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Potentiometric Studies of 1,4-bis[o-(quinoline-2-carboxamidophenyl)]-1,4-dithiobutane as a Sensing Material for Tb(III) Ions

Hassan Ali Zamani[1], *Mina Ranjkesh*[2], *Mohammad Reza Abedi*[2,*], *Soraia Meghdadi*[3]

[1]Department of Applied Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran
[2]Department of Applied Chemistry, Quchan Branch, Islamic Azad University, Quchan, Iran
[3]Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran
[*]E-mail: mohamadrezaabedi@yahoo.com

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A new Tb^{3+} ion-selective PVC membrane sensor has been developed, based on 1,4-bis[o-(quinoline-2-carboxamidophenyl)]-1,4-dithiobutane (QCD), as a suitable sensing material. The sensor performance includes a Nernstian slope of 20.1 ± 0.4 mV decade^{-1} across a wide concentration range between 1.0×10^{-6} and 1.0×10^{-2} mol L^{-1} and a detection limit of 6.4×10^{-7} mol L^{-1} in the pH range of 3.2 –9.0. The sensor possesses the advantages of short conditioning time, fast response time (~ 5 s) and, especially, great selectivity towards transition and heavy metal and some mono, di and trivalent cations. The recommended sensor was effectively used as an indicator electrode in the potentiometric titration of Tb^{3+} ions with EDTA. The membrane sensor was also applied to the Tb^{3+} ions determination in some water samples.

Keywords: PVC membrane, Sensor, Ion selective electrode, Potentiometry

1. INTRODUCTION

Because the lanthanides illustrate similar chemical and physical properties, the lanthanides analysis is an extremely time consuming and complicated procedure, when several of their members are present, since separation as well as pre-concentration are required [1]. Terbium is classified as a rare earth element. Terbium is used to dope calcium fluoride, calcium tungstate and strontium molybdate, materials that are used in solid-state devices, and as a crystal stabilizer of fuel cells which operate at elevated temperatures, together with ZrO_2. The main applications include; firstly, the use of mixed rare-earth as gasoline-cracking catalysts, and as starting materials for making misch metal, secondly, the use of rare-earth silicides for various metallurgical applications as polishing compounds, and for carbon arcs used in movie projectors and searchlights [2].

Many techniques have been used for determination of terbium which most of them have been spectroscopic methods such as inductively coupled plasma mass spectroscopy (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES), electron spin resonance, high resolution γ-spectroscopy, atomic emission spectroscopy, spectrophotofluorimetric, laser-based multi step resonance ionization and some nucleic methods.Nevertheless, almost all of these methods are expensive and time consuming, with the exception of one; the ion selective electrode (ISE) method. As a matter of fact, it is one of the most popular electrochemical methods and it can be employed as a sensor for the determination of ions. These sensors are, relatively short response times, wide linear dynamic ranges, selective and can be prepared easily [3-16].

We have currently developed some ISEs for the potentiometric determination of some metal ions, where polymeric membranes were prepared with increasingly selective ionophores, sensing analyte selectively [16-21]. In this work we report a Tb^{3+} membrane sensor based on 1,4-bis[o-(quinoline-2-carboxamidophenyl)]-1,4-dithiobutane (QCD) (Fig. 1) with a nice Nernstian response over a relatively wide working range.

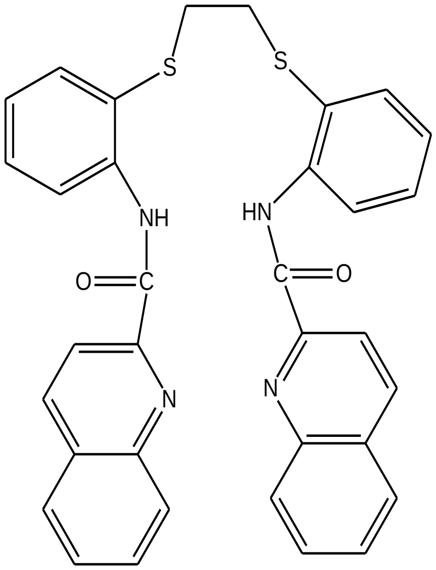

Figure 1. The chemical structure of QCD.

