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# Potentiometric Utility of the New Solid-State Sensor Based on Crowned Ionophore for the Determination of $K^+$

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All solid-state contact poly vinyl chloride (PVC) membrane potassium-selective electrode has been developed. The construction of the ion selective electrode membrane was organized using ionophore 4,4$'$-bis[4$''$-phenoxy(15-crown-5) methyl]benzyl in PVC cocktail. The potentiometric performance characteristics of the electrode were investigated by a computerized system. The electrode was found highly selective to $K^+$ions over a wide variety of other cations. The electrode almost exhibited a Nernstian response ($\geq 55$ ($\pm 15$) mV/decade of K activity) to $K^+$ within the concentration range $1.5 \times 10^{-1} - 1.0 \times 10^{-5}$ M. The operational pH range of the electrode was 5–7. The response time of the electrode was fast (<10 s), and the life time was long (at least 2 months). The electrode has been successfully used in real sample analysis. The values obtained by the electrode were in good agreement with the certified values.

**Key Words:** Ion-selective electrodes, Solid-state contact PVC-membrane, $K^+$ determination.

## Introduction

Ion-selective electrodes (ISE) are the chemical sensors with the longest and probably the most frequent routine application. Potentiometric detection based on ion-selective electrodes, as a simple method, offers several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity, and low cost. Besides, they are ideally suitable for on-site analysis and, nowadays, they are found to be applicable in the analysis of some biologically relevant ions, process control, and environmental analysis.[1−5] In recent years, there has been an increasing interest in the field of ion-selective electrodes, mainly those based on the use of all-solid state contact types[6,7] similar to coated-wire electrodes. The all solid-state contact prepared uses a mixture of graphite-epoxy resin in suitable

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ratios. In these types of electrodes, the sensing membrane adhered better to the surface of all-solid-state contact without an internal reference solution.[8]

Macrocyclic compounds have attracted considerable attention for the development of carrier-based PVC membrane sensors sensitive toward cationic species.[9-16] Crown ether classes of macrocyclic compounds, containing only oxygen as the heteroatom in the macrocyclic ring, exhibit ionophore properties, e.g. a strong affinity for alkali metal cations within the PVC membrane.[17-20] Potassium-selective potentiometric electrodes based on crown ether derivatives[21-23] and the ones incorporating the neutral carrier valinomycin in PVC membrane have been reported.[24-26] $K_2Zn_3[Fe(CN)_6]_2$ has also been used as electroactive material in preparation of silicone rubber and PVC matrix based potassium selective electrodes.[27-30]

A significant number of macrocyclic compounds, from crown ethers to calixarene derivatives, exhibit ionophore properties. Using these compounds as ionophore in PVC membranes, highly selective electrodes for alkali metal and alkaline earth metal ions can be developed. In the present study, all-solid-state PVC membrane $K^+$ selective sensor using 4,4$'$-bis[4$''$-phenoxy(15-crown-5) methyl]benzyl is reported. The chemical structure of the ionophore is shown in Figure 1.

