Int. J. Electrochem. Sci., 7 **(2012)** 5147 - 5162

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Determination of Neodymium(III) in Aqueous and Soil Samples with Use of a High-Sensitive and Selective Membrane Sensor

Mohammad Reza Pourjavid[1,2,*], *Seyed Reza Yousefi*[1], *Majid Haji Hosseini*[1], *Mohammad Rezaee*[1], *Taherehsadat Razavi*[3], *Ali Akbari Sehat*[4]

[1] NFCRS, Nuclear Science & Technology Research Institute, AEOI, P.O. Box 11365-8486, Tehran, Iran
[2] Department of Medicinal Chemistry, Pharmaceutical Sciences Branch, Islamic Azad University, Tehran, Iran
[3] Instrumental Analysis Department, Research Institute of Petroleum Industry (RIPI), P.O. Box 14665-137, Tehran, Iran
[4] Department of Analytical Chemistry, Faculty of Chemistry, University College of Science, University of Tehran, P.O. Box 14155-6455, Tehran, Iran
[*]E-mail: pourjavid@gmail.com

Received: 25 April 2012 / *Accepted:* 19 May 2012 / *Published:* 1 June 2012

N-(furfuralidene)-N -isonicotinoylhydrazine (FIH) have been explored as a suitable neutral ionophore for preparation a highly selective Nd(III) PVC-based membrane sensor with sodium tetraphenyl borate (NaTPB) and oleic acid (OA) as anionic additives and benzyl acetate (BA), dibutyl phthalate (DBP), o-nitrophenyloctyl ether (NPOE) and acetophenone (AP) as plasticizing solvent mediators. The best performance was obtained with the sensor having membrane of FIH-PVC-NaTPB-NPOE. The proposed sensor exhibits a Nernstian response over a wide concentration range (from 1.0×10^{-7} to 5.0×10^{-1} mol L^{-1} of Nd(III)). The detection limit of designed membrane is 8.6×10^{-8} mol L^{-1}. The sensor response is independent of pH of the solution in the pH range 3.0 – 8.4 and possess the advantages of fast response time (~8) and in particular, good selectivity and sensivity to the neodymium ions with regard to most common metal ions, and especially all lanthanide ions. The sensor can be used over a period of 11 weeks without any considerable divergence in the potentials. It was applied successfully as an indicator electrode in potentiometric titration of Nd(III) ions with EDTA and also used in the trace determination of Nd(III) ions in some binary mixtures, mouth washing solutions, soil and sediment samples.

Keywords: Membrane sensor, Nd(III) selective, N-(furfuralidene)-N -isonicotinoylhydrazine, PVC, Potentiometry.

1. INTRODUCTION

Rare earth metals and their compounds have been widely used in all walks of life due to their spectroscopic physical and chemical characteristics. The property of the metal alloy can be improved by adding some rare earth metals or compounds in it. Therefore, rare earth elements are known as vitamin of metallurgical industry [1]. Neodymium is one of the rare earth metals that has a bright silvery metallic luster and is one of the more reactive rare-earth metals and quickly tarnishes in air, forming an oxide that spalls off and exposes the metal to further oxidation. It is present in Misch metal and didymium glass. Neodymium is added to glass to create violet, red or gray colors. Some types of glass containing neodymium are used by astronomers to calibrate spectrometers and other types are used to create artificial rubies for lasers. Some neodymium salts are used to color enamels and glazes [2].

Several analytical methods have been reported for low-level monitoring of Nd(III) and other lanthanide ions in various sample matrices. These methods include ICP-MS, ICP-AES, isotope dilution mass spectrometry, resonance light scattering, voltammetry, CE, XRF, fluorimetry and finally potentiometric sensors. These sensors have shown to be very effective tools for analysis of a wide variety of cations and anions. They are very simple, inexpensive, and capable of reliable response in wide concentration ranges. In addition to their simplicity, sensor based potentiometric detections, offer several other advantages such as speed and ease of preparations and procedures, simple instrumentations, relatively fast responses, wide dynamic ranges, reasonable selectivity, and low costs. This has led to an increasing interest in the development of sensors for several ionic species, increasing the number of available electrodes over the last few years and many articles published about theoretical and experimental principles of ion selective electrodes [3-9].

We and other researchers have recently introduced a number of lanthanide selective membrane sensors based on different noncyclical and macro cyclic ionophores [10-26]. This study describes another ion selective sensor for Nd(III) potentiometric determination based on N-(furfuralidene)-N -isonicotinoylhydrazine (FIH), as a novel neutral ionophore (as shown in Fig. 1).

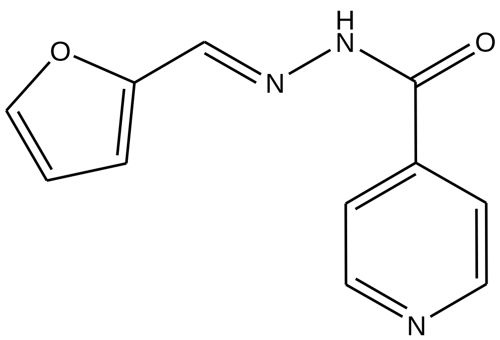

Figure 1. Chemical structure of N-(furfuralidene)-N -isonicotinoylhydrazine.

Three noticeable benefits demonstrated by this sensor are the fast response time, low detection limit and also great selectivity.

2. EXPERIMENTAL

2.1. Apparatus

A corning ion analyzer 250 pH/mV meters was used for the potential measurements at 25.0±/0.1 ◦C. The emf observations were made relative to a double-junction saturated calomel electrode (SCE, Philips), with its chamber filled with an ammonium nitrate solution.

2.2. Reagents and materials

Reagent grade sodium tetraphenyl borate (NaTPB), oleic acid (OA), benzyl acetate (BA), dibutyl phthalate (DBP), o-nitrophenyloctyl ether (NPOE), acetophenone (AP), tetrahydrofuran (THF), acetonitrile (AN), hydrochloric acid, sodium hydroxide, perchloric acid, hydrofluoric acid and high relative molecular weight PVC of the highest purity available were purchased from Merck and Aldrich, and used without any further treatments, except for the vacuum drying. The nitrate and chloride salts of cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. The ionophore (FIH) was prepared as described [27].

