Full Paper

A Novel Thulium Selective All-Solid-State Electrode

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Abstract- A new all-solid-state ion selective electrode (ASS-ISE) was developed for the determination of thulium trivalent cation. The potentiometric sensor was made by depositing a thin PVC membrane containing N′-[(2-hydroxyphenyl)methylidene]-2-furohydrazide (L) as a selectophore on a conducting solid-state electrode. The solid-state electrode was a thin copper wire coated by a mixture of multi-walled carbon nanotubes (MWCNTs) and an epoxy resin. The optimal composition of the PVC membrane was 25%wt. of PVC powder, 68% wt. of benzyl acetate, 2% wt. of sodium tetraphenyl borate (NaTPB)), and 5% wt. of L. The sensor showed good selectivity for Tm^{3+} ion with a Nernstian calibration plot slope of 19.6±0.4 mV/decade in Tm^{3+} ion solutions with concentrations ranging from 1.0×10^{-8} M to 1.0×10^{-3} M, and its limit of detection was as low as 6.3×10^{-9} M. The proposed sensor was able to detect Tm^{3+} cations in the wastewater matrix.

**Keywords-** Sensor; All-solid-state; Potentiometry; Tm^{3+} cation; Wastewater

1. INTRODUCTION

The construction of accurate sensitive analytical tools has always been very important. Given the widespread applications of Tm^{3+} compounds, the element, in its ionic form, is widely distributed in the environment, gradually finding its way into and bioaccumulating in

organisms and the human and animal food chains. Consequently, the design and construction of fast and accurate analytical tools and techniques for the analysis of Tm^{3+} is always an interesting topic. Commonly, spectroscopic techniques or advanced instruments are used for this purpose [1,2]. In contrast, ion-selective electrodes have proven to be versatile tools for use in the analysis of various ions, due to their numerous advantages in terms of accuracy, sensitivity, and selectivity, moderate construction and application costs, have made them powerful candidates for various applications the mentioned techniques [3-10].

All solid-state ISEs (ASS-ISEs), on the other hand, are known due to their figures of merit over common symmetrical ISEs, in terms of improved detection limits, and lifetimes, which attracted a great deal of focus on the part of researchers [11-15].

Based on these facts and in the light of the extensive knowledge about the various classes of ionophores used in ISEs, this work was focused on the design of a Tm^{3+} selective ASS-ISE, using a film of a conductive polymeric composite (CPC) of MWCNTs and an epoxy on a copper wire, as the all-solid-state element to be coated by a thin film of a Tm^{3+}-selective PVC membrane containing a known Tm^{3+} selective ionophore, namely N′-[(2-hydroxyphenyl)methylidene]-2-furohydrazide (Scheme 1).
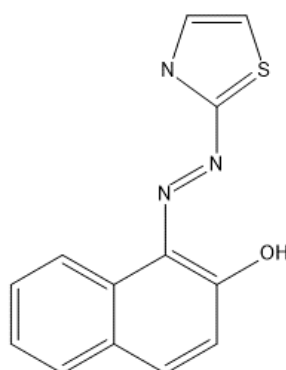
Scheme 1. N′-[(2-hydroxyphenyl)methylidene]-2-furohydrazide chemical structure

N′-[(2-hydroxyphenyl)methylidene]-2-furohydrazide (L) has been previously reported as a suitable ionophore for thulium trivalent cation [16]. Sensing materials known as selectophores are an important part of potentiometric ion-selective sensors. A good selectophore interacts selectively with a target ion in presence of the other similar ions.

Thulium is one of the rare members of the lanthanide series which is used in the construction of lasers, portable X-ray devices as bombarded material in a nuclear reactor, and some high technology industries [17,18].

Soluble thulium salts are slightly toxic, but insoluble forms are rather non-toxic [19]. In humans, thulium can adsorb in the liver, kidneys, and bones. Humans typically consume several micrograms of thulium per year. The roots of plants do not take up thulium, and the dry matter of vegetables usually contains one part per billion of thulium [20].

According to the above-mentioned, the design and construction of ion-selective electrodes for trace determination of Tm^{3+} cations can be an interesting field of research [16,21-30]. Most of the previously reported Tm^{3+} selective electrodes are symmetric PVC membrane electrodes in which the membrane is placed between two internal and external solutions [16,21-27]. And there are fewer reports on wire-coated and other solid-state electrodes [28-30].

