

Tm³⁺-PVC Membrane Electrochemical Sensor Based on N-[(E)-1-(2-thienyl)methylidene]-N-{4-[(4-[(Z)-1-(2-thienyl)methylidene]amino}phenyl)sulfonyl]phenyl}amine

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The N - [(E) - 1 - (2 - thienyl) methylidene] - N - { 4 - [(4 - { [(Z) - 1 - (2 - thienyl) methylidene] amino } phenyl) sulfonyl] phenyl } amine (TAS) was used as a suitable ionophore for fabrication of a new thulium(III) ion selective potentiometric sensor. The sensor displays a Nernstian response (19.4±0.3 mV/decade) in the concentration range of 1.0×10⁻⁶ to 1.0×10⁻² mol L⁻¹ with the detection limit of 6.9×10⁻⁷ mol L⁻¹ at a pH range of 3.1–8.9. The electrode shows a fast response time (~5 s). This sensor shows very good selectivity and sensitivity towards thulium ion over a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The sensor revealed a great enhancement in selectivity coefficients for thulium ions, in comparison to the previously reported thulium sensors. For testing applicability of the sensor, it was used as an indicator electrode in the potentiometric titration of Tm³⁺ ions with EDTA and in the titration of Tm³⁺ ion solutions in certified reference materials.

Keywords: Sensor, PVC membrane, Ion-selective electrode, Potentiometry

1. INTRODUCTION

The quick determination of minute quantities of ionic species by simple methods is of special interest in analytical chemistry. During the last decade, there has been a renewed resurgence in developing potentiometric membrane electrodes as devices for rapid, accurate, low cost and nondestructive analysis of different samples with small volume samples. Ion-selective sensors based on plasticized PVC membranes were successfully applied to the determination of many cations in various industrial, environmental and biochemical samples [1-3].

One prominent application of thulium, is the use of a (0.1–0.2)-g pellet of the metal or oxide as a portable source of diagnostic X-radiations and also be used as a dopant in tunable fiber lasers [4]. ICP-MS and ICP-AES and spectrofluorimetry are among the available methods for the low-level monitoring of thulium ions in solutions. Isotope dilution mass spectrometry, neutron activation analysis, X-ray fluorescence spectrometry, etc, are also used in some laboratories. Characteristics all these method share are their being either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories [5-8].

Ion selective electrodes are used widely in analysis of a wide variety of ions [9-17] because of some advantages such as portability, simplicity, fast, inexpensive, and reliable response in a wide concentration range in comparison with new electrochemical methods. Potentiometric sensors on the other hand offer inexpensive and convenient analysis methods for of lanthanide ions as well as a number of cations and anions, providing that they have acceptable sensitivity and selectivity. To the best of our knowledge, however, there are only three reports on thulium(III) sensors [18-22].

Recently, our team and other researchers have recently introduced a number of PVC-membrane ion-selective membrane sensors for anions and metal ions [23–30]. This research focuses on the introduction of a highly Tm(III)-selective sensor based on N-[(E)-1-(2-thienyl)methylidene]-N-{4-[(4-[(Z)-1-(2-thienyl)methylidene]amino}phenyl)sulfonyl] phenyl}amine (TAS) (Fig. 1), as an ionophore for determination of Tm(III) ion concentration.

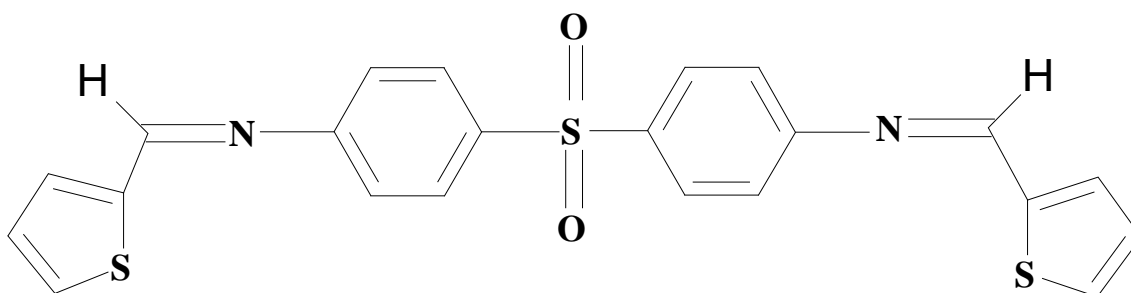


Figure 1. Chemical structure of TAS.

