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A PVC Membrane Electrode for Zirconium Based on 4-Nitrophenylazo-n-(2-hydroxypropylamine) Salicylidine

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ABSTRACT
A potentiometric zirconium sensor based on the use of 4-nitrophenylazo-N-(2-hydroxypropylamine)salicylidine (NHPS) as an ion carrier in poly (vinyl chloride) (PVC) matrix, was developed. The best performance was observed for the membrane composition including 26.27% PVC, 65.67% N-POE, 5.43% NaTPB and 2.63% ionophore.The electrode which can be used for at least 1 month without observing any deviation exhibited a Nernstian slope of 29.37 mV per decade and a linear range of 1.0×10^{-2} to2.0×10^{-7} mol L^{-1}, with a detection limit of 2.0×10^{-8} mol L^{-1}, for zirconium ion. Also it showed a fast response time of about 10 s. The proposed membrane sensor revealed good selectivity for zirconium ion over a wide variety of other metal ions and could be used in pH range of 5–9.5. It was successfully used as an indicator electrode in potentiometric titration of zirconium ion.

Keywords: Ion selective electrode; Zirconium; Potentiometry; Schiff base.

1. INTRODUCTION

Zirconium is a significant engineering material which has become important as secondary metal for carrying out certain kind of industrial processes such as manufacturing of photoflash bulbs, surgical equipments, and tanning of leather [1]**.** Naturally occurring isotopes of zirconium are non radioactive in nature and some isotopes like Zr_{93} and Zr_{95} are produced as a result of uranium fission and dissolution of "Zircaloy" fuel cladding. Due to its long half life (1.5×10^{6} years), it has importance in nuclear fuel cycle [2]. Thus, because of increasing industrial uses of zirconium compounds, its determination is the subject of considerable efforts.

Potentiometric sensors possess many advantages such as accuracy, reproducibility, relatively fast response, lower costing, time saving, affectivity and facility in preparation. Also, the ion-selective electrodes (ISEs) allow non-destructive, and on line monitoring of particular ions in small volume of sample without any pretreatment. These characteristics have inevitably led to the preparation of numerous sensors for several ionic species, and the list of available electrodes has grown substantially over the past years [3-6].

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In the present work, a highly selective and sensitive potentiometric Poly Vinyl Chloride (PVC) membrane electrode based on 4-nitrophenylazo-N-(2-hydroxypropylamine)saicylidine (NHPS) (Fig.1) is reported for zirconium ion. NHPS is a new Schiff base that recently synthesized in our laboratory [7].
The proposed electrode has been preliminary applied to zirconium solutions and as indicator electrode in potentiometric titration of zirconium ion.

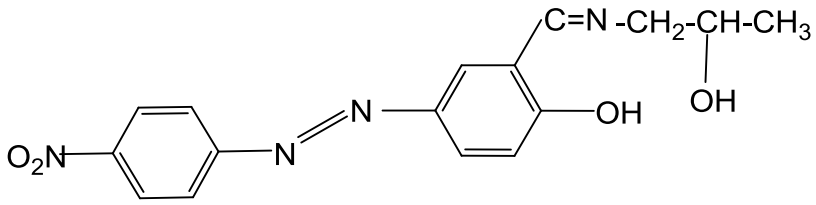

Fig.1: The structure of ionophor 4-nitrophenylazo-N-(2-hydroxypropylamine)salicylidine (NHPS)

2. EXPERIMENTAL

2.1. Apparatus

All potentiometric measurements were made at 25±0.1ºC with a pH/mV meter (Zag Chimi, Iran) using the proposed sensor in conjunction with a double junction Ag/AgCl (Azar Electrode, Iran) as a reference electrode.

2.2. Reagents and materials

All aqueous solutions were prepared using the chemicals of Analytical reagent grade and double distilled water. High molecular weight Poly Vinyl Chloride powder, diocthyl phthalate (DOP), dibuthyl phthalate (DBP), dimethyl sebacate (DMS), and tetrahydrofuran (THF), were supplied from Aldrich. Sodium tetraphenyl borate (NaTPB) and o-nitrophenyl octyl ether (NPOE) were obtained from Fluka. zirconylchloride ($ZrOCl_2.8H_2O$) was purchased from Merck. Also all salts of metal nitrates (all from Merck) were of the highest purity available and used without any further purification except vacuum drying over P_2O_5. Ligand (NHPS) was synthesized and purified as previously reported [7].

