Full Paper

A Novel Potentiometric Ni^{2+}-Sensor based on a Ni^{2+} Ion-Imprinted Polymer

Negin Hamidi,[1] Taher Alizadeh[1,*] and Mohammad Madani[2]

[1]*Department of Analytical Chemistry, School of Chemistry, College of Science, University of Tehran, Tehran, Iran*
[2]*Nanotechnology Department, Agricultural Biotechnology Research Institute of Iran (ABRII), AREEO, 3135933151 Karaj, Iran*

*Corresponding Author, Tel +982161112788
E-Mail: talizadeh@ut.ac.ir

Abstract- A novel Ni^{2+} ion-imprinted polymer (IIP) was synthesized through a precipitation polymerization technique using itaconic acid (as functional monomer) and ethylene glycol dimethacrylate (as cross-linking agent). NIP was next used to construct a Ni^{2+} ion-selective membrane electrode through dispersing its particles in a poly (vinyl chloride)(PVC) based membrane plasticized with dibutylphthalate. The electrode revealed a Nernstian response of 24.2 ± 0.5 mV decade-1 to Ni^{2+} from 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} and had a lower detection limit of 5.0×10^{-6} mol L^{-1}. A control electrode based on non-imprinted polymer (NIP) was also prepared and evaluated, and found to be insensitive to the analyte ions in aqueous media. The satisfactory qualities of the developed IIP sensor make it a suitable candidate for the determination of Ni^{2+} ions.

Keywords - Imprinted polymer, Potentiometric, Nickel, Ionophore, Ni^{2+}-selective sensor

1. INTRODUCTION

Analysis of nickel is very critical due to the toxic nature, widespread industrial applications and it's the emission of Ni^{2+} ions through various effluents [1]. Traces of Ni^{2+} are also found in meat, chocolate, hydrogenated and unsaturated oils, corn meal, cotton seed, dairy products, conserved food, etc. The carcinogenic effects of the elements and its cations have been proven

by various animal experiments over the years, and some of the health conditions associated with nickel are nasal cavity and lung cancers, dermatitis, asthma, acute pneumonia and damages to the central nervous system, which further highlight the importance of the analysis of nickel contents of various products and samples [1-3].

Varied analytical techniques like inductively coupled plasma atomic emission (ICP-AES) [4, 5], atomic adsorption spectroscopy (AAS) [6,7], polarography and stripping voltammetry [8-11] have been evaluated for this purpose, yet the complexity of techniques such as AAS, ICP together with high costs, and long analysis times, difficult operations and being unsuitable for routine application especially in the case of large numbers of samples, are among the disadvantages of these techniques [12].

The development and application of potentiometric sensors has recently attracted a great deal of focus in academic and scientific circles due to the simplicity, low-cost and the potentials of use in in-vivo experiments, as well as biomedical, environmental and industrial analyses as opposed to rivaling methods [13-23]. Although the application of potentiometry has been common for a long time, advances made in the area of ion-selective electrodes, change them to robust alternatives for other techniques [24]. Ion-selective electrodes (ISEs) are a common analytical tool in various chemical analyses. Plasticized PVC membranes are especially interesting given their selectivity as a result of the incorporation of carrier. A major challenge in this area could be the design and synthesis of the various ionophores [25]. Myriad ionophores including crown ethers [26,27], porphyrins [1,28], pentacyclooctaaza [29], cyclams [30,31], and Schiff's bases [32, 33] have been used in the development of Ni^{2+} ISEs, which led to some drawbacks.

An essential quality of an ionophores is its high lipophilicity, which increases the life time and response stability of ensures through increasing the chances of the compounds remaining in the membrane phase for longer times through lowering their loss into the aqueous media during application. This requirement seriously limits the range of ionophores that can be used to this end [34, 35], and hence various efforts have been made to find new ionophores.