2. EXPERIMENTAL SECTION

2.1. Reagents

Analytical reagent grade dibutylphthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), dibutyl phthalate (DBP), acetophenone (AP), sodium tetraphenylborate (NaTPB), tertrahydofuran (THF), and the chloride/nitrate salts of cations were obtained from Merk Co. High-molecular weight polyvinylchloride, and the ion carrier, namely N′-[(2-hydroxyphenyl)methylidene]-2-furohydrazide (L) were procured from Fluka Co. The epoxy resin (Macroplast Su 2227 epoxy) was procured from Henkel Co. and the hardener (Desmodur® RFE) was from Bayer Ag. The materials were used as received and all solutions and cleaning operations were performed using doubly distilled deionized water.

2.2. Preparation of the ASS-ISEs

The CPC was formed by mixing various quantities of graphite powder, MWCNTs, epoxy, and hardener in tetrahydrofuran. The mixtures were left in the air for about half an hour to reach desirable viscosity. Next, a polished 15 cm copper wire (0.5 mm diameter) was dipped into the CPC mixtures, to be coated with a thin film thereof, and then the CPC-coated wires rested under atmospheric conditions to dry in order to form the all-solid-state elements, which were then repeatedly dipped into liquid mixtures of the Tm^{3+}-selective PVC membranes to form the ASS-ISEs. The electrodes were eventually aged in the air for one day prior to experimental evaluation [12-15].

Results of experiments (Table 1) revealed the optimal sensor response in the case of membranes containing 2% wt. of N′-[(2-hydroxyphenyl)methylidene]-2-furohydrazide (L), 66% wt. of BA, 30% wt. of PVC, and 2% wt. of NaTPB, and this composition was hence used in all experiments. The typical procedure for preparing the membrane involved admixing various amounts of the ionophore (L), PVC powder, a membrane solvent, and an ionic additive in THF. The resulting homogenous liquid was poured into a glass dish and the THF content was allowed to evaporate. A portion of the viscose liquid obtained in each case was next coated on the all-solid-state element through dipping. The resulting electrodes were left in the air for 24 hours to dry. Eventually, the ASS-ISEs were conditioned in a 10^{-3} M Tm^{3+} ion solution prior to use.

The Tm^{3+} ASS-ISE was used in a cell setup as below:

$$\text{Cu wire/CPC layer/ PVC membrane} \mid Tm^{3+} \text{ solution} \parallel \text{Ag-AgCl, KC1 (satd.)}$$

for measurements. The Ag/AgCl double junction reference electrode was obtained from Azar-Elelectrode Co., Iran. The reading of the cell potential values was made using an ion analyzer 250 pH/mV meter (±0.1 mV).

3. RESULTS AND DISCUSSION

An extensive review of the works on ion-selective electrodes (ISEs) reveals that most of the reported sensors are symmetrical devices; i.e. the sensing membrane is located between two external and internal solutions [27-31]. In the case of asymmetrical ISEs, like ASS-ISEs, however, the internal solution is eliminated which means only the outer surface of the electrode is in contact with solutions [32-38]. Symmetrical devices cannot function in the absence of an internal solution, yet the presence of this solution damages the robustness of these electrodes and severely limits their miniaturization. This means asymmetrical devices do not suffer such disadvantages increasing the potential of their application in different medical, biological, and in-vivo applications. The use of CPCs as the all-solid-state element together with ion-selective membranes with adjustable compositions, increases their potential for various applications. Therefore, different polymeric membrane compositions were prepared using L as the ionophore, and the results observed in each case are summarized in Table 1. These evaluations were performed based on some facts, revealed by various studies [39-44]; e.g. that the optimum electrode response usually occurs when the plasticizer/PVC ratios are between 2.0 to 3. However, some modifications were performed. The amount of PVC in the case of symmetrical PVC membrane is normally 30%wt. while in the case of ASS-ISEs, less amount improves the sensor response. Here 25%wt.

