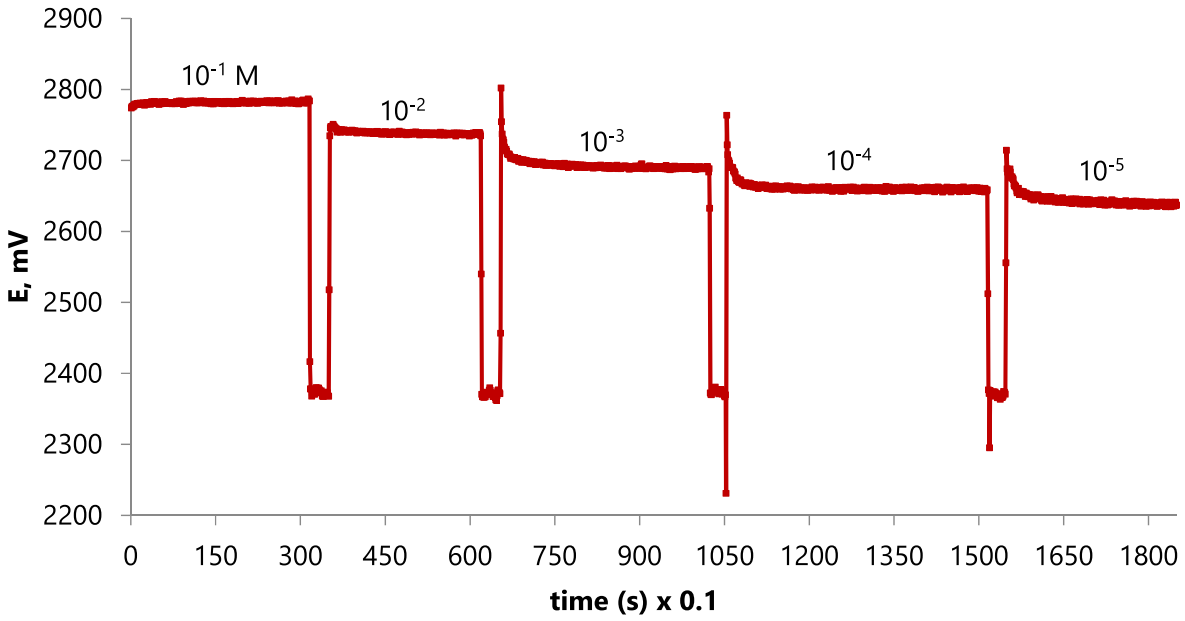

Fig. 6. The response time of the zinc(II)–selective electrode.

3.3. Potentiometric response and detection limit

The potential response of the Electrode 12 was determined using zinc(II) nitrate solutions with concentrations between 1.0×10^{-1} and 1.0×10^{-5} M. The potential behaviour of the electrode in this concentration range is given in Fig. 3. As seen, the electrode exhibits linear behaviour in the concentration range of $1.0 \times 10^{-1} - 1.0 \times 10^{-5}$ M. The detection limit of the proposed electrode was calculated using the calibration curve (Fig. 4). The limit of detection was calculated by substituting the potential value corresponding to the intersection point of