2. EXPERIMENTAL

2.1. Reagents

The Merck and the Aldrich Chemical Co. were the provider for the nitrate and chloride salts of all cations as well as for the following reagents; reagent-grades of phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), acetophenone (AP), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and relatively high molecular weight PVC. All reagents were used without any modification. The ligand QCD was synthesized as described elsewhere [22]. As far as the nitrate and chloride salts of all employed cations are concerned, they were of the highest available purity and were P_2O_5-vacuum dried. During the experiments, doubly distilled deionized water was used.

2.2. The measurements of EMF

The EMF measurements with the polymeric membrane were carried out with the following cell assemblies:

Ag–AgCl| 1.0×10^{-3} mol L^{-1} $TbCl_3$ | PVC membrane: test solution| Hg–Hg_2Cl_2, KCl (satd).

A Corning ion analyser 250 pH/mV meter was used for the potential measurements at 25.0 °C. The activities were calculated according to the Debye–Huckel procedure [23].

2.3. The fabrication of membrane

Firstly, 30 mg of the powdered PVC and 66 mg of the NB plasticizer were completely blended in 5 mL of THF. Then, 2 mg of NaTPB and 2 mg of the QCD ionophore were added to this mixture. The solution, after being mixed well, was transferred into a glass dish of 2 cm in diameter. The THF content of the mixture was evaporated slowly, until an oily concentrated mixture was obtained. A Pyrex tube (3–5 mm o.d.) was dipped into the mixture for about 10 s, in order to achieve a transparent membrane formation of about 0.3 mm in thickness [24-27]. In the end, the tube was removed from the solution, kept at room temperature for 12 h and filled with an internal filling solution (1.0×10^{-3} M $TbCl_3$). The electrode was conditioned for 24 h by soaking in a 1.0×10^{-2} M $TbCl_3$ solution. As an internal reference electrode, a silver-silver chloride electrode was used as an internal reference electrode.

3. RESULTS AND DISCISSION

3.1. The potential response of the Tb^{3+} sensor

In order to check the suitability of QCD as an ion carrier for Tb^{3+} and other metal ions, it was used to prepare PVC membrane ion-selective electrodes for a wide variety of cations including alkali, alkaline earth, and transition metal ions. The respective potential responses of the most sensitive ion-selective QCD-based electrodes clearly showed that only the Tb^{3+} ion illustrated a strong response (with a slope of 20.1±0.4 mV decade^{-1}) to the QCD-based membrane sensors in comparison with the other tested cations. This is most probably due to the proper size of Tb^{3+} ion to the semi-cavity of the QCD.

3.2. The membrane composition effect

Because the sensitivity and selectivity of any given membrane electrode is significantly related to the composition of the ion selective membrane, the nature of the solvent mediators and the used additives [28-30], it was decided to study such effects on the behavior of the proposed electrode. Thus, different aspects (the effect of the nature and the amount of the plasticizer, the amount of PVC and the additive) of the membrane preparation based on QCD for Tb^{3+} were optimized and the results are summarized in Table 1. It can be seen that the ionophore amount increase up to a 2 % value in the presence of 2 % of NaTPB and 66 % of NB results in the best sensitivity. As it is seen from Table 1, it is revealed that the four different plasticizers used, DBP, AP, NB and BA have almost the same results if the optimum composition is used. Also from Table1 (membraneno.6), NB is a more effective solvent mediator than DBP, AP and BA in preparing the Tb^{3+} ion-selective electrode. It is noteworthy that the plasticizer nature influences both the dielectric constant of the polymeric membranes and the mobility of the ionophore and its complex [29-31].

Generally speaking, the presence of lipophilic anions in a cation-selective membrane based on a neutral carrier 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 membrane electrode sensitivity [31, 32]. The data given in Table 1 revealed that in the absence of a proper additive, the sensitivity of the PVC membrane based on QCD is quite low (no. 4 with a slope of 10.4±0.3 mV $decade^{-1}$). However, the presence of 2% of NaTPB as a suitable lipophilic additive will improve the sensitivity of the Tb^{3+} sensor considerably (no. 6 with slope 20.1±0.4 mV $decade^{-1}$). All the same, the membranes with a composition of 30 % PVC, 2 % QCD, 2 % NaTPB and 66 % NB exhibit a Nernstian potential response.

