Nd(III)-PVC membrane sensor based on 2-{[(6-aminopyridin-2-yl)imino]methyl}-phenol

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Abstract

We report the development of a novel Nd(III) ion-selective PVC-based membrane sensor, based on 2-{[(6-aminopyridin-2-yl)imino]methyl}phenol (APIMP) as the membrane carrier. The sensor has a Nernstian slope of 19.6 ± 0.3 mV per decade over the concentration range of 1.0×10^{-5}–1.0×10^{-2} M, and a detection limit of 2.0×10^{-6} M of Nd(III) ions. The potentiometric response of the sensor is independent pH solution in the pH range 3.5–8.5. It has advantages of low resistance, very fast response time (< 10 s) and, most importantly, good selectivity with respect to a number of lanthanide ions. Using the proposed membrane sensor in a 6 weeks period caused no significant divergences in its potential response. To assess its analytical applicability the sensor was successfully applied as an indicator electrode in the titration of Nd(III) ion solution with EDTA.

1. Introduction

The most important application of neodymium is as the fundamental basis of neodymium-iron-boron (Nd2-Fe-B) permanent magnets. It is used extensively in the automotive industry with many applications including starter motor, brake systems, seat adjusters and car stereo speakers. Its largest application is in the voice coil motors used in computer disk drives. Neodymium is included in many formulations of barium titanate, used as dielectric coatings and in multi-layer capacitors essential to electronic equipment. Yttrium-aluminum-garnet (YAG) solid-state lasers utilize neodymium because it has optimal absorption and emitting wavelengths. Nd-based YAG lasers are used in various medical applications, drilling, welding, and material processing. Neodymium and other lanthanide oxides are widely used in the preparation of optical glasses, glass fibers for optical purposes, gasoline-cracking catalysts, polishing compounds and carbon arcs, and in the iron and steel industries to remove sulfur, carbon, and other electronegative elements from iron and steel [1].

The main available methods for low-level monitoring of rare-earth ions in solutions are spectrophotometry, inductively coupled plasma mass spectrometry and inductively coupled plasma atomic emission spectroscopy. Isotope dilution mass spectrometry, neutron activation analysis and X-ray fluorescence spectrometry, etc, are also used in some laboratories, These methods have either low sensitivities, are time consuming, involving multiple sample manipulations or are too expensive for most analytical laboratories.

However, a simple method that offers great advantages such as speed and ease of preparation and procedures, relatively short response times, reasonable selectivities, wide linear dynamic ranges and low cost is potentiometric detection based on ion-selective sensors. The list of available sensors has grown substantially over the past years [2].

A number of lanthanide ion ISEs, such as La^{3+}, Ce^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Nd^{3+} and Yb^{3+}) have recently been reported by our group and other researchers [3–20]. Due to the crucial importance of Nd(III) in industry, lack of good determination methods for this element and hence the urgent need for Nd(III)-selective electrodes for the fast monitoring of Nd(III), we were interested in the preparation of a selective and sensitive sensor 2-{[(6-aminopyridin-2-yl)imino]methyl}phenol (APIMP) for the determination of Nd(III) ions.

2. Experimental

2.1. Reagents

Reagent grade dibutyl phthalate (DBP), benzyl acetate (BA), acetophenon (AP), nitrobenzen (NB), sodium

tetraphenyl borate (TPB), tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from Merck and used as received. Neodymium chloride and the nitrate salts of neodymium and other cations used (all from Merck, Aldrich and Fluka) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. 2-furaldehyde, 2,6-diaminopyridine, acetic acid, ethanol and methanol (all from Merck), were of the highest purity available. Triply distilled de-ionized water was used throughout.

2.2. Synthesis of APIMP

2-{[(6-aminopyridin-2-yl)imino]methyl}phenol (Figure 1) was synthesized by refluxing a mixture of 2-hydroxybenzaldehyde (0.01 mol, 1.22 g), 2,6-diaminopyridine (0.01 mol, 1.09 g) and catalytic amount of acetic acid 5 h in absolute ethanol (20 ml). After this the reaction mixture was cooled to room temperature; the brown precipitate was filtered, washed with ethanol and dried under the reduced pressure.

M.p 225 °C (decomp), 1.8 g, yield 86%.

