Novel Tm(III) Membrane Sensor Based on 2,2'-Dianiline Disulfide and Its Application for the Fluoride Monitoring of Mouth Wash Preparations

Mohammad Reza Ganjali,* Parviz Norouzi, Atefeh Tamaddon,† and Syed Waqif Husain‡

Center of Excellence in Electrochemistry, Department of Chemistry, University of Tehran, Tehran, Iran
**E-mail: ganjali@khayam.ut.ac.ir*
†Department of Chemistry, Science and Research Unit, Islamic Azad University, Tehran, Iran
‡Faculty of Chemistry, University of Tarbiat Moallem, Tehran, Iran

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In this work the construction of a novel poly(vinyl chloride) membrane sensor based on 2,2'-dianiline disulfide (DADS) as a neutral carrier, *o*-nitrophenyloctyl ether (NPOE) as a plasticizer and sodium tetraphenyl borate (NaTPB) as an anionic site with unique selectivity towards Tm(III) ions is reported. The electrode has a linear dynamic range between 1.0×10^{-6} and 1.0×10^{-2} M, with a nice Nernstian slope of 19.5 ± 0.3 mV per decade and a detection limit of 4.0×10^{-7} M at the pH range of 4.8-8.5. It has a very fast response time (<15 s) in the whole concentration range, and can be used for at least 4 weeks without any considerable divergence in the electrode potentials. The proposed sensor revealed comparatively good selectivity with respect to most common metal ions, and especially lanthanide ions. It was used as an indicator electrode in the potentiometric titration of Tm(III) ions with EDTA and in direct determination of concentration of Tm(III) ions in binary mixtures. It was also applied in determination of fluoride ions in mouth wash preparations.

Key Words : Tm(III), Sensor, Potentiometry, PVC, 2,2'-Dianiline disulfide

Introduction

Thulium is the least abundant of the rare earths and its metal is easy to work, has a bright silvery-gray luster and can be cut by a knife. The element is never found in nature in pure form, but it is found in small quantities in minerals with other rare earths. It is principally extracted from monoazite (~0.007% thulium) ores found in river sands through ion-exchange. Thulium-silica fiber lasers are used for soft and hard tissue ablation.[1] Thulium doped fiber amplifiers (TDFAs) have unique behavior in photonic networks,[2] and thulium complexes are used as emitting materials in electroluminescence devices.[3]

Thulium and other lanthanides are widely distributed in low concentrations throughout the earths crust. The vapors or dusts of these elements are very toxic when inhalated.

The main methods for the low-level monitoring of Tm(III) and other lanthanide ions in solutions are ICP-MS and ICP-AES, spectrophotometry, and spctrofluorimetry. X-ray fluorescence spectrometry, isotope dilution mass spectrometry, neutron activation analysis, etc, are also used in some laboratories. Some electrochemical approaches have also been found in the literature.[4,5] Most of these methods are either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories.

Potentiometric membrane sensors have been shown to be very effective tools for the analysis of a wide variety of cations and anions. They are very simple to use, inexpensive, and capable of reliable responses in a wide concentration range. A wide variety of chemically, clinically or environmentally important analytes are now routinely monitored using ion-selective sensors based on impregnated polymeric membranes.[6]

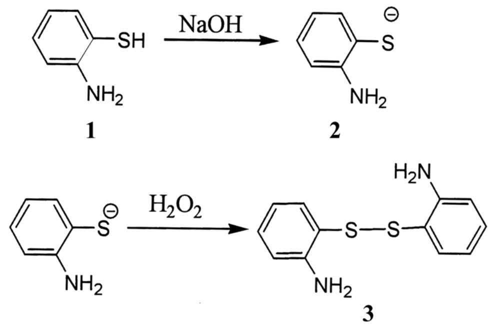
Recently, a number of lanthanide membrane sensors for La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) and Yb(III) based on different ion carriers have been reported.[7-38] In this work we wish to introduce a novel Tm(III) membrane sensor based on DADS for the fast direct monitoring of Tm(III) ions and indirect determination of fluoride ions in three mouth wash samples.