2.3. Conductometric procedure

The complexation of FIH with a number of cations was conductometricaly investigated in an acetonitrile solution, at 25±0.05 ◦C, in order to obtain a clue about the stability and selectivity of the resulting complexes. Cation solutions 20mL of were titrated with a 0.01M FIH solution in acetonitrile. The resulting molar conductance versus [FIH]/[M^{n+}] molar ratio showed the formation of 1:1 complexes between FIH and metal ions tested. The complex formation constants, K_f, were evaluated by computer fitting of the molar conductance/molar ratio data with appropriate equations, and the results are summarized in Table 1 [28].

Table 1. The formation constants of FIH-M^{n+} complexes at 25.0 ± 0.1 ºC.

Ion	Log K_f	Ion	Log K_f
Na^+	< 2.0	Nd^{3+}	5.84 ± 0.02
K^+	< 2.0	Sm^{3+}	2.84 ± 0.04
Cu^{2+}	< 2.0	Eu^{3+}	2.21 ± 0.02
Cd^{2+}	2.27 ± 0.04	Gd^{3+}	2.57 ± 0.06
Ba^{2+}	2.14 ± 0.05	Tb^{3+}	2.40 ± 0.01
Pb^{2+}	2.69 ± 0.06	Dy^{3+}	2.16 ± 0.04
Cr^{3+}	2.25 ± 0.02	Ho^{3+}	2.36 ± 0.05
Fe^{3+}	2.12 ± 0.01	Er^{3+}	2.05 ± 0.03
La^{3+}	2.60 ± 0.03	Tm^{3+}	2.31 ± 0.02
Ce^{3+}	2.76 ± 0.04	Yb^{3+}	2.10 ± 0.01
Pr^{3+}	2.95 ± 0.01	Lu^{3+}	2.02 ± 0.03

2.4. Preparation of membrane

The general procedure to prepare the PVC membrane was to mix thoroughly 30 mg of powdered PVC, 64 mg of plasticizer NPOE and 2 mg of additive NaTPB in 5 mL THF. To this solution was added 4 mg of ionophore FIH and mixed well. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm diameter on top) was dipped into the oily mixture for about 10 s so that a non-transparent film of about 0.3 mm thickness was formed [29-33]. The tube was then pulled out from the mixture and kept at room temperature for at least 1 h. The tube was then filled with an internal filling solution (1.0×10^{-4} mol L^{-1} $Nd(NO_3)_3$). The electrode was finally conditioned for 24h by soaking in a 1.0×10^{-4} mol L^{-1} solution of neodymium nitrate. Silver – silver chloride electrode was used as an internal reference electrode. The ratio of different membrane ingredients, concentration of equilibrating solution and the time of contact were optimized to provide membranes, which result in reproducible, noiseless and stable potentials.

2.5. EMF measurements

The electromotive force (EMF) measurements with the polymeric membrane electrodes were carried out with the cell assembly of:

Ag–AgCl | internal solution, 1.0×10^{-4} mol L^{-1} $Nd(NO_3)_3$ | PVC membrane | test solution | Hg–Hg_2Cl_2, KCl (Saturated)

The activities were calculated in agreement with the Debye–Huckel procedure.

3. RESULTS AND DISCUSSION

The ionophores having nitrogen and sulfur atoms as donor atoms are known to form very stable complexes with transition metal ions [10, 13, 15-26]. The resulting 1:1 complexes have been frequently used as catalysts in such diverse processes. Due to the radii of lanthanum ions (with the range of 1.02-0.80Å from Ce^{3+} to Lu^{3+} respectively), these elements have different properties such as charge densities, size and hydration energy (with the range of 3370–3760 kJ/mol from Ce^{3+} to Lu^{3+} respectively) [34].

Thus, by using a suitable ionophore having a semi-cavity and relatively high flexibility, it is possible to construct a highly selective lanthanide ion sensor. The existence of donating nitrogen and sulfur atoms in the FIH structure which causes a semi-cavity and forms a template complex, and considering soft–hard acid–base concept, the charge density and the size of the neodymium ion, it was expected that FIH can form a selective complex with neodymium ion more than the other transition metal ions. Thus, conductivity study of complexation in the acetonitrile solution was carried out as a primary test.

3.1. Preliminary study of FIH complexation with some metal ions

To examine ligand selectivity against various metal ions including Na, K, Cu, Cd, Ba, Pb, Cr, Fe and all 14 members of lanthanide series, the interaction of FIH with metal ions in an acetonitrile solution by conductometric method was investigated [10, 13-22, 35]. In all measurements, the cell should be thermo stated at the temperature of 25.0 °C, using a Phywe immersion thermostat. In typical experiments, 20 mL of an ion solution (1.0×10^{-4} mol L^{-1}) is placed in a water-jacketed cell, equipped with a magnetic stirrer and connected to the thermostat, circulating water at the desired temperature. Then, a known amount of an ionophore or a ligand (1.0×10^{-2} mol L^{-1}) solution is added in a stepwise manner, using a calibrated micropipette. The conductance of the solution is measured after each addition. The ligand addition is continued until the desired ionophore-to-ion mole ratio is achieved. The 1:1 binding of the cations with the ionophore and the complex formation constant in terms of the molar conductance can be expressed as [36]:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \tag{1}$$

where:

$$K_f = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})} \tag{2}$$

where, Λ_M is the molar conductance of the cation before the addition of the ionophore; Λ_{ML} is the molar conductance of the complexes, Λ_{obs} the molar conductance of the solution during titration, C_L the analytical concentration of the added ionophore and C_M the analytical concentration of the cation salt. The complex formation constant (K_f) and the molar conductance of the complex, Λ_{ML}, were obtained by computer fitting Eqs. (1) and (2) to the molar conductance–mole ratio data, using the nonlinear least-squares program KINFIT [36]. In this experiment, the ligand to cation mole ratio was equal to 1 in all cases. The formation-constant values of the resulting 1:1 complexes in Table 1 showed that log K_f is 5.84±0.02 for Nd^{3+} and between 2.02±0.03 to 2.95±0.01 for other lanthanide metal ions used. As can be seen from these results, FIH can be used as a sensing material in an Nd(III) sensor.