Table 1. Optimization of the membrane ingredients.

Sensor No.	Composition (wt%)				Linear Range (mol L^{-1})	Slope (mV $decade^{-1}$)
	PVC	Plasticizer	QCD	NaTPB		
1	30	DBP, 66	2	2	1.0×10^{-2}-1.0×10^{-6}	10.8±0.2
2	30	BA, 66	2	2	1.0×10^{-2}-1.0×10^{-6}	16.9±0.5
3	30	AP, 66	2	2	1.0×10^{-2}-1.0×10^{-6}	17.5±0.3
4	30	NB, 68	2	0	1.0×10^{-2}-1.0×10^{-5}	10.4±0.3
5	30	NB, 67	2	1	1.0×10^{-2}-1.0×10^{-5}	16.0±0.2
6	30	NB, 66	2	2	1.0×10^{-2}-1.0×10^{-6}	20.1±0.4
7	30	NB, 65	2	3	1.0×10^{-2}-1.0×10^{-6}	15.8±0.4
8	30	NB, 67	1	2	1.0×10^{-2}-1.0×10^{-5}	14.9±0.6
9	30	BA, 65	3	2	1.0×10^{-2}-1.0×10^{-6}	17.6±0.3

3.3. Calibration graph and statistical data

The critical response characteristics of the Tb(III) PVC-based membrane sensor were assessed according to the IUPAC recommendations [85]. The results may be summarized as follows: the emf membrane response at varying Tb^{3+} activities (Fig. 2) indicated a rectilinear range from 1.0×0^{-6} to

1.0×0^{-2} mol L^{-1}; the calibration curve slope was 20.1±0.4 mV $decade^{-1}$ of terbium concentration; moreover, the detection limit of the introduced sensor, as determined from the intersection of the two extrapolated segments of the calibration graph, was 6.4×10^{-7} mol L^{-1}; the standard deviation of nine replicate measurements was ± 0.6 mV; eventually, the sensor usage was found to be at least 10 weeks (one hour per day and then, washed and dried). After 10 weeks, the electrode slope reduced (from 20.1 to 18.2 mV $decade^{-1}$).

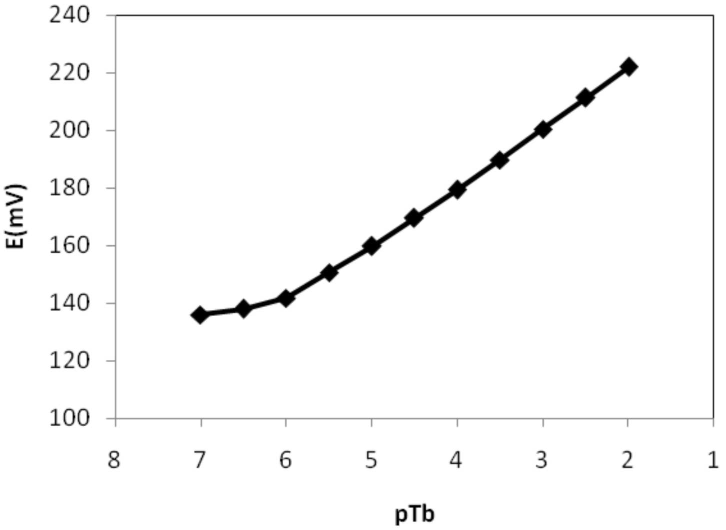

Figure 2. Calibration curves of the QCD-based Tb^{3+} sensor.