2.3. Electrode preparation

The procedure of preparation the PVC membrane was to dissolve a mixture of PVC powder, the plasticizer, ionophore (NHPS) and the additive NaTPB in 3 ml of THF, at the relative proportions given in Table 1. The resulting mixture was transferred into a glass dish of 2cm diameter. The solvent was evaporated slowly at room temperature until an oily concentrated mixture was obtained. A pyrex tube (3-5 mm id. on top) was dipped into the mixture for about 10 s so that a transparent membrane with the thickness of about 0.3 mm was formed. Pulled out from the mixture, the tube was kept at room temperature for about 1 h and then was filled by internal filling solution (1×10^{-3} mol L^{-1} of zirconylchloride). The electrode was finally conditioned for 24 h by soaking it in a 1×10^{-3} mol L^{-1}solution of zirconylchloride. A silver/silver chloride coated wire was used as an internal reference electrode. The ratio of various ingredients, concentrations of equilibrating solution and time of contact were optimized to provide membranes which resulted in reproducible and stable potentials with relatively little noise.

2.4. Emf measurements

All emf measurements were carried out with the following cell assembly: All measurements were carried out in a 50-ml double-walled glass cell, with constant magnetic stirring of the test solution. Activities were calculated according to Debye-Huckel procedure [8].

$$\text{Ag-AgCl}\,\big|\ \text{internal solution } (1\times10^{-3}\,\text{mol L}^{-1}\text{ of zirconylchloride})\ \big|\ \text{PVC membrane}\ \big|\ \text{test solution}\ \big|\ \text{Ag-AgCl.}$$

2. RESULTS AND DISCUSSION

The structure of NHPS as an ion-selective ionophore is presented in Fig. 1. In preliminary experiments, it was used as a neutral carrier to prepare PVC-based membrane electrodes for a variety of metal ions. The potential responses of the most sensitive electrodes, prepared under the same experimental conditions (except for 24 h conditioning in a 1.0×10^{-2} M of the corresponding cations) are shown in Fig. 2. As it can be seen, except for the zirconium ion-selective electrode, for all other cations, the slope of the corresponding potential pM plots is much lower than the expected Nernstian slopes.

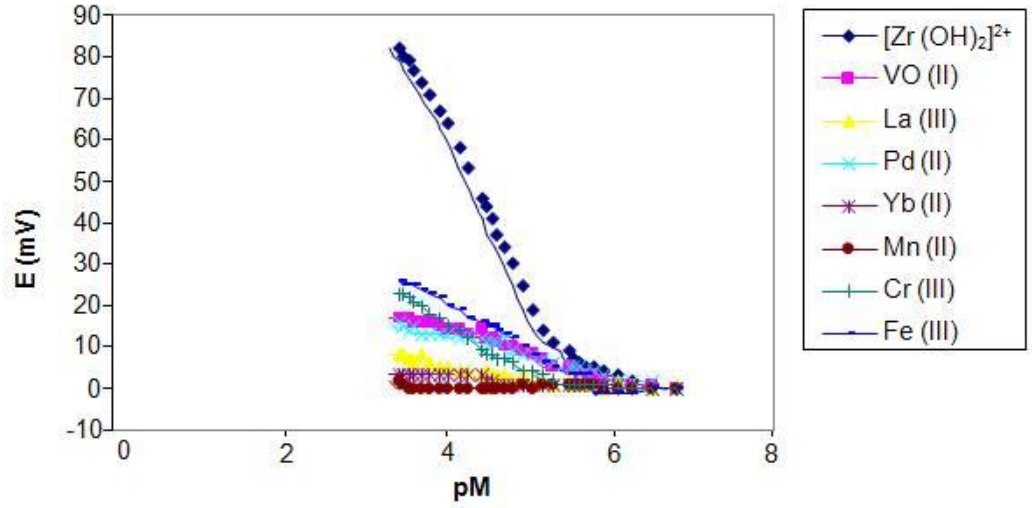

Figure 2. Potential response of different ion-selective electrode based on NHPS ligand

It is well known that the sensitivity and selectivity obtained for a given sensor significantly depend on the membrane composition [9-20]. Thus, some important features of the PVC membrane such as the nature and amount of ionophore, the properties of the plasticizer, the plasticizer/PVC ratio, and especially, the nature of additives used are reported to be significantly effective the sensitivity and selectivity of the ion selective electrode. To find the best plasticizer, different membranes containing NHPS as ionophore were prepared. The obtained results are shown in Table 1. Among four different plasticizers which are often used with PVC-membrane electrodes, including NPOE, DOP, DBP, and DMS, the best calibration parameters and mechanical characteristics of the membranes were observed in the case of NPOE; hence, this plasticizer was used in further studies.