3.2. Potential response

In order to check the suitability of FIH as an ion carrier for Nd(III) and other metal ions, it was used to prepare PVC membrane ion-selective electrodes for a wide variety of cations including a number of lanthanide (La^{3+}, Ce^{3+}, Sm^{3+}, Gd^{3+} and Nd^{3+}) and some common metal ions (K^+, Cr^{3+}, Cu^{2+}, Cd^{2+} and Ba^{2+}). At first experiment we used 30 mg PVC, 64 mg BA, 4 mg FIH and 2 mg NaTPB for membrane fabrication. The potential responses different ion-selective electrodes based on FIH are depicted in Fig. 2. With the exception of Nd(III) ions, all the tested cations showed relatively weak responses in the concentration range 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1}, due to their weak interactions with the ionophore.

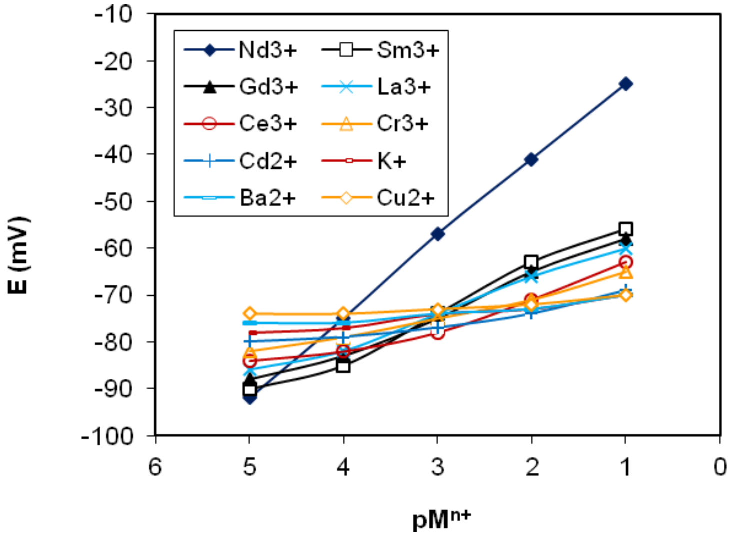

Figure 2. The potential response of various metals ion-selective electrodes based on FIH.

3.3. The influence of membrane composition on the sensor response

The properties of the ion-selective membrane sensors, namely response time, lifetime, selectivity, and chemical stability depend on the nature and amount of ionophore, the plasticizer properties, the plasticizer/PVC ratio and, especially, the nature of additives used [3, 4]. Thus, in this work, ten PVC membranes with plasticizer/PVC ratios of about 1.97-2.23, but with varying nature and amount of other ingredients were prepared (Table 2). It is noteworthy that the best membrane characteristics are reported to be usually obtained at a plasticizer/PVC ratio of about 1.6–2.3 [12, 15, 29-32].

Table 2. Optimization of membrane ingredients during design of Nd(III) selective membrane sensor.

No.	Composition (wt.%)				Slope (mV decade^{-1})	Linear Range (mol L^{-1})
	PVC	Plasticizer	FIH	Additive		
1	30	BA, 64	4	NaTPB, 2	16.7 ± 0.6	1.0×10^{-7} to 1.0×10^{-2}
2	30	DBP, 64	4	NaTPB, 2	15.1 ± 0.1	5.0×10^{-7} to 1.0×10^{-2}
3	30	NPOE, 64	4	NaTPB, 2	17.7 ± 0.5	1.0×10^{-7} to 5.0×10^{-1}
4	30	AP, 64	4	NaTPB, 2	14.2 ± 0.2	1.0×10^{-6} to 1.0×10^{-2}
5	30	NPOE, 65	3	NaTPB, 2	17.0 ± 0.1	1.0×10^{-7} to 5.0×10^{-1}
6	30	NPOE, 63	5	NaTPB, 2	17.5 ± 0.4	1.0×10^{-7} to 5.0×10^{-1}
7	30	NPOE, 59	4	OA, 7	16.4 ± 0.3	5.0×10^{-7} to 5.0×10^{-1}
8	30	NPOE, 63	4	NaTPB, 3	20.1 ± 0.3	1.0×10^{-7} to 5.0×10^{-1}
9	30	NPOE, 66	4	-, 0	14.6 ± 0.2	1.0×10^{-6} to 1.0×10^{-2}
10	30	NPOE, 67	0	NaTPB, 3	7.9 ± 0.4	1.0×10^{-5} to 1.0×10^{-2}

As it is well known, plasticizers are solvent mediators that lead to optimum physical properties as well as ensure high mobility of ions in the membrane. The presence of 61–65% plasticizer can influence the working concentration range of ISEs [3, 7, 8]. As addition of appropriate amount of plasticizer leads to improve the electrochemical properties of conventional ISEs, the effect of different plasticizers on Nd(III) selective membrane sensor was first investigated. The potential response obtained for prepared membrane sensors with use of BA, DBP, NPOE and AP at the same membrane composition (having FIH – PVC – NaTPB – Plasticizer with the ratio 4.0: 30.0: 2.0: 64.0) is shown in Fig. 3. Due to the increased polarity of NPOE over BA, DBP and AP, it can be seen that membrane with NPOE as plasticizer gave better slope (17.7 ± 0.5 mV decade^{-1}) and higher order of magnitude widening of the measuring concentration range of the corresponding membrane sensor over the membrane based on other plasticizers. Also the result is in tune with earlier reports that high dielectric constant of plasticizers cause better sensivity to lanthanide(III) ions [15 -26].

