

Full Paper

Taguchi OA₂₅ Orthogonal Array Design for the Optimization of La³⁺-Selective Electrode Prepared by Sol-gel Technique

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Abstract- A sol-gel electrode, based on ethyl 1,2,3,4-tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxylate (ETMPTC) as a neutral ionophore, was successfully developed for the detection of La³⁺ in aqueous solutions. The electrode responds to La³⁺ ion with a sensitivity of 19.7±0.1 mV/ decade over the range 1.0×10⁻⁸–1.0×10⁻¹ M and in a pH range of 3.0–10.0. The sol-gel electrode shows detection limit of 3.5×10⁻⁹ M. The influence of membrane composition, the pH of the test solution, and the interfering ions on the electrode performance was investigated. The proposed electrode shows good discrimination of La³⁺ ion from several cations. The effect of temperature on the electrode response showed that the temperature higher than 65°C deteriorates the electrode performance. The electrode was found to work well under laboratory conditions. This sensor not only was used as an indicator electrode in potentiometric titration of lanthanum ion against EDTA but also was used to determination of La³⁺ concentration in the presence of certain interfering ions.

Keywords- La³⁺-Selective Electrode, Organic–Inorganic Sol–gel Matrices, Neutral Carrier, Potentiometry

1. INTRODUCTION

Research involving rare earths monitoring in the environment has become an increasingly popular area in the research community in the last 20 years. The rare earths are considered only slightly toxic according to the Hodge–Sterner classification system and thus can be handled safely with ordinary care [1].

Against this viewpoint, Lanthanum ions accelerate the phosphate ester hydrolysis binding by 13 orders of magnitude. This suggests that the phosphate diester in DNA may also suffer such destruction. Thus, lanthanum should be situated among the class of highly toxic metal ions that are potentially effective against micro and higher organisms. On the other hand, Lanthanum chloride manifests as antitumor. Therefore, Lanthanum is both toxic and essential [2].

The introduction of new ion-selective membrane electrodes has played a fundamental role in the development of potentiometric measurements. In the area of membrane-based ISEs, emphasis has been focused on the development of new ionophores and on the composition of the membrane phase, aiming at enhancing the potentiometric responses of the ISEs [3].

The determination of La^{3+} ion has been carried out directly or indirectly by a variety of instrumental methods. These methods include flame photometry [4], atomic absorption spectrometry, inductively coupled plasma-mass spectrometry (ICP-MS), ion chromatography [5], etc. In spite of excellent precision and accuracy of mentioned methods, all of them suffer from some limitations such as: high cost, time consuming and tedious requirement of sample preparation. In these circumstances, a convenient potentiometric determination by ion-selective electrode is beneficial. This is due to their several advantages, such as speed, ease of preparation, simple instrumentation, relatively fast response, wide dynamic range, selectivity and low cost. ISEs are also appropriate for on-site monitoring. Therefore, the analysis by ISEs is a preferred procedure for those ions for which selective electrodes are available [6].

Sol-gel chemistry involves the fabrication of materials through the hydrolysis and condensation of suitable alkoxysilane precursors. Due to the inherent low temperature process, sol-gel technology has gained great popularity in the field of electrochemical sensors. The driving force for these efforts is that sol-gel chemistry provides a relatively simple way to incorporate recognition species in a stable host environment [7–10].

In fact, the sol-gel technology provides a unique means to prepare inorganic and organic-inorganic hybrid materials for use in sensing devices. The simple doping of the sol-gel solution with the desired compound is the most popular technique for immobilization because of its generality, simplicity, and retention of the properties of the compound in the immobilized state. This can be readily achieved by simply doping the reagent in to the sol prior to its gelation, as demonstrated by Avnir et al. [11] and

Collinson [12]. In the recent years several PVC-based La^{3+} -selective electrode has been reported [2, 13-20]. According to many advantages of the sol-gel derived materials, we decided to add our highly selective ionophore ethyl 1,2,3,4-tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxylate (ETMPTC) to the sol for incorporation in a stable host matrix. To the best of our knowledge, sol-gel method has not previously been used in the development of a La^{3+} -selective electrode.

In order to determine the optimum condition of preparation, Qualitek-4(QT4) software package [21] was used. QT4 can design simple of mixed level experiments based on Taguchi method .

The calculations of interaction energy between metal ions-ionophore compounds were performed with the second-order Møller–Plesset (MP2) perturbation theory [22]. All these calculations were performed using the Gaussian 98 package.