Table 1. The different membrane compositions

No.	Composition (wt.%)				Linear range (M)	Slope* (mV/decade)	Response time* (s)
	PVC	Plasticizer	L	NaTPB			
1	30	BA, 67	3	0	1.0×10^{-7}–1.0×10^{-4}	13.6±0.5	15.7±0.6 s
2	30	BA, 65	5	0	1.0×10^{-8}–1.0×10^{-3}	18.4±0.3	12.3±0.3 s
3	30	BA, 63	7	0	1.0×10^{-8}–1.0×10^{-3}	17.9±0.4	12.4±0.2 s
4	20	BA, 75	5	0	1.0×10^{-8}–1.0×10^{-3}	16.8± 0.5	15.7±0.4 s
5	25	BA, 70	5	0	1.0×10^{-8}–1.0×10^{-3}	19.1±0.3	10.2±0.3 s
6	25	BA, 68	5	2	1.0×10^{-8}–1.0×10^{-3}	19.6±0.4	7.0±0.2 s
7	25	BA, 67	5	3	1.0×10^{-8}–1.0×10^{-3}	19.5±0.5	8.5±0.2 s
8	25	NB, 68	5	2	1.0×10^{-8}–1.0×10^{-3}	17.2±0.7	9.6±0.4 s
9	25	DBP, 68	5	2	1.0×10^{-8}–1.0×10^{-3}	16.4±0.3	11.3±0.6 s
10	25	AP, 68	5	2	1.0×10^{-8}–1.0×10^{-3}	17.3±0.4	10.2±0.5 s
11	25	BA, 65	0	2	1.0×10^{-6}–1.0×10^{-4}	3.3±0.7	21.3±0.6 s

*Standard deviation of five repeated measurements

A very important membrane ingredient is the sensing element or selectophore, which affects the selectivity of the sensor toward a target ion. As mentioned above previously selectivity of the L toward Tm^{3+} ions, was studied [16]. Here, its amount for ASS-ISE was optimized. As can be seen from test no. 1 to no. 3, 5%wt. showed the best response and the membrane without any L inside (no. 11) did not show any reasonable response.

Another ingredient that needs to be selected is a non-volatile liquid (membrane solvent), which allows for physical dissolution and homogenization of the membrane components. This inert component, should evidently not intervene with the role of the ion-carrier, yet its polarity can influence ISE response and should hence be optimized. DBP, NB, AP, and BA were evaluated as various membrane solvents and the results can be seen in Table 1 (membrane no. 7 to 10), which indicate that membranes based on BA produce the best results.

A further component of PVC membrane sensors is an ionic additive for enhancing membrane polarity for optimal extraction and exchange of the analyte by the membrane, as well as minimizing its Ohmic resistance. Sodium tetraphenylborate (NaTPB) was used as an ionic additive in the PVC membrane compositions and the optimum response was produced by membranes containing 2% wt. of NaTPB (membrane no. 6).

Based on the results in Table 1, the best results were with membrane composition no. 6, the ASS-ISE based on which produced a Nernstian slope of 19.6±0.4 mV/decade. Consequently, this composition was used in the rest of the evaluations.

The linear response range of the optimal ASS-IE was determined using various Tm^{3+} solutions with concentrations in the range of 1.0×10^{-9} to 1.0×10^{-2} M (Figure 1).


y = -19.596x + 231.15
R² = 0.9951
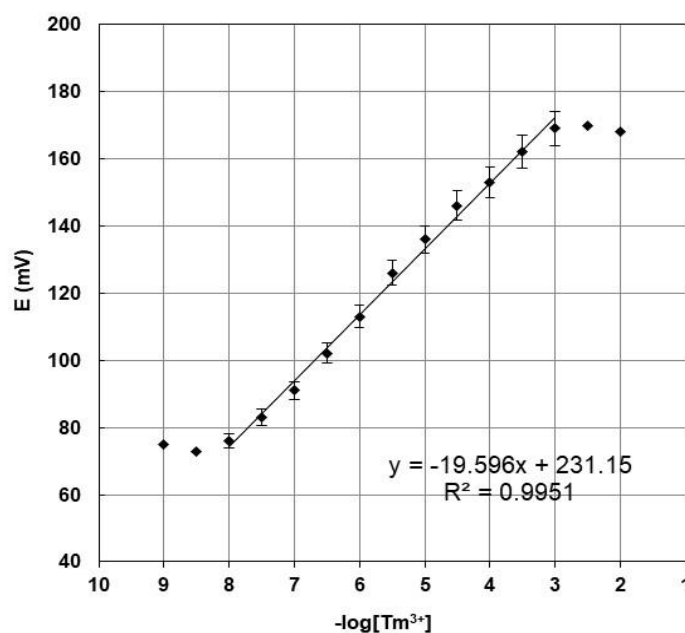
Figure 1. Calibration curve of the Tm^{3+}-ASS-ISE

The resulting calibration curve indicated that the sensor response was linear from 1.0×10^{-8} to 1.0×10^{-3} M, and the detection limit, which was determined by extrapolating the two linear segments of the calibration plot at low concentrations reached 6.3×10^{-9} M.