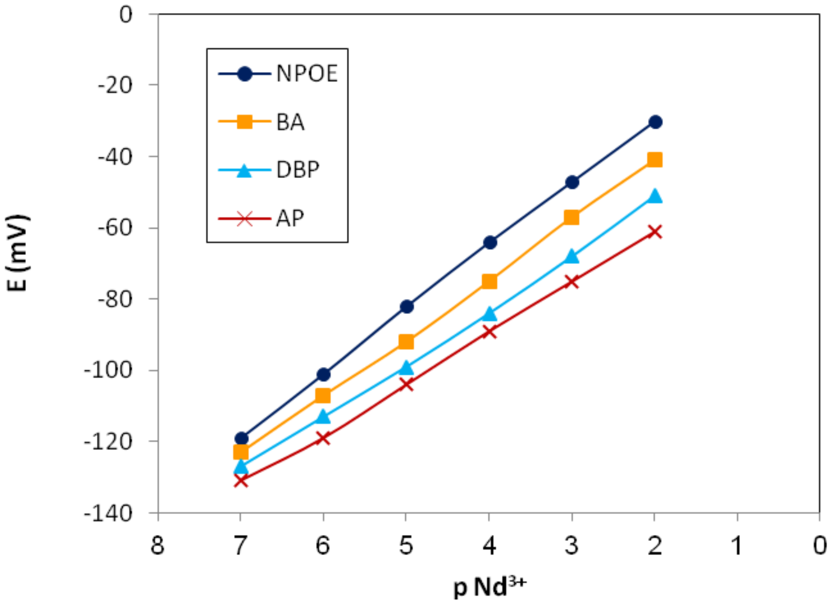

Figure 3. The potential responses of the Nd(III) membrane ISEs prepared with different plasticizers.

It has been well established that, the presence of lipophilic negatively charged additives improves the potentiometric behavior of certain cationic selective electrodes not only by reducing the ohmic resistance, improving the response behavior and selectivity, but also, in cases where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the membrane electrode. Moreover, the additives may catalyze the exchange kinetics at the sample-membrane interface [4, 16-19, 37-39]. Table 2 shows that in the absence of ionic additive, the slope of the proposed sensor is 14.6 mV decade^{-1} (No. 9) whereas in the presence of 3% NaTPB as a suitable additive, the slope increases 20.1 mV decade^{-1} (No.8). It is interesting to note that a membrane, having a composition like membrane 8, but lacking FIH, (No.10) showed no promising responses towards Nd(III) ions. However, membrane with a PVC: NB: FIH: NaTPB percent ratio of 30: 63: 4: 3 had a Nernstian behavior over a wide concentration range.

The optimum responses of the electrodes were tested after conditioning (soaking) for different periods of time in 1.0×10^{-4}M Nd(III) ions. As can be seen in Table 3, the slopes obtained after conditioning for 18 hours were close to the theoretical slopes expected on the basis of the Nernst equation. Longer conditioning times produced no further improvements in response.

Table 3. Effect of soaking time on the response characteristics of Nd(III) selective membrane sensor.

Soaking Time (h)	Nernstian Response Range (mol L^{-1})
6	1.0×10^{-5} to 3.0×10^{-3}
12	4.0×10^{-6} to 6.0×10^{-2}
18	1.0×10^{-7} to 5.0×10^{-1}
24	1.0×10^{-7} to 5.0×10^{-1}

3.4. Linear concentration range and detection limit

The critical response characteristics of the Nd(III) sensor were assessed according to IUPAC recommendations [40]. The potential response of the membrane at varying concentrations of Nd(III) ions was investigated. Fig. 4 indicates a rectilinear range from 1.0×10^{-7} to 5.0×10^{-1} mol L^{-1}. The slope of the calibration curve was 20.1 ± 0.3 mV decade^{-1} of Nd(III) concentration. The detection limit, as determined from the intersection of the two extrapolated segments of the calibration graph, was 8.6×10^{-8} mol L^{-1}.

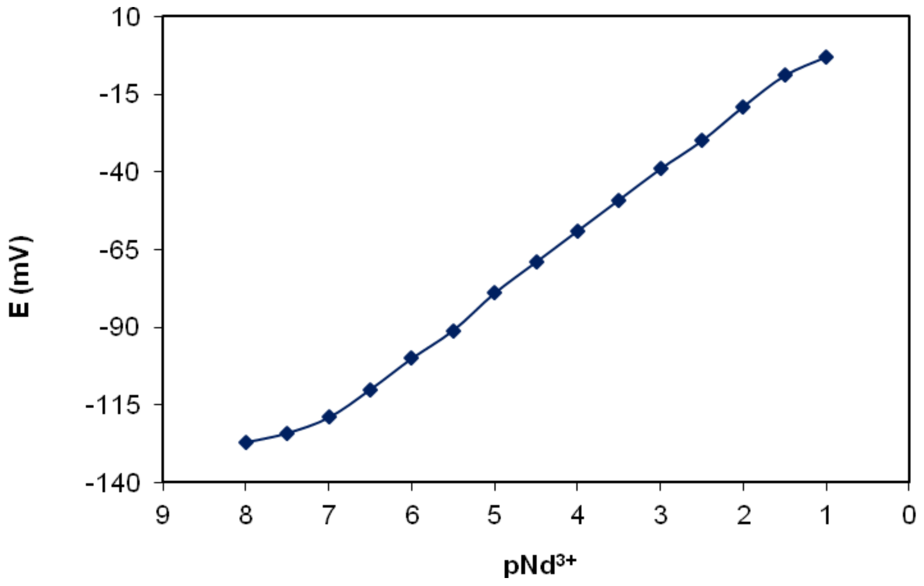

Figure 4. The Calibration curve of the Nd(III) membrane sensor based on FIH.

3.5. Response time

In analytical application, response time of an electrochemical sensor is very important. It is evaluated through measuring the average time required to achieve potential values within ±0.1 mV of the steady-state potential of the electrode after its immersion in a series of solutions of the target ions, each having a ten-fold difference in concentration [15-17]. A numbers of experimental parameters such as temperature of testing solution, type and speed of stirring, the concentration and composition of each test solution, and preconditioning of the electrode can affect the response time of any sensor [29-33]. In this study, the practical response time was recorded by changing the Nd(III) concentration in solution, over a concentration range from 1.0×10^{-7} mol L^{-1} to 1.0×10^{-2} mol L^{-1}, and the results are shown in Fig. 5. The response time of the proposed membrane sensor was between 6 s (for high concentrations) to 9 s (for low concentrations) of Nd(III) ions. This is probably due to the fast exchange kinetics of complexation-decomplexation of Nd(III) with FIH on the test solution-membrane interface.

