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Evaluation and Characteristics of a Tb^{3+} Electrochemical Sensor Based on Plasticized Poly(vinyl chloride) Membrane

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A new greatly selective and sensitive PVC membrane sensor has been developed as a Tb^{3+} ion selective electrode, using an ionophore named 3-Hydroxybenzaldehyde azine (HBH). The best performance was obtained with a membrane composition of 30% poly(vinyl chloride), 66% nitrobenzen (NB), 2% HBH and 2% sodium tetraphenylborate (NaTPB). Fortunately, the benefits illustrated by the use of this sensor basically include a fast response time, lower detection limit, comparatively good selectivity with respect to alkali, alkaline earth, some transition, and heavy metal ions. The sensor works satisfactorily in the concentration range of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} with detection limit of 8.3×10^{-7} mol L^{-1} and a Nernstian slope of 20.2±0.2 mV $decade^{-1}$ of activity. This electrode showed a fast response time (~5 s). The proposed sensor was successfully applied as an indicator electrode for the potentiometric titration of a Tb^{3+} solution, with EDTA. It was also applied to the monitoring of terbium ion in various mixtures of different metal ions and the fluoride ion determination in some mouth washing solutions.

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

1. INTRODUCTION

Terbium is rare and expensive, so it has few commercial uses. Some minor uses are in lasers, semiconductor devices, and phosphorous in colour television tubes. It is also used in solid-state devices, optical fibers, as stabilizer of fuel cells which operate at high temperature [1]. Terbium is not found free in nature but is found in a number of minerals: mainly monazite, zenotime and euxenite. Commercially it is produced from monazite using a complex ion-exchange process. A terbium-iron alloy is used to provide metallic films for magneto-optic recording of data. Terbium has 26 isotopes whose half-lives are known, with mass numbers 140 to 165. Of these, one is stable, ^{159}Tb [2]. Spectroscopy, inductively coupled plasma mass spectroscopy (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) are the main methods for determination of terbium ions in solutions. These methods are time consuming, involving sample preparations, and too expensive for most analytical laboratories. Also, the sample was destroyed after measurement. Ion selective electrodes (ISEs) are one of the selective methods for monitoring and determination of rare earth elements. ISEs offer advantages of low cost, portability, selectivity, and simple operatory. They also provide an analysis method without destruction of sample [3-10]. There are only a limited number of reports on the development of highly selective ionophores for terbium [11-13].

Recently, our research team and other researchers were reported several membrane electrodes for metal ions [14-40]. In this work, a relatively sensitive and selective Tb^{3+} ion-selective membrane electrode was employed with the help of 3-Hydroxybenzaldehyde azine (HBH) (Fig.1) as an neutral ionophore for the Tb^{3+} ion determination with relatively low detection limit and fast response time.

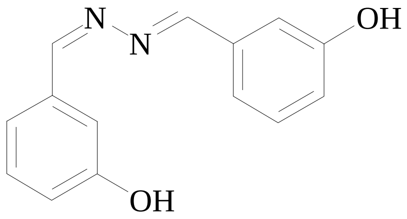

Figure 1. The chemical structure of HBH.

2. EXPERIMENTAL

2.1. Reagents

The Merck and the Aldrich Chemical Co. were the provider for the nitrate and chloride salts of all cations as well as for the following reagents; reagent-grades of phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), acetophenone (AP), oleic acid (OA), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and relatively high molecular weight PVC. All reagents were used without any modification. As far as the nitrate and chloride salts of all employed cations are concerned, they were of the highest available purity and were P_2O_5-vacuum dried. During the experiments, doubly distilled deionized water was used.

2.2. The EMF measurements

The EMF measurements with the polymeric membrane were carried out with the following cell assemblies:

Ag–AgCl| 1.0×10^{-3} mol L^{-1} $TbCl_3$ | PVC membrane: test solution| Hg–Hg_2Cl_2, KCl (satd).