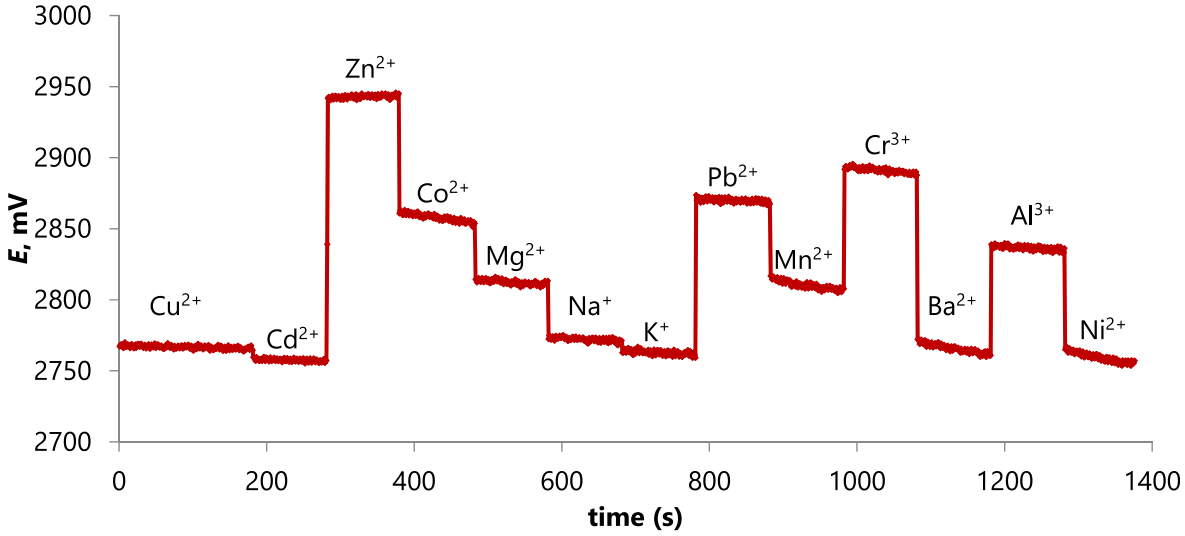

Fig. 7. The potential values of all ions at 1.0×10^{-2} M.

Table 2
The potentiometric selectivity coefficients of the zinc(II)–selective electrode.

Interfering ions	Selectivity coefficient		Interfering ions	Selectivity coefficient	
	$log\ K^{pot}_{Zn^{2+},\,M^{n+}}$	$K^{pot}_{Zn^{2+},\,M^{n+}}$		$log\ K^{pot}_{Zn^{2+},\,M^{n+}}$	$K^{pot}_{Zn^{2+},\,M^{n+}}$
Cr^{3+}	−1.78	1.66×10^{-2}	Na^{+}	−4.65	2.24×10^{-5}
Pb^{2+}	−2.02	9.54×10^{-3}	Mg^{2+}	−5.27	5.37×10^{-6}
Co^{2+}	−2.81	1.55×10^{-3}	Ba^{2+}	−6.15	7.08×10^{-7}
Al^{3+}	−3.86	1.38×10^{-4}	Cu^{2+}	−6.58	2.63×10^{-7}
K^{+}	−4.41	3.89×10^{-5}	Cd^{2+}	−6.91	1.23×10^{-7}
Mn^{2+}	−4.43	3.71×10^{-5}	Ni^{2+}	−7.27	5.37×10^{-8}

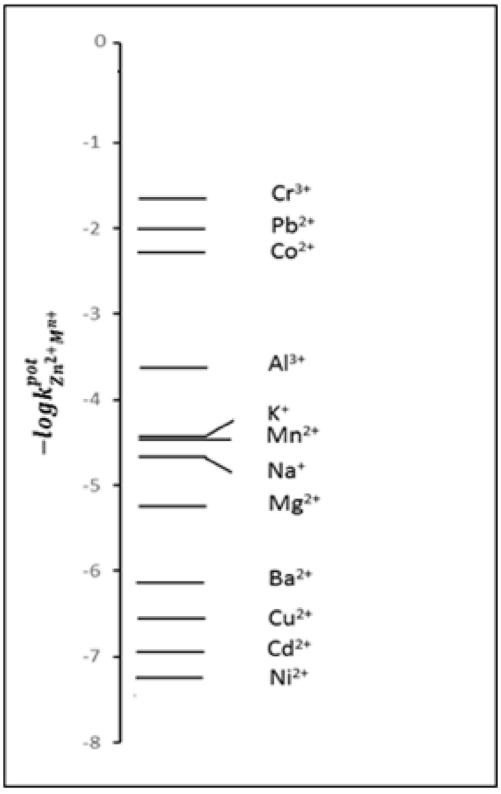

Fig. 8. The potentiometric selectivity coefficients of the zinc(II)–selective electrode.

the extrapolations of the two linear regions in the graph in the linear equation. The detection limit of the developed electrode was calculated as 6.50×10^{-6} M.