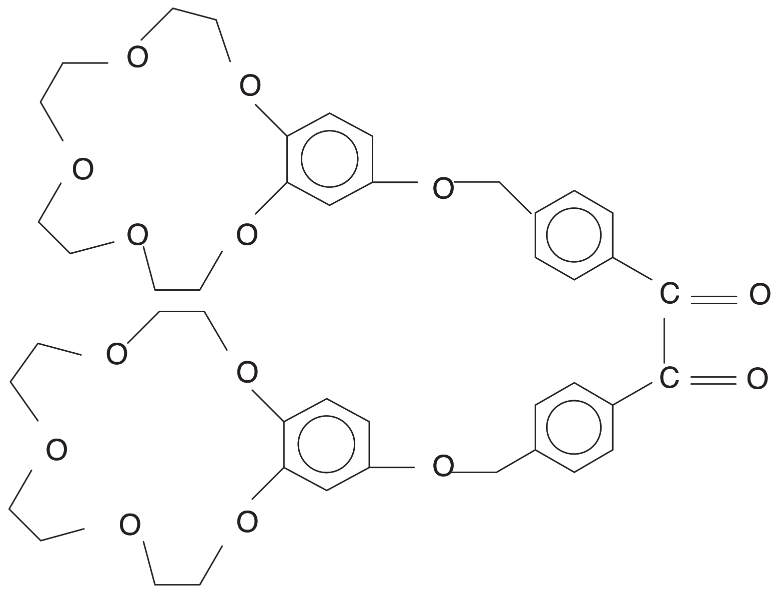

**Figure 1.** The chemical structure of ionophore.

# Experimental

## Reagents and apparatus

Tetrahydrofuran (THF), polyvinylchloride (PVC), dioctylsebacate (DOS), potassium tetrakis(p-chloropheny) brote (KTClPB), and sodiumtetrapenylborate (NaTPB) were purchased from Fluka (Buchs, Switzerland). Epoxy (macroplast Su 2227) and Hardener (desmodur RFE) were purchased from Henkel (Germany) and Bayer Ag (Germany), respectively. All salts used in the experiments are nitrate form and analytical reagent grade obtained from Merck (Darmstadt, Germany). The ionophore 4,4$'$-bis[4$''$-phenoxy(15-crown-5) methyl]benzyl was synthesized following a literature method published previously. [31]

The potential measurements were carried out at room temperature with an Ionmeter (ELIT 9808, Serial No: 1254100 CE). The ionmeter was connected to a personal computer with Athlon AMD Processor. Glass electrode as a pH electrode and silver/silver chloride as reference electrode (Mettler Toledo inlab 302) were used in the potentiometric cell.

## Preparation of sensors

The general procedure for preparing solid-state PVC membrane sensors was used.[32–33] For the construction of all solid-state contact material, the powdered graphite, epoxy, and hardener were mixed in various proportions. Experimentally established that the most appropriate solid-state contact composition was determined as 0.5 g of graphite (50%, w/w), 35 g of epoxy (35%, w/w), and 0.15 g of hardener (15%, w/w). The mixture was placed in THF solvent and left for aging for approximately 30 min. After obtaining appropriate viscosity, a shielded copper wire (0.5 mm diameter and 15 cm length) was polished and dipped in the solution about 10 times. The wire was covered with the mixture, and it was ripened for overnight in an oven at 60 °C. PVC membrane cocktails were composed of 4% (w/w) ionophore, 55% (w/w) plasticizer (DOS), 40% (w/w) PVC, and 1% (w/w) KTClPB or NaTPB (if required). The solid-state contact material was immersed into the membrane cocktail for 5 times and then allowed to dry in open air for 24 h. The prepared membrane electrodes were conditioned in a $10^{-1}$ M solution of $K^+$.

## EMF measurements

The electrode potential (EMF) measurements were performed at room temperature. Measurements were carried out in 50 mL solutions. The electrochemical cell was Cu/all-solid state PVC membrane/test solution/reference solution. Measurement apparatus with continuous stirring contain a developed electrode and a reference electrode in the same cell. Before every measurement, electrodes were washed with deionized water. All the standard or test solution concentrations of the studied ions were in the range of $10^{-1}$– $10^{-7}$M. The performances of the electrodes were evaluated measuring the EMFs of the test solutions in the same concentration range.

Test operation was as follows: All electrodes were conditioned for 3–24 h in main solutions before use, and were kept dry or in deionized water.

## Sampling

Water samples were taken from tap water and Değirmendere River, which is the main water resource for Trabzon Province and Karadeniz Technical University. Polyethylene bottles were used to store the samples. Before the collection of the water samples, polyethylene bottles were thoroughly washed with detergent, tap water, diluted $HNO_3$, and distilled/deionised water, in that order. After filtration through 0.45 $\mu$m nitrocellulose membrane filter, water samples were used for the analysis. The certified standard reference drinking water was supplied from CRM-TMDW-500.

# Results and Discussion

## Performance characteristics of the sensor

In preliminary experiments, the potentiometric response of the all-solid state PVC membrane electrode based on 4,4$'$-bis[4$''$-phenoxy(15-crown-5) methyl]benzyl to alkali and alkaline earth ions was measured.

In the first place, $K^+$ and similar cations such as $Na^+$, $Li^+$, $Mg^{2+}$, $Ca^{2+}$, and $Ba^{2+}$ were tested and the results of 5 repeated measurements were plotted as mV potential versus log[C] graphs, and is shown in Figure 2. The potentiometric response of the $K^2$ selective electrode was examined in the concentration range $1.0 \times 10^{-1}$ - $1.0 \times 10^{-7}$ M. Furthermore, 10 numbered standard solutions of $K^+$ were prepared and measured. The average of the results is shown in Figure 3. The electrode showed a linear response in $1.5 \times 10^{-1}$ - $1.0 \times 10^{-5}$ M concentration range with a Nernstian slope of ($\geq 55$ ($\pm$ 15) mV/decade.