3.4. pH effect

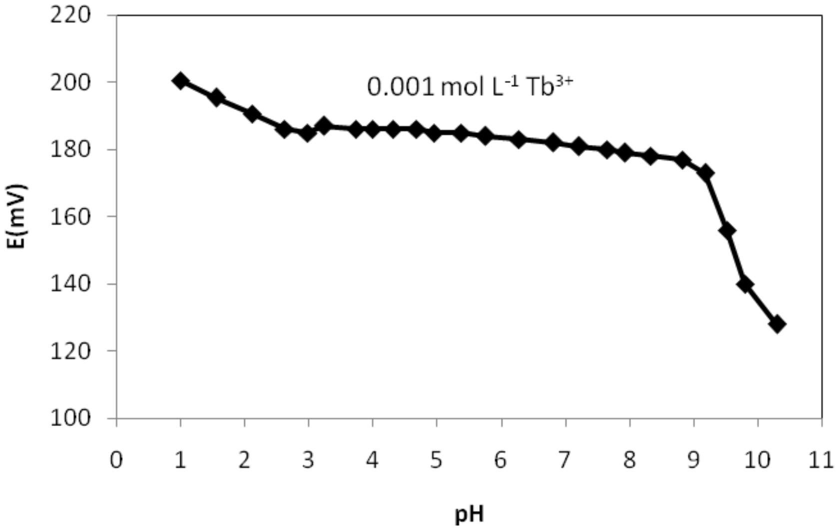

Figure 3. pH effect of the test solution (1.0×10^{-3} mol L^{-1} of Tb^{3+}) of the Tb^{3+}sensor based on QCD.

The influence of pH of the test solution (containing 1.0×10^{-3} mol L^{-1} of Tb^{3+} ions) on the potential responses of the three membrane sensors was tested in the pH range of 1.0 - 10.0 and the results are shown in Figure 3. As can be seen, potentials remain constant over a pH range of 3.2-9.0. At lower and higher pH values, the potential changes sharply. The observed drifts at lower (<3.2) and higher (>9.0) pH could be due to the protonation of the ionophore and the formation of some hydroxyl complexes of Tb^{3+} ions in solution, respectively.

3.5. Dynamic response time

For analytical applications, dynamic response time is very important for any sensor. The dynamic response time of the membrane was measured at various concentrations (1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}) of the test solutions and results are illustrated in Figure 4. As can be seen, in the whole concentration range the electrode reaches its equilibrium response, very fast (~5 s).

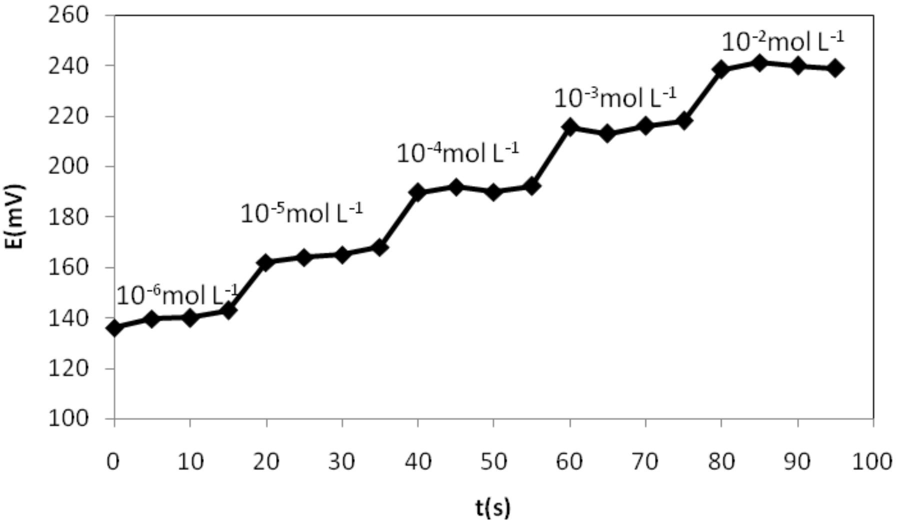

Figure 4. Dynamic response time of Tb^{3+} sensor based on QCD.

3.6. The selectivity of the sensor

For the selectivity coefficients measurement, the matched potential method [33-35] was used. The MPM was recommended by IUPAC in 1995 [36]. According to the MPM, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion and the interfering ion, which gives the same potential change in a reference solution. Subsequently, the potential change should be measured upon changing the primary ion activity. Then, the interfering ion would be added to an identical reference solution until the same potential change would be obtained. The MPM selectivity coefficient, K^{MPM}, is then given by the resulting primary ion (A) to the interfering ion (B) activity (concentration) ratio, $K^{MPM} = a_A/a_B$. The resulting values are listed in Table 2. Clearly, the selectivity coefficients for mono and divalent metal ions (Na^+, K^+, Co^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, and Ca^{2+}) are in the range of 5.2×10^{-3} or smaller. For the trivalent ions (Ho^{3+}, Sm^{3+}, Pr^{3+}, Nd^{3+} and Eu^{3+}), the selectivity coefficients are in the range of 6.4×10^{-3} or smaller, indicating they would not radically disturb the function of the developed Tb^{3+} membrane sensor. Therefore, the electrode could be used for the Tb^{3+} ions detection in the presence of certain interfering ions. Also, the same Table reveals that the proposed electrode is superior to the formerly published terbium sensor.