3.4. Repeatability

The repeatability was determined by immersing the electrode in zinc(II) solutions of different concentrations (10^{-1}, 10^{-2} and 10^{-3} M). Potentiometric measurements were carried out at room temperature and care was taken to wash the surface of the electrode with deionized water during the transition from one solution to another solution during the measurements. The potential–time plot of the repeatability study is given in Fig. 5. As can be seen in this figure, the developed electrode exhibited a highly reproducible and stable potentiometric behaviour.

3.5. Response time

The response time of the electrode was determined according to IUPAC recommendations [27]. The response time of the zinc(II)–selective electrode was calculated by immersing it in zinc(II) solutions in a concentration range of 1.0×10^{-1}– 1.0×10^{-5} M, and recording the time taken for the equilibrium potential to occur during the transition of the electrode from one solution to the other. The obtained potential–time graph is given in Fig. 6. As seen in Fig. 6 it is clear that the response time of the zinc(II)–selective electrode is approximately 5s. This experimental result shows that the electrode reaches equilibrium very quickly.

3.6. Selectivity

Selectivity is one of the most important properties of ion–selective electrodes and is a measure of the electrode's sensitivity to analyte ion in the presence of interfering ions. The selectivity coefficient is a numerical value used to express the selectivity of an ion–selective electrode. In this study, the selectivity coefficients were determined using the separate solution method reported by IUPAC [28]. The potential values of all ions at 1.0×10^{-2} M were used in the calculations. The potential values exhibited by all ions at 1.0×10^{-2} M are given in Fig. 7. The calculated selectivity coefficients are given in Table 2 and Fig. 8. According to the data in Table 2 and Fig. 8, the potential value of the electrode to the zinc(II) ion is higher than the potential value it shows against to the other ions. The data show that the electrode is highly selective towards Zn^{2+} ions.

3.7. Effect of pH

The effect of pH on the potential response of the developed zinc(II)–selective electrode was studied over the pH range of 2.0–12.0, and test solutions were prepared using the 1.0×10^{-2} and 1.0×10^{-3} M zinc(II) solutions adjusted with HCl (for pH 2.0–7.0) and NaOH (for pH 8.0–12.0).

The pH working range was determined by directly immersing the zinc(II)–selective electrode into the prepared solutions. The potential behaviour of the zinc(II)–selective electrode against the pH change of the solution is given in Fig. 9. Fig. 9 shows that the zinc(II)–selective electrode performed well in the pH range of 5.0–10.0 at both concentrations (1.0×10^{-2} and 1.0×10^{-3} M), without being effected by the changes in pH. It is observed that there are deviations in the measured potential values at pH $<$ 5.0 and pH $>$ 10.0. At lower pH values (pH $<$ 5.0), increases in potential are due to the electrode's response to the hydronium ion, while at higher pH values (pH $>$ 10.0), decreases in potential can be attributed to the formation of $Zn(OH)_2$.

3.8. Real samples analysis

The proposed zinc(II)–selective electrode was applied in the analysis of a zinc(II) containing drug sample. The one tablet of the drug obtained from a local pharmacy contains 50 mg of zinc(II). After the drug sample was ready for measurement, direct potentiometric measurements were performed. Zinc(II) content was calculated by substituting the obtained potential value in the calibration equation. The potentiometric