A Corning ion analyser 250 pH/mV meter was used for the potential measurements at 25.0 °C. The activities were calculated according to the Debye–Huckel procedure [41].

2.3. The construction of membrane

The PVC membrane was prepared by blending 2 mg HBH ionophore, 2 mg NaTPB, 66 mg NB, and 30 mg PVC and dissolving in 3 mL THF. The resulting homogeneous mixture was transferred into a glass dish with a 2 cm diameter. The solvent was then evaporated slowly, until an oily concentrated mixture was obtained. A Pyrex tube (3–5 mm in top) was dipped into the oily mixture for about 5 s, so that a transparent film of about 0.3 mm thickness was formed [42-60]. Afterwards, the tube was removed from the mixture, kept at the room temperature for about 24 h and filled with the internal filling solution (1.0×10^{-3} mol L^{-1} $TbCl_3$). The electrode was, finally, conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} $TbCl_3$ solution. A silver–silver chloride electrode was used as an internal reference electrode.

2.4. The selectivity study of the sensor

The potentiometric selectivity coefficient, which reflects the relative response of the membrane sensor for the primary ion over other ions that are present in solution, is perhaps the most important characteristic of an ion-selective electrode. The selectivity coefficients for the proposed sensor were determined by the matched potential method (MPM) [61-65]. In accordance with the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion (A) and the interfering ion (B), $K^{\mathrm{MPM}}_{A,B}=a_A/a_B$, which gives some potential change in a reference solution.

3. RESULTS AND DISCISSION

3.1. The potential response of the sensor

In the HBH structure, four donor atoms (two N and two O) exist. The existence of this donating atoms in the HBH structure was expected to increase both the stability and selectivity of its complexes with transition and heavy metal ions, rather than alkali and alkaline earth metal ions. For this purpose, in preliminary experiments, in order to evaluate the suitability of the HBH as a sensing ionophore for different cations, it was used to prepare plasticized polymeric membrane for a wide variety of metal ions, including alkali, alkaline earth, transition, and heavy metal ions. The potential responses obtained of some of the most sensitive electrodes based on HBH are shown in Figure 2. As it is seen from Figure 2, except for the Tb^{3+} ion-selective electrode, for all other cations, the slope of the corresponding potential pM^{n+} plots is much lower than the expected Nernstian slopes of 59, 29.5, and 20 mV $decade^{-1}$ for the univalent, bivalent, and trivalent metal ions, respectively. Due to the existence of a semi cavity with donor atoms in the structure of HBH, it can form relatively strong complex with transition metal ions, and especially lanthanide metal ions. The selective behavior against Tb^{3+} is likely due to the high ionophore selectivity for cobalt ions over other metal ions as well as the rapid exchange kinetics of the resulting Tb^{3+}-HBH complex.