Ionic imprinted polymers (IIPs), were introduced as a novel class of ionophores for use in potentiometric ISEs, which function due to the reversible binding of ionic analytes to the imprinted binding sites of IIPs [24, 34]. In theory various target agents can be used for preparing corresponding imprinted materials and hence imprinting constitutes a flexible complementary approach for preparing ionophore for different analytes. The selectivity of IIP ionophores has been reported to be better than conventional ionophores in many cases [34]. A unique quality of IIP-based ISEs is that they do not require the analyte to diffuse through the membrane and hence the template compounds are not limited [24]. In the face of all of the above-mentioned advantages, only few IIP-based ISEs have been developed so far [15, 34, 36]. In the present work, a Ni^{2+}-IIP was prepared and used to construct a novel PVC-based ISE for

Ni^{2+} ions. The development of a Ni^{2+} selective sensor using an IIP-based ISE is expected to be an interesting development in the area.

2. EXPERIMENTAL

2.1. Reagents

The analytical reagent grade chemicals used included nickel nitrate (Merck, Germany); and itaconic acid, ethylene glycol dimethacrylate (EGDMA), 2, 2-azobisisobutyronitrile (AIBN), di-butylphthalate (DBP), tetrahydrofurane (THF), sodium tetraphenyl borate (NaTPB) and high molecular PVC.

2.2. Synthesis of the Ni^{2+}-imprinted polymer

A typical precipitation polymerization approach used for preparing the Ni^{2+} IIP involved dissolving 2 mmol of itaconic acid (as both the functional monomer and complexing ligand) and 1 mmol of $Ni(NO_3)_2.6H_2O$ in 30mL of acetonitrile (porogen) and stirring the resulting solution the resulting reaction solution for 0.5 h to reach the equilibration state of the complexation reaction. To this solution, was then added 8 mmol of EGDMA and 0.06 g of the initiator solution, and the mixture was next purged with N_2 gas for 10 min to eliminate O_2 which cam trap the radicals and consequently slow the polymerization reaction, which was then performed in an oil bath at 60 °C for 1 day under stirring.

The resulting IIP powder was then separated and washed with ethanol (2 times) to remove the residual reactants and then with a 0.1 mol L^{-1} EDTA solution (pH=10) to leach of the nickel ions. This washing process was continued until the washing solution did not contain Ni^{2+} ions. The particles were finally washed with distilled water to reach a neutral pH, and dried at 60 °C.

The non-imprinted polymer (NIP) sample was prepared under identical conditions in the absence of Ni^{2+}.

2.3. Ni^{2+}-IIP ISE

To prepare the electrode membrane a 21.4:64.5:3 (w=w%) mixture of PVC, a plasticizer (DBP), and an anion excluder (NaTPB) was dissolved in 2.5mL of tetrahydrofuran (THF). Then 11% w of the Ni^{2+} IIP (or NIP) particles were added to the mixture and the resulting mixture was mixed well, and sonicated for 5 min to dissolve the PVC and DBP in THF. The sonication process also dispersed the IIP (or the control NIP) particles in the mixture. This mixture was next poured into a Teflon mold, and the solvent (THF) was allowed to evaporate under ambient conditions. The resulting membranes had a ~0.5mm thickness. These membranes were glued to the tip of a glass tube, which was next filled with a 10^{-2} mol L^{-1} of

nickel nitrate solution (as the internal filling solution), and the resulting assembly was sensor was stored in the air when it was not used.

2.4. Procedure of analyses

The resulting ISEs was conditioned in 25 ml of a 10^{-2} mol L^{-1} nickel solution for 5h, and their responses were evaluated through measuring the electromotive force (EMF) of an electrochemical cell as bellow:

Hg_2Cl_2, KCl (satd.) (internal reference electrode)| internal solution (1.0×10^{-2} mol L^{-1} $Ni(NO_3)_2$) | PVC-IIP membrane | sample solution | Hg_2Cl_2, KCl (satd.) (external reference electrode)

The internal and external reference electrodes were linked to a Corning Ion Analyzer 250/pH mV meter at 25±0.1°C for performing the potential readings on sample solution containing different amounts of Ni^{2+}. The EMF values were plotted against Ni^{2+} concentration.