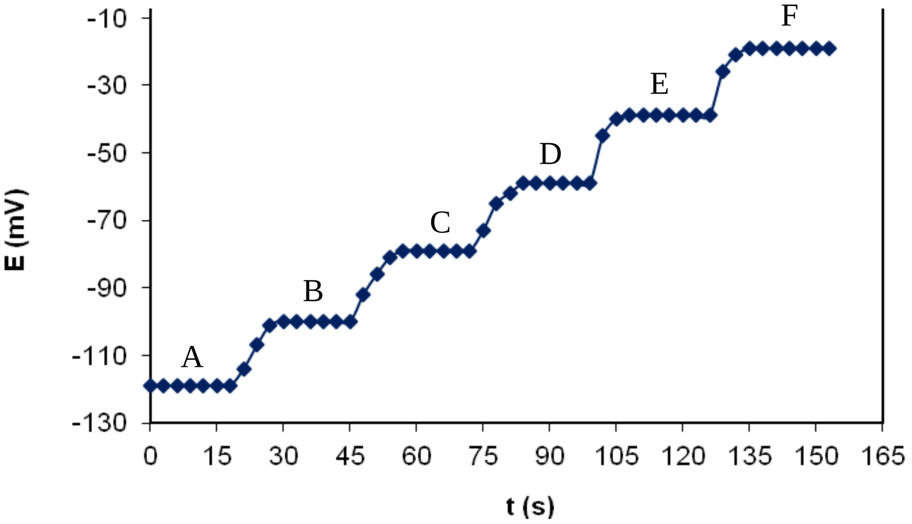

Figure 5. The practical response time of the Nd(III) membrane sensor for step changes in the Nd(III) concentration: (A) 1.0×10^{-7} M, (B) 1.0×10^{-6} M, (C) 1.0×10^{-5} M, (D) 1.0×10^{-4} M, (E) 1.0×10^{-3} M, (F) 1.0×10^{-2} M.

3.6. pH effect on the electrode response

The pH response profile for the electrode was tested by using 1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1} $Nd(NO_3)_3$ solutions over the pH range of 2.0-10.5. The pH was adjusted by introducing small drops of hydrochloric acid (0.1-0.01 mol L^{-1}) or sodium hydroxide (0.1-0.01 mol L^{-1}). The influence of pH on the response of PVC membrane electrode is shown in Fig. 6. As is seen, the potential remained constant from pH 3.0 to 8.4, beyond which some drifts in the potentials were observed. The observed drift at higher pH values could be due to the formation of some hydroxyl complexes of Nd(III) in the solution. At the lower pH values, the potentials decreased, indicating that the membrane sensor also responded to H^+ ions, by the protonation of the nitrogen atoms of the ionophore.

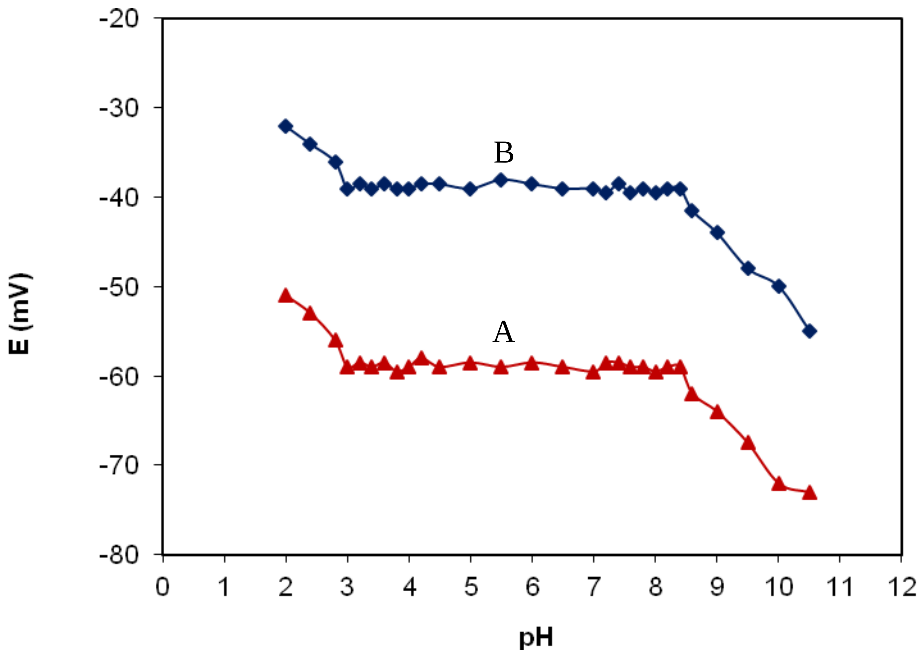

Figure 6. Effect of pH on the potential response of the Nd(III) membrane sensor based on FIH in the test solutions of Nd(III) ions: (A) 1.0 × 10^{-4} M, (B) 1.0 × 10^{-3} M.

3.7. Potentiometric selectivity

Potentiometric selectivity coefficients of the Nd(III) membrane sensors were evaluated by a matched potential method (MPM) [6, 37, 38].

Table 4. The selectivity coefficients of various interfering cations for the membrane sensor.

Cation	$K^{MPM}_{Nd^{3+},B}$	Cation	$K^{MPM}_{Nd^{3+},B}$
Pr^{3+}	2.4×10^{-3}	Eu^{3+}	2.9×10^{-4}
Sm^{3+}	1.7×10^{-3}	Dy^{3+}	1.6×10^{-4}
Ce^{3+}	1.2×10^{-3}	Ba^{2+}	1.3×10^{-4}
Pb^{2+}	9.8×10^{-4}	Yb^{3+}	8.4×10^{-5}
Gd^{3+}	9.5×10^{-4}	K^{+}	6.4×10^{-5}
Tb^{3+}	8.3×10^{-4}	Er^{3+}	5.6×10^{-5}
Ho^{3+}	7.4×10^{-4}	Lu^{3+}	4.0×10^{-5}
Tm^{3+}	5.1×10^{-4}	Cu^{2+}	2.2×10^{-5}
Cd^{3+}	3.7×10^{-4}	Na^{+}	7.8×10^{-6}

Table 4 shows potentiometric selectivity coefficients of the FIH-based Nd(III) selective membrane sensor. For all diverse ions, the selectivity coefficients of the electrode are in the order of 2.4×10^{-3} or smaller, indicating they would not significantly disturb the function of the Nd(III) PVC-membrane sensor.