2. EXPERIMENTAL

2.1. Reagents

The Merck and the Aldrich Chemical Co. were the providers of the following reagent. grades: benzyl acetate (BA), nitrobenzene (NB), dibutyl phthalate (DBP), o-nitrophenyloctylether (NPOE), acetophenone (AP), oleic acid (OA), high relative molecular weight PVC, sodium tetraphenyl borate (NaTPB) and tetrahydrofurane (THF). 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. Doubly distilled de-ionized water was used throughout.

2.2. The synthesis of TAS

N - [(E) - 1 - (2 - thienyl) methylidene] - N - { 4 - [(4 - { [(Z) - 1 - (2 - thienyl) methylidene] amino } phenyl) sulfonyl] phenyl } amine was synthesized in the usual manner by reaction of thiophene-2-carbaldehyde with diamine in a 2:1 molar ratio in methanol as follows. Thiophene-2-carbaldehyde (0.01 mol, 1.12 g) and 4,4'-diaminodiphenylsulfone (0.005 mol, 1.24 g); were placed in 100 ml round-bottom flask equipped with a condenser and a magnetic bar. Methanol (50 ml) was then added to the mixture and the mixture was refluxed for 3 h while stirring, and then cooled to room temperature. The solid product was filtered, and the product was recrystallized from chloroform. Anal. calcd for $C_{22}H_{16}N_2O_2S_3$: C, 60.53; H, 3.69; N, 6.42. Found: C, 60.35; H, 3.50; N, 6.53%; IR bands (KBr, cm^{-1}), $\nu_{C=N}$, 1622 cm^{-1} ; Yield = 78%; M.P. = 205 $^{\circ}C$; 1H -NMR (400 MHz, $CDCl_3$, internal reference TMS): δ , 8.87 (2H, s, CH=N), 7.32 (4H, ddd, aminophenyl), 7.10 (4H, ddd, aminophenyl), 7.23 (2H, m, C_4H_3S), 7.48 (2H, m, C_4H_3S), 7.59 (2H, m, C_4H_3S).

2.3. The preparation of membrane

The PVC membranes were prepared by mixing 3 mg TAS ionophore, 10 mg OA, 57 mg NPOE and 30 mg PVC and dissolving in 3 mL THF. The resulting homogeneous mixture was transferred into a glass dish of 2 cm diameter. A Pyrex tube (5 mm o.d.) was dipped into the mixture for about 5 s, so that a transparent membrane of about 0.3 mm thickness was formed [31-35]. The tube was then pulled out from the mixture and kept at room temperature for at least 12 h. The tube was then filled with internal filling solution ($1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ TmCl}_3$). The electrode was finally conditioned for 36 h by soaking in a $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ TmCl}_3$ solution. A silver/silver chloride electrode was used as an internal reference electrode.

2.4. The emf measurements

All electromotive force (emf) measurements were carried out with the following cell assembly:

Ag-AgCl | internal solution, $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ TmCl}_3$ | PVC membrane | test solution | Hg-Hg₂Cl₂, KCl (satd.)

Using a Corning ion analyzer 250 pH/mV meter at 25.0 $^{\circ}C$. The activities of the ions tested were calculated according to the Debye-Huckel procedure [36].

3. RESULTS AND DISCUSSION

In order to check the TAS suitability as an ion carrier for different metal ions, it was used to prepare PVC membrane ion-selective electrodes in preliminary experiments for a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. Among different metal ions tested, Tm^{3+} ion displays a strong response (with a slope of $19.4 \pm 0.3 \text{ mV per decade}$) to the TAS-based membrane sensors in comparison with the other tested cations.

