

Application of Pyridine-2-carbaldehyde-2-(4-methyl-1,3-benzothiazol-2-yl)hydrazone as a Neutral Ionophore in the Construction of a Novel Er(III) Sensor

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A piridina-2-carbaldeído-2-(4-metil-1,3-benzotiazol-2-il) hidrazona (PCMHT) pode ser usada como um ionóforo neutro apropriado à preparação de uma membrana sensora a Er(III), com alta seletividade. A composição ótima encontrada foi PCMHT-PVC-KTpCIPB-BA com as razões de 6,0:30,0:5,0:59,0, respectivamente. A resposta Nernstiniana foi de $21,8 \pm 0,5$ mV década⁻¹ para a atividade de Er(III). O intervalo linear encontrado para o sensor foi relativamente grande (de $1,0 \times 10^{-5}$ a $1,0 \times 10^{-2}$ mol L⁻¹). Sua funcionalidade no intervalo de pH entre 2,5 e 12,0 o torna adequado para aplicações analíticas. O limite de detecção mais baixo do sensor foi $5,0 \times 10^{-6}$ mol L⁻¹. A excelente seletividade a Er(III) do sensor proposto, frente aos íons metálicos mais comuns e, especialmente íons lantanídeos, é uma outra vantagem. O sensor foi usado com sucesso como eletrodo indicador na titulação de 25 mL de $1,0 \times 10^{-4}$ mol L⁻¹ de íons Er(III) com $1,0 \times 10^{-2}$ mol L⁻¹ de EDTA. O sensor proposto foi usado na monitoração direta de Er(III) em misturas binárias e na determinação indireta de íons fluoreto em duas preparações de enxágue bucal.

We found that pyridine-2-carbaldehyde-2-(4-methyl-1,3-benzothiazol-2-yl) hydrazone (PCMHT) can be used as a suitable neutral ionophore for preparing an Er(III) membrane sensor with high selectivity. The optimum composition was found to be PCMHT-PVC-KTpCIPB-BA with the ratios of 6.0:30.0:5.0:59.0, respectively. The Nernstian response was of 21.8 ± 0.5 mV decade⁻¹ of Er(III) activity, the linear range of the sensor was found to be relatively wide (from 1.0×10^{-5} to 1.0×10^{-2} mol L⁻¹). Its applicability pH range of 2.5-12.0 seems to make it suitable for analytical applications. The lower detection limit (LDL) of the sensor was 5.0×10^{-6} mol L⁻¹. The excellent Er(III)-selectivity of the proposed sensor with regard to most common metal ions, and especially, lanthanide ions is another advantage. It was successfully used as an indicator electrode for titration of 25 mL of a 1.0×10^{-4} mol L⁻¹ Er(III) ions with a 1.0×10^{-2} mol L⁻¹ EDTA. The proposed sensor was used for direct monitoring of Er(III) in binary mixtures and indirect determination of fluoride ions in two mouth wash preparations.

Keywords: Er(III), ion selective electrode, PVC, pyridine-2-carbaldehyde-2-(4-methyl-1,3-benzothiazol-2-yl)hydrazone

Introduction

It is estimated that the erbium concentration of the earth's crust reaches 24 ppm. Its commercial sources are monazite and bastnasite. Although the conclusion of the investigators is to classify the rare earths as having low acute toxicity rating, the studies of toxicity of various erbium compounds show that when inhaled, taken orally, or injected into the blood stream, erbium salts can cause serious problems.¹

Voltammetry has been used for the determination of trace of erbium in alkali halides. Secondary ion mass spectroscopy and Rutherford back-scattering techniques were used for the analysis of erbium profiles in lithium niobate crystals. Higher order derivative spectrometric procedures were developed for the determination of erbium in selective rare earth mixtures. Recently, preconcentrative ICP-MS and NAA procedures have been developed to ascertain individual rare earth element concentration in seawater samples from various locations.²⁻⁸

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The utility of ion-selective electrodes (ISEs) is being increasingly realized by analytical chemists in view of the rapid growth of industry and technology all over the world as they represent a rapid, accurate and low-cost method of analysis.