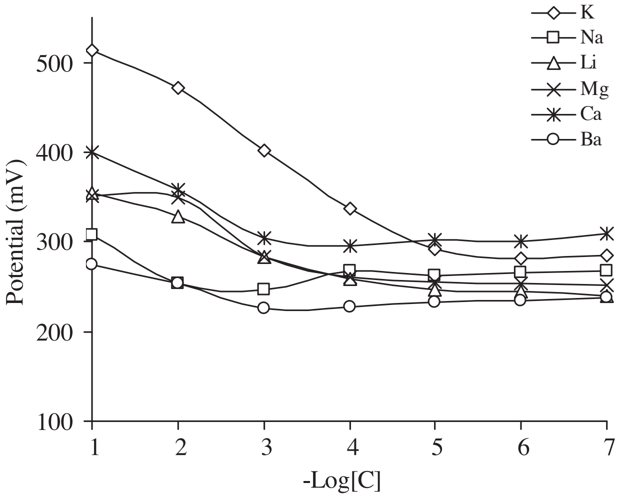

**Figure 2.** Potentiometric response of all solid-state contact PVC membrane ion selective electrode to different cations (The electrode was conditioned in $10^{-1}$ M $K^+$ for 24 h).

The selectivity behavior is one of the important characteristics of the ion selective electrodes. Figure 2 indicates that the electrode showed good selectivity towards $K^+$ ions compared to other alkali and alkaline earth ions. As can be seen in Figure 2, the most convenient cation was $K^+$ in terms of sensitivity and selectivity. Potentiometric selectivity of all solid state $K^+$ selective electrodes towards $K^+$ ions relative to alkali and alkaline earth metal ions was determined by the separate solution method.[34] The potentiometric selectivity coefficients ($k^{pot}_{K,M^{n+}}$) of each electrode for various cations were calculated by the separate solution method for $K^+$ selective electrode are given in Table 1. The smaller its value, the higher the performance for the primary ion relative to the interfering ion, and the more selective the electrode.

The response time of ion-selective electrodes is a very important feature. In order to determine this, after the electrode was taken out from $10^{-2}$M $K^+$ solution, it was immersed into $10^{-3}$ M $K^+$ solution. The response time ($t_{95}$%) of the electrode was measured as the time required to reach 95% of the steady potential value for a $10^{-3}$M solution. In this situation, the actual potential versus time traces is shown in Figure 4. The response time for the electrode was less than 10 s.

**Table 1.** Selectivity coefficient values for solid–state contact $K^+$ selective membrane electrode as obtained by separate solution method.

| Interfering ions | Selectivity coefficient, $\log k^{pot}_{K,M^{n+}}$ |
|---|---|
| $Ca^{2+}$ | – 2.0 |
| $Li^+$ | – 2.9 |
| $Mg^{2+}$ | – 2.9 |
| $Na^+$ | – 3.6 |
| $Ba^{2+}$ | – 4.2 |

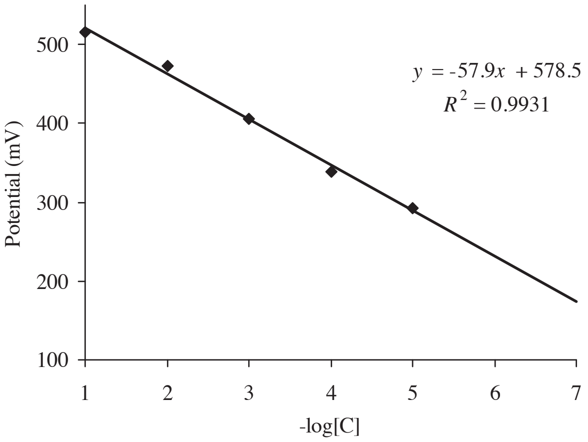

**Figure 3.** The variation of average potential values (mV) with log[C] for $K^+$ solutions in the range $10^{-1}$–$10^{-5}$ M (The electrode was conditioned in $10^{-1}$M $KNO_3$ for 24 h, $N= 10$).

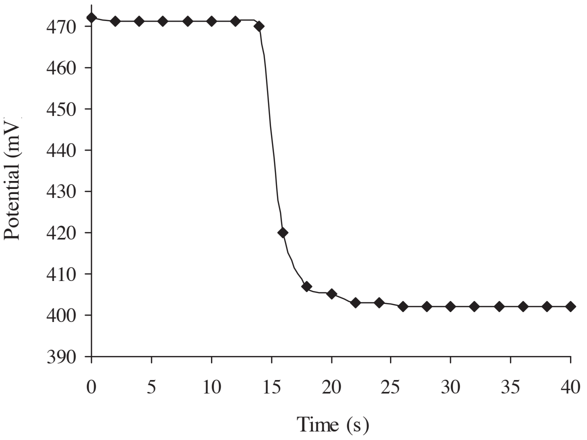

**Figure 4.** Potentiometric response – time of the solid-state contact $K^+$ selective membrane electrode for step changes in concentration of $10^{-2}$ M $K^+$ solution to $10^{-3}$ M $K^+$ solution (The electrode was conditioned in $10^{-1}$ M $K^+$ solution for 24 h).

