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Development of PVC membrane potentiometric sensor for the determination of potassium ion and its applications

Potasyum iyonunun tayini için PVC membran potansiyometrik sensör geliştirilmesi ve uygulamaları

Ömer IŞILDAK[1], Oğuz ÖZBEK[2], Meliha Burcu GÜRDERE[3], Alper ÇETİN[4]*

[1,3]Tokat Gaziosmanpaşa University, Faculty of Science and Arts, Department of Chemistry, Tokat, Turkey.
omer.isildak@gop.edu.tr, burcugurdere@gmail.com
[2]Zonguldak Bülent Ecevit University, Science and Technology Application and Research Center, 67600, Zonguldak, Turkey.
oguzozbek60@gmail.com
[4]Tokat Gaziosmanpaşa University Faculty of Science and Arts Department of Molecular Biology and Genetics, Tokat, Turkey.
alper.cetin044@gmail.com

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Abstract

In this study, a novel all-solid-state contact poly(vinylchloride) (PVC) membrane potassium selective sensor with a pyrazole derivative molecule as an ionophore has been developed. The potassium selective sensor has a composition of poly(vinyl chloride) (PVC), ionophore, anion excluder (potassium tetrakis (p-chlorophenyl) borat (KTpClPB)) and plasticizer (bis(2-ethylhexyl) adipate (DEHA)) in the ratio of 32.0 : 4.0 : 1.0 : 63.0 (mg). The potassium selective sensor works in a linear concentration range of 1.0×10^{-5} to 1.0×10^{-1} M with a low detection limit of 6.02×10^{-6} M The developed potassium selective sensor works in pH range of 6.0 - 10.0 and has good repeatability, selectivity and a short response time of 10 seconds. Finally, the developed potassium selective sensor was successfully used in the determination of potassium in tap water and a drug sample.

Keywords: potassium, PVC membrane, potentiometry

Öz

Bu çalışmada, pirazol türevi bir molekülünün iyonofor olarak kullanıldığı yeni tümüyle katı hal kontak poli(vinilklorür) (PVC) membran potasyum sensörü geliştirildi. Potasyum seçici sensör poli (vinilklorür), iyonofor, anyon dışlayıcı (potasyum tetrakis (p-klorofenil) borat (KTpClPB)) ve plastikleştirici (bis (2-etilheksil) adipat (DEHA)'ın 32.0 : 4.0 : 1.0 : 63.0 (mg) bileşimine sahiptir. Geliştirilen potasyum seçici sensör, 6.02×10^{-6} M'lık düşük algılama limiti ile 1.0×10^{-5} - 1.0×10^{-1} M konsantrasyon aralığında doğrusal olarak çalışmaktadır. Geliştirilen potasyum seçici sensör pH 6.0 - 10.0 aralığında çalışmaktadır ve iyi tekrarlanabilirlik, seçicilik ve 10 saniyelik kısa cevap zamanına sahiptir. Son olarak, geliştirilen potasyum seçici sensör musluk suyu ve ilaç örneğinde potasyum tayininde başarıyla kullanılmıştır.

Anahtar kelimeler: potasyum, PVC membran, potansiyometri

1 Introduction

The use of the ion selective electrodes (ISEs) is increasingly preferred by chemists, due to the rapid growth of the technology world-wide. ISEs offer good advantages such as, speed, ease of preparation, accuracy, reasonable selectivity, wide dynamic range, lower cost procedures, simple instrumentation and shorter analysis time for different ions [1]-[4]. One of the most important advantages of ISEs is in routine monitoring, especially in environmental, clinical and chemical fields. Therefore, ISEs have continued to be an important topic in sensor field for over half a century [5].

Solid-contact PVC membrane ion-selective electrodes with their very low cost, ease of preparation and durability, quite easy maintenance are regarded as the most promising type in the production of potentiometric based ion selective electrodes [6]. In addition, polymer containing structures particularly poly(vinylchloride) can easily hold the ionophore based membrane mixture. Therefore, most researchers have focused on the PVC-based sensors [7]. Furthermore, ion-selective electrodes are superior to other analytical techniques due to all these properties. Therefore, it is much more reasonable to prefer ion selective electrodes compared to other analytical techniques in the analysis of different samples [8].