2. EXPERIMENTAL

2.1. Apparatus and reagents

All potentiometric measurements were made with a pH/mV meter ion analyzer (Metrohm, 691) in stirred solutions. In all instances, a saturated calomel electrode (Azar Electrode Co., Urmia, Iran) was used in conjunction with the respective indicator electrode. A Haake Model FK2 circulation water bath was used to control the temperature of the test solution. A digital pH meter (Corning Model 125) was used for measuring pH. All reagents used were of analytical reagent grade. Oleic acid (OA), ethanol ($\text{C}_2\text{H}_5\text{OH}$), tetraethoxysilane (TEOS), diethoxydimethylsilane (DEDMS) were obtained all from Merck, Fluka or Aldrich chemical company. Chloride and nitrate salts of all other cations (all from Merck) were of the highest purity available and used without any further purification. Double distilled deionized water was used throughout.

2.2. Synthesis of ionophore ETMPTC

ETMPTC was synthesized under solvent-free conditions: A mixture of the substrate (1 mmol), β -keto ester (1.2 mmol) urea or thiourea (1.2 mmol) and $\text{Fe}(\text{HSO}_4)_3$ (1 mmol) was heated in an oil bath (100 °C) for 2 h. After completion (monitored by TLC), the reaction was cooled to room temperature and poured onto crushed ice and the solid product separated was filtered and recrystallised from ethanol.

The product has m.p.=208-210°C and its structure is shown in Fig. 1. FT-IR (KBr), $\text{V}(\text{Cm}^{-1})$: 3440(m), 3240(m), 3105(w), 2990(w), 1725(s), 1700(s), 1640(s), 1450(s), 1415(s), 1310(m), 1285(m), 1220(m), 1085(s), 780-755(s), 700(w), $^1\text{HNMR}(\text{CDCl}_3)$, $\delta(\text{ppm})$: 1.19-1.21(t,3H), 2.39(s,3H), 4.09-4.15(m,2H), 5.44-5.45(d,1H), 5.57(bs,1H), 7.29-7.55(m,

5H), 7.55(bs,1H), ^{13}C NMR(CDCl_3 , 125MHZ): 14.49, 18.89, 56.15, 60.3, 101.81, 126.96, 128.4, 129.62, 144.22, 146.74, 153.97, 166.01.

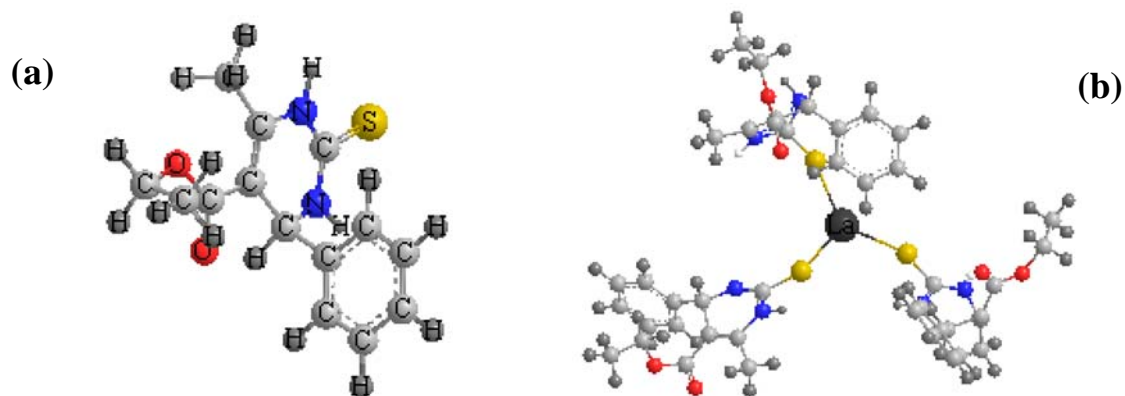


Fig. 1. Optimal conformation of ionophore before (a) and after (b) complexation with La^{3+}

2.3. Preparation of sol-gel-based electrodes

Polymerization and drying processes for the sol–gel membranes were performed according to previously reported details [23].

TEOS (90 μL), DEDMS (260 μL), ethanol (270 μL), 0.1 M HCl aqueous solution (90 μL), additive OA (6 mg) and ionophore ETMPTC (3 mg) were mixed in a sample tube, and the mixture was then allowed to stand at 70 $^{\circ}\text{C}$ for 2 h to afford a viscous sol-gel solution. The clean graphite electrode was then coated by viscous sol-gel solution and allowed to dry for 48 h at room temperature. The electrodes were then rinsed with water and conditioned in 1.0×10^{-1} M La^{3+} solution.