The pH dependence of the electrode potential was also investigated over the pH range of 2–12 for $10^{-1}$ M $K^+$ ions. As shown in Figure 5, potentials remain constant between pH 5–7 which was determined as the operational pH range.

The detection limit of the electrode was found as $8 \times 10^{-6}$ M for $K^+$ ions and its lifetime was at least 2 months.

Consequently, from the results discussed in this paper, the solid-state electrode produced by ionophore can be considered as a convenient electrode for direct determination of $K^+$ ion in aqueous solution.

## Analytical application

The selectivity of potassium ions exhibited by the developed all solid state membrane electrode makes it potentially useful for the determination of $K^+$ in water samples. The concentration of $K^+$ was determined in real environmental samples, unspiked and spiked tap water, and river water samples. The obtained results are given in Table 2. The results of $K^+$determination in certified reference drinking water materials (CRM-TMDW-500) are given in Table 3. Table 4 shows that the values of K obtained by the electrode are in good agreement with certified values. Therefore, the developed sensor can be used for the determination of $K^+$ in real samples. Table 4 shows the values of $K^+$ in environmental water samples.

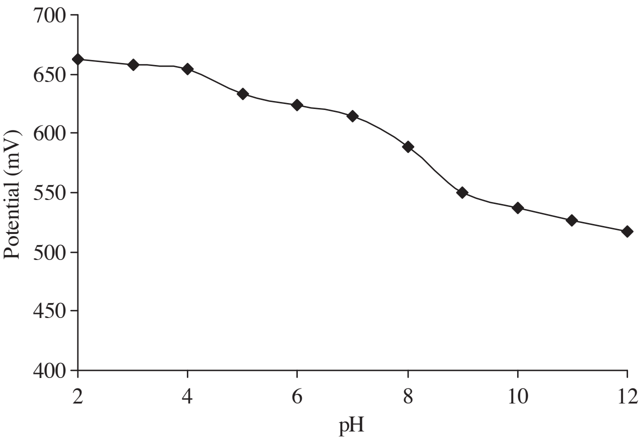

**Figure 5.** Effect of pH on potential of the solid-state contact $K^+$ selective membrane electrode at $[K^+]$: $1\times10^{-1}$ M.

**Table 2.** Spiked recovery results of $K^+$ in tap water and stream water ($N$= 3, V: 10 mL).

| Sample | Added (mg) | Found (mg) | Recovery (%) |
|---|---|---|---|
| KTU Tap Water* | 0 | 2.70 ± 0.01 | - |
| | 5 | 7.63 ± 0.02 | 97 |
| | 10 | 12.73 ± 0.04 | 101 |
| Değirmendere Stream | 0 | 1.72 ± 0.01 | - |
| | 5 | 6.66 ± 0.02 | 97 |
| | 10 | 11.75 ± 0.03 | 102 |

*Karadeniz Technical University main water line

**Table 3.** The level of potassium ($K^+$) in the standard reference material ($N$= 3, V: 10 mL).

| Sample | Certified value ($\mu$g $L^{-1}$) | Found value ($\mu$g $L^{-1}$) | Recovery (%) |
|---|---|---|---|
| CRM-TMDW-500* | 2500 ± 12.5 | 2500 ± 75 | 100 |

**Table 4.** The level of potassium in the water samples ($N$= 3, V: 10 mL).

| Sample | Concentration (mg $L^{-1}$) |
|---|---|
| KTU Tap water | 270.60 ± 0.72 |
| Degirmendere River | 172.40 ± 0.75 |

## Conclusions

The $K^+$selective electrode, based on 4,4$'$-bis[4$''$-phenoxy(15-crown-5) methyl]benzyl has sufficient characteristics in view of selectivity, response time, detection limits, linear response range, and independent pH range. Developed electrode has higher selectivity for $K^+$ ions than other ions such as $Ca^{2+}$, $Mg^{2+}$, $Li^+$, $Na^+$, and $Ba^{2+}$. Electrode sensitivity was relatively low, and it was approximately $10^{-5}$M. $K^+$ ion concentrations had linear responses versus potential in the range of $1.5 \times 10^{-1} - 1.0 \times 10^{-5}$M. The potential difference was nearly (55 ± 15 mV) for every 10-fold concentration change. Independency of pH versus potential increase was sufficient for reasonable $K^+$ determination. Therefore, the electrode was successfully used in real sample analysis for the determination of $K^+$ ion.