IR (KBr) (v_{max}/cm^{-1}): 3472, 3380, and 3200 (–OH and –NH$_2$), 1614 (–C=N), 1481, 1452, 1277, 1229, 1150, 1117, 1090, 754. MS, m/z (%): 213 (M^+, 28), 197 (10), 129 (44), 92 (20), 87 (8), 77 (24), 55 (17), 40 (44), 32 (100).

Anal. Calcd for $C_{12}H_{11}N_3O$ (213.24): C, 67.59; H, 5.20; N, 19.71. Found: C, 67.70; H, 5.40; N, 19.90%.

^{1}H NMR (250 MHz, DMSO-d_6 solution): δ 6.25 (1 H, d, J = 7.5 Hz, –CH), 6.79 (1 H, d, J = 7.9 Hz, –CH), 7.05 (1 H, d, J = 5.9 Hz, –CH), 7.10–7.40 (4 H, m, 4 – CH), 8.25 (2 H, br., –NH$_2$), 8.55 (1 H, s, –N=CH), 11.02 (1 H, fairly br., –OH).

^{13}C NMR: δ 108.24, 113.55, 117.94, and 120.63 (4 – CH), 129.21 (C), 133.71, 135.43, and 139.21 (3 –CH), 154.25, 159.09, and 160.25 (3 C), 160.32 (–CH).

2.3. Electrode preparation

In order to prepare the membrane, 30 mg of powdered PVC, 62 mg of BA, 6 mg of APIMP and 2 mg of TPB were completely dissolved in 5 ml of fresh THF, the mixture was transfered into a glass dish of 2 cm diameter and its solvent was allowed to evaporate slowly so as to produce an oily concentrated mixture. In the next step, a Pyrex tube (with a outer diameter of 3– 5 mm) was dipped into the mixture for about 10 s, so that a transparent membrane of 0.3 mm thickness was
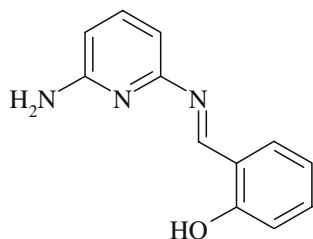
formed on its tip [15–19]. The tube was then pulled out of the mixture and kept at room temperature for 10 h, before being filled with its internal filling solution ($1.0×10^{-3}$ M NdCl$_3$). The final step was conditioning the electrode for 24 h by soaking in a $1.0×10^{-2}$ M solution of neodymium nitrate.

For a comparative study, a membrane containing no active component was also prepared. The ratio of different membrane ingredients, concentration of equilibrating solution and the time of contact were optimized to provide membranes which resulted in reproducible, noiseless and stable potentials.

2.4. Emf measurements

All emf measurements were carried out with the following assembly:

Ag–AgCl| internal solution $(1.0 × 10^{-3}$ MNdCl$_3$)| PVC membrane| test solution |Hg − Hg$_2$Cl$_2$, KCl (satd).

A Corning ion analyzer 250 pH/mV meter was used for potential measurements at $25 ± 1$ °C.

3. Results and discussion

As mentioned above, a number of carriers based lanthanide membrane sensors based, on different ion carriers containing nitrogen and sulfur donor atoms have been reported during recent years [3–20]. Due to its flexible structure and, especially because of the presence of three donating nitrogen atoms in its structure, APIMP was expected to act as a suitable ion carrier in the PVC membranes with respect to transition and heavy metal ions of appropriate size and charge. To determine the selectivity potentials of APIMP, in the preliminary experiments, the APIMP complexation with a number of transition and heavy metal ions was investigated conductometrically in acetonitrile solution at $25 ± 0.1$ °C $(1.0×10^{-4}$ M of cation solution and $1.0×10^{-2}$ M of ionophore) [21]. Twenty-five milllitres of each cation solution was titrated with 0.01 M of APIMP solution in order to obtain a clue about the stability and selectivity of the resulting complexes. The formation constants (K_f) of the resulting 1:1 complexes are given in Table 1. As can be seen, the APIMP with the most stable complex with Nd(III) ion is expected to act as a suitable ion-carrier for the fabrication of a Nd(III) ion-selective membrane sensor.