2.4. Potentiometric measurements

The sol-gel membranes containing ETMPTC were equilibrated with 1.0×10^{-1} M La^{3+} solution for 48 h, the optimum time necessary for generating reproducible and stable potentials with low noise when interposed between the test solution and graphite rod. The conditioned electrodes were used as the measuring electrode in conjunction with saturated calomel electrode (SCE). All measurements were performed at ambient temperature (25 ± 1 $^{\circ}\text{C}$) using a pH/mV meter. The performance of each electrode was investigated by measuring its potential in solutions with concentrations ranging from 1.0×10^{-10} to 1.0×10^{-1} M by serial dilution at constant pH.

The potentiometric cell used was:

$\text{Hg}, \text{Hg}_2\text{Cl}_2, \text{KCl (saturated)} \parallel \text{sample solution} \mid \text{sol-gel membrane} \mid \text{C electrode (graphite)}$

The EMF readings were made after the potential reached a constant value. Selectivity coefficients were obtained by using the matched potential method (MPM) [24]. Also, for the calibration curve, concentration instead of activity was used.

3. RESULTS AND DISCUSSION

3.1. Theoretical calculations

Some ab initio quantum mechanical calculations were carried out using second-order Møller–Plesset (MP2) perturbation theory with Gaussian 98 program package. The lan12dz basis set for all atoms was used for optimizing molecules. The optimized structures of ionophore and its La³⁺ complex are shown in Fig. 1.

3.2. Optimization of sol-gel membranes preparation

Taguchi's design methodology has wide ranging application. In the Taguchi method the results of the experiments are analyzed to achieve one or more of the following three objectives:

1. To establish the best or the optimum condition for a product or a process
2. To estimate the contribution of individual factors
3. To estimate the response under the optimum conditions

The power and popularity of the method lies in the discipline rather than the technique itself. The composition of sol-gel membrane was optimized by Taguchi method in order to achieve better slope. Table 1 summarizes the factors and their levels in membrane composition optimization. The resulting values of the slope are shown in Table 2.

Table 1. The factors and their levels in membrane composition optimization

Levels	Factors					
	TEOS (μL)	DEDMS (μL)	Ethanol (μL)	HCl (μL)	OA (mg)	ETMPTC (mg)
1	60	230	250	60	2	4
2	70	240	260	70	3	5
3	80	250	270	80	4	6
4	90	260	280	90	5	7
5	100	270	290	100	6	8

Table 2. Optimization of membrane ingredient by Taguchi method

No.	TEOS (μL)	DEDMS (μL)	Ethanol (μL)	HCl (μL)	OA (mg)	ETMPTC (mg)	Slope (mV/decade)	Linear range (μM - M)
1	60	230	250	60	2	4	17.9	0.10–0.010
2	60	240	260	70	3	5	18.0	1.0–0.10
3	60	250	270	80	4	6	18.5	1.0–0.10
4	60	260	280	90	5	7	18.4	0.50–0.50
5	60	270	290	100	6	8	18.8	0.80 – 0.10
6	70	230	260	80	5	8	18.9	0.50–0.010
7	70	240	270	90	6	4	18.0	0.10–0.10
8	70	250	280	100	2	5	18.2	5.0–0.25
9	70	260	290	60	3	6	18.6	0.10–0.10
10	70	270	250	70	4	7	18.5	0.25–0.10
11	80	230	270	100	3	7	18.9	0.50–0.50
12	80	240	280	60	4	8	18.5	0.10–0.10
13	80	250	290	70	5	4	18.2	0.25–0.010
14	80	260	250	80	6	5	18.8	0.10–0.050
15	80	270	260	90	2	6	19.0	0.50 – 0.10
16	90	230	280	70	6	6	19.5	0.10–0.50
17	90	240	290	80	2	7	19.2	1.0–0.010
18	90	250	250	90	3	8	19.7	0.010–0.10
19	90	260	260	100	4	4	19.5	0.10–0.10
20	90	270	270	60	5	5	19.3	1.0–0.10
21	100	230	290	90	4	5	20.2	0.10–0.10
22	100	240	250	100	5	6	20.3	0.10–0.10
23	100	250	260	60	6	7	20.4	0.50–0.010
24	100	260	270	70	2	8	20.2	0.50–0.10
25	100	270	280	80	3	4	20.3	0.10–0.010

3.3. The pH effect

The pH influence of the test solution (1.0×10^{-3} M) on the potential response of the sol-gel membrane sensor (membrane no. 18) was tested in the pH range 1.0–13.0. The pH of solutions was adjusted with either HCl or NaOH solutions. It can be seen from Fig. 2 that the potentials remain constant in the pH range 3.0–10.0, but below pH 3, the change in the potential is due to co fluxing of hydrogen ions and above pH 10, the variation of potential may be due to formation of some hydroxyl complex of the La^{3+} ions in the solution.