Experimental Section

Reagents. PVC of high relative molecular weight, benzyl acetate (BA), dibuthyl phthalate (DBP), *o*-nitrophenyloctyl ether (NPOE), tetrahydrofuran (THF), sodium tetraphenyl borate (NaTPB), chloride and nitrate salts of cations were of the highest purity available from Merck, Aldrich and Fluka, and were used without further purification, except THF, which was distilled before use. All aqueous solutions were prepared with de-ionized, distilled water. The pH adjustments were made with dilute nitric acid and potassium hydroxide.

Synthesis of 2,2'-dianiline disulfide. 2-Aminothiophenol **1** (2.34 g, 18.7mmol) was dissolved in a concentrated sodium hydroxide solution (NaOH) at 75-80 °C. Then 30% hydrogen peroxide (0.6 mL, 18.7 mmol) is added dropwise to the flask containing 2-Aminothiophenolate **2**, during two hours the temperature of the reaction mixture is maintained at 65-70 °C.

The reaction mixture is cooled and the crude 2,2' dianiline disulfide **3**, is collected on a buchner funnel. It is dissolved in 10 mL of hot ethanol, and a small amount of insoluble material is removed by filtration. To the hot solution is then



added 50 mL of water containing several grams of sodium hydrosulfite. The solution is cooled, and an additional 300 mL of water is added with stirring. The precipitate is removed on a buchner funnel and crystallized by *n*-hexane and ethyl acetate.

Electrode preparation. To prepare the PVC membranes, we used dipping method[7,9,13,15] where, after thoroughly mixing 32.0 mg of powdered PVC, 59.5 mg of plasticizer NPOE, 3.0 mg of additive NaTPB, 5.5 mg of DADS and 3 ml of fresh THF, the resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was slowly evaporated to yield an oily concentrated mixture was obtained. A Pyrex tube with an outer diameter of 3.0-5.0 mm was dipped into the mixture for about 10 s so that a transparent membrane of about 0.3 mm thickness was formed on its tip. To dry the membrane the tube was next pulled out from the mixture and kept at the room temperature for about 2 h, before being filled with an internal filling solution of 1.0×10^{-3} M of $TmCl_3$. The electrode conditioning was finally done by its soaking in a 1.0×10^{-2} M $TmCl_3$ solution for 24 h. A silver/silver chloride wire was used as an internal reference electrode.

Apparatus. Potentials were measured with a Corning ion analyzer Model 250-pH|mV meter. The pH of the sample solutions was monitored simultaneously with a conventional glass pH electrode.

EMF-measurement. All emf measurements were carried out with the following assembly:

Ag-AgCl |internal solution (1.0×10^{-3} M $TmCl_3$)| PVC membrane| sample solution| Hg-Hg_2Cl_2, KC1 (satd.)

Results and Discussion

Potential response of the sensors based on DADS. Due to the existence of two sulfur as well as two nitrogen atoms as soft base in the structure of DADS, it was expected to increase both the stability and selectivity of its complexes with transition and heavy metal ions, rather than transition metal alkali and alkaline earth metal ions. Thus, in order to check the suitability of DADS as an ion carrier for different metal ions, in preliminary experiments, it was used to prepare PVC membrane ion-selective electrodes for a wide variety of cations, including alkali, alkaline earth and transition metal ions, the potential response of the most sensitive ion-selective electrodes based on DADS are shown in Figure 1(a, b). As can be seen from Figures 1a, and 1b, among the thirteen metal ions used, Tm(III) with the most sensitive response seems to be suitably determined with the PVC membrane based on DADS. This is probably due to both the selective behavior of the ion carrier against Tm(III) (proper size of Tm(III) ion to the semi cavity of DADS) in comparison to other metal ions used, and the rapid exchange kinetics of the resulting DADS-Tm(III) complex.

Influence of membrane composition on the potential response of the Tm(III) sensor based on DADS. The PVC-based membrane sensor based on DADS generates stable potential response in aqueous solutions containing Tm (III) ions after conditioning for about 24 h in a 1.0×10^{-2} M $Tm(NO_3)_3$ solution. Table 1 shows the data obtained with membranes having various ratios of different constituents. The potential responses of all of the membrane sensors were studied in a wide range of concentrations of Tm(III) solution. Table 1 reveals that the total potentiometric response of the electrode towards Tm(III) ions is relatively dependent on the concentration of the DADS that incorporated within the membrane (Nos. 3, 4). As can be seen from Table 1, increasing the amount of DADS up to 5.5% (in the membrane No. 4) displays larger slope. A maximum slope of 13.1 mV per decade of Tm(III) concentration in the absence of additive was observed for the membrane No. 4 with 5.5% of DADS.