Table 2. Selectivity coefficients $(K^{MPM}_{Tb^{3+},B})$of proposed Tb^{3+} sensor.

Ion	$K^{MPM}_{Tb^{3+},B}$
Eu^{3+}	6.4×10^{-3}
Pr^{3+}	2.0×10^{-4}
Nd^{3+}	8.6×10^{-4}
Sm^{3+}	7.2×10^{-4}
Ho^{3+}	3.9×10^{-3}
Ca^{2+}	1.9×10^{-3}
Na^{+}	2.5×10^{-4}
K^{+}	1.3×10^{-4}
Pb^{2+}	4.8×10^{-3}
Ni^{2+}	8.1×10^{-4}
Co^{2+}	4.7×10^{-4}
Cd^{2+}	5.2×10^{-3}

Table 3 summarizes and compares the detection limit, pH range, slope, concentration range, response time, and the selectivity coefficients for the previously reported and the presented sensor [37-40]. As it is seen, the proposed sensor not only in the case of the selectivity, but also in the case of the detection limit, pH range, response time and slope is superior to the previously reported Tb^{3+} ion-selective membrane electrode.

Table 3. Comparison of different Tb(III) electrodes.

Parameter	Ref. 37	Ref. 38	Ref. 39	Ref. 40	This work
LR (mol L^{-1})	1.0×10^{-6}-1.0×10^{-1}	1.0×10^{-6}-1.0×10^{-1}	1.0×10^{-5}-1.0×10^{-1}	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-2}
DL (mol L^{-1})	8.0×10^{-7}	8.6×10^{-7}	7.0×10^{-6}	8.3×10^{-7}	6.4×10^{-7}
Response time (s)	~10	15	<20	~5	~5
pH range	3.5-8.0	3.8-8.2	3.5-7.7	2.8-9.2	3.2-9.0
Slope(mVdecade^{-1})	19.7	19.4	19.8	20.2	20.1
Log K_{sel}>-2	Gd	Gd	Ce, La, Dy, Yb, Sm	-	-

3.7. Analytical application

The proposed Tb^{3+} PVC membrane sensor was successfully applied as an indicator electrode in the potentiometric titration of Tb^{3+} (1.0×10^{-4} mol L^{-1}) with a standard EDTA solution (1.0×10^{-2} mol L^{-1}). The resulting titration curve is displayed in Figure 5, where it can be observed that the Tb^{3+} amount in solution could be accurately detected by the electrode.

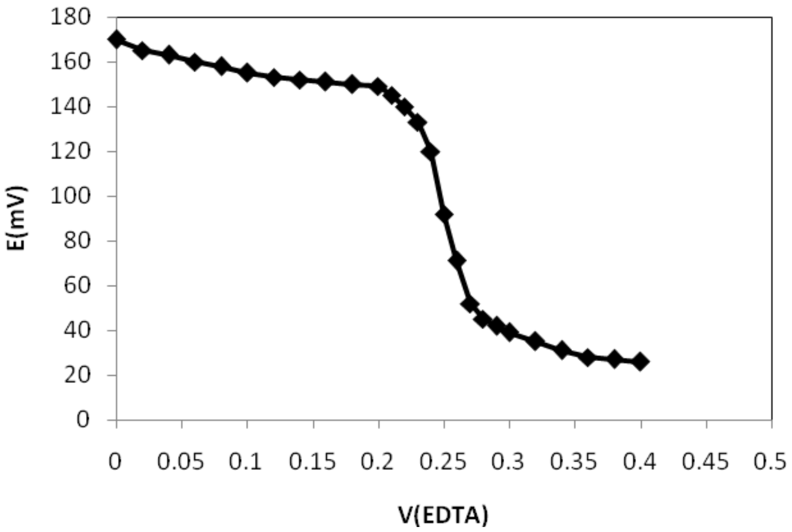

Figure 5. Potential titration curves of 25 mL 1.0×10^{-4} mol L^{-1} Tb^{3+} solution with 1.0×10^{-2} mol L^{-1} of EDTA.