Table 1: Optimization of membrane ingredients

No	**Composition(%w/w)**				**Slope** (mVper decade)	**Linear rang**
	PVC	**Plasticizer**	**Ligand**	**NaTPB**		
1	30.67	DOP,66.46	2.87	_	1.1	_
2	76.14	_	7.62	16.24	13.16	1.0×10^{-5}–1.0×10^{-3}
3	28.18	DOP,61.82	3.36	6.64	12.76	1.0×10^{-5}–1.0×10^{-3}
4	30.74	N-POE,60.03	2.87	6.63	20.52	1.0×10^{-6}–5.0×10^{-2}
5	33.73	DOP,59.46	_	6.81	2.19	_
6	32.93	DOP,55.63	5.46	5.98	9.35	1.0×10^{-5}–1.0×10^{-3}
7	30.60	DBP,60.11	3.42	5.87	2.2	_
8	28.24	DOP,60.72	3.09	7.95	11.67	1.0×10^{-5}–1.0×10^{-3}
9	26.27	N-POE,65.67	2.63	5.43	29.37	2.0×10^{-7}–1.0×10^{-2}
10	28.90	DMS,62.12	3.38	5.6	18.37	5.0×10^{-6}–5.0×10^{-2}

Although neutral-carrier-based ISE membranes may work properly even when they contain only a very small number of ionic sites, the addition of a salt of lipophilic ion is advisable and beneficial. In fact, it has been demonstrated that the presence of lipophilic negatively charged additives in cation selective membrane electrodes not only diminishes the ohmic resistance and enhances the response behavior and selectivity but also, in cases where the extraction capability is poor, it increases the sensitivity of the membrane electrodes [21-27]. Considering the data presented in Table 1, it is seen that the addition of NaTPB can increase the sensitivity of the electrode response considerably. Use of 5.43 %(w/w) NaTPB resulted in Nernstian behavior of the electrode (No. 9).

The obtained results indicated that the best sensitivity and linear range were obtained using membrane number 9 resulted in Nernstian behaviors of the membrane electrode over a wide concentration range.

Zirconium is present in aqueous solution in the form of $[Zr(OH)]^{3+}$, $[Zr(OH)_2]^{2+}$, $[Zr(OH)_3]^{+}$, $[Zr(OH)_4]$, $[Zr(OH)_5]^{-}$, $[Zr_3(OH)_4]^{8+}$, $[Zr_3(OH)_5]^{7+}$, $[Zr_4(OH)_8]^{8+}$ and ZrO_2. The dissolution and hydrolysis of zirconyl chloride (that was used as source of zirconium in this study) is a multivariate process. The existence of each of these species or others depends on different variables such as pH, temperature, zirconium concentration and chloride concentration [28]. In the crystal structure of zirconylchloride, the dominant from of zirconium is $[Zr_4(OH)_8]^{8+}$ ion, with water molecules grouped around this polymeric ion and no cross-linking between the units of zirconium species [29]. When the crystal is added to water, it is readily dissolved and the zirconium polymers are simply lifted out of the lattice into solution. The obtained slope of 29.37 mV/decade was equivalent to Nernstian slope for a double-charged cation. Accordingly, it can be concluded that the response of the electrode may be due to $[Zr(OH)_2]^{2+}$ cation.

The effect of H_3O^+ ion concentration on the electrode response was studied in a 1.0×10^{-3} M zirconium solution in which the pH adjustment was carried out in the presence of HNO_3 and NaOH. The corresponding results are depicted in Fig. 3, showing that the potential electrode based on (NHPS) seems to be hardly affected by pH in the range of 5.0–9.5. The observed changes of potential at lower and higher pH values could be due to the protonation of the ion carrier and formation of some mono hydroxyl complexes of zirconium ion in solution [29], respectively.