It is well understood that the presence of lipophilic anions in cation-selective membrane electrodes diminishes the ohmic

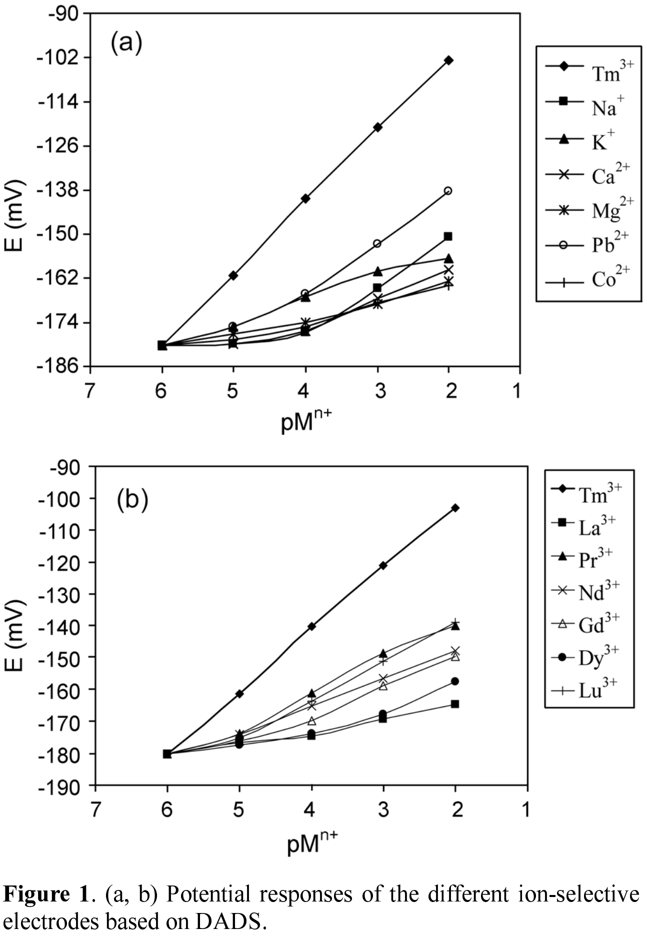


Figure 1. (a, b) Potential responses of the different ion-selective electrodes based on DADS.

Table 1. Optimization of membrane ingredients

No.	Components in membranes (% W/W)				Working concentration range (M)	Slope (mV/decade)	LOD (M)
	PVC	Ionophore	Additive NaTPB	Plasticizer			
1	32	5	–	63, DBP	$1 \times 10^{-2} \sim 1 \times 10^{-5}$	11.9	$< 10^{-5}$
2	32	5	–	63, BA	$1 \times 10^{-2} \sim 1 \times 10^{-5}$	12.5	$< 10^{-5}$
3	32	5	–	63, NPOE	$1 \times 10^{-2} \sim 1 \times 10^{-5}$	12.7	$< 10^{-5}$
4	32	5.5	–	62.5, NPOE	$1 \times 10^{-2} \sim 1 \times 10^{-5}$	13.1	$< 10^{-5}$
5	32	5.5	2	60.5, NPOE	$1 \times 10^{-2} \sim 1 \times 10^{-6}$	17.3	$< 10^{-6}$
6	32	5.5	3	59.5, NPOE	$1 \times 10^{-2} \sim 1 \times 10^{-6}$	19.5	$< 10^{-6}$
7	32	–	3	65, NPOE	$1 \times 10^{-2} \sim 1 \times 10^{-4}$	3.1	$< 10^{-4}$
8	32	5.5	3	59.5, BA	$1 \times 10^{-2} \sim 1 \times 10^{-6}$	18.7	$< 10^{-5}$
9	32	5.5	3	59.5, DBP	$1 \times 10^{-2} \sim 1 \times 10^{-5}$	16.5	$< 10^{-5}$

resistance, enhances the response behavior and selectivity, and increases the sensitivity of the membrane electrodes.[39,40] As can be seen from Table 1, the slope of the sensor in the absence of NaTPB is lower than the expected Nernstian value, while, addition of 3% NaTPB will increase the sensitivity of the electrode response considerably, so that the membrane electrode demonstrates a nice Nernstian behavior (membrane no. 6). However, the membrane sensor with composition of 32% PVC; 59.5% NPOE; 3% NaTPB, and 5.5% DADS exhibits the best performance.