3. RESULTS AND DISCUSSION

3.1. Comparative evaluation of the analytical and control ISEs

Fig. 1 shows the response of the Ni^{2+} IIP-ISE against the concentration of the analyte solutions. Clearly the IIP-based membrane exhibits a Nernstian response of 24.5 mVdecade^{-1} for Ni^{2+} over a rather wide concentration range; while the control ISE (based on the with non-imprinted polymer) did not show any sensitivity to analyte under identical conditions, suggesting that the Ni^{2+} IIP-ISE cavities suitably fitted the size of the Ni^{2+} leading to the sensitivity of the IIP.
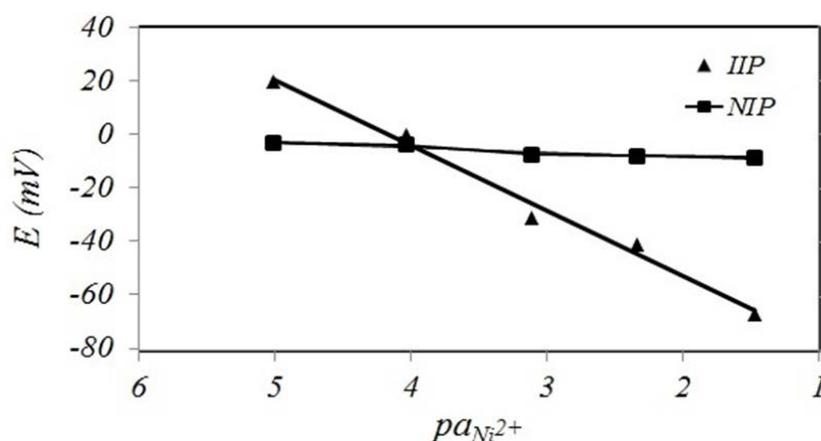

Fig. 1. Potentiometric responses of the membrane electrodes containing IIP and NIP

3.2. Optimization of the Ni^{2+} IIP-ISE composition

Various aspects of the composition of Ni^{2+} IIP-ISE membrane were studied and optimized (Table 1). The amount of the IIP was found to influence the working rang of the electrode (Nos. 1–3). To assess the role of the nature of the plasticizer on the response two plasticizers with distinctly different dielectric constants (i.e. DBP, NPOE) were used to prepare the membrane and according to the experimental data (Table 1), DBP was found to lead to a wider working range.

Table 1. Optimization of membrane ingredients

Sensor	% w/w each ingredient					Working concentration range (mol L^{-1})	Slope (mV/decade of activity)
	PVC	DBP	NPOE	NaTPB	% IIP		
1	27.5	64.5	0	3	5	10^{-3}-10^{-1}	19.5
2	21.5	64.5	0	3	11	10^{-5}-10^{-1}	24.4
3	14.5	64.5	0	3	18	10^{-4}-10^{-1}	21
4	16	70	0	3	11	10^{-3}-10^{-1}	21
5	21.5	0	64.5	3	11	10^{-3}-10^{-1}	24

3.3. Effect of test solution pH

Using a 10.0 mL sample of a 1.0×10^{-3} mol L^{-1} solution of nickel nitrate in water, and by varying the pH of the solution from 3 to 8 through adding concentrated acid and base solutions, the effect of the pH of the sample solution on the response of the Ni^{2+} IIP-ISE was studied. Based on the results are illustrated (Fig. 2) the potential of the electrode was constant in the range of 4.0–7.0. Beyond this range considerable changes were observed in the potential of the electrode. At pH values below 4.0, the changes in the potential were attributed to the competition of the H$^+$ with Ni^{2+}, while and at pH values above 7, the drift was related to the hydrolysis of the analyte (Ni^{2+}) and formation of hydroxyl complexes of Ni^{2+}.
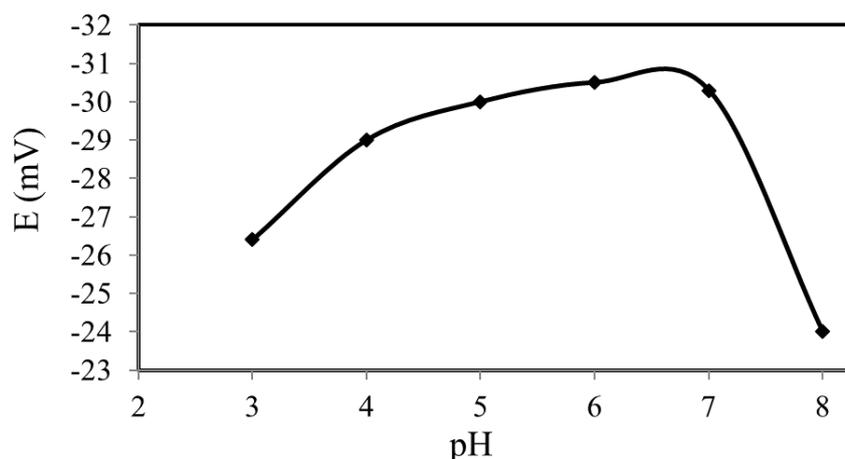
Fig. 2. Effect of the test solution pH on the potential response of the Ni^{2+}-ISE