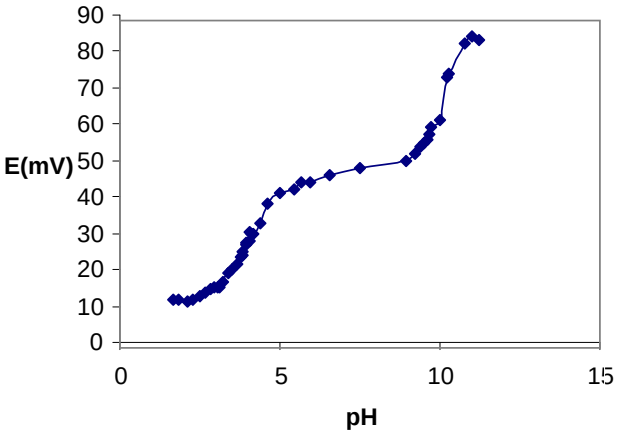

Fig. 3. Effect of pH of the test solution on the potential response of the zirconium ion-selective electrode.

The potential response of the electrode displayed a linear response to the concentration of zirconium ion in the range of 1.2×10^{-2} to 2.0×10^{-7} mol L^{-1} (Fig. 4). The slope of calibration graph was 29.37 mV per decade of the activity of the ion. The detection limit of the sensor determined by the intersection of the two extrapolated segments of the calibration graph was 2.0×10^{-8} mol L^{-1}. The prepared membrane electrode could be used for at least 1 month without any measurable divergence.

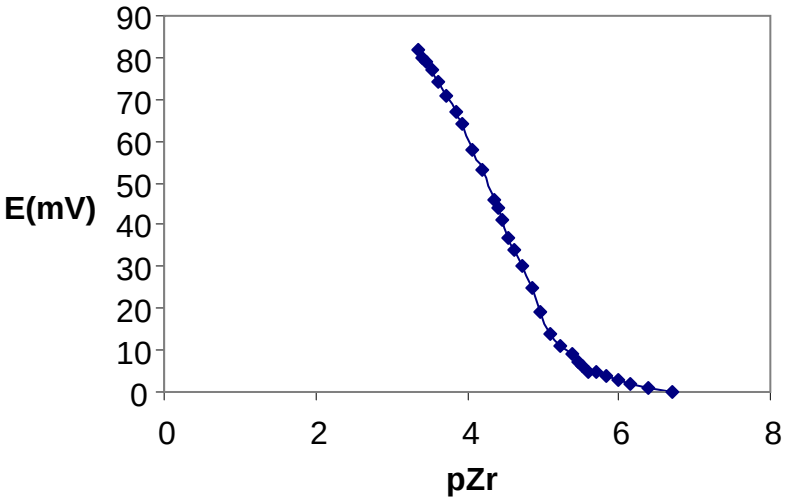

Fig.4. Calibration curves of zirconium electrode based on NHPS ligand.

The influence of interfering ions on the response behavior of ion-selective membrane electrodes is usually described in terms of selectivity coefficients, $\mathbf{K}^{pot}_{A,B}$. In this work, matched potential method (MPM) [30] and fixed interference method (FIM) [31-32] were used for calculation of selectivity coefficient. According to the MPM, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion to the interfering ion, which gives the same potential change in a reference solution. Thus one should measure the change in potential up on changing the primary ion activity. Then the interfering ion would be added to an identical reference solution until the same potential change is obtained. The selectivity coefficient, $\mathbf{K}^{pot}_{A,B}$ is determined as follows,

$$\mathbf{K}^{pot}_{A,B} = \Delta A / aB$$

Where aB is the activity of interfering ion and $\Delta A = a'A - aA$, that aA is the initial primary ion activity and $a'A$ is the activity of A in the presence of interfering ion. The concentration of zirconium ion used as primary ion in this study was 5.0×10^{-5} mol L^{-1}. The resulting values are shown in Table 2. In the other method (FIM), the emf of a cell comprising an ion-selective electrode and a reference electrode is measured for solutions of constant activity of the interfering ion, aB, and varying activity of the primary ion, aA. The obtained emf values are plotted vs. the logarithm of the activity of the primary ion. The intersection of the extrapolated linear portions of this plot indicates the value of aA that is to be used to calculate $\mathbf{K}^{pot}_{A,B}$ from the following equation:

$\mathbf{K}^{pot}_{A,B} = a\mathrm{A}/(a\mathrm{B})^{zA/zB}$ where both zA and zB have the same sign (positive).