Fig. 1. Structure of APIMP

Table 1. The formation constants of APIMP–M^{n+} complexes

Cation	log K_f	Cation	log K_f
Nd^{3+}	4.47 ± 0.14	K$^+$	2.28 ± 0.12
Sm^{3+}	2.85 ± 0.17	Mg^{2+}	2.20 ± 0.09
La^{3+}	2.76 ± 0.12	Ca^{2+}	2.15 ± 0.15
Gd^{3+}	2.54 ± 0.10	Dy^{3+}	2.13 ± 0.11
Na$^+$	2.30 ± 0.14	Yb^{3+}	2.09 ± 0.15
		Cu^{2+}	2.25 ± 0.15

In the next experiment APIMP was used as a neutral carrier to prepare PVC-based membrane electrodes for a variety of transition and heavy metal ions.

The responses of various ion-selective electrodes based on APIMP are shown in Figure 2. As seen, except for Nd(III) ion, the slopes of emf *vs.* log $a_{m^{n+}}$ were smaller than the expected Nernstian response for mono, di and trivalent cations and, among the different metal ions tested, only Nd(III), with the most sensitive response, can be suitably determined with the PVC membrane sensor based on APIMP.

This is probably due to both the selective behavior of the ion carrier against Nd(III), in comparison to other metal ions and the rapid exchange kinetics of the resulting APIMP-Nd(III)complex.

Previously reported experiments have revealed that some important features of the PVC membranes such as the properties of the plasticizer, the plasticizer/PVC ratio, the nature and amount of ionophore and, especially, the nature and amount of the additives used, significantly influence the sensitivity and selectivity of the ion-selective electrodes.

Different aspects of the preparation of APIMP-based Nd(III)-selective membranes were optimized and the results are summarized in Table 2. Since the nature of the plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands [3–20, 22, 23] it was expected to play a key role in determining the ion-selective characteristics. Thus, in some preliminary experiments, we found that BA was better than other common plasticizers such as DBP and NB in construction of the Nd(III) ion-selective membrane sensor.
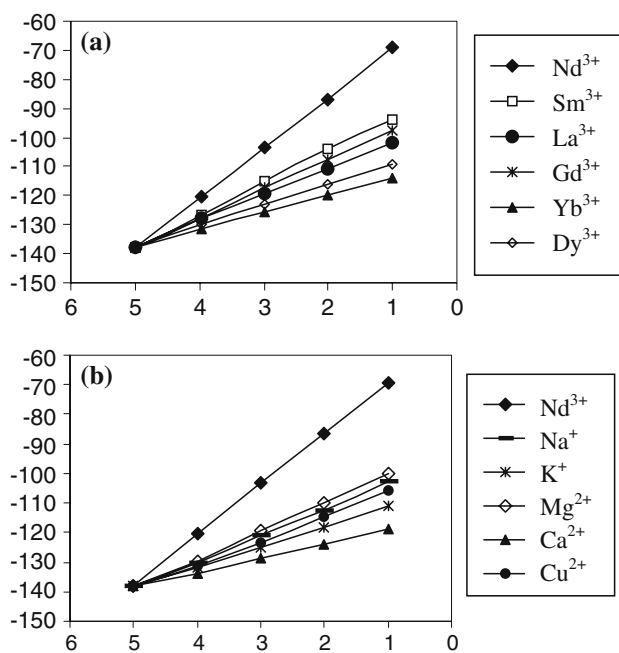
Table 2 shows a 6% of APIMP as the optimum amount of ionophore in the PVC-based membrane (no. 6).

The optimization of perm-selectivity of membrane sensors is known to be highly dependent on the incorporation of additional membrane components. In fact, it has been demonstrated that the presence of lipophilic negatively charged additives improves the potentiometric behavior of certain cation-selective electrodes by reducing the ohmic resistance and improving the response behavior and selectivity, in some cases, by catalyzing the exchange kinetics at the sample-membrane interface [24–26]. The data in Table 2 show that, in the absence of appropriate additive, the sensitivity of the PVC membrane based on APIMP is quite low (no. 4 with a slope of 13.1 ± 0.3 mV decade^{-1}). However, the presence of 2% TPB as a suitable lipophilic additive improves the sensitivity of the Nd(III) membrane sensor considerably (no. 6 with a slope of 19.6 ± 0.3 mV decade^{-1}).