3.4. Response time and memory effect study

IUPAC defines the practical response time of an ISE as the time required for the response of an ion selective electrode to reach ±1mV of its equilibrium value after a tenfold change in the concentration of the sample solution. To determine the response time of the sensor, the concentration of a test solution was successively increased from 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} while measuring the potential of the electrode and a corresponding plot was drawn (Fig. 3). According to the results, the response time of the electrode was around 20 s. The rather quick response time was attributed to the fast exchange kinetics of the complexation–decomplexation interaction among the Ni^{2+} ions and the active site of the IIP at the solution/membrane interface.
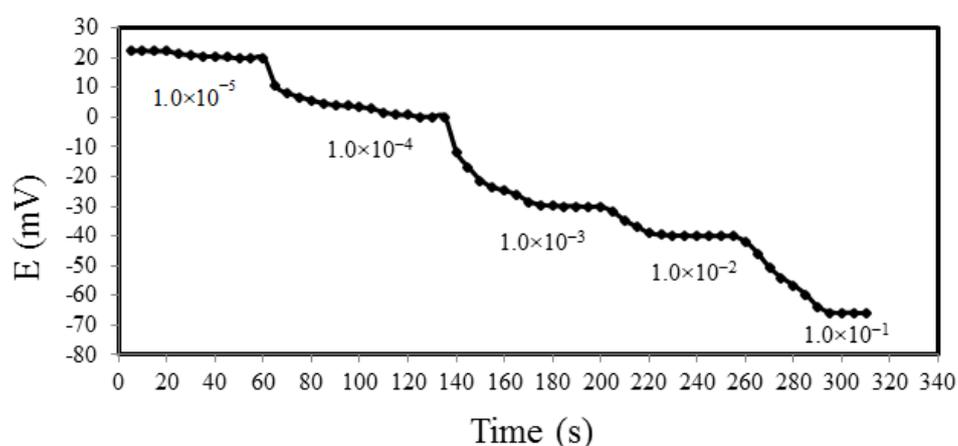

Fig. 3. Dynamic response of the proposed Ni^{2+}-selective electrode for reversibility with step changes in concentration of Ni^{2+} 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} at pH 6.