The high degree of terbium selectivity, the sensor was used for the recovery of Tb^{3+} ions spiked in tap and river water samples. The 10.0 mL of each water samples was taken and diluted with distilled water in a 25.0 mL volumetric flask and the results of triplicate measurements are summarized in Table 4, clearly showing that the accuracy of terbium recovery in different solution samples is almost quantitative.

Table 4. Recovery of Tb^{3+} spiked in tap and river water samples by use of the proposed electrode

Sample	Tb^{3+} added (mg mL^{-1})	Found (mg mL^{-1})	Recovery (%)
River water	0.25	($0.27^{a} \pm 0.03$)	108
	0.5	(0.53 ± 0.02)	106
Tap water	0.25	(0.27 ± 0.03)	108
	0.5	(0.52 ± 0.04)	104

4. CONCLUSION

In the present study, 1,4-bis[o-(quinoline-2-carboxamidophenyl)]-1,4-dithiobutane (QCD) as a selective and sensitive chemical material has been used to develop a Tb^{3+}-selective sensor with a wide concentration range 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}, Nernstian slope of 20.1±0.4 mV $decade^{-1}$and the limit of detection 6.4×10^{-7} mol L^{-1} in the pH range of 3.2–9.0. The sensor exhibited terbium selectivity with very low interference from common alkali, alkaline earth, transition and heavy metal ions. It was used as an indicator electrode in the potentiometric titration of Tb^{3+} ions with EDTA and it could be applied to the Tb^{3+} monitoring in some water samples.

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References

1. J. G. S. Gupta, *J. Anal. At. Spectrom.* 8 (1993) 93.
2. O. R. Kirk, and F. D. Othmer, *Encyclopedia of Chemical Technology.* Vol. 19, John Wiley & Sons, New York, 1982.
3. H. A. Zamani, B. Feizyzadeh, F. Faridbod, and M. R. Ganjali, *Sensor Lett.* 9 (2011) 1767.
4. M.R. Ganjali, M. Rezapour, P. Norouzi, and M. Salavati-Niasari, *Electroanalysis* 17 (2005) 2032.
5. P. Norouzi, M.R. Ganjali, A. Ahmadalinezhad, and M. Adib, *J. Braz. Chem. Soc.* 17 (2006) 1309.
6. M.R. Ganjali, A. Ahmadalinezhad, P. Norouzi, and M. Adib, *J. Appl. Electrochem.* 36 (2006) 931.
7. S. Chandra, and D.R. Singh, *Mater. Sci. Eng. A* 502 (2009) 107.
8. A. K. Singh, A. Panwar, S. Kumar, and S. Baniwal, *Analyst* 124 (1999) 521.
9. M. B. Gholivand, and F. Sharifpour, *Talanta* 60 (2003) 707.
10. A. K. Singh, R. Singh, and P. Saxena, *Sensors* 4 (2004) 187.
11. V. K. Gupta, A. K. Jain, P. Kumar, S. Agarwal, and G. Maheshwari, *Sens. Actuators B* 113 (2006) 182.
12. H. A. Zamani, M. R. Ganjali, F. Faridbod, and M. Salavati-Niasari, *Mater. Sci. Eng. C* 32 (2012) 564.
13. V. K. Gupta, A. K. Jain, S. Agarwal, and G. Maheshwari, *Talanta* 71 (2007) 1964.
14. V. K. Gupta, R. N. Goyal, M. K. Pal, and R. A. Sharma, *Anal. Chim. Acta* 653 (2009) 161.
15. S. K. Mittal, S. K. A. Kumar, and H. K. Sharma, *Talanta* 62 (2004) 801.
16. A. K. Singh, R. P. Singh, and P. Saxena, *Sens. Actuators B* 114 (2006) 578.
17. P. S. Ramanjaneyulu, P. Singh, Y. S. Sayi, H. M. Chawla, and K. L. Ramakumar, *J. Hazard. Mater* 175 (2010) 1031.
18. S. Chandra, and D. R. Singh, *Mater. Sci. Eng. A* 5029 (2009) 107.
19. H. A. Zamani, Fatemeh Naghavi-Reyabbi, M. Mohammadhossieni, Babak Feizyzadeh, M. R. Abedi, F. Faridbod, and M. R. Ganjali, *Sensor Lett.* 10 (2012) 112.
20. H. A. Zamani, B. Feizyzadeh, F. Faridbod, and M. R. Ganjali, *Sensor Lett.* 9 (2011) 1767.
21. H. A. Zamani, M. Rohani, M. Mohammadhosseini, M. R. Ganjali, F. Faridbod, and S. Meghdadi, *Sensor Lett.* 9 (2011) 1745.
22. S. Meghdadi, V. Mirkhani, and P. C. Ford, *Synth. Commun.* 42 (2012) 246.
23. S. Kamata, A. Bhale, Y. Fukunaga, and A. Murata, *Anal. Chem.* 60 (1998) 2464.
24. V. K. Gupta, A. K. Jain, S. Agarwal, and G. Maheshwari, *Talanta* 71 (2007) 1964.
25. H. A. Zamani, F. Faridbod, and M. R. Ganjali, *Mater. Sci. Eng. C* 33 (2013) 608.
26. H. A. Zamani, F. Naghavi-Reyabbi, F. Faridbod, M. Mohammadhosseini, M. R. Ganjali, A. Tadjarodi, and M. Rad, *Mater. Sci. Eng. C* 33 (2013) 870.
27. H. A. Zamani, A. Zanganeh-Asadabadi, M. Rohani, M. S. Zabihi, J. Fadaee, M. R. Ganjali, F. Faridbod, and S. Meghdadi, *Mater. Sci. Eng. C* 33 (2013) 984.