3.8. Stability and lifetime

For the investigation of the stability and lifetime of the Nd(III) membrane sensor, two electrodes were tested over a period of 14 weeks and the results are in Table 5. The main factor limiting the lifetime of the ion-selective membrane in potentiometric measurements is the leakage of ionophore into the aqueous solutions. The proposed PVC-based membrane sensor could be used for at least 11 weeks (use of 1 hour daily). After its utilization, it was washed and kept dry. During this certain time period, the membrane sensor could be used without any measurable divergence. After 11 weeks changes were observed in the slope and detection limit (from 20.1 to 18.0 mV decade^{-1} and 8.6×10^{-8} from 5.3×10^{-7} mol L^{-1}, respectively) [21-24].

Table 5. Lifetime of Nd(III) selective membrane sensor.

Week	Slop (mV decade^{-1})	DL (mol L^{-1})
1	20.1 ± 0.3	8.6×10^{-8}
2	20.1 ± 0.1	8.7×10^{-8}
3	20.0 ± 0.3	8.9×10^{-8}
4	19.8 ± 0.2	9.2×10^{-8}
5	20.0 ± 0.4	9.1×10^{-8}
6	19.8 ± 0.2	9.3×10^{-8}
7	19.9 ± 0.1	9.5×10^{-8}
8	19.7 ± 0.2	9.4×10^{-8}
9	19.5 ± 0.2	9.7×10^{-8}
10	19.5 ± 0.1	9.8×10^{-8}
11	19.4 ± 0.2	9.7×10^{-8}
12	18.0 ± 0.4	5.3×10^{-7}
13	16.8 ± 0.4	6.8×10^{-7}
14	15.6 ± 0.3	8.7×10^{-7}

3.9. Reversibility of the electrode response

To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements were performed in the sequence of high-to-low (from 1.0×10^{-2} to 1.0×10^{-3} mol L^{-1}) sample concentrations and the results showed that, the potentiometric responses of the electrode was reversible; although the time needed to reach equilibrium values (30 s) were longer than that of low-to-high sample concentrations [3] (Fig.7).

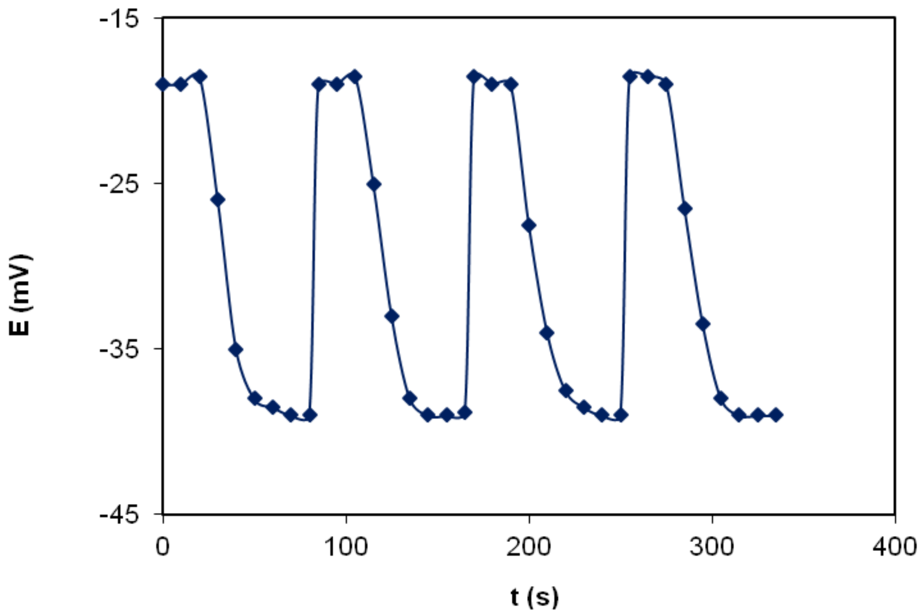

Figure 7. Dynamic response characteristics of the Nd(III) membrane sensor for several high-to-low sample cycles.

3.10. Analytical applications

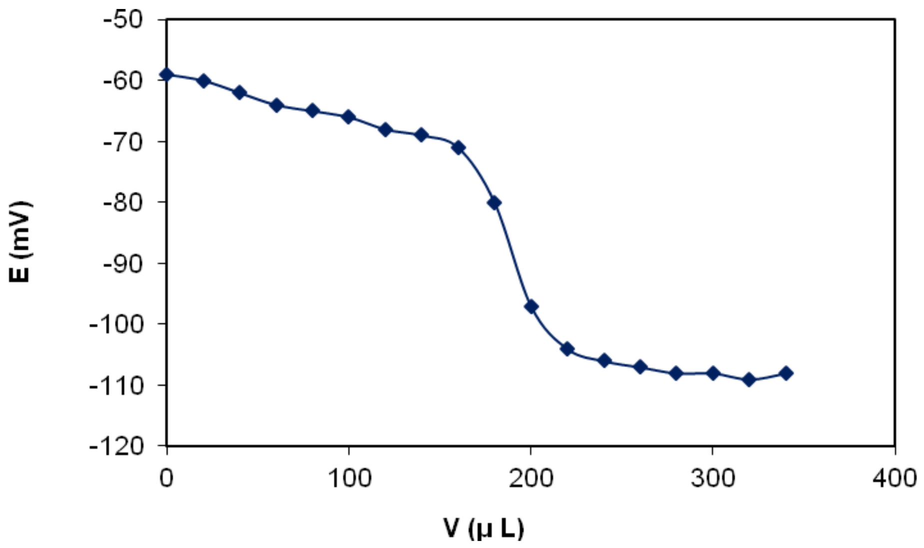

Figure 8. Potential titration curves of 20.0 mL from a 1.0×10^{-4} M Nd(III) solution with 1.0×10^{-2} M of EDTA.