Further the potential–time plot in Fig. 4 was obtained by changing the Ni^{2+} concentration from 1.0×10^{-4} to 1.0×10^{-3} mol L^{-1} (through rapid injection of μL amounts of a concentrated Ni^{2+} solution to the diluter sample). Then, by reducing the Ni^{2+} concentration from 1.0×10^{-3} to 1.0×10^{-4} mol L^{-1} through an appropriate dilution step, the memory or hysteresis effects of the sensor was checked. Clearly, the potentiometric response reached its equilibrium value rapidly (in about 20 s) and was reversible. Also in spite of the longer recovery times (90–100 s) in the dilution stage, no memory or hysteresis effects were observed.
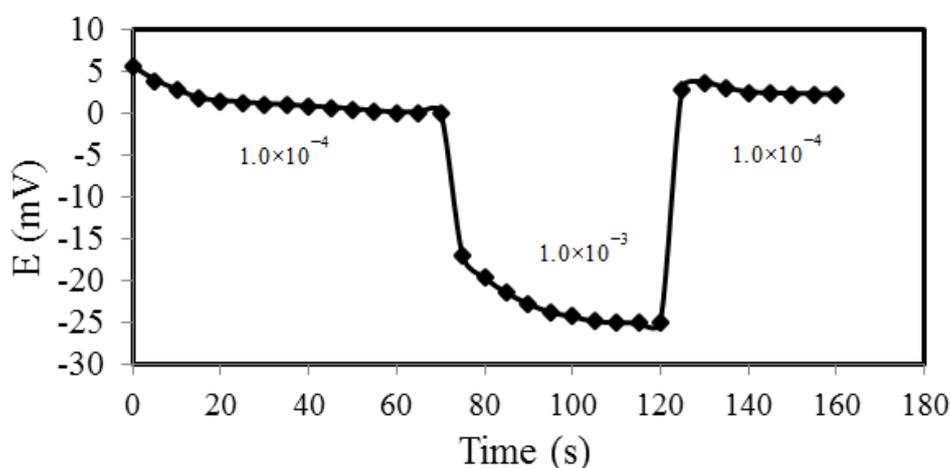

Fig. 4. Evaluation of the response time and the memory effect of the sensor

3.5. Interference study

The matched potential method (MPM) [34-36] was used to determine the potentiometric selectivity coefficients of possible interfering species. These coefficients illustrate the preference of the developed ISE to an interfering ion (X) in comparison to Ni^{2+} ions. To determine the MPM coefficients a specified activity (concentration) of Ni^{2+} ions (1.0×10^{-5} mol L^{-1}) is added to a reference solution and the equilibrium potential response is recorded. In other experiments, the interfering ions (X) are gradually added to a similar reference solution until its potential reaches matches that obtained before the addition of the primary ions. Using the data the MPM selectivity coefficient, $K_{Ni,X}$ is determined from the equation below:

$$K_{Ni,x} = a_{Ni} / a_x$$

The in which a_{Ni} and a_x are the activities of the nickel and the interfering ions, respectively.

The experimentally determined MPM selectivity coefficients are listed in Table 2, indicating that none of the interfering ions has a serious effect on the response of the analyte.

Table 2. Selectivity coefficients of sensor using the

Interfering ion (X)	$K_{Ni,x}$
Ag^+	4.7×10^{-2}
K^+	4.5×10^{-3}
Cd^{2+}	2.9×10^{-3}
Cu^{2+}	7.5×10^{-3}
Co^{2+}	1.3×10^{-2}
Zn^{2+}	2.4×10^{-2}
Pb^{2+}	4.1×10^{-2}
Mg^{2+}	2.2×10^{-2}

3.6. Analytical characteristic of the optimized membrane electrode

The responses of the Ni^{2+}-imprinted membrane sensors with the optimal concentration (sensor 2, Table 1) were recorded to plot a calibration curve (Fig. 5). The points used to draw the curve were obtained through triplicate measurements, and as it can be seen, the plot is linear from 1×10^{-5} to 1×10^{-1} mol L^{-1}, with a slope of 24.5 ±0.5 (mV decade^{-1}) indicating a Nernstian behavior. The detection limit of the sensor was also found to be 5×10^{-6} mol L^{-1} based on the IUPAC recommendation.
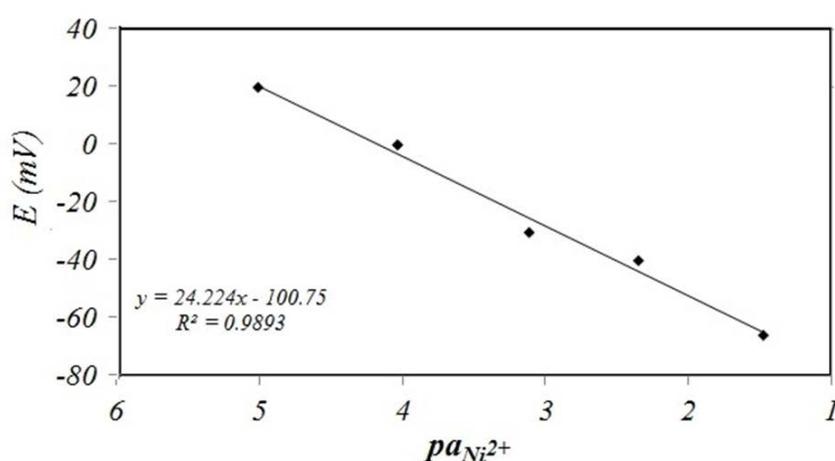