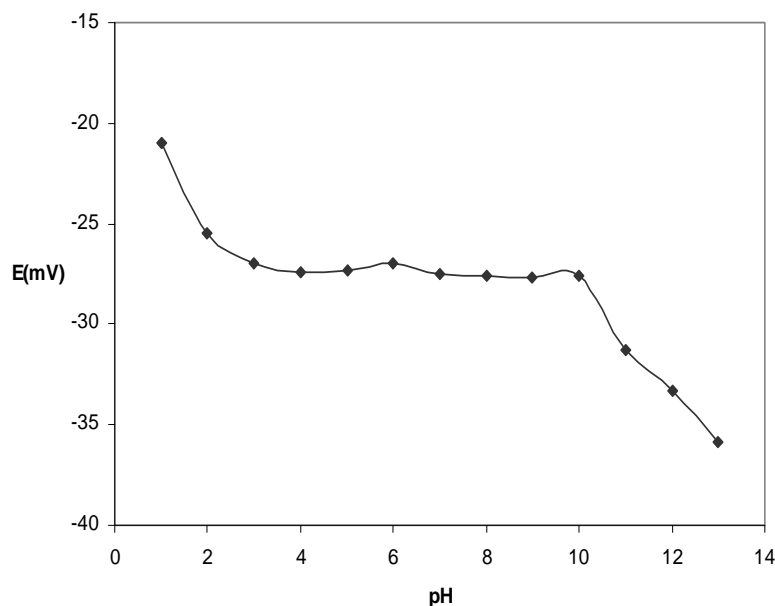


Fig. 2. Effect of pH at 1.0×10^{-3} M La^{3+} solutions on the potential response of La^{3+} -selective sol-gel membrane no. 18 at 25 °C

3.4. Potentiometric selectivity

The basic parameter characterizing the analytical properties of each new electrode is its selectivity coefficient. The influence of interfering ions on the response behavior of ion-selective membrane electrode is usually described in terms of selectivity coefficient ($k_{\text{La},j}^{\text{pot}}$). The potentiometric selectivity coefficients $k_{\text{La},j}^{\text{pot}}$ of lanthanum electrode were evaluated by matched potential method [24].

The resulting values of the selectivity coefficients are summarized in Table 3. Clearly, for all diverse ions used, the selectivity coefficients are in the order of 10^{-4} or smaller, indicating they would not significantly disturb the La^{3+} ion-selective electrode function. Comparison of the selectivity of the most recently described Lanthanum ion selective electrodes (Table 4) with our La^{3+} -selective sol-gel electrode reveals that, the present electrode exhibits a better selectivity, especially in the presence of Pr^{3+} , Gd^{3+} , Cu^{2+} and Yb^{3+} cations.

3.5. Response time and lifetime

The response time of a sensor is one of the most important factors in its evaluation. In this study, to measure the practical response time of the La^{3+} -selective sol-gel membrane sensor the concentration of the test solution was changed from 1.0×10^{-6} M to 1.0×10^{-3} M. The results showed that electrodes reach the equilibrium response in a short time of about 6 s. The reproducibility of the slope of calibration graphs was within ± 0.5 mV/decade over a period of six months ($n=18$).

Table 3. Selectivity coefficients ($k_{La,j}^{pot}$) of various ions with La³⁺-selective electrode, determined by MPM

Interfering ion	$k_{La,j}^{pot}$	Interfering ion	$k_{La,j}^{pot}$
Na ⁺	1.5×10^{-6}	Fe ³⁺	9.3×10^{-5}
Al ³⁺	4.0×10^{-5}	Yb ³⁺	2.7×10^{-5}
Cr ³⁺	3.0×10^{-4}	Th ⁴⁺	7.1×10^{-6}
Tb ³⁺	1.0×10^{-4}	ZrO ²⁺ ^a	8.9×10^{-4}
Nd ³⁺	2.5×10^{-4}	Gd ³⁺	2.0×10^{-5}
Zn ²⁺	2.5×10^{-6}	Pr ³⁺	8.7×10^{-4}
Cd ²⁺	4.0×10^{-5}	Sm ³⁺	6.2×10^{-5}
Mn ²⁺	5.0×10^{-6}	Pb ²⁺	5.0×10^{-5}
Cu ²⁺	1.8×10^{-6}	Hg ⁺	5.5×10^{-4}
Bi ³⁺	4.7×10^{-4}	Ba ²⁺	1.0×10^{-6}
Sn ²⁺	8.5×10^{-6}	Ni ²⁺	3.8×10^{-6}