Potassium is an essential ion that the body requires for a wide range of biological functions, such as water balance, nerve impulses, blood pressure, digestion, pH balance (acidity and alkalinity) and heart rhythm. In addition, potassium deficiency can cause kidney disease, excessive sweating, diarrhea, and vomiting [9], [10]. Therefore, the amount of potassium in the human body is quite important. To date, different techniques of potassium ions determination have been developed and applied, such as ion chromatography [11], electrochemical methods [12], [13], flame photometry [14], [15].

Pyrazole derivative and sulfur-containing compounds have a wide range of chemical, physical and biological properties such as antimicrobial, antioxidant, antiinflammatory, antitubercular characteristics etc [16]-[18]. The presence of the pyrazole in different chemical structures leads to many applications in different areas such as technology, medicine and material industry [19].

The ionophore, the most important component of an ISE is responsible for a selective response to the target ion. In this study, 5,5'-(1,4-phenylene)bis(3-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide) (Figure 1) was used

*Corresponding author/Yazışılan Yazar

as an ionophore and a potassium selective sensor was developed.

Potentiometric properties of the novel sensor were investigated. In addition, the developed potassium selective sensor was successfully used in different real sample (drug and water) analysis.

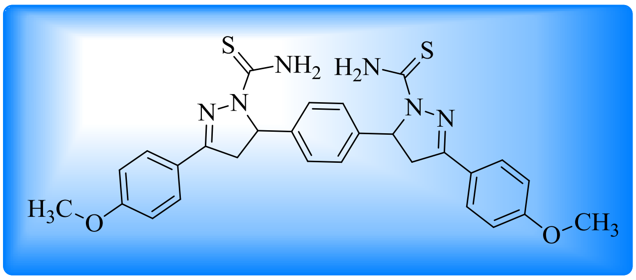

Figure 1: Structure of ionophore

2 Material and Methods

2.1 Materials

All reagents (DEHA, KTpClPB, PVC and THF) required to prepare the PVC membrane were of analytical grade. These reagents were purchased from Aldrich, Fluka and Merck companies. Nitric acid (HNO_3) and sodium hydroxide (NaOH) which are used to prepare the pH solution and sodium salts of the cations were also purchased from the same companies. Epoxy (Denlaks TP3100), Graphite (Sigma Aldrich) and hardener (Desmodur RFE) were purchased and used in the preparation of solid state contact. Metal solutions were prepared with double distillated deionized water (DI 800 deionize water system). The ionophore (Figure 1) was synthesized in the our laboratory.

2.2 Apparatus

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance DPX-400 instrument. FT-IR spectra was saved by Jasco FT/IR-4700 spectrometer. Melting point was measured on an Electrothermal 9100 apparatus. All potentiometric measurements were performed using a laboratory-made multi-channel potentiometric measurement system. In current study, Ag/AgCl electrode (Thermo-Orion) was used as the reference electrode.

2.3 Method

2.3.1 Synthesis of Ionophore

In this study, the synthesis of 5,5'-(1,4-phenylene)bis(3-(4-methoxyphenyl)-4,5-dihydro-1*H* -pyrazole-1-carbothioamide) molecule was performed according to a previously published method [20] and spectroscopic data of the molecule is identical to that reported in the literature.

White solid, Yield: 55%; mp: 284–286 °C. IR (KBr, cm^{-1}): 3449, 3244, 3138, 1609, 1588, 1484, 1375, 1304, 1249, 1179, 1036, 831. ^{1}H NMR (400 MHz, DMSO, ppm): δ 7.96 (s, 2H), 7.80–7.77 (m, 6H), 7.04 (d, J = 7.6 Hz, 4H), 6.94 (d, J = 8.4 Hz, 4H), 5.86 (d, J = 10.8 Hz, 2H), 3.85–3.76 (m, 8H), 3.11–3.03 (m, 2H). ^{13}C NMR (100 MHz, DMSO, ppm): δ 176.4 (2C), 161.8 (2C), 155.3 (2C), 142.0 (2C), 129.6 (4C), 126.1 (4C), 123.9 (2C), 114.4 (4C), 62.6 (2C), 55.9 (2C), 43.0 (2C).