It is interesting to note that a membrane without APIMP (no. 9), but otherwise of about the same composition as membrane (no. 6), resulted in poor sensitivity for Nd(III) ions. As seen from Table 2, membrane no. 6 with PVC:BA:APIMP:TPB percent ratio of 30:62:6:2 resulted in Nernstian behavior of the membrane electrode over a wide concentration range.

The potential response of the electrode was considered in the pH range 2.0–10.0 (the pH was adjusted by using concentrated NaOH and HNO$_3$) and the results are depicted in Figure 3. The response of the sensor remains constant in the pH range 3.5–8.5. The observed drift at higher pH values could be due to the formation of insoluble Nd(OH)$_3$ ions in the solution. It is noteworthy that, in such an acidic solution, the ionophore used could be protonated to some extent (nitrogen atom in NH$_2$ with a pKa of 11.53), which results in the improper functioning of the membrane electrode to the Nd(III) ion concentration.

The critical response characteristics of the Nd(III) ion-selective electrode were assessed according to IUPAC recommendations [27]. The Emf response of the membrane at varying Nd(III) concentrations (Figure 4) depicts a rectilinear range from 1.0×10^{-2} to 1.0×10^{-5} M with a Nernstian slope of 19.6 ± 0.3 mV decade^{-1}. The detection limit was 2.0×10^{-6} M, as determined from the intersection of the two extrapolated segments of the calibration plots. The standard deviation of eight replicate measurements is ± 0.3 mV.

3.1. Stability and lifetime

To study the stability and lifetime of the sensor, two similar membrane sensors were selected and their slopes were recorded over the 8 weeks; the results showed that the proposed Nd(III) PVC-based membrane sensor could be used for at least 6 weeks without significant change in its slope. After this time a slight decrease in the slope (19.4–18.1 mV per decade) was observed.

Fig. 2. Potential responses of different membrane sensors based on APIMP (a) other lanthanid.

Table 2. Optimization of membrane ingredients

Membrane no.	Composition/%				Slope/mV decade^{-1}	D.L	r
	PVC	Plasticizer	Ionophore	TPB			
1	30	BA, 67	3	–	10.9 ± 0.2	1.0×10^{-4}	0.995
2	30	BA, 65	5	–	11.4 ± 0.4	1.0×10^{-4}	0.993
3	30	BA, 63	7	–	12.6 ± 0.2	1.0×10^{-4}	0.990
4	30	BA, 64	6	–	13.1 ± 0.3	1.0×10^{-4}	0.996
5	30	BA, 63	6	1	17.7 ± 0.2	5.0×10^{-6}	0.996
6	30	BA, 62	6	2	19.6 ± 0.3	2.0×10^{-6}	0.998
7	30	NB, 62	6	2	15.3 ± 0.2	1.0×10^{-5}	0.985
8	30	DBP, 62	6	2	14.7 ± 0.4	1.0×10^{-5}	0.992
9	30	BA, 68	0	2	3.9 ± 0.4	1.0×10^{-4}	0.989
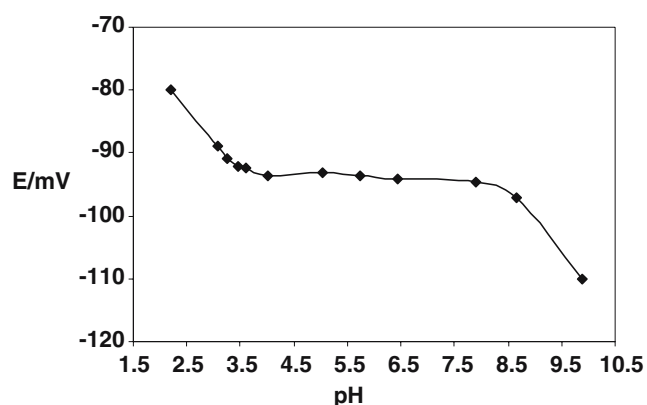
Fig. 3. Effect of pH of the test solution (1.0×10^{-4} M of Nd(III) ions) on potential response of the sensor based on APIMP.