The recent introduction of a number of lanthanide selective membrane sensors for La(III),⁹⁻¹⁴ Ce(III),¹⁵⁻¹⁷ Nd(III),¹⁸ Eu(III),¹⁹ Sm(III),^{20,21} Gd(III),²² Tb(III),²³ Dy(III),²⁴ and Yb(III),²⁵ ions based on different noncyclic and macrocyclic ionophores, by our own and other groups, inspired us to try the construction of an Er(III)-selective electrode based on a PCMHT as an ion carrier. The resulting electrode shows to be suitable for the determination of Er(III) concentration in the range of 1.0×10^{-5} mol L⁻¹- 1.0×10^{-2} mol L⁻¹, with a lower detection limit of 5.0×10^{-6} mol L⁻¹ and within pH values between 2.5-12.0. To the best of our knowledge this is the first report on Er(III) membrane sensor.

Experimental

Reagents

Reagent grade benzyl acetate (BA), nitrobenzene (NB), *o*-nitrophenyloctyl ether (NPOE), high relative molecular weight poly vinyl chloride (PVC), potassium tetrakis(*p*-chlorophenyl) borate (KTpCIPB), and tetrahydrofuran (THF) were purchased from Aldrich and used as received. Chloride and nitrate salts of the cations used (from Merck and Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P₂O₅. Triply distilled deionized water was used through out.

Synthesis of pyridine-2-carbaldehyde-2-(4-methyl-1,3-benzothiazol-2-yl) hydrazone

The procedure for the preparation of pyridine-2-carbaldehyde-2-(4-methyl-1,3-benzo-thiazol-2-yl)-hydrazone was to reflux a mixture of 2-hydrazino-4-methyl-1,3-benzo-thiazole (0.01 mol, 1.79 g), pyridine-2-carbaldehyde (0.01 mol, 1.07 g) and catalytic amount of toluene-4-sulfonic acid in benzene (70 mL) for 6 h. Then the solvent was evaporated to 20 mL and the product was obtained as yellow crystals.

mp 208-211 °C, 2.41 g, yield 90%; IR (Shimadzu IR-460 spectrometer) (KBr) ν_{\max} /cm⁻¹: 3165 (NH), 1595, 1549, 1463, 1425, 1356, 1311, 1280, 1254, 1142, 1079, 991, 899, 871, 766, 732; MS (FINNIGAN-MATT 8430 mass spectrometer), *m/z* (%): 268 (M⁺, 70), 239 (20), 225 (5), 190 (100), 164 (40), 148 (15), 136 (25), 121

(10), 105 (15), 92 (20), 78 (15), 65 (12). Anal. Calc. for C₁₄H₁₂N₄S (268.34): C, 62.66; H, 4.51; N, 20.88. Found: C, 62.6; H, 4.6; N, 20.7%. ¹H NMR (90 MHz, DMSO-*d*₃ solution): δ 2.50 (3 H, s, CH₃), 7.00-7.20 (2 H, m), 7.40 (1H, dd, *J* 7.0 and *J* 6.8 Hz, CH), 7.65 (1 H, dd, *J* 7.0 and *J* 2.1 Hz, CH), 7.92 (2 H, m), 8.15 (1 H, s, N=CH), 8.60 (1 H, dd, *J* 6.9 and *J* 1.2 Hz, CH), 12.25 (1 H, br, NH). ¹³C NMR (22.5 MHz, DMSO-*d*₃ solution): 15.97 (CH₃), 119.38, 120.25, 121.66, and 123.44 (4 CH), 126.31 (C), 130.22 and 135.14 (2 CH), 137.77 (C), 147.33 and 148.91 (2CH), 152.46, 156.48, and 166.85 (3 C).