^a Various hydroxide species exist simultaneously

Table 4. Comparison of the selectivity coefficient of the best La³⁺ sensor with the proposed sensor

Ion	$-\log k_{La,j}^{pot}$								
	Ref. 2	Ref. 13	Ref. 14	Ref. 16	Ref. 17	Ref. 18	Ref. 19	Ref. 20	This work
Pr ³⁺	2.6	---	1.7	---	---	---	---	---	3.06
Gd ³⁺	3.9	---	---	---	4.38	---	4.4	3.3	4.70
Cu ²⁺	5.2	1.77	2.5	2.85	4.30	1.7	---	3.4	5.75
Yb ³⁺	3.2	---	1.9	---	4.19	---	---	---	4.57

3.6. Effect of temperature

Drift of changes of electrode performance with temperature, at test solution temperatures 10, 20, 30, 40, 50, 55, 60, 65 and 70 °C for the La³⁺-selective sol-gel electrode was studied. The electrode exhibits good Nernstian behavior in the temperature range (10–65 °C). At higher temperatures, the slope of electrode deviates from a good

Nernstian behavior. This behavior maybe due to the disturbances occurring in phase boundary equilibrium at the membrane layer test solution [25].

The standard cell potentials (E° cell), were determined at different temperatures from the respective calibration plots as the intercepts of these plots at $pLa=0$, and were used to determine the isothermal temperature coefficient (dE°/dt) of the cell with the aid of the following equation [26]:

$$E^{\circ} \text{ cell} = E^{\circ} \text{ cell}(25^{\circ}\text{C}) \pm (dE^{\circ}/dt)_{\text{cell}}(t-25)$$

Plot of E° cell versus $(t-25)$ produces a straight line, which its slope was taken as the isothermal temperature coefficient of the cell. It amounts to $0.00054 \text{ V}^{\circ}\text{C}$. The standard potentials of the reference electrode ($\text{Hg}/\text{Hg}_2\text{Cl}_2$; KCl (saturated)) were calculated using the following equation:

$$E^{\circ} \text{ Hg}/\text{Hg}_2\text{Cl}_2 = 0.241 - 0.00066(t-25)$$

The values of the standard potentials of La^{3+} -selective electrode were calculated at the different temperatures from the following relation:

$$E^{\circ} \text{ cell} + E^{\circ} \text{ reference} = E^{\circ} \text{ electrode}$$

Plot of E° electrode versus $(t-25)$ produces a straight line. The slope of the line was taken as the isothermal temperature coefficient of our Lanthanum selective electrode. It equals to $0.00021 \text{ V}^{\circ}\text{C}$. The small values of $(dE^{\circ}/dt)_{\text{cell}}$ and $(dE^{\circ}/dt)_{\text{electrode}}$ reveal the high thermal stability of the electrode within the investigated temperature range.

4. ANALYTICAL APPLICATION

The proposed sol-gel electrodes were found to work well, under laboratory conditions. It should be noted that the La^{3+} selective membrane electrode not only can be used for direct determination of the La^{3+} ions but also it was found useful as an indicator electrode in titration of La^{3+} ions in aqueous solutions .

Several spiked samples were prepared by adding aliquots (a few mL) of La^{3+} solution to Pr^{3+} , Cr^{3+} , Tb^{3+} and Hg^{+} solutions and the results are shown in Table 5. The recovery and relative standard deviation values given in the table were calculated from eight determinations. The results, given in Table 5, indicate the high accuracy and precision of the present work.

In the next step, a 50 ml solution of La^{3+} ($1.0 \times 10^{-3} \text{ M}$) was titrated against EDTA solution ($1.0 \times 10^{-2} \text{ M}$) at pH 10 using ammonia buffer, and the potentials obtained are plotted in Fig. 3. The titration plot is not conventional sigmoid-type because the sensor, though selective towards La^{3+} , is not specific to it and responds to a small extent to other ions. This type of behavior is characteristic for many ISEs, which are not specific to the

primary ion and have been used to determine the concentration of primary ions by potentiometric titration [27]. Thus, the present sensor might be used as an indicator electrode for determining La^{3+} by potentiometric titration.

