

A Novel Ho(III) Sensor based on *N,N'*-Bis(2- pyridinecarboxamide)-1,2-benzene as a Neutral Ion Carrier

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N,N'-bis(2- piridinacarboxamida)-1,2-benzeno (H_2BPB) apresentou um comportamento seletivo e sensível, frente ao íon Ho(III), em comparação a um grande número de íons de metais de transição interna, representativos e de lantanídeos, tendo sido portanto, aplicado como um ionóforo neutro para preparação de uma membrana sensora Ho(III), com alta seletividade e sensibilidade. As membranas também contêm tetraquis(*p*-clorofenil) borato de potássio (KTPCIPB) como um aditivo aniônico, e foram testadas pelo uso de diferentes solventes mediadores plastificantes, tais como benzil acetato (BA), nitrobenzeno (NB), e éter *o*-nitrofeniloctil (NPOE). A composição ótima encontrada foi H_2BPB -PVC- KTPCIPB-BA, com razão de 6,0: 30,0: 4,0: 60,0, respectivamente. Com uma resposta Nernstiniana de $19,6 \pm 0,2$ mV *per* década de atividade de Ho(III), o intervalo linear encontrado para o sensor foi relativamente grande (de $1,0 \times 10^{-5}$ a $1,0 \times 10^{-2}$ mol L⁻¹), podendo trabalhar bem no intervalo de pH de 3,0 a 11,5. O limite de detecção mais baixo (LDL) calculado para o sensor foi de $8,0 \times 10^{-6}$ mol L⁻¹. A excelente seletividade do sensor proposto para Ho(III), considerando os íons metálicos mais comuns e, especialmente todos os íons lantanídeos, é uma outra vantagem deste sensor. O sensor foi usado com sucesso como eletrodo indicador na titulação de 25 mL de solução de íons Ho(III) a $1,0 \times 10^{-4}$ mol L⁻¹, com EDTA a $1,0 \times 10^{-2}$ mol L⁻¹, e *vice-versa*. Este é o primeiro sensor seletivo para Ho(III).

N,N'-bis(2- pyridinecarboxamide)-1,2-benzene (H_2BPB) was found to have a selective and sensitive behavior towards Ho(III) ion, in comparison to a large number of lanthanide, inner transition and representative metal ions and was hence applied as a neutral ionophore, for preparing an Ho(III) membrane sensor, with high selectivity and sensitivity. The membranes, also contain potassium tetrakis(*p*-chlorophenyl) borate as an anionic additives, and were tested by using different plasticizing solvent mediators such as benzyl acetate (BA), nitrobenzene (NB), and *o*-nitrophenyloctyl ether (NPOE). The optimum composition was found to be H_2BPB -PVC- KTPCIPB-BA with the ratios of 6.0: 30.0: 4.0: 60.0, respectively. Having a Nernstian response of 19.6 ± 0.2 mV *per* decade of Ho(III) activity, the linear range of the sensor was found to be relatively wide (from 1.0×10^{-5} to 1.0×10^{-2} mol L⁻¹). It can work well in the pH range of 3.0-11.5. The lower detection limit (LDL) of the sensor was calculated to be 8.0×10^{-6} mol L⁻¹. The excellent Ho(III)-selectivity of the proposed sensor with regard to most common metal ions, and especially, all lanthanide ions, is another advantage that can be mentioned about this sensor. The sensor was successfully used as an indicator electrode for titration of 25 mL of a 1.0×10^{-4} mol L⁻¹ Ho(III) ions with a 1.0×10^{-2} mol L⁻¹ EDTA, and *vice versa*. To the best of our knowledge this is the first Ho(III)-selective sensor.

Keywords: Ho(III), ion selective electrode, PVC, *N,N'*-bis(2-pyridinecarboxamide)-1,2- benzene

Introduction

Holmium, being a rare earth, can absorb fission-bored, so is used in nuclear reactors to keep a chain reaction under control. Its very high magnetic moment makes it

suitable for use in yttrium-iron-garnet (YIG) and yttrium-lanthanum-fluoride (YLF) solid-state lasers found in microwave equipment (which are in turn found in a variety of medical and dental settings). It is one of the rare earths that can be found in equipment such as color televisions, fluorescent lamps, energy-saving lamps and glasses. The use of holmium is still growing, due to the fact that it is

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studied to produce catalysts and to polish glass.¹ Holmium can be a threat to the liver when it accumulates in the human body. Today we know that with water animals, holmium causes damage to cell membranes, which has several negative influences on reproduction the functions of the nervous system. This makes the analysis of this element greatly important. However conventional methods that can be used for the analysis of this element, such as ICP-AES, neutron activation analysis, are either expensive or difficult to work with. Hence the ability to analyze this element in different matrixes is of great importance.