The selectivity coefficient values calculated using FIM and MPM are reported in Table 2. The results indicate that the proposed sensor is sufficiently selective for zirconium ion over a large number of foreign ions.

Table 2. Selectivity coefficients of various interfering ions

Interfering ion	$-\mathbf{Log}\ \mathbf{K}^{pot}_{Zr,M}$	
	FIM	MPM
Cr^{+3}	2.90	2.48
Pb^{+2}	2.31	2.869
Fe^{+3}	2.95	2.759
Co^{+2}	2.9	2.103
Mn^{+2}	2.98	2.804
Ni^{+2}	2.1	2.471
Fe^{+2}	2.3	3.346
Yt^{+2}	2.98	2.167
K^{+}	3.2	2.647
Cu^{+2}	2.746	2.869
Zn^{+2}	2.2	2.484
Cd^{+2}	2.1	3.346

The proposed zirconium sensor was found to be able to work well under laboratory conditions. It was successfully applied as an indicator electrode in the potentiometric titration of zirconylchloride with NaOH and resulting titration curve is shown in Fig. 5. As it can be seen, the amount of zirconium ions in solution can be accurately determined using the sensor.

The proposed zirconium sensor was found to work well under laboratory conditions. It was successfully applied as an indicator electrode in the potentiometric titration of zirconylchloride with NaOH and resulting titration curve is shown in Fig. 5. As seen the amount of zirconium ions in solution can be accurately determined with the sensor

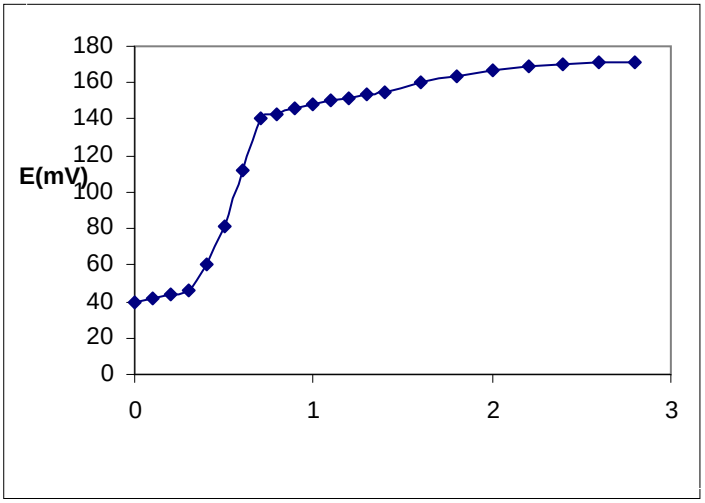

Fig.5. Potentiometric titration of 50.0 ml of 1 $\times 10^{-4}$ mol L^{-1} zirconium solution with 1 $\times 10^{-2}$ mol L^{-1} NaOH, using the proposed membrane sensor as an indicator electrode

The electrode was successfully applied to the direct determination of zirconium in different water samples and the results are given in Table 3.As can be seen, the accuracy of zirconium determination in different water samples is almost quantitative.

Table3. Recovery of zirconium from different water samples

No	Zr (μgL^{-1}) Added	Found	Recovery (%)
1	160	158	98.75
2	230	223	97
3	330	338	102.4
4	16	16.6	103.75
5	23	23.1	100.4
6	33	32.3	97.9

CONCLUSION

The main advantages of the proposed potentiometric sensor are its simplicity of preparation, fast response time, short conditioning time, low detection limit, low cost, wide dynamic range, Nernstian behavior, and life time at least 1 month. The electrode has a fairly good selectivity. Consequently, the proposed sensor is on the one hand, superior to the existing sensors in terms of response time and lifetime, on the other hand, comparable with regards to other parameters such as slope, pH range, concentration range (Table 4).

Table 4. Comparison of the proposed ion selective sensor with the existing sensors

Ref. no.	Working concentration range (M)	pH	Response time (s)	Lifetime (days)
33	1.0×10^{-1}-5.0×10^{-5}	3-6	18	30
29	1.0×10^{-1}- 1.0×10^{-7}	4.1–7.8	15	30
34	0.39–3.1	2.5	300	10
Proposed sensor	1.0×10^{-2} -2.0×10^{-7}	5–9.5	10	30

REFERENCES

1. Faghihian, H. and Kabiri-Tadi, M., "Removal of zirconium from aqueous solution by modified clinoptilolite", ***J. Hazard. Mater.***, 178: 66–73, (2010).