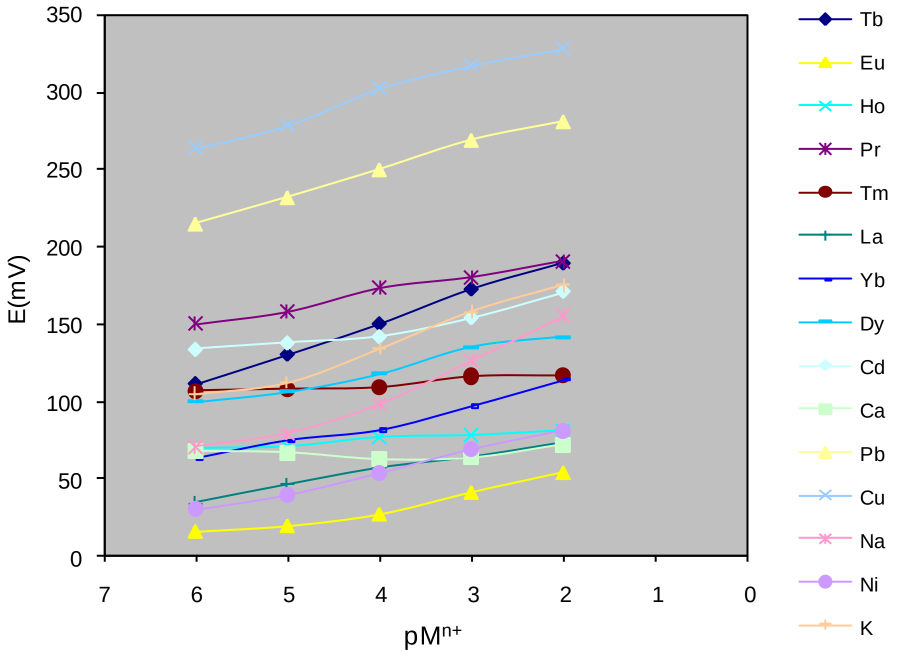

Figure 2. Potential responses of various ion-selective electrodes based on HBH.

3.2. The membrane composition effect on the potential response

It is well established that some important features of the PVC based membranes, such as the properties of the plasticizer, the nature and the amount of ionophore, the plasticizer/PVC ratio and, particularly, the nature of the used additives, significantly influence the sensitivity and selectivity of the ion-selective electrodes [66-72]. Thus, the influences of the membrane composition, the nature and the amount of plasticizer and the amount of sodium tetraphenylborate and oleic acid (OA) as additives on the potential response of the terbium electrodes were investigated and the results are given in Table 1. As can be seen from Table 1, increasing the amount of HBH up to 2% resulted in the membranes (No. 2 and 10-14) that display larger slopes. A maximum slope of 20.2 ± 0.2 mV decade^{-1} of terbium concentration was observed for the membrane No. 2 with 2% of HBH. It is reported that the selectivity and the working concentration range of the membrane sensor are affected by the nature and the amount of the used plasticizer [66, 73-80]. From Table 1, it is evident that among the four tried plasticizers, NB offers the best sensitivity. This phenomenon can be attributed to the plasticizer influence on the dielectric constant of the membrane phase, the ionophore molecules mobility, and the state of ligands. Obviously from Table 1, the sensor slope in the absence of the used additives is lower than the expected Nernstian value (membranes No. 9). As it is obvious from Table 1, the presence of 2% NaTPB, gave the provided the electrode with Nernstian potential responses. In fact, it is accepted that the presence of lipophilic negatively charged additives such as NaTPB in cation-selective membrane electrodes diminishes the ohmic resistance, enhances the response behavior and selectivity, and increases the sensitivity of the membrane electrodes [80-85]. However, the membrane sensor with composition of 30% PVC; 66% NB; 2% NaTPB, and 2% HBH exhibits the best performance.

Table 1. Optimization of membrane ingredients.

Sensor No.	Composition (wt%)				Slope (mV decade^{-1})	Concentration range (mol L^{-1})
	HBH	Additive	Plasticizer	PVC		
1	2	NaTPB,2;OA,0	AP, 66	30	16.8 ± 0.4	1.0×10^{-6}-1.0×10^{-2}
2	2	NaTPB,2;OA,0	NB, 66	30	20.2 ± 0.2	1.0×10^{-6}-1.0×10^{-2}
3	2	NaTPB,2;OA,0	BA, 66	30	15.3 ± 0.3	1.0×10^{-5}-1.0×10^{-2}
4	2	NaTPB,2;OA,0	DBP, 66	30	14.8 ± 0.4	1.0×10^{-5}-1.0×10^{-2}
5	1	NaTPB,2;OA,0	NB, 67	30	15.5 ± 0.2	1.0×10^{-6}-1.0×10^{-2}
6	1.5	NaTPB,2;OA,0	NB, 66.5	30	18.7 ± 0.5	1.0×10^{-6}-1.0×10^{-2}
7	2.5	NaTPB,2;OA,0	NB, 65.5	30	19.3 ± 0.3	1.0×10^{-6}-1.0×10^{-2}
8	3	NaTPB,2;OA,0	NB, 65	30	18.4 ± 0.6	1.0×10^{-6}-1.0×10^{-2}
9	2	NaTPB,0;OA,0	NB , 68	30	12.6 ± 0.3	1.0×10^{-5}-1.0×10^{-2}
10	2	NaTPB,1;OA,0	NB, 67	30	16.9 ± 0.5	1.0×10^{-6}-1.0×10^{-3}
11	2	NaTPB,3;OA,0	NB, 65	30	17.8 ± 0.4	1.0×10^{-6}-1.0×10^{-3}
12	2	NaTPB,2;OA,5	NB , 61	30	15.3 ± 0.2	1.0×10^{-6}-1.0×10^{-2}
13	2	NaTPB,2;OA,10	NB, 56	30	17.2 ± 0.3	1.0×10^{-6}-1.0×10^{-2}
14	2	NaTPB,2;OA,15	NB, 51	30	18.4 ± 0.5	1.0×10^{-6}-1.0×10^{-2}