2.3.2 Praparation of potassium selective sensors

Potassium selective sensor was prepared as in literature [21], [22]. First, all-solid-state contact electrode was prepared. 50.0% graphite, 35.0% epoxy and 15.0% hardener were mixed in 3 mL THF and, after obtaining the proper viscosity, a copper wire was immersed in the solution several times. Then, PVC membrane was prepared by dissolving 4.0% ionophore, 32.0% PVC, 1.0% KTpClPB and 63.0% DEHA in 5 mL THF. The prepared all solid state contact electrodes were immersed in the PVC membrane mixture and then left to dry for 12 h. The potentiometric measurement scheme of the Ag/AgCl reference electrode with the developed potassium selective electrode is given in Figure 2.

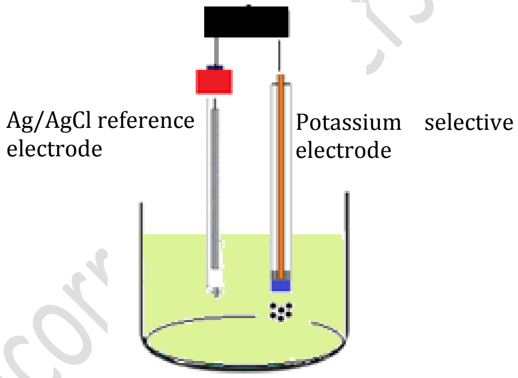

Figure 2: Potentiometric measurement of the developed sensor

3 Results and Discussion

In this study, the synthesized pyrazole derivative molecule was used as an ionophore in the development of a potassium selective sensor. The potentiometric behavior of the proposed potassium selective sensor was tested under laboratory conditions.

The working concentration and calibration curve of the developed potassium selective sensor was presented in Figure 3. The PVC membrane sensor showed linear behavior in the 1.0 × 10^{-5} to 1.0 × 10^{-1} M concentration range. Also, the developed potassium selective sensor shows a low detection limit of 6.02 × 10^{-6} M. Response time is a very important feature in ISEs. The response time of potassium selective sensor was found to be 10 seconds.

In this study, reusability of the novel potassium selective sensor was investigated by taking repeated measurements at 1.0 × 10^{-2} – 1.0 × 10^{-4} M potassium concentrations. Figure 4, shows that the developed potassium selective sensor is highly reusable.

The effect of pH dependence of the sensor was studied over pH range 2.0 – 12.0 at the 1.0 × 10^{-2} M potassium ion concentration after adjusting the pH solutions with HNO_3 and NaOH Figure 5 shows that the response of the developed potassium selective electrode response does not change in the pH range of 6.0 - 10.0. The developed potassium selective sensor can be used in this range without being affected by the change in pH.