Table 5. Potentiometric determination of La^{3+} in aqueous solutions in presence of interfering ion(s) a by the standard addition method, at 25 °C

Sample	La^{3+} concentration (M)/added	La^{3+} concentration (M)/ found	Recovery (% of nominal value)	R.S.D. (%)
La^{3+} , Pr^{3+}	5.00×10^{-4}	5.20×10^{-4}	104	3.1
La^{3+} , Cr^{3+}	5.00×10^{-4}	4.85×10^{-4}	97	3.0
La^{3+} , Tb^{3+}	5.00×10^{-4}	4.90×10^{-4}	98	3.2
La^{3+} , Hg^+	5.00×10^{-4}	4.80×10^{-4}	96	2.8
La^{3+} , Tb^{3+} , Hg^+	5.00×10^{-4}	5.20×10^{-4}	104	3.2
La^{3+} , Pr^{3+} , Cr^{3+}	5.00×10^{-4}	4.75×10^{-4}	95	3.3
La^{3+} , Pr^{3+} , Cr^{3+} , Hg^+	5.00×10^{-4}	5.15×10^{-4}	103	3.5
La^{3+} , Pr^{3+} , Cr^{3+} , Hg^+ , Tb^{3+}	5.00×10^{-4}	4.80×10^{-4}	96	3.6

^aThe concentration of interfering ion(s) in each sample: 1.0×10^{-4} M

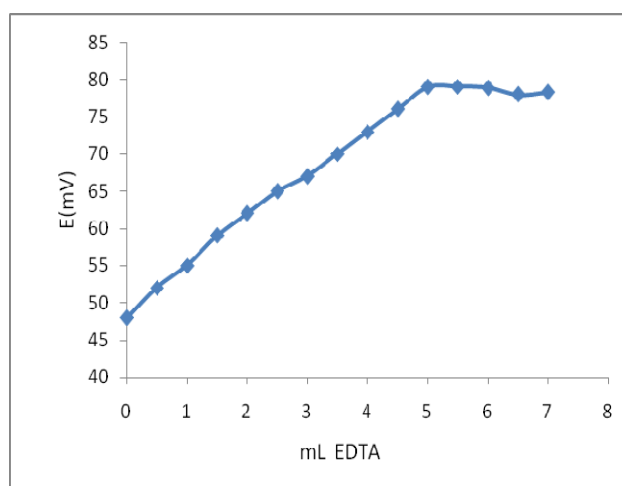


Fig. 3. Potentiometric titration plot of 1.0×10^{-3} M La^{3+} solution (50 ml) with EDTA (1.0×10^{-2} M)

In order to investigate the analytical performance of the proposed potentiometric method in real samples, the sol-gel electrode was applied to the determination of La^{3+} content in pharmaceutical samples. 1.0-2.0 g of each sample was taken and diluted by distilled water, in a 10.0 mL volumetric flask. The resulting solution was titrated with a La^{3+} solution (1.0×10^{-4} M). The results are summarized in Table 6. As is seen from the table, there is a satisfactory agreement between the declared fluoride content and the determined values by the La^{3+} sensor and the commercial solid state fluoride electrode. Therefore, it can be concluded that, the proposed electrode may have applications in the pharmaceutical analysis of La^{3+} .

Table 6. Fluoride determination in the different mouth washes samples

Sodium fluoride mouth wash solution (Shahre Daru Co., Tehran, Iran)*	Labeled (%)	Found (%)
Sample no. 1	0.20	0.19±0.05
Sample no. 2	0.20	0.20±0.08

5. CONCLUSION

The results of the present work show that sol-gel electrodes based on ethyl 1,2,3,4-tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxylate (ETMPTC) reveal high sensitivity and selectivity for lanthanum ion. This sensor acts in a neutral carrier mechanism and show Nernstian responses over a wide range of La^{3+} concentration. The proposed sol-gel sensor reveals excellent selectivity for La^{3+} over a wide variety of alkali, alkaline earth, some transitions and heavy metal ions. Analytical features of the electrode are either comparable or better than those previously reported. The thermal stability and performance of the electrode is adequate within the tested temperature of 10–65 °C. Practical pH range, lower detection limit, higher thermal stability, high sensitivity and accuracy of the proposed sol-gel sensor make it a superior device both compared to other sensors used for the determinations of La^{3+} ion.

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