3.1. The effect of the membrane composition

Sensitivity and selectivity of any given membrane sensor are significantly related to the composition of the ion-selective membrane (the properties of the plasticizer, the nature and amount of the ionophore, the plasticizer/PVC ratio and the nature additives used) [37-39]. Thus, different aspects of preparation of membranes based on TAS were optimized and the results are given in Table 1. Solvent polymeric membrane ion-selective electrodes are usually based on a matrix of the solvent mediator/PVC ratio of about 2. Polymeric films with such a plasticizer/PVC ratio will result in optimum physical properties and high enough mobility of their constituents. It can be observed that the ionophore amount increase up to a value of 3 %, in the presence of 10 % OA and 57 % of polar solvent (NPOE), results in the best sensitivity (membrane no. 9).

A maximum slope of 19.4 ± 0.3 mV per decade of thulium concentration was observed for the No. 9 membrane with 3 % of TAS. Since the plasticizer nature influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands [39-41], the plasticizer nature was expected to play a key role in the determination of the selectivity, in the definition of the working concentration range and the response time of the membrane electrode. Of the five tried solvent mediators (NPOE, NB, AP, DBP and BA), NPOE was found to provide the best sensitivity for the construction of the Tm(III) membrane sensor.

It is well known that the presence of lipophilic anions in a cation-selective membrane, based on neutral carrier, presents the following noticeable benefits; i) ohmic resistance reduction, ii) enhancement of the response behavior and selectivity and iii) membrane electrode sensitivity increase (when the extraction capability is poor) [41, 42]. The data given in Table 1 showed that in the presence of 10% OA as a suitable lipophilic additive improved the sensitivity of the Tm³⁺ sensor considerably (no. 9 with a slope 19.4 mV decade⁻¹). However, the membranes with the composition of 30 % PVC, 3 % TAS, 10 % OA and 57 % NPOE illustrate a Nernstian potential response.

Table 1. Optimization of the membrane ingredients.

No.	Composition (wt %)				Linear range (mol L ⁻¹)	Slope (mV/decade)
	PVC	Plasticizer	TAS	Additive		
1	30	NB, 66	2	NaTPB,2;OA,0	1.0×10^{-2} - 1.0×10^{-5}	11.4 ± 0.4
2	30	BA, 66	2	NaTPB,2;OA,0	1.0×10^{-2} - 1.0×10^{-5}	10.2 ± 0.3
3	30	AP, 66	2	NaTPB,2;OA,0	1.0×10^{-2} - 1.0×10^{-5}	12.7 ± 0.2
4	30	DBP, 66	2	NaTPB,2;OA,0	1.0×10^{-2} - 1.0×10^{-5}	13.1 ± 0.4
5	30	NPOE, 66	2	NaTPB,2;OA,0	1.0×10^{-2} - 1.0×10^{-6}	14.8 ± 0.3
6	30	NPOE, 63	2	NaTPB,0;OA,5	1.0×10^{-2} - 1.0×10^{-6}	15.6 ± 0.3
7	30	NPOE, 59	1	NaTPB,0;OA,10	1.0×10^{-2} - 1.0×10^{-5}	16.2 ± 0.2
8	30	NPOE, 58	2	NaTPB,0;OA,10	1.0×10^{-2} - 1.0×10^{-6}	18.0 ± 0.2
9	30	NPOE, 57	3	NaTPB,0;OA,10	1.0×10^{-2} - 1.0×10^{-6}	19.4 ± 0.3
10	30	NPOE, 53	2	NaTPB,0;OA,15	1.0×10^{-3} - 1.0×10^{-6}	16.8 ± 0.5

3.2. The calibration curve

The potential response of the developed TAS-based sensor (composition No. 9) shows a linear response to the concentration of Tm(III) ions in the range 1.0×10^{-6} - 1.0×10^{-2} mol L⁻¹ (Fig. 2). The results may be summarized as follows. The calibration graph slope is 19.4 ± 0.3 mV per decade of the Tm(III) concentration. The detection limit of the sensor, as determined from the intersection of the two extrapolated segments of the calibration graph, is 6.9×10^{-7} mol L⁻¹. The standard deviation of eight replicate measurements is ± 0.5 mV.