3.3. Slope and detection limit of the Tb^{3+} sensor

As it can be observed from Figure 4, the developed sensor exhibits a Nernstian response slope of (20.2±0.2 mV decade^{-1}) across a broad concentration range of 1.0×10^{-6}-1.0×10^{-2} mol L^{-1}. The detection limit, defined as the Tb(III) concentration obtained after the extrapolation of the linear region of the standard plot to the baseline potential, was 5.3×10^{-7} mol L^{-1}. The standard deviation for ten replicate measurements was ±0.6 mV.

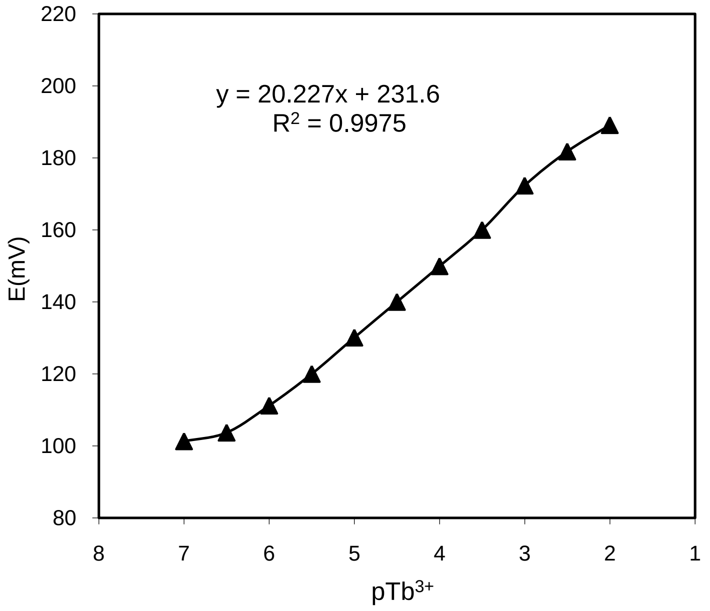

Figure 3. Calibration curve of the terbium sensor based on HBH.

3.4. pH effect

The behavior of the sensor in relation to the pH values variation (1.0–12.0) was studied at one particular concentrations of the Tb^{3+} activity of 1.0×10^{-3} mol L^{-1}, adjusted with nitric acid (0.1 M) and sodium hydroxide (0.1 M) as acidic and alkaline media. The reported data of Figure 4 exhibit that the potential remained constant from the pH value of 2.8 up to 9.2, beyond which some drifts in the potentials were observed. At values above pH 9.2, the potential decreased owing to the terbium hydroxide formation in the solution, while at lower pH values (<2.8), the potential increased, indicating that the membrane sensor responded to protonium ions, as a result of the extent nitrogen atom protonation of the ionophore.