The recent introduction of a number of lanthanide selective membrane sensors for La(III), Ce(III), Gd(III), Sm(III), Eu(III), Dy(III), and Yb(III) ions based on different noncyclic and macrocyclic ionophore, by our own and other groups,²⁻²⁸ inspired us to try the construction of a Ho(III)-selective electrode based on a H₂BPB as an ion carrier. The resulting electrode shows to be suitable for the determination of Ho(III) concentration in the range of 1.0×10^{-5} - 1.0×10^{-2} mol L⁻¹, with a lower detection limit of 8.0×10^{-6} mol L⁻¹ and within pH values between 3.0-11.5. To the best of our knowledge this is the first report on Ho(III) sensor.

Experimental

Reagents

Reagent grade benzyl acetate (BA), nitrobenzene (NB), *o*-nitrophenyloctyl ether (NPOE), high relative molecular weight PVC, tetrakis(*p*-chlorophenyl) borate (KTPCIPB), and tetrahydrofuran (THF) were purchased from Aldrich and used as received. 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. Triply distilled deionized water was used throughout. H₂BPB was synthesized by a famous method in the literature.²⁹

Electrode preparation

To prepare the electrodes 30 mg of powdered PVC, 60 mg of BA and 6 mg of additive KTPCIPB were dissolved in 3 mL of THF, and 6 mg of H₂BPB was added to the resulting solution, which had a low viscosity. After completely mixing the solution it was transferred into a glass dish of 2 cm diameter, and then its solvent was let evaporate so as to gain an oily concentrated mixture. The membrane was then formed on the tip of a Pyrex tube of (3-5 mm o.d.), by inserting

the tube into the viscose mixture for about 10 s, so that a transparent membrane of about 0.3 mm thickness was formed. Before being filled with an internal filling solution (1.0×10^{-3} mol L⁻¹ HoCl₃), the tube was pulled out and given enough time to dry at room temperature for about 10 h. The final step was to condition the electrode for 24 h, by soaking in a 1.0×10^{-3} mol L⁻¹ Ho(NO₃)₃ solution. A Silver/Silver chloride coated wire was used as an internal reference electrode.

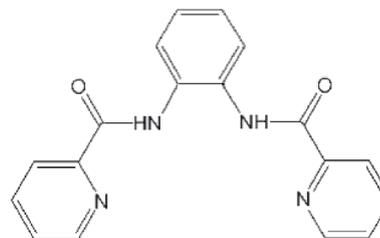


Figure 1. Structure of H₂BPB.

EMF measurements

The cell assembly Ag-AgCl/ internal solution (1.0×10^{-3} mol L⁻¹ HoCl₃) / PVC Membrane / test solution / Hg₂Cl₂, KCl (satd.) was used for all measurements.

All potential measurements were carried out by means of a Corning ion analyzer 250 pH / mV meter at 25.0 ± 0.1 °C.

Results and Discussion

Regarding that some neutral ion carriers, containing nitrogen and sulfur donor atoms, have been reported, to be used in construction of highly selective transition and heavy metal ion membrane sensors, lately²⁻²⁸ and considering the existence of four nitrogen donor atoms in the semi cavity of H₂BPB, it was expected to act as a suitable ion carrier for special transition and heavy metal ions (specially, higher charge density), in the PVC membranes.

To investigate the possible ions towards which, H₂BPB is selective, during the initial experiments this carrier was used in the construction of membrane sensors for lanthanide ions like Er³⁺, La³⁺, Pr³⁺, Sm³⁺, Dy³⁺, Ho³⁺, Tm³⁺, Nd³⁺, and other representative and transition metal ions like Na⁺, K⁺, Ca²⁺, Mg²⁺, Pb²⁺, Cu²⁺ ions. The curves of the best potential responses of the resulting membranes vs. changing the concentration of each ion, that are shown in Figure 2(a, b), revealed that among the lanthanide, transition and representative ions tested, Ho(III) with the most Nernstian response, can be suitably determined with the PVC membrane sensor based on H₂BPB.

This behavior may be considered to be the result of the selective tendency of the ionophore against Ho(III) (with relatively low charge density and hydration energy), in comparison to other metal ions, and the rapid exchange kinetics of the resulting H_2BPB - Ho(III) complex.