Electrode preparation

The viscous solution that was used for the formation of the membrane was prepared by the mixing 30 mg of powdered PVC, 59 mg of BA and 5 mg of additive KTpCIPB in 5 mL of THF, and 6mg of PCMHT. The resulting low-viscosity mixture was thoroughly mixed and transferred into a glass dish of 2 cm diameter and then its solvent was slowly evaporated to gain an oily concentrated mixture. The membrane was then formed on the tip of a Pyrex tube of (3-5 mm o.d.) and by dipping the tube into the mixture for about 10 s, a transparent membrane of about 0.3 mm thickness was formed. Before being filled with an internal filling solution (1.0×10^{-3} mol L⁻¹ ErCl₃), the tube was pulled out and given enough time to dry at room temperature for about 10 h. The final step was to condition the electrode for 24 h by soaking in a 1.0×10^{-3} mol L⁻¹ Er(NO₃)₃ solution. A silver/silver chloride coated wire was used as an internal reference electrode.

emf measurements

The cell assembly, Ag-AgCl|internal solution (1.0×10^{-3} mol L⁻¹ ErCl₃)|PVC Membrane|test solution|Hg₂Cl₂, KCl (sat.), was used for all measurements.

All potential measurements were carried out by means of a Corning ion analyzer 250 pH/mV meter at 25.0 ± 0.1 °C.

Results and Discussion

Regarding that some neutral ion carriers containing nitrogen and sulfur donor atoms have been reported to be used in construction of highly selective transition and heavy metal ion membrane sensors, such as, La(III),⁹⁻¹⁴ Ce(III),¹⁵⁻¹⁷ Nd(III),¹⁸ Eu(III),¹⁹ Sm(III),^{20,21} Gd(III),²² Tb(III),²³ Dy(III),²⁴ and considering the existence of both nitrogen and sulfur donor atoms in the structure of

PCMHT, it was expected to act as a suitable ion carrier for special transition and heavy metal ions (specially, higher charge density) in the PVC membranes.

Many experimental and theoretical investigations have been carried out to understand better the fundamental interaction between metal ions and neutral molecules and their relationship to molecular recognition. Computational models capable of reliably predicting ligand selectivity in a variety of cations have been shown to be valuable tools for the advancement of practical works.²⁶⁻²⁹ In order to have a clear picture about the selectivity of ligand for various metal ions, in this work, we investigated its binding to Ce³⁺, Th³⁺, Eu³⁺, Sm³⁺, Gd³⁺, Pb²⁺, Cu²⁺ and Er³⁺ ions by using the Extended Hückel semi-empirical calculations. Because system contains atom (Er) which have not been assigned any basis function in *ab initio* calculation, Extended Hückel semi-empirical calculations have been used. The influence of the nature, size and charge of metal ions on the complexation reaction with the neutral ligand is explained on the basis of the calculation of gas-phase binding energies.

Table 1. Interaction energy between metal ions-ligand

Compounds	Interaction energy/ (kcal mol ⁻¹)
Er ³⁺ -ligand	-7308.654
Gd ³⁺ -ligand	-4410.996
Eu ³⁺ -ligand	-3716.814
Th ³⁺ -ligand	-3149.231
Sm ³⁺ -ligand	-3020.702
Ce ³⁺ -ligand	-590.089
Cu ²⁺ -ligand	-5883.444
Pb ²⁺ -ligand	-1389.752
Zn ²⁺ -ligand	-6100.670
Co ²⁺ -ligand	-5846.003
Ni ²⁺ -ligand	-4722.321
Cd ²⁺ -ligand	-3837.167
Hg ²⁺ -ligand	-3808.395

The binding energy of the uncomplexed ligand and its complexes with Er³⁺ and other metal ions were carried out using Hyper Chem software (Version 6.01). The binding energy (ΔE) was calculated using equation 1:

$$\Delta E = \Delta E_{\text{complex}} - (\Delta E_{\text{ligand}} - \Delta E_{\text{cation}}) \quad (1)$$

where, $\Delta E_{\text{complex}}$, ΔE_{ligand} and ΔE_{cation} are the total energies

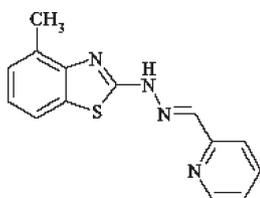


Figure 1. Structure of PCMHT.

of the complex, uncomplexed ligand and metal ion, respectively. Table 1 summarizes the theoretical data relating the stability of the ligand complexes with Ce³⁺, Th³⁺, Eu³⁺, Sm³⁺, Gd³⁺, Pb²⁺, Cu²⁺ and Er³⁺ ions. Inspection of Table 1 reveals that the cation binding energy with ligand shows a pronounced dependence on the nature of metal ions used.