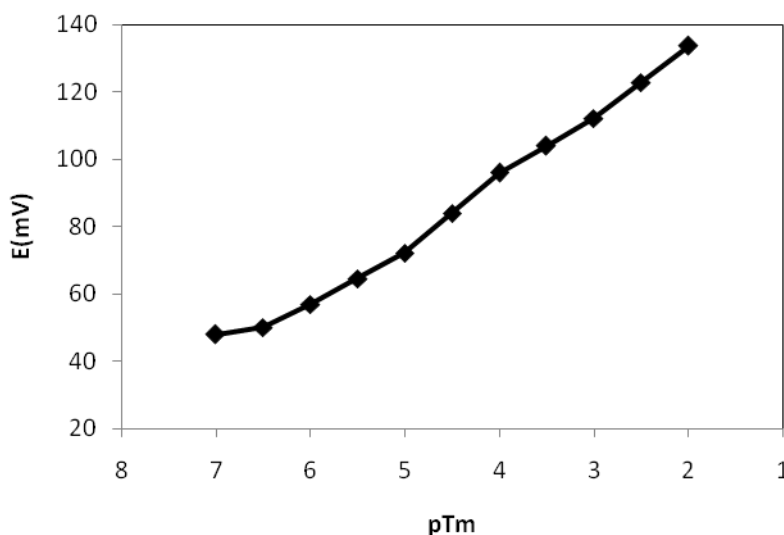


Figure 2. Calibration curves of the TAS-based Tm³⁺ sensor.

3.3. The pH effect

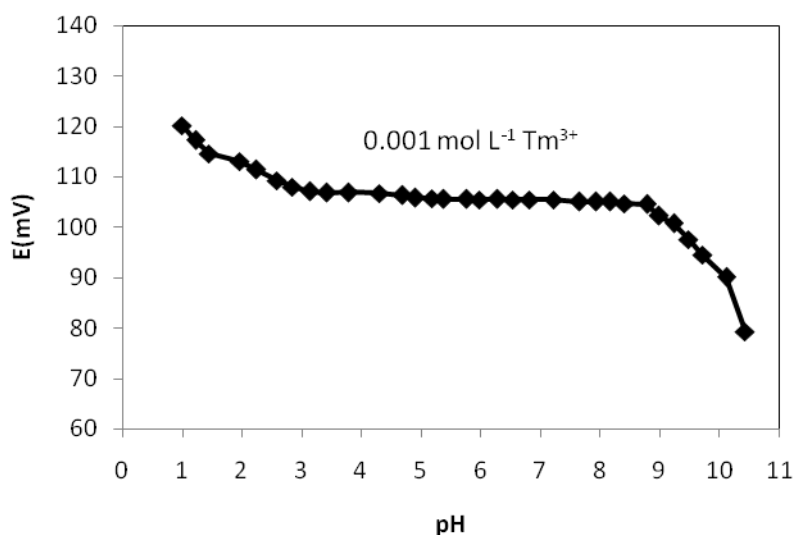


Figure 3. pH effect of the test solution (1.0×10^{-3} mol L⁻¹ of Tm³⁺) of the Tm³⁺ sensor based on TAS.

In order to study the effect of pH on the performance of the sensor, the potentials were determined in the pH range of 1.0-10.5 (the pH was adjusted by using concentrated NaOH or HCl) at concentrations ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) of Tm^{3+} and the results is depicted in Figure 3. As it is seen, the potential remained constant from pH 3.1 to 8.9, 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 Tm^{3+} in the solution. At the lower pH values, the potentials increased, indicating that the membrane sensor responded to protonium ions, as a result of the some extent protonation of nitrogen atoms of the ionophore.

3.4. Dynamic response time of the Tm^{3+} sensor

For any ion-selective, response time is one of the most important factor. The average time required for the Tm(III) sensor to reach a potential within $\pm 1\text{mV}$ of the final equilibrium value after successive immersion of a series of Tm(III) ion solutions, each having a 10-fold difference in concentration, was measured. The potentials versus time traces are shown in Figure 4. As can be seen, over the entire concentration range the plasticized membrane electrode reaches its equilibrium responses in a very short time ($\sim 5 \text{ s}$). The lifetime of the membrane sensor was at least 8 weeks (using 1 h per day, and then washed and kept dry), during which it could be used without any measurable divergence.