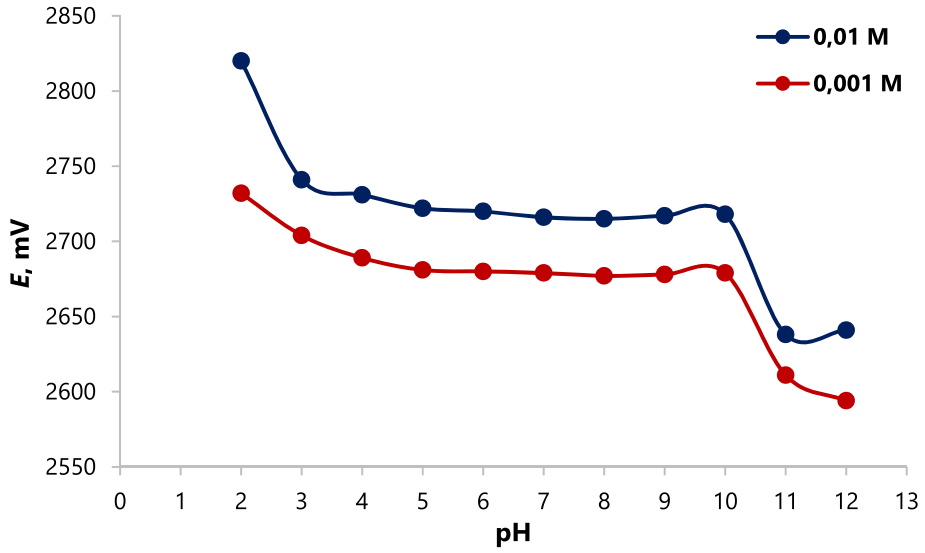

Fig. 9. Effect of pH on the potential response of zinc(II)–selective electrode.

Table 3
The zinc(II) analysis in drug samples.

	Zn^{2+} quantity, (mg)		
Drug sample	Zn^{2+} drug content	Found (± SD) with ISE[a]	% Recovery
Zinc tablet	50.0	47.3 (±0.87)	94.6

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

measurement results are given in Table 3. Based on these data, it can be said that the developed electrode can detect zinc(II) concentrations in drug samples with very high recoveries.

3.9. Comparative study

In this study, zinc(II)–selective electrodes prepared using tetrabutylthiuram disulphide were compared with the zinc(II)–selective potentiometric electrodes previously reported in the literature according to the parameters given in Table 4. When Table 4 is evaluated, the proposed electrode is similar to those in the literature in terms of linear working range. The electrode is better than some the earlier reported zinc(II) ion–selective electrodes regarding limit of detection (Table 4). The response time of the developed zinc(II)–selective electrode is < 5 s, while the response time of the compared electrodes varies between 5 and 30 s. The pH working range of the proposed electrode is better than the electrodes presented in Table 4.

4. Conclusion

Ionophores play an important role in the selectivity of polymeric membrane electrodes. In recent years, a large number of ionophore compounds have been produced and continuous progress has been made in this regard. In this study, four different ionophore species were used and their selectivity towards Zn^{2+} ions was investigated. The used tetrabutylthiuram disulfite exhibited a more selective and ideal potentiometric behaviour to Zn^{2+} ions compared to other ionophores. All–solid–state contact PVC–membrane electrodes prepared using tetrabutylthiuram disulfite work in a wide concentration range. Zinc(II)–selective electrodes have fast response time, very good selectivity, repeatability and high stability. The proposed electrode successfully performed the zinc(II) analysis in a drug sample. The electrode, which can work in a wide range without being affected by pH changes, can be used for the potentiometric determination of Zn^{2+} ions present in different real samples.

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 4
Comparison of the potentiometric performance properties of the developed electrode with the electrodes in the literature.

Ionophore	concentration range (M)	limit of detection (M)	pH working range	response time (s)	Ref.
Hematoporphyrin IX	1.0×10^{-5} – 1.0×10^{-1}	Not reported	2.0–5.5	30	29
bis(2,4,4-trimethylpentyl) dithiophosphinic acid	2.8×10^{-5}–1.0×10^{-1}	Not reported	2.1–6.9	15	30
4-tert-butylcalix [4]arene	9.8×10^{-6} – 1.0×10^{-1}	5.0×10^{-7}	2.5–4.3	30	31
3,7,12,17-tetramethyl-8,13-divinyl 2,18-porphine dipropionic acid	1.3×10^{-5} – 1.0×10^{-1}	Not reported	3.0–7.4	10	32
dibenzo-24-crown-8	9.2×10^{-5} –1.0×10^{-1}	2.0×10^{-7}	4.8–6.2	12	33
tartrazine azo dye	1.0×10^{-5} – 1.0×10^{-1}	8.0×10^{-6}	4.0–6.0	50	34
tetrabutylthiuram disulphide	1.0×10^{-5} – 1.0×10^{-1}	6.5×10^{-6}	5.0–10.0	<5	This work

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