Asymmetric electrodes, like ASS-ISEs are known to produce lower detection limits in the range of 10^{-8} M and lower [12-15], which are much more improved as opposed to conventional symmetric PVC membrane sensors with detection limits as low as 10^{-5} to 10^{-6} M. In the case of the present work, the limit of detection was improved in comparison to that of a symmetrical PVC membrane sensor based on the same ionophore which is about 8.7×10^{-7} M [16]. The upper limit of detection of the electrode was as high as 10^{-3} M, which is in order of magnitude lower than the PVC-based membrane sensor based on the same ionophore [16], which is also anticipated given the smaller surface area values of asymmetrical devices in comparison to the symmetrical ones.

Also, the dynamic response time of the ASS-ISE, defined as the time required for reaching ±1 mV of the equilibrium potential of the electrode, after a 10-fold change in the concentration of the test solution [31-38] was evaluated. This factor was evaluated by successively immersing the electrodes in TM solutions with 10-fold concentration differences (in the concentration window of 1.0×10^{-8} to 1.0×10^{-3} M) and determining the time they took to reach the equilibrium potential. The results showed that the electrode quickly reached the equilibrium potential after an average time of only 7.0 ± 0.2 seconds.
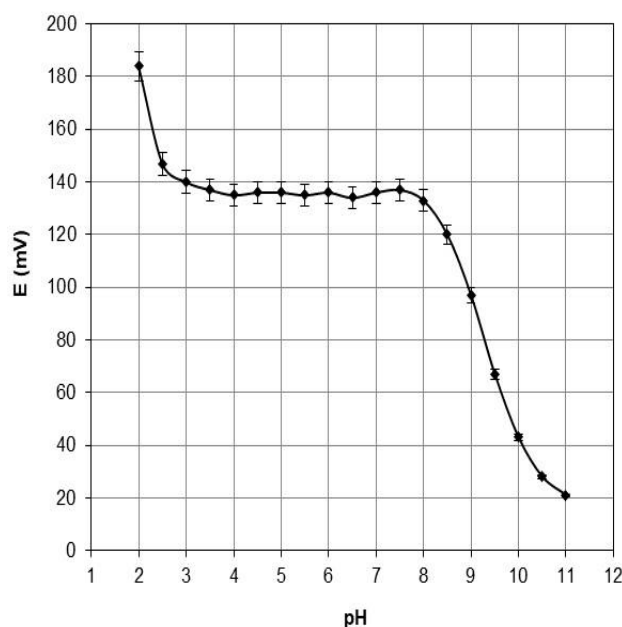
Figure 2. Effect of solution pH on the response of the Tm^{3+}-ASS-ISE in a 1.0×10^{-5} M solution of Tm^{3+}

The influence of the pH of the test solution, on the response of the electrode, was evaluated via monitoring the ASS-ISE response to a fixed concentration of the Tm^{3+} solution (1.0×10^{-5} M of Tm^{3+}) while the solution pH was altered by adding small volumes of concentrated NaOH or HCl solutions, while minimizing changes in the concentration of the Tm^{3+} solution. In this test, the pH of the test solution was changed between 2.0 to 11.0 (Figure 2). The results indicate that the response of the all-solid-state electrode was independent of the pH of the test solution from 3.0 to 8.0.

The sharp change in potentials at the higher pH values may be due to changes observed beyond the upper and lower pH values corresponding to the formation of soluble $Tm(OH)^{2+}$, $Tm(OH)_2^+$ or $Tm(OH)_3$ in higher pH values, as well as the protonation of the donor atoms of L (competition of the H^+ ions with the Tm^{3+} ions) at lower pH.

The lifetime of the ASS-ISE was evaluated by using the device for 60 minutes a day for three months and recording the calibration plot slope and detection limit (Table 2). Based on the results the ASS-ISE produces reliable results for at least 10 weeks, after which the Nernstian slope and detection limit undergo considerable changes, which can be attributed to the leakage of the membrane ingredients like the ion carrier, plasticizer, and ionic additive [39-44].