3.2. *Static and dynamic response time*

The average time required for the Nd(III) membrane sensor to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of neodymium ion solutions, each having a 10-fold difference in concentration, was measured. The static response time of the membrane electrode thus obtained was < 10 s over the entire concentration range. The standard deviation of 10 replicate measurements was ± 0.3 mV.
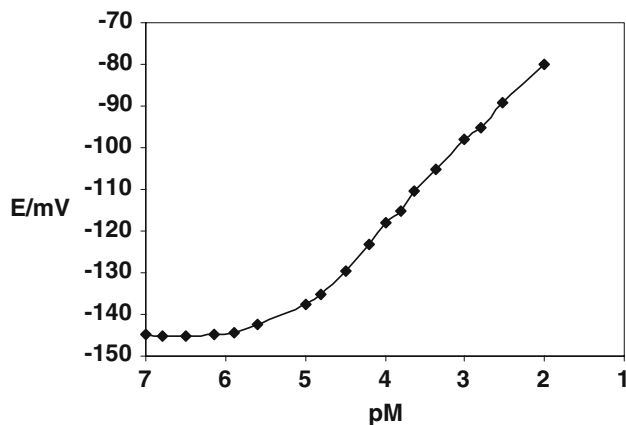
The response time of the proposed sensor was recorded by changing the Nd(III) concentration in a series of solutions (1.0×10^{-2} to 1.0×10^{-5} M), and the results are shown in Figure 5. Over the whole concentration range, the plasticized membrane sensor reaches its equilibrium response rapidly (< 10 s).

3.3. *Determination of selectivity coefficients*

To determination the selectivity coefficients the matched potential method (MPM) and separation solution method (SSM) were used [28, 29]. According to the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion (A = 1.0×10^{-4} M neodymium ions) and the interfering ion (B = 10^{-3}–10^{-2} M) which gives the same potential change in a reference solution (1.0×10^{-5} M neodymium ions). Thus, first the change in the potentials, upon changing the primary ion activity is measured, and then the interfering ion is added to an identical reference solution until the same potential change is obtained. The selectivity coefficient K_{AB} is determined as:

$$K_{AB}^{Pot} = \Delta A / a_B$$

where $\Delta A = á_A - a_A$, a_A is the initial primary ion activity and $á_A$ the activity of A, in the presence of interfering ion, a_B. In the separation solution method

Fig. 4. Calibration graph of the Nd(III) sensor based on APIMP.

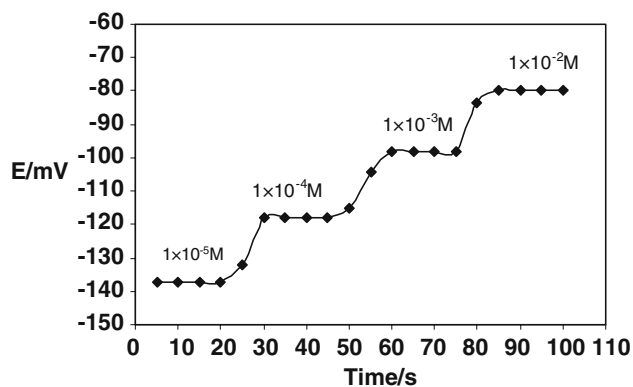*Fig. 5.* Dynamic response time of the Nd(III) electrode for step changes in the concentration of Nd(III): (A) 1.0×10^{-5} M, (B) 1.0×10^{-4} M, (C) 1.0×10^{-3} M, (D) 1.0×10^{-2} M.

Table 3. Selectivity Coefficients

Ion	$K_{sel(MPM)}$	$K_{sel(SSM)}$
Na^+	2.1×10^{-3}	2.3×10^{-3}
K^+	2.1×10^{-3}	2.2×10^{-3}
Mg^{2+}	2.9×10^{-3}	2.7×10^{-3}
Ca^{2+}	3.2×10^{-3}	3.0×10^{-3}
Cu^{2+}	8.9×10^{-3}	8.8×10^{-3}
La^{3+}	2.5×10^{-2}	2.7×10^{-2}
Gd^{3+}	1.5×10^{-2}	1.8×10^{-2}
Sm^{3+}	2.7×10^{-2}	2.5×10^{-2}
Dy^{3+}	7.1×10^{-3}	7.0×10^{-3}
Yb^{3+}	5.8×10^{-3}	5.9×10^{-3}
Al^{3+}	2.7×10^{-3}	2.5×10^{-2}
Cr^{3+}	7.1×10^{-3}	7.0×10^{-3}
Ce^{3+}	2.7×10^{-2}	2.5×10^{-2}
Fe^{3+}	5.8×10^{-3}	5.9×10^{-3}