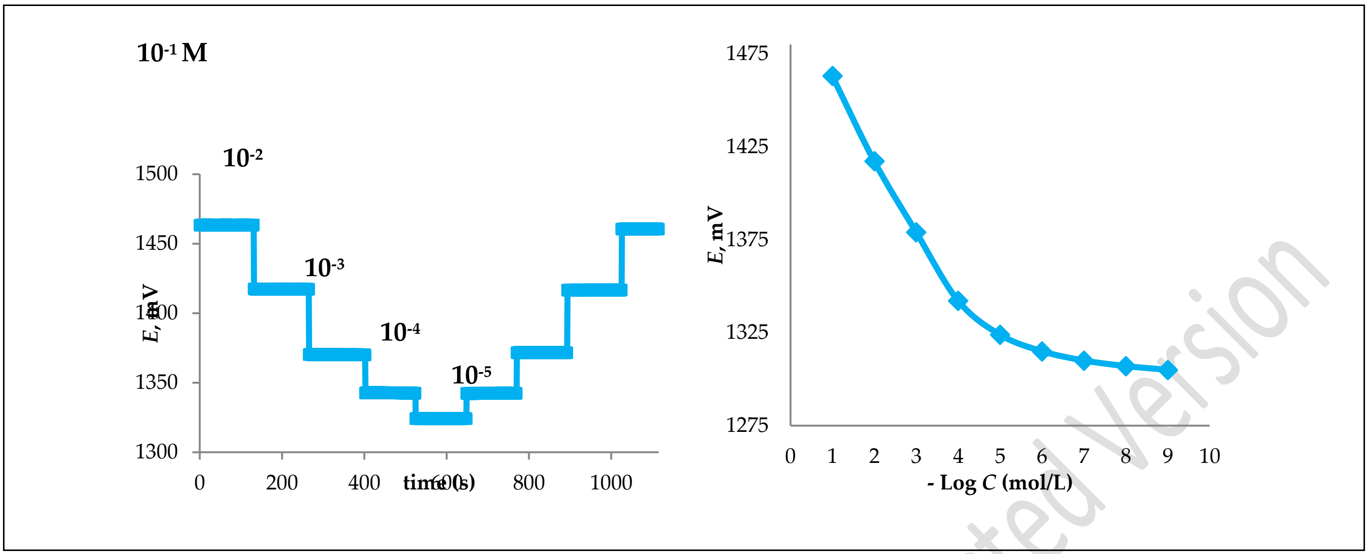

Figure 3: The potential response of potassium selective sensor and its calibration curve.

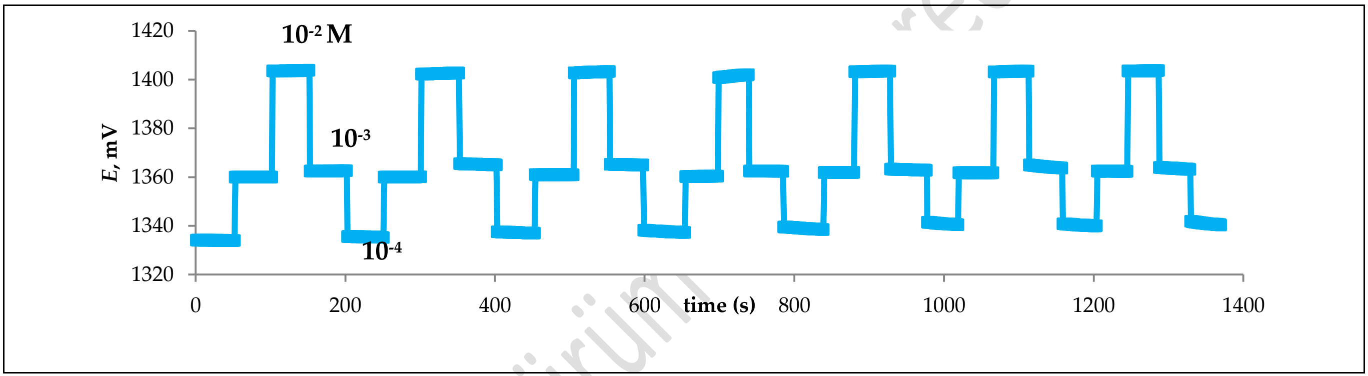

Figure 4: Reusability of potassium selective sensor.

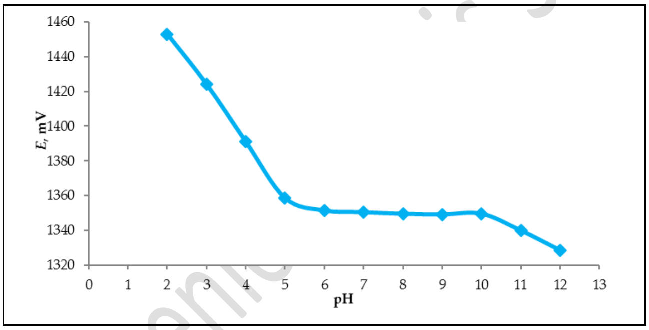

Figure 5: pH depedence of potassium selective sensor.

The selectivity coefficients of the developed potassium selective sensor towards other cationic ions were evaluated by using separate solution method [23].

$$logK_{A,B}^{pot} = \frac{(E_{B-} E_A)Z_A F}{RTln10} + (1 - \frac{Z_A}{Z_B})loga_A$$

The potentiometric response of potassium selective sensor was studied in presence of NH_4^+, Li^+, Na^+, Ni^{2+}, Cu^{2+}, Mg^{2+}, Zn^{2+}, Co^{2+} ions. The values of selectivity coefficient are summarized in Table 1.