2. Akhtar, K., Akhtar, M.W. and Khalid, A.M., "Removal and recovery of zirconium from its aqueous solution by Candida tropicalis", ***J. Hazard. Mater.***, 156: 108–117, (2008).

3. Bakker, E,. Bühlmann, P..and Pretsch, E., "Carrier based ion-selective electrodes and bulk optodes. I. General characteristics", ***Chem. Rev***., 97: 3083–3132, (1997).

4. Mashhadizadeh, M.H., Mostafavi, A., Razavi, R., and Shamsipur, M., "Highly selective Cu(II) PVC membrane electrode based on 3,6,9,14-tetrathiabicyclo[9.2.1]tetradeca-11,13-diene as a suitable neutral ionophore" , ***Sens. Actuat. B***, 86: 222-228, (2002)**.**

5. Sheikhshoaie, I., Shamspur, T. and Ebrahimipur, S.Y., **"**Asymmetric Schiff base as carrier in PVC membrane electrodes for manganese (II) ions**",** ***Arabian J. Chem.***, 5: 201–205 (2012).

6. Fakhari, A.R., Shamsipur, M. and Ghanbari, Kh., " Zn(II)-selective membrane electrode based on tetra(2-aminophenyl) porphyrin" ***Anal. Chim. Acta.***, 460, 177-183, (2002).

7. Sheikhshoaei I, Saeed-Nia S Monadi N. And khabazzadeh, H., "Theoretical Study of Second-Order Non-Linear Optical Properties of Two Imino Chromophores Containing Salicylidine Group", ***Asian. J.Chem.***, 19: 1925-1929, (2007).

8. Kamata, S., Bhale, A., Fukunaga, Y. and Murata, H., "Cu (II)-selective electrode using thiuram disulfide neutral carriers", ***Anal. Chem.***, 60: 2464-2467, (1988) .

9. Mashhadizadeh, M.H. and Momeni, A. "Nickel(II) selective membrane potentiometric sensor using a recently synthesized mercapto compound as neutral carrier" , ***Talanta***, 59: 47-53, (2003).

10. Yang, X., Hibbert, D.B. and Alexander, P.W. "Continuous flow analysis of lead (II) and mercury (II) with substituted diazacrown ionophore membrane electrodes", ***Talanta***, *45*: 155-165, (1997).

11. Gupta, V.K., Jain, S. and Khurana, U.," A PVC-based pentathia-15-crown-5 membrane potentiometric sensor for mercury (II)", ***Electroanalysis***, 9P: 478-480, (1997).

12. Shamsipur, M., Yousefi, M. and Ganjali, M.R." PVC-Based 1,3,5-Trithiane Sensor for Cerium(III) Ions", ***Anal. Chem***., 72: 2391-2394, (2000).

13. Javanbakht, M., Shabani-Kia, A., Darvich, M.R., Ganjali, M.R. and Shamsipur, M. "Cadmium(II)-selective membrane electrode based on a synthesized tetrol compound", ***Anal. Chim. Acta***, 408: 75-81, (2000).

14. Gholivand, M.B. and Mozaffary, Y.," PVC-based bis(2-nitrophenyl)disulfide sensor for zinc ions " ***Talanta***, 59: 399-407, (2003).

15. Gholivand, M.B. and Raheedayat, F." Chromium(III) Ion Selective Electrode Based on Oxalic Acid Bis(Cyclohexylidene Hydrazide)", ***Electroanalysis***, 16: 1330-1335, (2004).

16. Chung, S., Kim, W., Park, S.B., Kim, D.Y. and Lee, S.S." Silver(I)-selective membrane electrodes based on sulfur-containing podands", ***Talanta***, 44: 1291-1298, (1997).

17. Rostazin, T., Bakker, E., Suzuki, K. and Simon, W. ") Lipophilic and immobilized anionic additives in solvent polymeric membranes of cation-selective chemical sensors", ***Anal. Chim. Acta***, 280: 197-208, (1993).