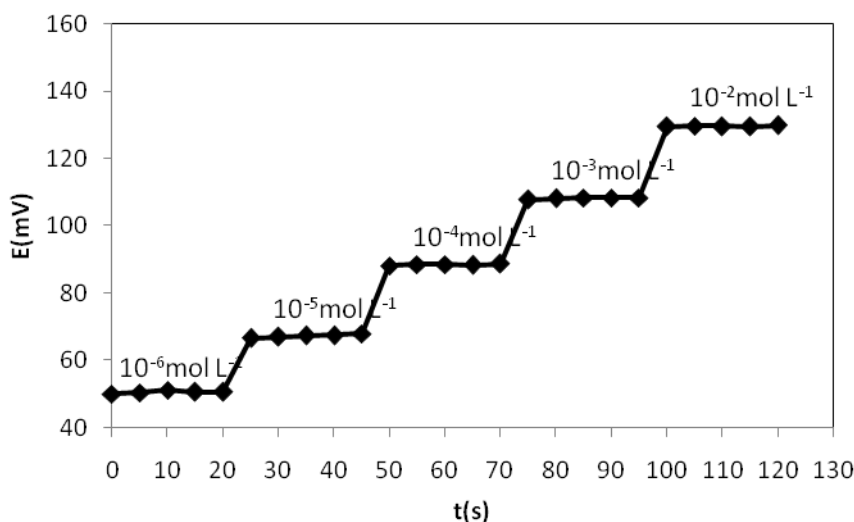


Figure 4. Dynamic response time of Tm^{3+} sensor based on TAS.

3.5. Selectivity coefficient

The selectivity behavior is obviously one of the most important characteristics of an ion-selective electrode, determining the feasibility of a reliable measurement in the target sample. To investigate the membrane electrode selectivity, its potential response was monitored in the presence of various interfering foreign cations using the matched potential method (MPM) [43-45]. According to the MPM, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion

and the interfering ion, which gives the same potential change in a reference solution. Thus, the potential change should be measured upon changing the primary ion activity. Then, the interfering ion would be added to an identical reference solution until the same potential change would be obtained. The matched potential method selectivity coefficient, K^{MPM} , is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{MPM} = a_A/a_B$. The resulting potentiometric selectivity coefficients values are summarized in Table 2. The data given in Table 2, revealed the selectivity coefficients of the electrode for all the diverse ions are in the order of 4.1×10^{-3} or smaller, indicating they would not significantly disturb the function of the Tm(III) selective membrane sensor. 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 molecules for Tm(III) ions.

Table 2. Selectivity coefficients ($K_{Tm^{3+},B}^{MPM}$) of proposed Tm³⁺ sensor.

Ion	K_{MPM}
Eu ³⁺	2.4×10^{-3}
Pr ³⁺	8.1×10^{-4}
Tb ³⁺	4.1×10^{-3}
Sm ³⁺	1.9×10^{-3}
Ho ³⁺	7.6×10^{-4}
Ca ²⁺	3.6×10^{-3}
Na ⁺	1.4×10^{-3}
Fe ³⁺	3.1×10^{-3}
Pb ²⁺	2.2×10^{-3}
Zn ²⁺	1.7×10^{-3}
Co ²⁺	8.3×10^{-4}
Cd ²⁺	3.5×10^{-3}

Table 3 compares the linearity range, response time, detection limit and selectivity coefficients of the suggested sensor with the best previously reported Tm(III) sensors [18-22]. It is evident that the newly developed sensor is superior to the formerly reported Tm(III) sensors in terms of selectivity, detection limit and response time.

Table 3. Comparison of previously reported Tm³⁺ sensor with the proposed sensor.