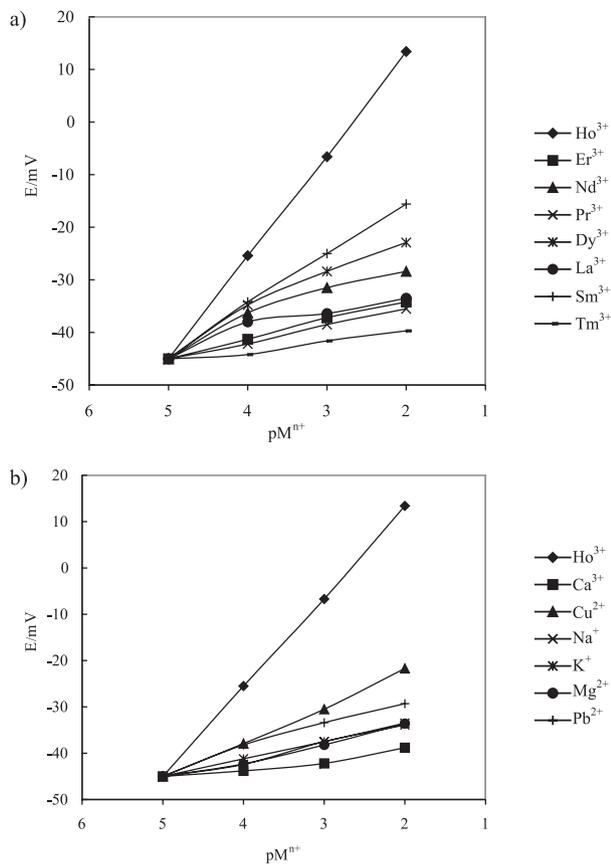


Figure 2. (a) and (b) Potential response various metal ion-selective electrodes based on H_2BPB .

Because the sensitivity and selectivity of any given membrane sensor is significantly related to, the composition of the ion selective membrane, and the nature of the solvent mediators and additives used,^{2-28,30,31} we decided to study such effects on the behavior of the proposed sensor. The effect of the nature and amount of the plasticizer and the additive on the potential

response of the proposed Ho(III) sensor were investigated, and the results are summarized in Table 1. These data revealed that the three different plasticizers used, BA, NB, and *o*-NPOE have almost the same results if the optimum composition is used, however, because NB, and *o*-NPOE are very polar, leading to the extraction of the polar interfering ions such as other rare earth ions which may have negative effects on the selectivity behavior of the sensor, BA was chosen as the solvent mediator. This may lead to the poorer extraction of Ho(III) ion, that has very high charge density, by the average-polar solvent. However, considering the experimental results, it seems that this effect is compensated by the selective complexation of H_2BPB with the Ho(III) ions. This way, not only was the slope of the sensor response maintained, but its selectivity pattern was also improved.

In addition, one can understand from the data in Table 1 that increasing the amount of the ion carrier, up to a value of 6%, increases the sensitivity, while the slope of the resulting emf vs. log Ho(III) concentration plot is about two-thirds of the expected Nernstian value (membranes No. 2). However, addition of 4% KTpCIPB (membranes No. 5) will increase the sensitivity of the electrode response to a great extent. The fact that the presence of lipophilic anions in the composition of cationic-selective membrane sensors, not only diminishes the ohmic resistance and enhances the potential behavior and selectivity, but also in poor extraction capacities, increases the sensitivity of the membrane electrodes, has long been known.³²

The potential response of the sensor was evaluated using the optimum composition of all ingredients, while lacking the ionophore, and it was found that under these conditions the response of the sensors falls to very low values of 6.2 mV decade⁻¹, indicating that the sensitivity of the sensor is majorly due to the complexing behavior of H_2BPB .

The optimum equilibration time for the membrane electrode, after which it generates stable potentials when placed in contact with Ho(III) solutions, is found to be 20 h.

Table 1. Optimization of membrane ingredients

Membrane	Composition / (%)				Slope / (mV decade ⁻¹)
	PVC	Plasticizer	H_2BPB	Additive	
1	30	65, BA	5	-	10.1±0.3
2	30	64, BA	6	-	10.5±0.7
3	30	62, BA	5	4, KTpCIPB	14.3±0.3
4	30	61, BA	5	5, KTpCIPB	16.8±0.2
5	30	60, BA	6	4, KTpCIPB	19.6±0.2
6	30	65, BA	-	5, KTpCIPB	5.0±0.3
7	30	60, NB	6	4, KTpCIPB	18.7±0.2
8	30	60, NPOE	6	4, KTpCIPB	19.1±0.3

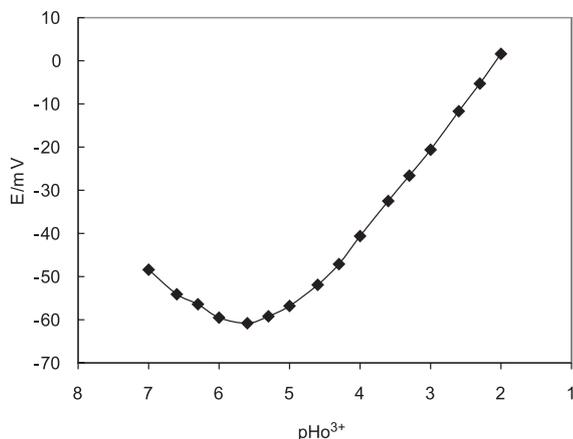


Figure 3. Calibration curve of the Ho(III) sensor of membrane.