Thus, based on the previous *ab initio* calculation results, ionophore could possibly be used as a suitable ionophore in preparation of an erbium ion-selective membrane electrode. The optimized results revealed that the erbium ion was coordinated with four donor atoms (N and S atoms in the five members ring, N of pyridine ring, and the N in neighbor of NH group).

In the next experiment, PCMHT was used in the construction of membrane microelectrodes for lanthanide ions (Ce³⁺, Th³⁺, Eu³⁺, Sm³⁺, Gd³⁺) and other transition metal ions like Pb²⁺ and Cu²⁺ ions.

This behavior may be due to the result of the selective tendency of the ion carrier against erbium(III) (with relatively high charge density and hydration energy), in comparison to other metal ions and the rapid exchange kinetics of the resulting PCMHT - erbium(III) complex.

Due to the radii of lanthanum ions (from Ce³⁺ to Lu³⁺ with the range of 1.02-0.80 Å, respectively) these elements have different properties such as charge densities and size and hydration energy (from Ce³⁺ to Lu³⁺ with the range of 3370-3760 kJ mol⁻¹).³⁰ Thus, it is possible that by using a suitable ionophore which having the semi-cavity and relatively high flexibility, construct a highly selective lanthanide ion sensors.

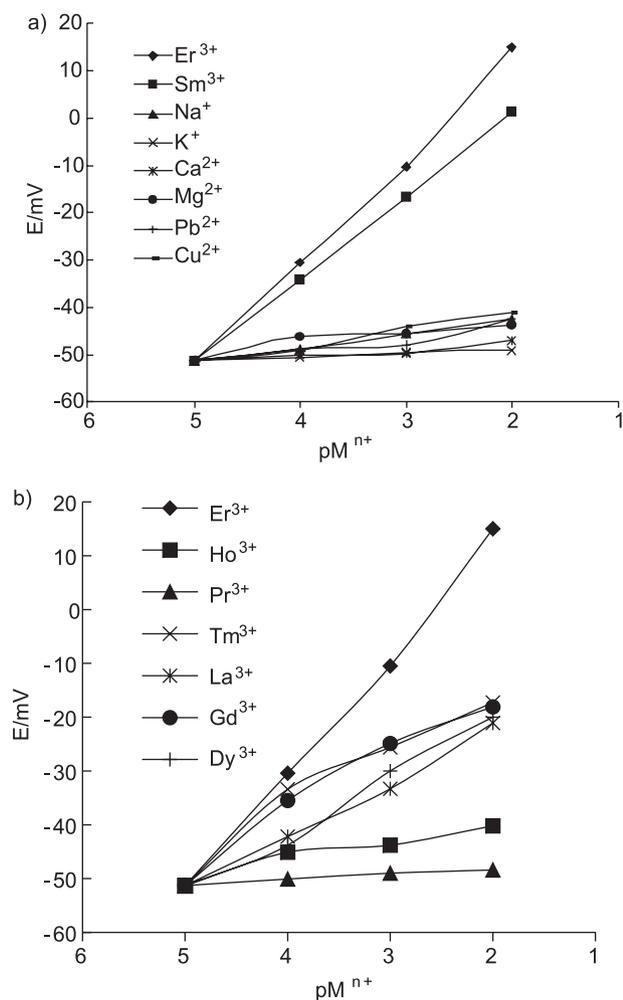
To investigate the possible ions towards which PCMHT is selective, during the next experiments this carrier was used in the construction of membrane sensors for Er³⁺, La³⁺, Pr³⁺, Sm³⁺, Gd³⁺, Dy³⁺, Ho³⁺, Tm³⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Pb²⁺, and Cu²⁺ ions. The best potential responses of the resulting membranes towards the mentioned ions are shown in Figure 2 (a, b). As it is obvious from these figures, among the lanthanide ions tested, Er(III), with the most Nerstian response, can be suitably determined with the PVC membrane sensor based on PCMHT.

This behavior may be considered to be the result of the selective tendency of the ionophore against Er(III) (with relatively low charge density and hydration energy), in comparison to other metal ions, and the rapid exchange kinetics of the resulting PCMHT-Er(III) complex.