28. T. Rostazin, E. Bakker, K. Suzuki, and W. Simon, *Anal. Chim. Acta* 280 (1993) 197.
29. E. Ammann, E. Pretsch, W. Simon, E. Lindner, A. Bezegh, and E. Pungor, *Anal. Chim. Acta* 171 (1985) 119.
30. P. Buhlmann, E. Pretsch, and E. Bakker, *Chem. Rev.* 98 (1998) 1593.
31. E. Bakker, P. Buhlmann, and E. Pretsch, *Electroanalysis* 11 (1999) 915.
32. G.G. Guilbault, R.A. Durst, M.S. Frant, H. Freiser, E.H. Hansen, T.S. Light, E Pungor, G. Rechnitz, N.M. Rice, T.J. Rohm, W. Simon, and J.D.R. Thomas, *Pure. Appl. Chem.* 46 (1976) 127.
33. IUPAC Analytical Chemistry Division, Commission on Analytical Nomenclature, *Pure Appl. Chem.* 48 (1976) 127.
34. Y. Umezawa, K. Umezawa, H. Sato, *Pure Appl. Chem.* 67 (1995) 507.
35. S. Matysik, F. M. Matysik, J. Mattusch, and W. D. Einicke, *Electroanalysis* 10 (1998) 57.
36. R.P. Buck, E. Lindner, IUPAC Recommendations for nomenclature of ion- selective electrodes, *Pure Appl. Chem.* 66 (1994) 2527.
37. H.A. Zamani, M.R. Ganjali, P. Norouzi, A. Tadjarodi, and E. Shahsavani, *Mater. Sci. Eng. C* 28 (2008) 1489.
38. H.A. Zamani, G. Rajabzadeh, and M.R. Ganjali, *J. Braz. Chem. Soc.* 17 (2006) 1297.
39. M.R. Ganjali, A. Ghesmi, M. Hosseini, M.R. Pourjavid, M. Rezapour, M. Shamsipur, and M. Salavati-Niasari, *Sens. Actuators B* 105 (2005) 334.
40. H. A. Zamani, and S. Sahebnasagh, *Int. J. Electrochem. Sci.* 8 (2013) 3696.