The optimum equilibration time for the membrane electrode, after which it generates stable potentials when placed in contact with Tm(III) solutions, is found to be 24 h.

The critical response characteristics of the Tm(III) sensor were assessed according to IUPAC recommendations.[41] The potential response of the membrane at varying concentration of Tm(III) ions (Figure 2) indicates a rectilinear range from 1.0×10^{-6} - 1.0×10^{-2} M. The slope of the calibration curve was 19.5 ± 0.3 mV/decade of Tm(III) concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 4.0×10^{-7} M.

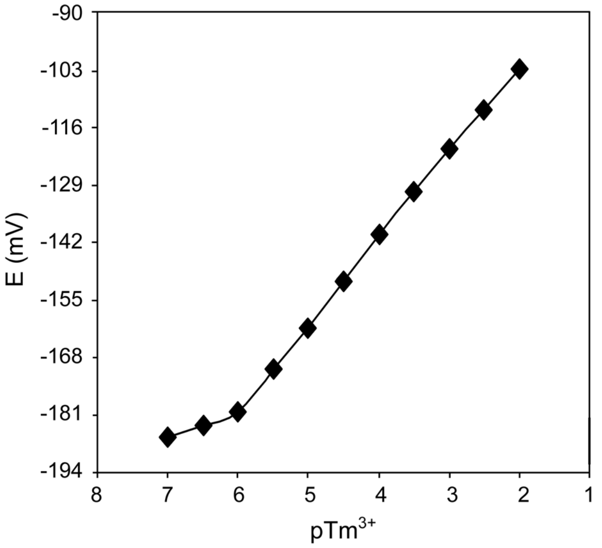


Figure 2. Calibration curve of Tm(III) membrane sensor based on DADS for the membrane no. 6.

The effect of the pH of the solution on the response of the proposed membrane sensor to a 1.0×10^{-4} M Tm(III) solution, was studied over a pH range from 4.0 to 9.7, and the results are depicted in Figure 3. It is obvious that the potential remains constant from pH 4.8 to 8.5, beyond which, a drastic drifts were observed. The observed drift at higher pH values could be due to the formation of insoluble thullium hydroxide in the solution. It is noteworthy that in such acidic solution, the ionophore used could be protonated to some extent, which results in improper functioning of the membrane sensor to the Tm(III) ion concentration.

Dynamic response time. Dynamic response time is one of the most important factors for any ion-selective sensor. In this study, the practical response time of the Tm(III) sensor was recorded by changing the concentration of thulium ion in solution in the range of 1.0×10^{-6} to 1.0×10^{-2} M and the results are shown in Figure 4. As can be seen from Figure 4, in the whole concentration range the electrode reaches its equilibrium response, very fast (< 12 s).

Lifetime study. For evaluation of stability and lifetime of the proposed membrane sensor, three same electrodes were chosen and tested over a period of eight weeks. The electrodes were kept dry and only 1-2 hours before use were conditioned by filling with and soaking in a 1.0×10^{-3} M $TmCl_3$ solution. During this period, the electrodes were used over extended period of time (one hour per day). After four

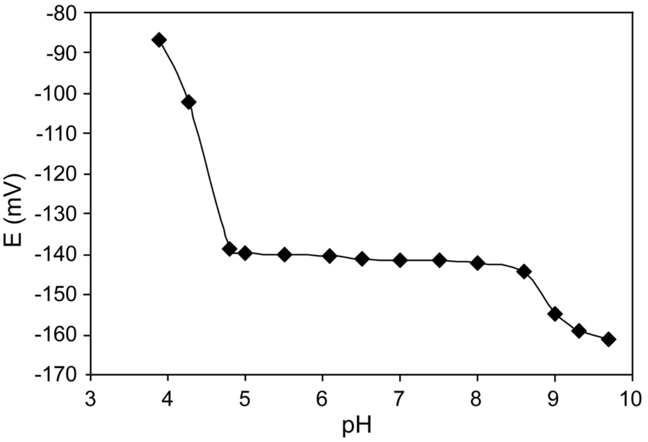


Figure 3. Dynamic responses of the proposed membrane electrode for step changes in concentration of Tm(III) solution.