The fact that the sensitivity and selectivity obtained for a given ionophore is significantly related to and dependent on the membrane composition and the nature of the solvent mediators and additives used^{31,32} urged us

Table 2. Optimization of membrane ingredients

Membrane	Composition/(%)				Slope/(mV decade ⁻¹)
	PVC	Plasticizer	PCMHT	Additive	
1	30	65, BA	5	-	10.1 ± 0.3
2	30	64, BA	6	-	10.5 ± 0.7
3	30	61, BA	5	4, NaTPB	14.3 ± 0.3
4	30	60, BA	5	5, NaTPB	16.8 ± 0.2
5	30	59, BA	6	5, NaTPB	21.8 ± 0.5
6	30	65, BA	-	5, NaTPB	5.0 ± 0.3
7	30	61, NB	5	4, NaTPB	19.2 ± 0.4
8	30	60, NPOE	6	4, NaTPB	19.6 ± 0.2

**Figure 2.** (a, b) Potential response various metal ion-selective electrodes based on (PCMHT).

to investigate such effects on the behavior of the proposed sensor. To investigate these effects, the nature and amount of the plasticizer and the additive on the potential response of the proposed Er(III) sensor were investigated and the results are summarized in Table 2. These data revealed that the three different plasticizers used, BA, NB, and *o*-NPOE have almost the same results if the optimum composition is used. However, as NB, and *o*-NPOE are

very polar and lead to the extraction of polar interfering ions such as other rare earth ions, which may have negative effects on the selectivity behavior of the sensor, BA was chosen as the solvent mediator. This may seem to lead a poor extraction of Er(III) ion, having a very high charge density by the average-polar solvent, but this seemed to be compensated by the selective complexation of PCMHT with the Er(III) ions. This way, not only was the slope of the sensor response maintained, but its selectivity pattern was also improved.

In addition, one can understand from the data in Table 2 that increasing the amount of the ion carrier up to a value of 6%, the sensitivity increases, while the slope of the resulting emf vs. log Er(III) concentration plot is about two-thirds of the expected Nernstian value (membrane No. 2). However, addition of 5% KTpCIPB (membrane No. 5) will increase the sensitivity of the electrode response to a great extent. The fact that the presence of lipophilic anions in the composition of cationic-selective membrane sensors not only diminishes the ohmic resistance and enhances the potential behavior and selectivity, but also, in poor extraction capacities, increases the sensitivity of the membrane electrodes has long been known.^{33,34}

The potential response of the sensor was evaluated using the optimum composition of all ingredients, while lacking the ionophore and it was found that under these conditions the response of the sensors falls to very low values of 5.0 mV decade⁻¹, indicating that the sensitivity of the sensor is mainly due to the complexing behavior of PCMHT.

The optimum equilibration time for the membrane electrode, after which it generates stable potentials when placed in contact with Er(III) solutions, was found to be 24 h. The critical response characteristics of the Er(III) sensor were assessed according to IUPAC recommendations.³⁵ The potential response of the membrane at varying concentration of Er(III) ions (Figure 3) indicates a rectilinear range from 1.0×10^{-5} - 1.0×10^{-2} mol L⁻¹. The slopes of the calibration curves

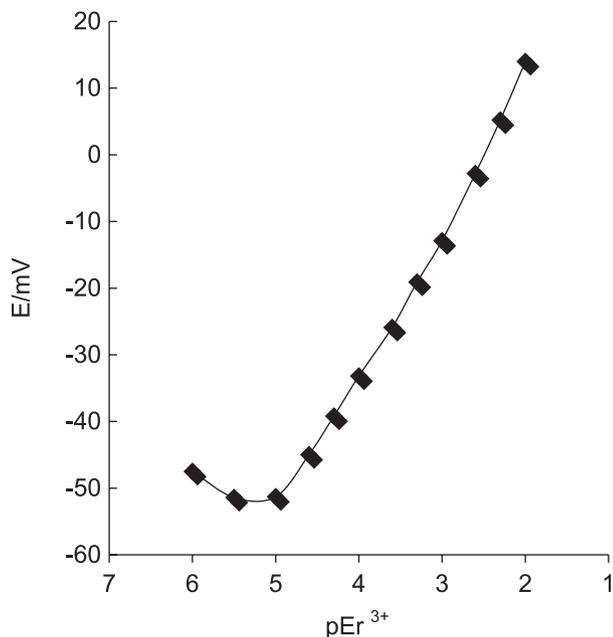


Figure 3. Calibration curve of the Er(III) sensor of membrane.

were 21.8 ± 0.5 mV decade⁻¹ of Er(III) concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 5.0×10^{-6} mol L⁻¹.