Table 1: Selectivity coefficient values for K^+ selective sensor by the separate solution method.

Interfering ions	Selectivity coefficient, $\log k_{K^+,M^{n+}}^{pot}$	Interfering ions	Selectivity coefficient, $\log k_{K^+,M^{n+}}^{pot}$
Ni^{2+}	-2.27	Na^+	-2.79
Mg^{2+}	-2.46	Co^{2+}	-3.00
NH_4^+	-2.59	Zn^{2+}	-3.06
Li^+	-2.70	Ca^{2+}	-3.10

As seen, it is clear that the developed potassium selective sensor is highly selective when compared with different cations.

The developed potassium selective sensor was successfully applied to a drug sample and water sample. The water sample was prepared by the standard addition method. Potassium ion solution (1.0 × 10^{-2} mol L^{-1}) was added to the water sample. The measurement results obtained are given in Table 2. As seen, high rates of recovery are obtained. In this study, the developed potassium selective sensor was used to determine the amount of potassium in a drug sample. Drug tablet (0.2844 g) was crushed in a muller and dissolved in 50 mL of water. Then, the potential of the fully water-soluble drug sample was measured with the developed potassium selective sensor. The drug sample contains 5.85 mg potassium per tablet. The result of 5.41 (±0.11) mg was obtained by the developed sensor. The results obtained for drug sample are summarized in Table 3.

The comparison of the proposed potassium selective sensor with the previously reported potassium selective sensors or ion selective electrodes is given in Table 4. The other potassium selective sensor studies demonstrated that the PVC membrane potassium selective sensor was superior to the existing electrodes. While the ionophore used in the other studies is the same, it is completely different in this study. This supports in fact that different molecules can be selective against potassium ions. According to Table 4, the proposed potassium selective sensor is superior to other sensors in terms of its wide pH working range and response time. In addition, the detection limit value is very close to that of other studies. Potassium analysis was performed on a drug sample with the sensor developed differently from other studies.

Table 2: The determination of potassium in the water sample using the developed sensor.

Sample	K^+ amount, (M)		
	Added K^+	Measured (± SD) by sensor*	% Recovery
Tap water (Tokat, Turkey)	1.00×10^{-3}	$0.9772 (\pm 0.493) \times 10^{-4}$	97.72

*Average value (n = 3)

Table 3: The determination of potassium in the drug sample using the developed sensor.

	K^+ selective sensor (mg)*	Drug content K^+ (mg)	% Recovery
Drug sample	5.41 (± 0.11)	5.85	92.48

*Average value (*n* = 3)

Table 4: The comparison of the developed potassium selective sensor with other reported potassium selective electrodes.

Ionophore	**concentration range (M)**	**limit of detection (M)**	**pH working range**	**response time (s)**	**real samples applications**	**Ref.**
4,4'-bis[4''-phenoxy(15-crown-5) methyl]benzyl	1.0×10^{-5} – 1.0×10^{-1}	1.0×10^{-7}	5.0 – 7.0	< 10	various water samples	[24]
Valinomycin	1.0×10^{-6} – 1.0×10^{-2}	Not reported	Not reported	30	serum	[25]
Valinomycin	1.0×10^{-5} – 1.0	1.58×10^{-6}	Not reported	Not reported	artificial serum	[26]
Valinomycin	5.0×10^{-5} – 1.0×10^{-1}	4.0×10^{-5}	5.0 – 9.0	< 15	some vegetables	[27]
5,10,15,20-tetrakis(p-chlorophenyl)porphyrin	1.0×10^{-5} – 1.0×10^{-1}	6.02×10^{-6}	6.0 – 10.0	10	water and drug sample	This work

4 Conclusions

A novel sensor sensitive to potassium ions has been developed using a molecule completely different from the molecules used as ionophores in ion selective electrodes. Besides the used of a different ionophore used, the number of potassium selective potentiometric sensors is limited in the literature. The sensor developed in this study can be used as a new alternative to few potassium ion selective electrodes currently in application. The potassium selective potentiometric sensor developed in the current study has short response time, good reusability, good selectivity, a wide pH working range and low detection limit. In addition, the developed potassium selective sensor has been used successfully to determine potassium in the drug sample and tap water (Tokat, Turkey) sample.

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