The membrane sensor has been successfully used as an indicator electrode in the potentiometric titration of Nd(III) (20.0 mL, 1.0×10^{-4} mol L^{-1}) with a standard EDTA (1.0×10^{-2} mol L^{-1}) solution. The results are shown in Fig. 8 and as can bee seen, the amount of Nd(III) can be determined with the sensor. It should be noted that for the titration of trivalent cations with EDTA for obtaining a sharp end-point titration, adjusting the pH is necessary because, the stability constants of these complexes are pH dependent.

Due to the high selectivity and the very low detection limit of the constructed Nd(III) sensor, it was applied for the monitoring of the neodymium ions concentration in various binary mixtures and the resulting data are given in Table 6. It is clear from the table that the recoveries of the Nd(III) ions in all mixtures are in the range of 99.3-103.2 %, therefore being acceptable the high degree of neodymium selectivity exhibited by the membrane sensor.

Table 6. Determination of Nd(III) ions in various binary mixtures by the designed selective membrane sensor.

Nd^{3+} (ppm)	Added cation (ppm)	Recovery[a] (%)
35	La^{3+}, 90	101.4 ± 0.3
35	Nd^{3+}, 90	102.2 ± 0.1
35	Gd^{3+}, 90	100.6 ± 0.5
35	Tb^{3+}, 90	99.5 ± 0.2
35	Er^{3+}, 90	101.2 ± 0.4
35	Tm^{3+}, 90	102.4 ± 0.5
35	Pb^{2+}, 90	100.4 ± 0.3
30	Ba^{2+}, 100	102.3 ± 0.6
30	Cd^{2+}, 100	99.3 ± 0.1
20	Cu^{2+}, 120	99.7 ± 0.4
20	K^{+}, 120	101.0 ± 0.5
20	Na^{+}, 120	103.2 ± 0.2

[a] Results are based on three measurements.

Table 7. Determination of fluoride ions in mouth washes.

Sample	Labeled (ppm)	Found ISE[a,b] (ppm)	Commercial fluoride ISE[b] (ppm)
Sodium fluoride mouth wash solution (Aquafresh, Brentford, UK)	1350	1366 ± 34	1342 ± 12
Sodium fluoride mouth wash solution (Eurodont, DuroDont GmbH)	1450	1470 ± 14	1440 ± 16

[a] Designed Nd(III) membrane sensor
[b] Results are based on three measurements

The proposed sensor was used for the determination of fluoride ion concentration in two mouth wash preparations [18]. One gram of each sample of the sodium fluoride mouth wash solutions (Aquafresh, Brentford, UK and Eurodont, Dr. Scheller, DuroDont GmbH, Germany) was taken and diluted with distilledwater in a 100 mL flask and titrated with a Nd(III) solution (1.0×10^{-3} mol L^{-1}). The corresponding results (after triplicate measurements) are summarized in Table 7. Evidently, there is a satisfactory agreement among the declared fluoride content, the determined values by the sensor and the commercial solid fluoride sensor.

The proposed sensor was effectively employed for the determination of neodymium ions in soil and sediment samples [17]. A sample (1 g) was weighed into a PTFE beaker. Then, 5 mL of 70% $HClO_4$ and 10 mL of 48% HF were added. The sample was heated in a sand bath to incipient dryness. The acid attack with $HclO_4$ and HF (1 + 2) was repeated three times to complete the digestion of the silicate matrix. Afterwards, the samples were transferred into flasks, diluted with 5mL of NaOH 5% and distilled water to 50mL (pH~5) [41]. Then, the potential of these solutions was measured by employing the developed Nd(III) sensor as well as its calibration curve (1.0×10^{-7} to 5.0×10^{-1} mol L^{-1}), which was obtained after measuring a series of neodymium ion standard solutions. Afterwards, the Nd(III) ion concentration in the samples was determined. The result, derived from triplicate measurements with the same sensor, was found to be in satisfactory agreement with that determined by the Arsenazo method. This is a spectrophotometric method in which the Arsenazo reagent (*o*-(1,8-dihydroxy-3,6-disulfo- 2-naphthylazo)benzene arsenic acid, tri-sodium salt) forms a colored complex with the lanthanide ions and it is also used as a standard method for determination of lanthanides. There was a color change from red-orange to blue-violet, denoting the complex formation [42]. The results can be seen in Table 8.

Table 8. Determination of Nd(III) ions in soil samples.

Sample No.	Designed membrane sensor[a] (ppm)	Arsenazo method[a] (ppm)
1	75.4 ± 0.3	76.3 ± 0.2
2	39.2 ± 0.2	38.4 ± 0.5
3	51.6 ± 0.4	52.4 ± 0.3
4	58.4 ± 0.1	58.0 ± 0.1
5	64.0 ± 0.2	64.2 ± 0.4

[a] Results are based on three measurements

4. CONCLUSIONS

The above studies showed that N-(furfuralidene)-N -isonicotinoylhydrazine (FIH) is a selective ionophore for Nd(III) ions. This can be related to the presence of three intermediately soft N-donor atoms in its structure, and also to the size of the semi-cavity formed as a result of the arrangement of the different parts of the ligand around the desired ion in the solution. Another determining property which leads to the applicability of FIH as a proper ion carrier, is the relatively fast ion exchange kinetics that governs the formation of its complexes, at least those with Nd(III) ions. This can be indirectly concluded from the relatively short response time of the sensor (~8 s). The lipophilicity of the ionophore, decreasing its leaching from the membrane to the test solution drastically, is the reason for the long life-times of the electrodes based on FIH. All these advantages, together with the other improvements that are the result of the optimized composition of the membrane ingredients make FIH-based membrane sensors, acceptable potentiometric devices for the determination of Nd(III) concentrations in different samples.

ACKNOWLEDGEMENT
The authors would like to thank NFCRS, Nuclear Science & Technology Research Institute (Tehran, Iran) for their financial support.