Ion	Ref. 18	Ref. 19	Ref. 20	Ref. 21	Ref. 22	This work
Linearity rang (molL ⁻¹)	1.0×10^{-6} - 1.0×10^{-2}	1.0×10^{-5} - 1.0×10^{-2}	1.0×10^{-6} - 1.0×10^{-2}	1.0×10^{-6} - 1.0×10^{-2}	1.0×10^{-6} - 1.0×10^{-2}	1.0×10^{-6} - 1.0×10^{-2}
Detection limit (molL ⁻¹)	4.0×10^{-7}	8.0×10^{-6}	8.7×10^{-7}	6.8×10^{-7}	7.2×10^{-7}	6.9×10^{-7}
Response time (s)	15	7	~10	<10	<10	~5
Slope (mV decade ⁻¹)	19.5	19.5	19.5	19.6	19.6	19.4
$K^{MPM} > 10^{-2}$	Er, Lu, Yb, Pb	Er, Nd, Ho, Mg	Lu, Yb	-	-	-

3.6. Analytical application

The proposed membrane electrode was also used as an indicator electrode in the potentiometric titration of a 1.0×10^{-4} mol L⁻¹ Tm(III) ion solution with a standard 1.0×10^{-2} mol L⁻¹ of EDTA. The resulting titration curve is shown in Figure 5. As seen, the sensor is capable of monitoring of the amount of Tm(III) ions.

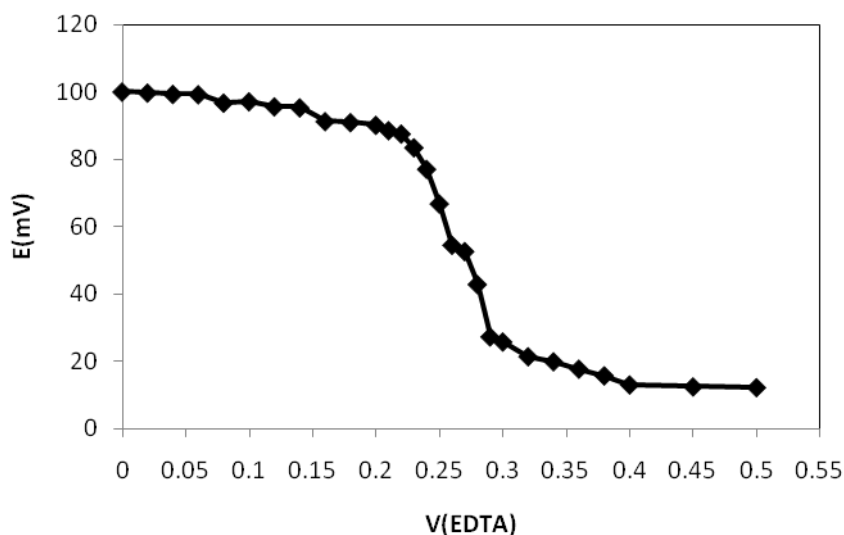


Figure 5. Potential titration curves of 25 mL 1.0×10^{-4} mol L⁻¹ Tm³⁺ solution with 1.0×10^{-2} mol L⁻¹ of EDTA.

Further, to evaluate the accuracy of the proposed sensor, it was successfully applied to direct monitoring of Tm³⁺ in thulium ICP/DCP standard solution ($10,000 \mu\text{g mL}^{-1}$ Tm in 3 wt. % HNO₃) as a certified reference material and the results showed that the recovery of thulium ions to be very good (103.3%-104.9%).

4. CONCLUSION

A simple construction procedure was used to develop ion-selective electrodes for the detection of Tm³⁺ ions at low concentrations. The use of N-[(E)-1-(2-thienyl)methylidene]-N-{4-[(4-[(Z)-1-(2-thienyl)methylidene]amino}phenyl)sulfonyl] phenyl}amine (TAS) as an ionophore and o-nitrophenyloctyl ether, being the solvent mediator, results in the best response characteristics with Nernstian behavior over a wide concentration range of 1.0×10^{-6} - 1.0×10^{-2} mol L⁻¹ Tm³⁺. The recommended sensor displayed a Nernstian response (19.4 ± 0.3 mV decade⁻¹) with the detection limit of 6.9×10^{-7} mol L⁻¹, a quick response time of 5 s and its potential responses were pH independent across the range of 3.1–8.9. Moreover, it was successfully applied as an indicator electrode to the thulium ion titration with EDTA as well as to the thulium ions detection in certified reference materials.

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