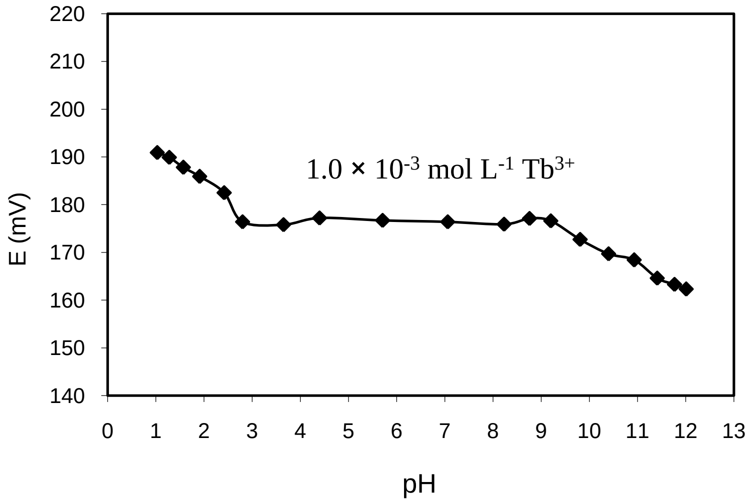

Figure 4. pH effect on the potential response of the Tb^{3+} electrode.

3.5. Dynamic response time

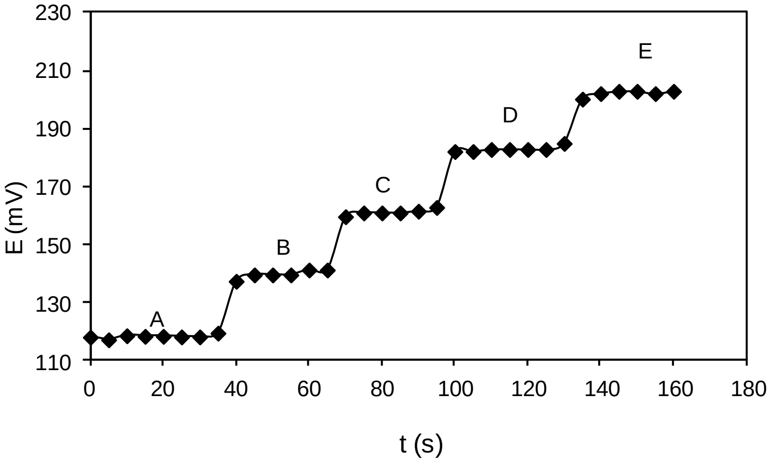

Figure 5. Dynamic response time of the terbium sensor for step changes in the Tb^{3+} concentration: A) 1.0×10^{-6} mol L^{-1}, B) 1.0×10^{-5} mol L^{-1}, C) 1.0×10^{-4} mol L^{-1}, D) 1.0×10^{-3} mol L^{-1}, E) 1.0×10^{-2} mol L^{-1}.

Dynamic response time is an important factor for any ion selective electrodes [86]. In this study, the practical response time of the sensor was recorded by changing the solution with different Tb^{3+} concentrations from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1}. The actual potential *versus* time trace for the electrode based on HBH is shown in Figure 5. As it can be seen, the electrode reaches its equilibrium response in a short time of about 5 s. This is most probably due to the fast exchange kinetics of complexation-decomplexation of Tb^{3+} ion with the ionophore at the test solution membrane interface.

3.6. The selectivity of the sensor

The selectivity coefficients for this work were calculated with the matched potential method (MPM). The potentiometric selectivity coefficients of the sensor towards different ions (Yb^{3+}, Sm^{3+}, La^{3+}, Eu^{3+}, Dy^{3+}, Tm^{3+}, Cr^{3+}, Fe^{3+}, Na^{+}, K^{+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, and Mg^{2+}) was determined and the results are summarized in Table 2. As can be seen, with the exception of Tb^{3+}, for all cations used, the selectivity coefficients are in the order of 4.6×10^{-3} or smaller, indicating they would not significantly disturb the functioning of the Tb^{3+} sensor.