Table 4. Determination of Nd(III) ions in various binary mixtures

Nd^{3+}/M	Added cation/M	Recovery/%
1×10^{-5}	$Na^+ (5 \times 10^{-2})$	102.3 ± 0.3
1×10^{-5}	$K^+ (5 \times 10^{-2})$	102.2 ± 0.2
1×10^{-5}	$Ca^{2+} (5 \times 10^{-2})$	103.5 ± 0.4
1×10^{-5}	$Mg^{2+} (5 \times 10^{-2})$	102.6 ± 0.3
1×10^{-5}	$Pb^{2+} (5 \times 10^{-2})$	101.3 ± 0.3
1×10^{-5}	$Co^{2+} (5 \times 10^{-2})$	99.7 ± 0.4
1×10^{-5}	$La^{3+} (1 \times 10^{-2})$	104.4 ± 0.3
1×10^{-5}	$Pr^{3+} (1 \times 10^{-2})$	103.6 ± 0.2
1×10^{-5}	$Eu^{3+} (5 \times 10^{-2})$	102.1 ± 0.3
1×10^{-5}	$Gd^{3+} (5 \times 10^{-2})$	103.6 ± 0.4
1×10^{-5}	$Dy^{3+} (1 \times 10^{-3})$	103.2 ± 0.3
1×10^{-5}	$Lu^{3+} (1 \times 10^{-3})$	102.4 ± 0.3

(SSM) the concentrations of a cell comprising an ion-selective electrode and a reference electrode (ISE cell) are adjusted with each of two separate solutions, one containing the ion A of the activity a_A (but no B), the other containing the ion B (but no A) of the activity as high as required to achieve the same measured cell voltage. From any pair of activities a_A and a_B giving the same cell voltage, the value of K_{AB}^{Pot} may be calculated from the equation:

$$K_{AB}^{Pot} = a_A a^{Z_A/Z_B}$$

The resulting selectivity coefficient values for the proposed Nd(III) sensor are given in Table 3 which shows that the selectivity coefficients are 2.7×10^{-3} or smaller. The selectivity coefficients of the sensor for the closer lanthanide ions to neodymium (lower hydration energy and charge density) in the lanthanide group are greater then those of lanthanides with higher hydration energy and charge density.

3.4. Analytical performance

It should be noted that the proposed Nd(III) membrane sensor can not only be used for the direct determination of the Nd(III) ions but also as an indicator electrode in the titration of EDTA ion with Nd(III) ion. Figure 6 shows the titration of 20 ml neodymium solution
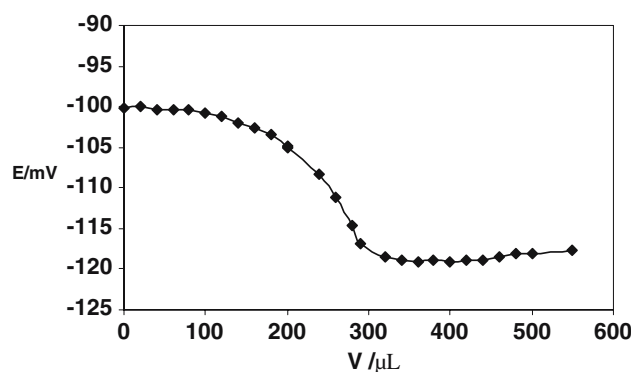
$(1.0 \times 10^{-3}$ M) with a standard solution of EDTA $(1.0 \times 10^{-1}$ M) at a pH about 9.0. As can be, the end point of the titration curve is sharp.

The sensor was applied to direct monitoring of Nd^{3+} in various binary mixtures and the results are summarized in Table 4. The recovery of Nd^{3+} ions is very good (97.7–104.4%). This is due to the relatively good selectivity of the proposed sensor.

Acknowledgement

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Fig. 6. Titration curve.

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