The influence of the pH on the response of the proposed membrane sensor to a 1.0×10^{-4} mol L⁻¹ Er(III) solution was studied over a pH range from 1.5 to 13.0 and the results are shown in Figure 4. It is obvious that the potential remained constant from pH 2.5 to 12.0, beyond which drastic drifts were observed. The observed drift at higher pH values could be due to the formation of insoluble Er(OH)₃ ion in the solution. It is noteworthy that, in such acidic solution, the ionophore used could be protonated to some extent, which results in an improper functioning of the membrane electrode to the Er(III) ion concentration.

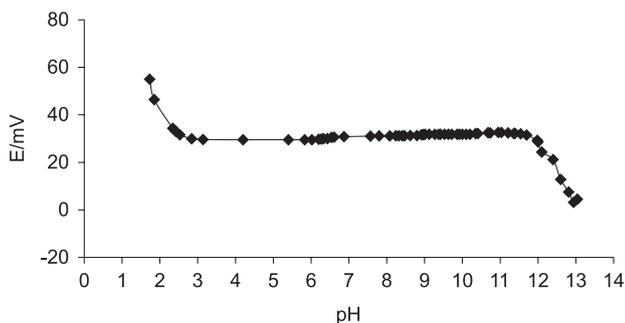


Figure 4. Effect of the pH of test solution (1.0×10^{-4} mol L⁻¹) on the potential response of the Er(III) ion-selective electrode.

One of the most important characteristics of any membrane sensor is its relative response for the primary ion over other ions present in solution, usually

expressed in terms of potentiometric selectivity coefficients. In this work, matched potential methods³⁶ was used for determination of selectivity coefficients of the sensor. According to MPM, a specified activity (concentration) of the primary ions (A, 5.0×10^{-4} - 1.0×10^{-3} mol L⁻¹ of Er(III) ion) is added to a reference solution (1.0×10^{-5} mol L⁻¹ of Er(III) ion) and the potential is measured. In a separate experiment, interfering ions (B, 1.0×10^{-3} - 1.0×10^{-2} mol L⁻¹) are successively added to an identical reference solution, until the measured potential matches the one obtained before by adding primary ions. The matched potential method selectivity coefficient, K_{MPM} , is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K_{MPM} = a_A/a_B$.

The resulting selectivity coefficients values are given in Table 3. It is immediately obvious from these data, that the proposed Er(III) sensor is highly selective with respect to the most of cations. In the case of lanthanide ions (except for Sm(III), and La(III) with the selectivity coefficient of 3.0×10^{-1} and 2.0×10^{-2}) the selectivity coefficients are in the order of 2.1×10^{-3} or smaller, which seems to indicate that the Er(III) ions can be determined in the presence of other lanthanide ions. The selectivity coefficients for other cations (Na⁺, K⁺, Mg²⁺, Ca²⁺, Cu²⁺, and Pb²⁺) are smaller than 3.1×10^{-3} and they can not disturb the functioning of the Er(III) membrane electrode. The surprisingly high selectivity of the membrane electrode for Er(III) ions over other cations used most probably arises from the strong tendency of the carrier molecule for Er(III) ions.

Table 3. Selectivity coefficients of various interfering cations for the membrane with the optimum composition

Ion	K_{set}
Dy ³⁺	3.2×10^{-2}
Gd ³⁺	3.7×10^{-2}
Tm ³⁺	3.7×10^{-2}
Sm ³⁺	3.0×10^{-1}
Pr ³⁺	1.01×10^{-3}
Ho ³⁺	3.5×10^{-3}
La ³⁺	3.0×10^{-2}
Ca ²⁺	2.1×10^{-3}
Na ⁺	1.0×10^{-3}
Pb ²⁺	1.4×10^{-3}
K ⁺	1.1×10^{-3}
Cu ²⁺	1.5×10^{-3}
Mg ²⁺	1.7×10^{-3}

Conditions: The concentration of the primary ions (A): 5.0×10^{-4} - 1.0×10^{-3} mol L⁻¹ of Er(III) ion; and the concentration of the interfering ions (B): 1.0×10^{-3} - 1.0×10^{-2} mol L⁻¹.