18. Schaller, U., Bakker, E., Spichiger, U.E. and Pretsch, E." Ionic additives for ion-selective electrodes based on electrically charged carriers", ***Anal. Chem***. 66: 391-398, (1994).

19. Kim, W., Sung, D.D., Cha, G.S. and Park, S.B." Chloride-selective membranes prepared with different matrices including polymers obtained by the sol–gel method", ***Analyst***, 123: 379-382, (1998).

20. Bakker, E., Malinowska, E., Schiller, R.D. and Meyerhoff, M.E. "Anion-selective membrane electrodes based on metalloporphyrins: The influence of lipophilic anionic and cationic sites on potentiometric selectivity", ***Talanta***, 41: 881-890, (1994).

21. Ammann, E., Pretsch, E., Simon,W., Lindner, E., Bezegh, A. and Pungor, E. " Lipophilic salts as membrane additives and their influence on the properties of macro- and micro-electrodes based on neutral carriers", ***Anal Chim Acta***, 171: 119-129, (1985).

22. Petrukhin, O.M., Kharitonov, A.B., Urusov, Y.I., Schipulo, E.V., Kruchinina, N.Y. and Baulin, V.E." Potentiometric selectivity of ion-selective electrodes for alkaline-earth elements based on podands with phosphoryl terminal groups", ***Anal. Chim. Acta***, 353: 11-27, (1997).

23. Shamsipur, M., Rouhani, S., Ganjali, M.R., Eshghi, H. and Sharghi, H." Zinc-selective membrane potentiometric sensor based on a recently synthesized benzo-substituted macrocyclic diamide", ***Sens. Actuat. B*** 59: 30-34, (1999).

24. Bakker, E., Buhlmann, P., and Pretsch, E." Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 1. General Characteristics", ***Chem. Rev***., 97: 3083-3132, (1997).

25. Zamani, H.A., Ganjali, M.R. and Adib, M." Cd(II) PVC-Based Membrane Sensor Based on *N′*-[1-(2-furyl)methylidene]-2-furohydrazide", ***Sensor Lett***., 4: 345-350, (2006).

26. Zamani, H.A., Ganjali, M.R. and Adib, M." electrode based on 3-{[2-oxo-1(2H)-acenaphthylenyliden]amino}-2-thioxo-1,3-thiazolidin-4-one", ***J. Braz. Chem. Soc***., 18: 215-222, (2007).

27. Zamani, H.A., Ganjali, M.R., Norouzi, P., Tadjarodi, A. and Shahsavani, E." Determination of terbium(III) ions in phosphate rock samples by a Tb^{3+}–PVC membrane sensor based on *N*, *N*-Dimethyl-*N′*, *N″*-bis(4-methoxyphenyl)phosphoramidate", ***Mater. Sci. Eng. C***, 28: 1489-1494, (2008).

28. Blumenthal, W.B. The Chemical Behavior of Zirconium, D. ***Van Nostrad Company, Inc***., Princeton, New Jersey, (1958).

29. Gholivand, M.B., Babakhanian, A. and Joshaghani, M." Zirconium ion selective electrode based on bis(diphenylphosphino) ferrocene incorporated in a poly(vinyl chloride) matrix", ***Anal. Chim. Acta***, 584: 302-307, (2007).

30. Umezawa, Y., Umezawa, K. and Sato, H." Selectivity coefficients for ion-selective electrodes: Recommended methods for reporting $K_{A,B}^{pot}$ values", ***Pure. Appl. Chem***., 67: 507-518, (1995).

31. Buck, R.P. and Linder, E. "Recommendations for nomenclature of ionselective electrodes", ***Pure. Appl. Chem***., 66: 2528-2537, (1994).

32. Inczedy, J., Lengyel, T. and Ure, A.M. Compendium of Analytical Nomenclature, Blackwell Science, ***Oxford***, 1998.

33. Nabi, S.A. and Shalla, A. H. "Poly (Vinyl Chloride) Based Ion Selective Electrode for Determination of Zr (IV) Ions Based on 2, 6-Dibenzylidenecyclohexanone", ***Sensors & Transducers Journal***, 95: 72-80, (2008).

34. Abbaspour , A. Baramakeh, L. "Novel zirconium optical sensor based on immobilization of Alizarin Red S on a triacetylcellulose membrane by using principle component analysis artificial neural network", ***Sens. Actuat. B,*** 114: 950–956, (2006).