Table 2. Data on the evaluation of the lifetime of Tm^{3+}-ASS-ISE

Week	ASS-ISE Performance	
	Slope (mV per decade)	DL (M)
First	19.6± 0.4	6.3×10^{-9}
Second	19.6± 0.5	6.3×10^{-9}
Third	19.5± 0.5	6.5×10^{-9}
Fourth	19.4± 0.4	6.7×10^{-9}
Fifth	19.3± 0.4	6.8×10^{-9}
Sixth	19.1± 0.5	7.0×10^{-9}
Seventh	19.0± 0.3	7.3×10^{-9}
Eighth	19.6± 0.4	7.7×10^{-9}
Ninth	19.6± 0.5	9.0×10^{-9}
Tenth	18.9± 0.7	1.0×10^{-8}
Eleventh	16.6± 0.5	5.0×10^{-7}
Twelfth	12.2± 0.7	8.3×10^{-6}

The selectivity behavior of the developed all-solid-state ISE was evaluated by measuring the response of the electrode to the target ion solutions also containing other interfering ionic species. The selectivity coefficients, calculated through the matched potential method (MPM) [37-44], are presented in Table 3. From these results, it is clear that the electrode has high

selectivity for Tm^{3+} in the presence of most interfering ions. For trivalent ions of other lanthanide series, the MPM selectivity coefficients were 7.9×10^{-3} M or smaller, while this value for other common cations was 1.0×10^{-3} M or smaller for all mono and divalent interfering species reflecting its considerable selectivity, and the applicability of the electrode in the determination of Tm^{3+} in the presence of rather large concentrations of these ions.

Table 3. Selectivity coefficients obtained for the sensor

Interfering species	Log (K_{MPM})	Interfering species	Log (K_{MPM})
Na^+	-4.4	La^{3+}	-3.0
K^+	-4.3	Ce^{3+}	-2.9
NH_4^+	-4.3	Dy^{3+}	-2.8
Ca^{2+}	-4.2	Nd^{3+}	-2.8
Mg^{2+}	-4.1	Eu^{3+}	-2.5
Co^{2+}	-3.8	Sm^{3+}	-2.7
Ni^{2+}	-3.9	Gd^{3+}	-2.6
Zn^{2+}	-3.3	Lu^{3+}	-2.1
Cd^{2+}	-3.5	Er^{3+}	-2.3
Pb^{2+}	-3.7	Yb^{3+}	-2.2
Fe^{3+}	-3.2	Eu^{3+}	-2.7
Cu^{2+}	-3.4	Tb^{3+}	-2.5
Hg^{2+}	-3.0	Ho^{3+}	-2.2

The optimal membrane ASS-ISEs were used in the determination of the concentration of Tm^{3+} ion in three wastewater samples obtained from some local companies without any sophisticated sample preparation. Since the obtained wastewater did not have thulium content, certain amounts of Tm^{3+} were spiked in the samples.

Table 4. Results of the Tm^{3+} content analysis of wastewater samples

Sample no.	Added (M)	Found (M)*	Recovery (%)
1	0	-	-
	1.0×10^{-7}	$9.4 \pm 0.3 \times 10^{-8}$	94
	5.0×10^{-7}	$9.6 \pm 0.2 \times 10^{-8}$	96
2	0	-	-
	1.0×10^{-7}	$9.7 \pm 0.3 \times 10^{-8}$	97
	5.0×10^{-7}	$5.1 \pm 0.3 \times 10^{-7}$	102
3	0	-	-
	1.0×10^{-7}	$1.1 \pm 0.4 \times 10^{-7}$	110

	5.0×10^{-7}	$5.3\pm0.2\times10^{-7}$	106

*The results are the mean of three replicate measurements.

The typical procedure involved filtering each sample and diluting a certain amount of liquid 10 times with distilled water in a 100 mL volumetric flask, following the addition of a certain concentration of a standard thulium nitrate solution. The potentiometric measurements were done through the standard addition method using the developed electrode as the indicator (Table 4). The recoveries concentration of Tm^{3+} ions were satisfied.

4. CONCLUSION

An all-solid-state Tm^{3+} selective potentiometric electrode was designed using a copper wire coated with a layer of conducting polymer composed of MWCNTs and an epoxy resin as the substrate for coating a liquid PVC membrane as a sensing element. The PVC film is composed of 25% wt. of PVC powder, 68% wt. of benzyl acetate as a plasticizer and solvent of the membrane, 2% wt. of sodium tetraphenylborate (NaTPB)) as an ion exchanger, and 5%wt. of a suitable selectophore named N′-[(2-hydroxyphenyl)methylidene]-2-furohydrazide. The response of the sensor was linear from 1.0×10^{-8} M to 1.0×10^{-3} M, it had a Nernstian response of 19.6 ± 0.3 mV/decade and its limit of detection was 6.3×10^{-9} M. Response of the sensor was 7.0 ± 0.2 s. The proposed sensor has good mechanical stability and its lifetime is about 10 weeks. The sensor can be applied in the determination of thulium trivalent cations in wastewater samples without any sophisticated sample preparations and interferences of common cations.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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