The dynamic response time of the sensor, being another very important parameter in the evaluation of a sensor, was studied by varying the concentration of a solution

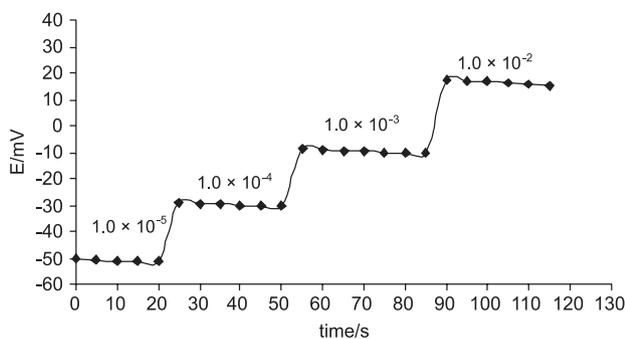


Figure 5. Dynamic response time of the electrode for step changes in the concentration of Er(III) solution.

from 1.0×10^{-5} mol L⁻¹ to 1.0×10^{-2} mol L⁻¹ and recording the times needed for the sensor to reach ± 1 mV of its equilibrium potential (Figure 5). The response time of the sensor was found to be between 5-8 seconds, depending on the concentration of the test solution.

The proposed Er(III) membrane electrode was found to work well under laboratory conditions. It was applied as an indicator electrode for the titration of 20.0 mL of 1.0×10^{-3} mol L⁻¹ of Er(III) solution with 1.0×10^{-1} mol L⁻¹ of standard EDTA and the resulting titration curve is shown in Figure 6. As it can be seen from Figure 6, the amount of Er(III) ions can be determined with good accuracy.

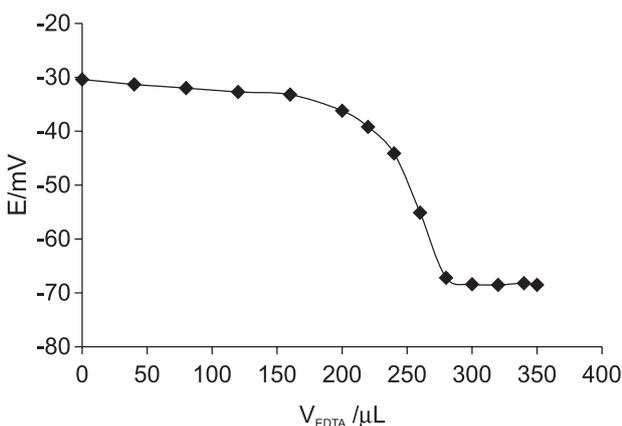


Figure 6. Potentiometric titration curve of 25 mL of a 1.0×10^{-4} mol L⁻¹ Er(III) solution, with a 1.0×10^{-4} mol L⁻¹ EDTA using the proposed membrane sensor as an indicator electrode.

The proposed Er(III) membrane sensor was also successfully used to the determination of fluoride ion concentration in three mouth wash samples. 1.0 g of each sample was taken and diluted with distilled water in a

Table 4. The results of the determination of fluoride ion concentration in mouth wash solution samples

Chimia Daru Co. Tehran, Iran	Labeled/(%)	Found/(%)
Sample 1	2.0	(2.06 ± 0.07)
Sample 2	0.2	(0.21 ± 0.05)
Sample 3	1.0	(0.98 ± 0.05)

100 mL flask and titrated with a Er³⁺ solution (1.0×10^{-3} mol L⁻¹) and the results of triplicate measurements are shown in Table 4. As it can be seen from Table 4, there is a good agreement between the declared fluoride content and the determined values.

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Received: May 17, 2006

Web Release Date: March 9, 2007