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### References

1. P. Bühlmann, E. Pretsch, E. Bakker, **Chem. Rev. 98**, 1593, (1998).
2. H.R. Pouretedal, A. Semnani, M.H. Keshavarz, **Turk. J. Chem. 30**, 711, (2006).
3. V.J. Wotring, D.M. Johnson, S. Daunert, L.G. Bachas, in: R.M. Nakamura, Y. Dasahara, G.A. Rechnitz (Eds.), Immunochemical Assays and Biosensor Technology for the 1990s, **American Society of Microbiology, Washington, DC, page 355**,(1992).
4. J. Janata, M. Josowicz, D. DeVaney, **Anal. Chem. 66**, 207,(1994).
5. S. Kim, H. Kim, K. H. Noh, S. H. Lee, S. K. Kim, J. S. Kim, **Talanta 61**, 709,(2003).
6. J.M.C.S. Magalhaes, F. Cespedes, S. Alegret, A.A.S.C. Machado, **Anal. Chim. Acta 355**, 24, (1997).
7. S. Alegret, A. Florido, **Analyst 116**, 473, (1991).
8. I. Isıldak, M. Yolcu, O. Isıldak, N. Demirel, G. Topal, H. Hosgoren, **Microchim. Acta 144**, 177, (2004).
9. M.M. Zareh, M.A. Akl, A. K. Gohneim, M.H.A. El-azız, **Turk. J. Chem. 31**, 449, (2007).
10. A. Ohki, J.P. Lu, R.A. Bartsch, **Anal. Chem. 66**, 651, (1994).
11. S. Daunert, L.G. Bachas, **Anal. Chem. 62**, 1428, (1990).
12. G.J. Moody, B.B. Saad, J.D.R. Thomas, **Ion Sel. Electrode 10**, 71, (1988).
13. T. Ito , **Anal. Sci. 14**, 89, (1998).
14. M.H. Mashhadizadeh, M. Shamsipur, **Anal. Chim. Acta 381**, 111, (1999).
15. R.K. Mahajan, M. Kumar, V. Sharma, T. Kaur, **Analyst 126**, 505, (2001).
16. L.Perez-Marin, H. Lopez-Valdivia, P. Avila-Perez, E. Otazo-Sanchez, G. Macedo-Miranda, O. Gutierrez-Lozano, J. Alonso, J. De Torres-Orazco, L. Carapia-Morales, **Analyst 126**, 501, (2001).
17. Y. Umezawa, **CRC handbook of ion selective electrodes**, CRC Press, Boca Raton, FL (1990).
18. I. Isildak, **Turk. J. Chem. 24**, 389, (2000).

19. H.C. Visser, D.N. Reinhoudt, F. De Jong, **Chem. Soc. Rev.** 75, (1994).
20. S. Faulkner, R. Kataky, D. Parker, A. Teasdale, **J. Chem. Soc. Perkin Trans 2**, 1761, (1995).
21. J.F. Alder, D.C. Ashworth, R. Narayanaswamy, **Analyst 112**, 1191, (1987).
22. G.J. Moody, B.B. Saad, J.D.R. Thomas, **Analyst 114**, 15, (1989).
23. R.E.Gyuresanyi, A.S. Nyback, K. Toth, G. Nagy, A. Ivaska, **Analyst 123**, 1339, (1998).
24. A.K. Covington, **Crit. Rev. Anal. Chem. 3**, 355, (1974).
25. J. Koryta, **Anal. Chim. Acta** 139, 1, (1982).
26. L.Y. Heng, E.A.H. Hall, **Anal. Chim. Acta 324**, 47, (1996).
27. P.A. Rock, T.L. Eyrich, S. Styer, **Electrochem. Soc. 124**, 530, (1977).
28. A.G. Fogg, A.S. Pathan, D.T. Burns, **Anal. Lett. 7**, 539, (1974).
29. C.J. Coetzee, **Ion selective electrode. Rev. 3**, 105, (1981).
30. H. A. Arida , R. F. Aglan, **Anal. Lett.36,** 895, (2003).
31. Y. Gök, Ü. Ocak, H.B. Senturk, **Indian J. Chem. B 38**, 1208, (1999).
32. S. Alegret, J. Alonso, J. Bartroli, E. Martinez-Fabregas, **Analyst 114**, 1443, (1989).
33. I. Isıldak, A. Asan, **Talanta 48**, 967,(1999).
34. W. Zhang, A. Fakler, C. Demuth, U.E. Spichiger, **Anal. Chim. Acta 375**, 211, (1998).