References

1. J. Yu, S.T. Yao and S. J. Chi, *J. Shenyang Univ. Technol.* 21 (1999) 83.
2. http://www.webelements.com/neodymium/
3. E. Bakker, P. Bühlmann and E. Pretsch, *Chem. Rev.* 97 (1997) 3083.
4. P. Bühlmann, E. Pretsch and E. Bakker, *Chem. Rev.* 98 (1998) 1593.
5. E. Pungor, *Anal. Sci.* 14 (1998) 249.
6. E. Bakker, E. Pretsch and P. Bühlmann, *Anal. Chem.* 72 (2000) 1127.
7. M.R. Ganjali, P. Norouzi, M. Rezapour, F. Faridbod and M.R. Pourjavid, *Sensors* 6 (2006) 1018.
8. M.R. Ganjali, P. Norouzi, F. Faridbod, M. Rezapour and M.R. Pourjavid, *J. Iran. Chem. Soc.* 4 (2007) 1.
9. V.K. Gupta, R.N. Goyal and R. A. Sharma, *Int. J. Electrochem. Sci.*, 4 (2009) 156
10. M. Shamsipur, M. Yousefi and M.R. Ganjali, *Anal. Chem.* 72 (2001) 2391.
11. T. Ito and C. Coto, *J. Trace. Microprobe Tech.* 19 (2001) 601.
12. M.R. Ganjali, M.R. Pourjavid, M. Rezapour and S. Haghgoo, *Sens. Actuators B* 89 (2003) 21.
13. M.R. Ganjali, M. Rezapour, M.R. Pourjavid and S. Haghgoo, *Anal. Sci.* 20 (2004) 1007.
14. A.A.A. Gaber, *Anal. Lett.* 36 (2003) 2585.
15. M.R. Ganjali, A. Ghesmi, M. Hosseini, M.R. Pourjavid, M. Rezapour, M. Shamsipur and M. Salavati-Niasari, *Sens. Actuators B* 105 (2005) 334.
16. M.R. Ganjali, S. Rasoolipour, M. Rezapour, P. Norouzi, M. Amirnasr and S. Meghdadi, *Sens. Actuators B* 119 (2006) 89.
17. H. Behmadi, H.A. Zamani, M.R. Ganjali and P. Norouzi, *Electrochim. Acta* 53 (2007) 1870.
18. M.R. Ganjali, P. Norouzi, A. Daftari, F. Faridbod and M. Salavati-Niasari, *Sens. Actuators B* 120 (2007) 673.
19. F. Faridbod, M.R. Ganjali, B. Larijani and P. Norouzi, *Electrochim. Acta* 55 (2009) 234.
20. H.A. Zamani, M. Nekoei, M. Mohammadhosseini and M.R. Ganjali, *Mater. Sci. Engin. C* 30 (2010) 480.
21. M.R. Abedi and H.A. Zamani, *Chinese Chem. Lett.* 22 (2011) 977.
22. H.A. Zamani, M. Rohani, A. Zangeneh-Asadabadi, M.S. Zabihi, M.R. Ganjali and M. Salavati-Niasari, *Mater. Sci. Engin. C* 30 (2010) 917.
23. M. Hosseini, M.R. Ganjali, B. Veismohammadi, F. Faridbod, P. Norouzi and S. Dehghan Abkenar, *Sens. Actuators B* 147 (2010) 23.
24. H.A. Zamani, M.S. Zabihi, M. Rohani, A. Zangeneh-Asadabadi, M.R. Ganjali, F. Faridbod and S. Meghdadi, *Mater. Sci. Engin. C* 31 (2011) 409.
25. H.A. Zamani, A. Imani, A. Arvinfar, F. Rahimi, M.R. Ganjali, F. Faridbod and S. Meghdadi, *Mater. Sci. Engin. C* 31 (2011) 588.
26. H.A. Zamani, A. Arvinfar, F. Rahimi, Alihossien Imani, M.R. Ganjali and S. Meghdadi, *Mater. Sci. Engin. C* 31 (2011) 307.
27. S. Satyabhama Devi and A.k. Manihar Singh, *J. Chem. Pharm. Res.* 3 (2011) 399.
28. M.R. Ganjali, M.H. Zargazi and A. Mohajeri, *Pol. J. Chem.* 75 (2001) 743.

29. M.R. Ganjali, M.R. Pourjavid, M. Shamsipur, T. Poursaberi, M. Rezapour, M. Javanbakht and H. Sharghi, *Anal. Sci.* 19 (2003) 995.
30. M.R. Ganjali, M. Rezapour, M.R. Pourjavid and M. Salavati-Niasari, *Anal. Sci.* 19 (2003) 1127.
31. M.R. Ganjali, M.R. Pourjavid, M. Rezapour, T. Poursaberi, A. Daftari and M. Salavati-Niasari, *Electroanalysis* 16 (2004) 922.
32. M.R. Ganjali, M. Rezapour, M.R. Pourjavid, M. Salavati-Niasari and T. Poursaberi, *Anal. Lett.* 36 (2003) 881.
33. M. Ghaedi, M. Montazerozohori, Z. Andikaey, A. Shokrollahi, S. Khodadoust, M. Behfar and S. Sharifi, *Int. J. Electrochem. Sci.*, 6 (2011) 4127.
34. D.A. Atwood, *Coord. Chem. Rev.* 195 (1997) 267.
35. M.R. Ganjali, R. Kiani-Anbouhi, M.R. Pourjavid and M. Salavati-Niasari, *Talanta* 61 (2003) 277.
36. J.L. Dye and V.A. Nicely, *J. Chem. Educ.* 48 (1971) 443.
37. M.R. Ganjali, A. Daftari, M.R. Pourjavid, M. Faal Rastegar and A. Moghimi, *Main Group Metal Chemistry* 25 (2002) 669.
38. M.R. Ganjali, M.R. Pourjavid, A. Mouradzadegun, M. Hosseini and M. Mizani, *Bull. Korean Chem. Soc.* 24 (2003) 1585.
39. T. Rosatzin, E. Bakker, K. Suzuki and W. Simon, *Anal. Chim. Acta.* 280 (1993) 197.
40. IUPAC Analytical Chemistry Division, Commission on Analytical Nomenclature. *Recommendations for nomenclature for ion selective electrodes, Pure Appl. Chem.* 48 (1976) p.127.
41. R. Djingova and Ju. Ivanova, *Talanta* 57 (2002) 821.
42. Z. Marczenko, *Separation and Spectrophotometric Determination of Elements*, Elis Horwood Limited, Chichester, UK, 1986.