Fig. 5. Calibration curve of the developed IIP-based membrane electrode for the determination of Ni^{2+}

3.7. Analytical performance

The Ni^{2+} sensor was evaluated in as an indicator electrode in the titrimetric determination of Ni^{2+} solutions with EDTA. To do this a 10 mL aliquot of a 1.0×10^{-3} mol L^{-1} Ni^{2+} solution was titrated using a 1.0×10^{-2} mol L^{-1} EDTA solution and the titration curve was drawn (Fig. 6). The plot had a typical sigmoid shape and the sharp break point indicates the stoichiometry of Ni^{2+}-EDTA complex, as well as the end point of titration.
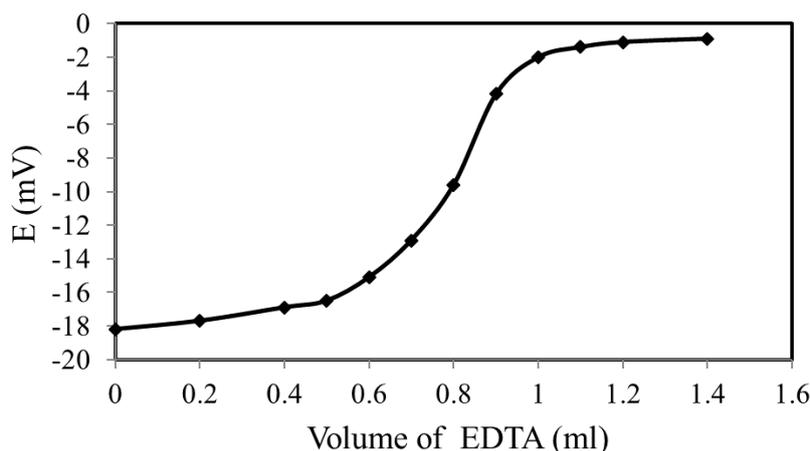

Fig. 6. Potentiometric titration curve plot of 10ml of 1.0×10^{-3} mol L^{-1} Ni^{2+} solution with 1.0×10^{-2} mol L^{-1} EDTA, using the proposed sensor as an indicator electrode.

4. CONCLUSION

The study involved the synthesis of an ion imprinted polymer (IIP) capable of selective recognition of Ni^{2+}, using a simple functional monomer. The IIP was next successfully used to construct a PVC membrane electrode for nickel ions. The Nernstian slope of about 25 mV decade^{-1} for the sensor indicated its Nernstian behavior. The sensor was found to have a high selectivity for Ni^{2+} ions and was satisfactorily used to the determination of Ni^{2+} ions through potentiometric titration.

Acknowledgement

REFERENCES

[1]   V. K. Gupta, A. K. Jain, and L. P. Singh, Anal. Chim. Acta 355 (1997) 33.
[2]   A. Yari, S. Azizi, and A. Kakanejadifard, Sens. Actuators B 119 (2006) 167.
[3]   K. G. Kumar, R. Poduval, and P. Augustine, Anal. Sci. 22 (2006) 1333.

[4]   A. Bortoli, M. Gerotto, and M. Marchiori, Microchem. J. 54 (1996) 402.

[5]   S. X. Xu, and D. M. Templeton, J. Anal. At. Spectrom. 8 (1993) 445.

[6]   M. A. Taher, J. Anal. At. Spectrom. 15 (2000) 573.

[7]   G. A. Zachariadis, D. G. Themelis, and D. J. Kosseoglou, Talanta 47 (1998) 161.