Table 2. Selectivity coefficients of the Tb^{3+} electrode

M^{n+}	$K^{MPM}_{Tb^{3+},B}$	M^{n+}	$K^{MPM}_{Tb^{3+},B}$
Yb^{3+}	6.2×10^{-4}	Fe^{3+}	3.8×10^{-3}
Sm^{3+}	6.9×10^{-4}	Na^{+}	6.4×10^{-4}
La^{3+}	7.4×10^{-4}	K^{+}	8.9×10^{-4}
Eu^{3+}	2.1×10^{-3}	Cd^{2+}	7.5×10^{-4}
Dy^{3+}	2.5×10^{-3}	Hg^{2+}	2.2×10^{-3}
Tm^{3+}	4.6×10^{-3}	Cu^{2+}	8.7×10^{-4}
Cr^{3+}	4.4×10^{-3}	Mg^{2+}	7.7×10^{-4}

Table 3 compares the selectivity, detection limit, pH range, slope, response time and dynamic linearity range of the proposed sensor with the best previously reported Tb^{3+} sensors [11-13]. As seen, the proposed sensor not only, in term of selectivity, but also, in terms of pH range, response time and detection limit is superior than the reported Tb^{3+} sensors.

Table 3. Comparison of different Tb(III) electrodes.

Parameter	Ref. 11	Ref. 12	Ref. 13	This work
LR (mol L^{-1})	1.0×10^{-6}-1.0×10^{-1}	1.0×10^{-6}-1.0×10^{-1}	1.0×10^{-5}-1.0×10^{-1}	1.0×10^{-6}-1.0×10^{-2}
DL (mol L^{-1})	8.0×10^{-7}	8.6×10^{-7}	7.0×10^{-6}	5.3×10^{-7}
Response time (s)	~10	15	<20	~5
pH range	3.5-8.0	3.8-8.2	3.5-7.7	2.8-9.2
Slope(mVdecade^{-1})	19.7	19.4	19.8	20.2
Log K_{sel}>-2	Gd	Gd	Ce, La, Dy, Yb, Sm	-

3.7. Analytical application

The selective terbium membrane sensor was used as an indicator electrode in titration of 1.0×10^{-4} mol L^{-1} solution of terbium ions with a standard 1.0×10^{-2} mol L^{-1} EDTA and the resulting titration curve is shown in Figure 6. As can be seen from Figure 6, the sensor can monitor the amount of terbium ions.

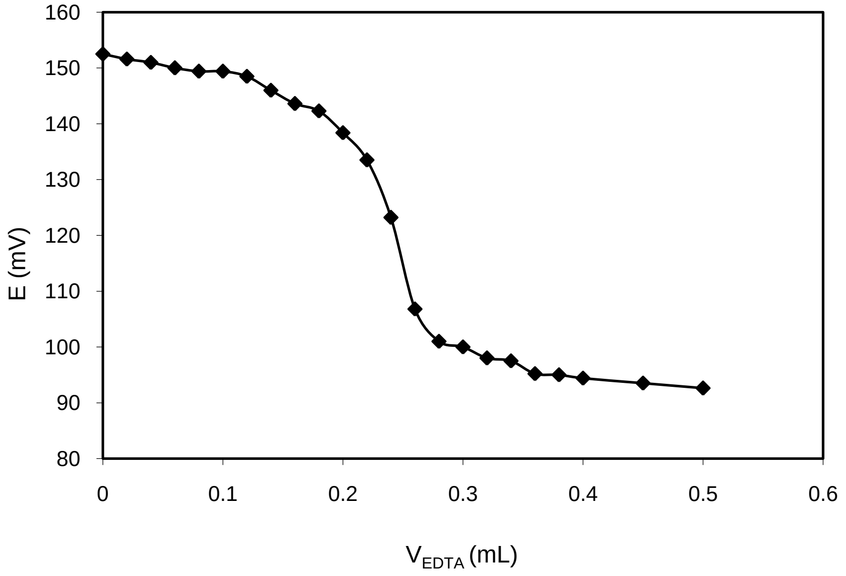

Figure 6. Potential titration curve of 25.0 mL from a 1.0×10^{-4} mol L^{-1} Tb^{3+} solution with 1.0×10^{-2} mol L^{-1} of EDTA.