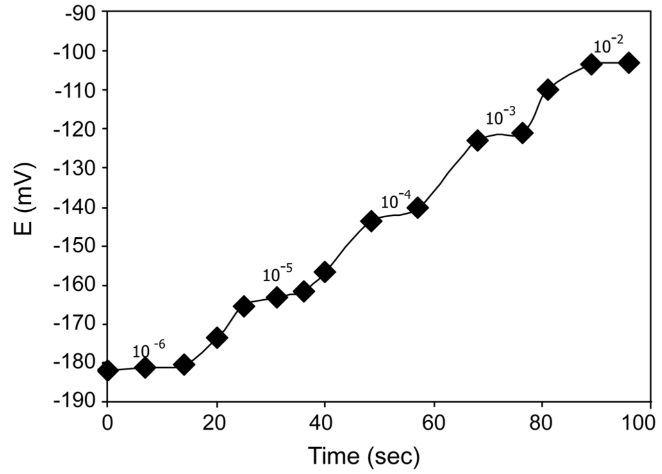


Figure 4. Effect of the pH of test solution (1.0×10^{-4} M of Tm(III)) on the potential response of the Tm(III) sensor.

weeks, a slight gradual decrease in the slopes (from 19.5 to 18.0 mV per decade) was observed.

Selectivity of the sensor. 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, the so-called matched potential method[42] was used for determination of selectivity coefficients of the sensor, according to which, a specified activity (concentration) of the primary ions (A, 5.0×10^{-4}-1.0×10^{-3} M of Tm (III) ion) is added to a reference solution (1.0×10^{-5} M of Tm(III) ion) and the potential is measured. In a separate experiment, interfering ions (B, 1.0×10^{-3}-1.0×10^{-2} M) 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 2. It is immediately obvious from these data, that the proposed Tm(III) sensor is highly selective with respect to the most of cations. In the case of lanthanide ions the selectivity coefficients are in the order of 1.2×10^{-2} or smaller, which seems to indicate that the Tm(III) ions can be determined in the presence of other lanthanide ions. The selectivity coefficients for other cations are smaller than 1.2×10^{-2}, indicating that they can not disturb the functioning of the Tm(III) membrane electrode.

Table 2. Selectivity coefficients of various interfering cations

M^{n+}	$k_{A,B}^{MPM}$	M^{n+}	$k_{A,B}^{MPM}$
Na^+	3.8×10^{-3}	La^{3+}	7.6×10^{-4}
K^+	1.7×10^{-3}	Pr^{3+}	1.0×10^{-2}
Ca^{2+}	1.2×10^{-3}	Nd^{3+}	4.5×10^{-3}
Mg^{2+}	8.9×10^{-4}	Dy^{3+}	1.6×10^{-3}
Pb^{2+}	1.2×10^{-2}	Gd^{3+}	3.7×10^{-3}
Co^{2+}	7.5×10^{-4}	Lu^{3+}	1.2×10^{-2}
Yb^{3+}	1.0×10^{-2}	Er^{3+}	1.4×10^{-2}

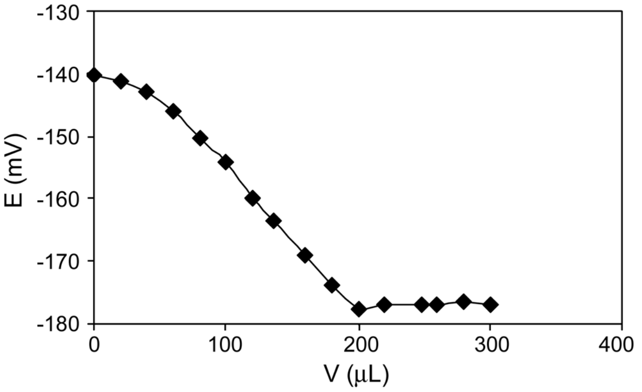


Figure 5. Potentiometric titration curve of 20.0 mL of 1.0×10^{-4} M Tm(III) with 1.0×10^{-2} M of EDTA, using the proposed membrane sensor as an indicator electrode.