[8]   A. M. Farias, A. K. Ohara, and I. Akase, Talanta 40 (1993) 1167.

[9]   I. Rutyna, and M. Korolczuk, Int. J. Environ. Anal. Chem. (2012) 1.

[10]   J. Wang, and J. Lu, Electrochem. Commun. 2 (2000) 390.

[11]   B. Bas, K. Wegiel, and K. Jedlinska, Anal. Chim. Acta 881 (2015) 44.

[12]   P. Kumar, Electroanalysis 24 (2012) 1.

[13]   M. Javanbakht, A. Shabani-Kia, M. R. Darvich, M. R. Ganjali and M. Shamsipur, Anal. Chim. Acta 408 (2000) 75.

[14]   M. Shamsipur, M. Javanbakht, M. F. Mousavi, M. R. Ganjali, V. Lippolis, A. Garau and L. Tei, Talanta 55 (2001) 1047.

[15]   T. Alizadeh, and M. Akhoundian, Electrochim. Acta 55 (2010) 3477.

[16]   H. A. Zamani, G. Rajabzadeh and M. R. Ganjali, J. Brazil. Chem. Soc. 17 (2006) 1297.

[17]   M. R. Ganjali, H. A. Zamani, P. Norouzi, M. Adib, M. Rezapour and M. Aceedy, Bull. Korean Chem. Soc. 26 (2005) 579.

[18]   M. R. Ganjali, A. Daftari, P. Nourozi and M. Salavati-Niasari, Anal. Lett. 36 (2003) 1511.

[19]   M. Shamsipur, M. Yousefi, M. Hosseini and M. R. Ganjali, Anal. Lett. 34 (2001) 2249.

[20]   H. A. Zamani, M. R. Ganjali, P. Norouzi and M. Adib, Sensor Lett. 5 (2007) 522.

[21]   M. R. Ganjali, M. Rahimi, B. Maddah, A. Moghimi and S. Borhany, Anal. Sci. 20 (2004) 1427.

[22]   H. A. Zamani, J. Abedini-Torghabeh and M. R. Ganjali, Electroanalysis 18 (2006) 888.

[23]   M. R. Ganjali, J. Ravanshad, M. Hosseini, M. Salavati-Niasari, M. R. Pourjavid and M. R. Baezzat, Electroanalysis 16 (2004) 1771.

[24]   T. Alizadeh, and M. Rashedi, Anal. Chim. Acta 16 (2014) 843.

[25]   K. G. Kumar, R. Poduval, and S. John, Microchim. Acta 156 (2007) 283.

[26]   M. F. Mousavi, N. Alizadeh, M. Shamsipur, and N. Zohari, Sens. Actuators B 66 (2000) 98.

[27]   M. Shamsipur, and S. Y. Kazemi, Electroanalysis 12 (2000) 1472.

[28]   M. D. Hampton, C. A. Peters, and L. A. Wellington, Anal. Chim. Acta 194 (1987) 171.

[29]   A. K. Jain, V. K. Gupta, R. D. Singh, U. Khurana, and L. P. Singh, Sens. Actuators B 40 (1997) 15.

[30]   V. K. Gupta, R. Prasad, P. Kumar, and R. Mangla, Anal. Chim. Acta 420 (2000) 19.

[31]   V. K. Gupta, R. Prasad, and A. Kumar, Sensors 2 (2002) 384.

[32]   H. Mashhadiazadeh, I. Sheikhshoaie, and S. Saeid-Nia, Sens. Actuators B 94 (2003) 241.

[33]   V. K. Gupta, A. K. Singh, and M. K. Pal, Anal. Chim. Acta 624 (2008) 223.

[34] T. Alizadeh, M. Rashedi, Y. Hanifehpour, and S. W. Joo, Electrochim. Acta 178 (2015) 877.

[35] K. N. Mikhelson, Ion-Selective Electrodes, Lecture Notes in Chemistry, Springer-Verlag Berlin Heidelberg (2013).

[36] S. Sadeghi, and D. Sheida Doosti, Sens. Actuators B 135 (2008) 139.