The high degree of terbium selectivity, the constructed Tb^{3+} membrane sensor was also successfully used for the monitoring of F^{-} ions in two mouth wash samples. In detail, 1.0 g of each sample was taken and diluted with distilled water in a 100 mL flask and titrated with a Tb^{3+} solution (1.0×10^{-3} mol L^{-1}). The corresponding results (after triplicate measurements) are summarized in Table 4. The measurement principle for the determination of fluoride ions was based on the monitoring of the Tb^{3+} ion concentration. Evidently, there is satisfactory agreement among the declared fluoride content and the values determined by the proposed electrode.

Table 4. Determination of fluoride ions in mouth wash solutions.

Sample	Labeled (mg L^{-1})	Found ISE[a] (mg L^{-1})
Sodium fluoride mouth wash solution (Aquafresh, Brentford, U.K.)	1350	(1378[b] ± 18)
Sodium fluoride mouth wash solution (Eurodont, DuroDont GmbH)	1450	(1481[b] ± 21)

a. Proposed Tb^{3+} sensor

b. Results are based on three measurements

The electrode was also applied to the monitoring of Tb^{3+} in various mixtures of different metal ions. The results (Table 5) obtained with the sensor, were close enough for us conclude that the proposed sensor could be used in the monitoring of Tb^{3+} ion.

Table 5. Determination of Tb^{3+} ions in mixtures of different ions.

Serial no.	Composition	Observed content(mol L^{-1})
1	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Ho(NO_3)_3$ + 0.0001 mol L^{-1} $Eu(NO_3)_3$	0.0000096
2	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Yb(NO_3)_3$ + 0.0001 mol L^{-1} $La(NO_3)_3$	0.0000103
3	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Er(NO_3)_3$ + 0.0001 mol L^{-1} $Pr(NO_3)_3$	0.0000101
4	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Sm(NO_3)_3$ + 0.0001 mol L^{-1} $Gd(NO_3)_3$	0.0000097
5	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Dy(NO_3)_3$ + 0.0001 mol L^{-1} $Nd(NO_3)_3$	0.0000097
6	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Tm(NO_3)_3$ + 0.0001 mol L^{-1} $Lu(NO_3)_3$	0.0000098
7	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Cr(NO_3)_3$+ 0.0001 mol L^{-1} $Fe(NO_3)_3$	0.0000096
8	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} KNO_3 + 0.0001 mol L^{-1} $Ni(NO_3)_2$	0.0000103
9	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Ca(NO_3)_2$ + 0.0001 mol L^{-1} $NaNO_3$	0.0000098
10	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Pb(NO_3)_2$+ 0.0001 mol L^{-1} $Co(NO_3)_2$	0.0000104

4. CONCLUSION

This study reveals that a potentiometric PVC constructed membrane sensor, which is based on the HBH functions, consists of an excellent Tb^{3+} selective sensor. The electrode exhibited a Nernstian response (slope of 19.8±0.4 mV $decade^{-1}$), low limit of detection (8.3×10^{-8} mol L^{-1}), applicable pH range of 2.2–9.7, fast response time (about 5 s) and wide linear range (1.0×10^{-7} to 1.0×10^{-2} mol L^{-1}) and very low interference from common alkali, alkaline earth, transition and heavy metal ions. The applicable pH range, lower detection limit, short response time and potentiometric selectivity coefficients of the proposed sensor make it a superior device compared with other methods used for the determinations of this ion. The selectivity coefficients of the sensor for the common alkaline and alkaline earth metal, transition and lanthanide ions are very low and makes it as suitable device for the determination of this ion in the presence of considerable concentrations of common interfering ions in solution samples.

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