The surprisingly high selectivity of the membrane electrode for Tm(III) ions over other cations used most probably arises from the strong tendency of the carrier molecule for Tm(III) ions.

Analytical applications. The proposed Tm(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^{-4} M of Tm(III) solution with a 1.0×10^{-2} M of standard EDTA (with pH 10.0), and the resulting titration curve is shown in Figure 5. As can be seen The proposed Tm(III) membrane electrode was found to work well under laboratory conditions.

As another analytical application of the proposed sensor, it was used for the determination of the concentration of Tm (III) ions in various binary mixtures. For the determination of the recovery of Tm(III) ions in binary mixtures, the potential responses of Tm(III) sensor in the presence and absence of added cations were measured and by using calibration curve method, concentration of Tm(III) in both cases were determined. The results are summarized in Table 3. As can be seen from Table 3, the determination of the Tm(III) ions in the presence of high concentrations of some other ions is successful.

It was also successfully applied to the determination of F^-

Table 3. Determination of Tm (III) ions in binary mixtures

Tm^{3+} (M)	Added cation (M)	Recovery (%)
1×10^{-5}	Na^+ (1×10^{-3})	100.3 ± 0.3
1×10^{-5}	K^+ (5×10^{-4})	101.2 ± 0.2
1×10^{-5}	Ca^{2+} (1×10^{-3})	100.5 ± 0.4
1×10^{-5}	Mg^{2+} (1×10^{-3})	100.6 ± 0.3
1×10^{-5}	Pb^{2+} (5×10^{-4})	101.3 ± 0.3
1×10^{-5}	Co^{2+} (1×10^{-3})	99.7 ± 0.4
1×10^{-5}	La^{3+} (1×10^{-3})	100.4 ± 0.3
1×10^{-5}	Pr^{3+} (1×10^{-4})	100.6 ± 0.2
1×10^{-5}	Nd^{3+} (5×10^{-4})	101.1 ± 0.3
1×10^{-5}	Gd^{3+} (5×10^{-4})	100.6 ± 0.4
1×10^{-5}	Dy^{3+} (1×10^{-3})	100.2 ± 0.3
1×10^{-5}	Lu^{3+} (1×10^{-4})	100.4 ± 0.3

Table 4. Results of determination of fluoride in the different mouth wash samples

Sodium fluoride mouth wash solution (Shahre Daru Co., Tehran, Iran)	Labled (%)	Found (%)
Sample no.1	0.2	0.18 ± 0.03
Sample no.2	0.2	0.19 ± 0.01
Sample no.3	0.2	0.22 ± 0.02

ions in three different pharmaceutical samples, and the results of triplicate measurements are summarized in Table 4. For this approach a diluted solution of pharmaceutical sample containing F^- was titrated by a standard solution of Tm(III) using the proposed sensor as an indicator electrode. Before the equivalent point we have TmF_3 in the solution and the potential is almost constant, but after the equivalent point addition of more Tm(III) ions will increase the potential. As seen, there is a satisfactory agreement between the declared fluoride content and the determined values.

Conclusion

Potentiometric PVC membrane sensor based on DADS as an ionophore is sensitive for the detection of thulium ions over a wide range of concentration (1.0×10^{-6} to 1.0×10^{-2} M) with a Nernstian slope of 19.5 ± 0.3 mV per decade and a detection limit of 4.0×10^{-7} M. The sensor exhibits a high selectivity towards Tm(III) with respect to many cations tested. It was used as an indicator electrode in the potentiometric titration of Tm(III) ions with EDTA and in direct determination of concentration of Tm(III) ions in binary mixtures. The proposed sensor was successfully applied for the determination of fluoride ions in mouth wash preparations.

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