The critical response characteristics of the Ho(III) sensor were assessed according to IUPAC recommendations.³³ The potential response of the membrane at varying concentration of Ho(III) ions (Figure 3) indicates a rectilinear range from 1.0×10^{-5} - 1.0×10^{-2} mol L⁻¹. The slopes of the calibration curves were 19.6 ± 0.2 mV decade⁻¹ of Ho(III) concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 8.0×10^{-6} mol L⁻¹.

The influence of pH on the response of the membrane sensor to 1.0×10^{-4} mol L⁻¹ and 1.0×10^{-3} mol L⁻¹ Ho(III) solutions, was studied over a pH range of 1.5 to 13.0, and the results are shown in Figure 4. For the 1.0×10^{-4} mol L⁻¹ Ho(III) solution the potential does not change with changing pH the pH range of 3.0 to 11.5, that indicates the applicability of this sensor in the mentioned pH range. Beyond these limits, however, relatively drastic drifts in the potential vs. pH behavior were observed. The observed drift at the higher pH values of this range could be due to the formation of insoluble Ho(OH)₃ in the solution. In acidic solutions having pH values of less than the minimum of this range, the ionophore used could be protonated to some extent, which results in improper functioning of the membrane electrode to the Ho(III) ion concentration. This can be further justified by the second curve, namely that of a 1.0×10^{-3} mol L⁻¹ Ho(III) solution. In this case slight changes in the applicability range of the sensor are observed and the potential is pH independent in the range of 2.5-10.5. This supports the fact that the formation of insoluble Ho(OH)₃ species that takes place at relatively lower pH values (10.5 instead of 11.5 in the former case) may be responsible for the potential drifts at higher pH values. It is also evident that at a relatively higher Ho(III) concentration,

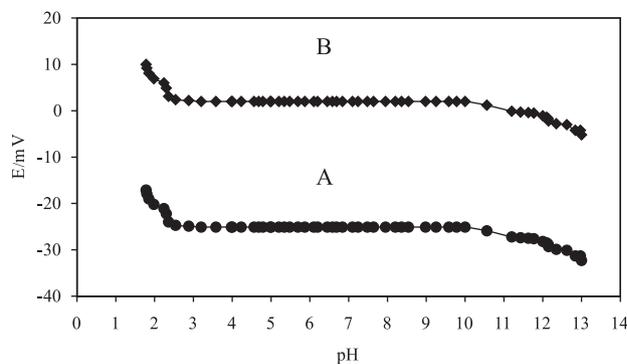


Figure 4. Effect of the pH of test solution (A= 1.0×10^{-4} mol L⁻¹, and B= 1.0×10^{-3} mol L⁻¹) on the potential response of the Ho(III) ion-selective electrode.

the target ions tend to compete more seriously with the proton ions at lower pH values which extends the applicability pH range of the sensor at to a value of 2 (rather than 3 in the case of the more dilute solution of 1×10^{-4} mol L⁻¹ solution).

The lifetime of the sensor, which is a measure of sensors durability, was also studied in a 4 months period. During this period the sensor was used for 2 hours a day, 5 days a week. After each usage it was washed completely. After three months only a relatively slight change in the sensor's slope and detection limit from 19.6 ± 0.2 mV decade⁻¹ of Ho(III) concentration and 8×10^{-6} mol L⁻¹ to 17.1 ± 0.4 mV decade⁻¹ of Ho(III) concentration and 5×10^{-5} mol L⁻¹ was observed. The results of this study are shown in Table 3.

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, matched potential and separated solution methods (MPM and SSM)³⁵ were used for determination of selectivity coefficients of the sensor. According to the general procedure for the determination of the matched potential method a specified amount of the target ion solution is added to a reference solution and the membrane potential is measured. In another experiment, known amounts of different interfering ion solutions are successively added to an identical reference solution until the membrane potential matches the one obtained before with the primary ion. The MPM selectivity coefficient is then defined by calculation of the ratio of the primary ion and interfering ion activity differences in the two experiments.³⁶

The other method namely the SSM involves the measurement of two separate solutions, each containing a salt of the determined ion only. The Nicolskii coefficient is then calculated from the two observed emf values.³⁶

The resulting selectivity coefficients values are given in Table 2. It is immediately obvious from these data, that the proposed Ho(III) sensor is selective with respect to the most of cations. In the case of lanthanide ions the selectivity coefficients are in the order of 5.0×10^{-2} or smaller, which seems to indicate that the Ho(III) ions can be determined in the presence of other lanthanide ions. The selectivity coefficients for other cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cu^{2+} , and Pb^{2+}) are smaller than 7.0×10^{-3} , and they can not disturb the functioning of the Ho(III) membrane electrode. The surprisingly high selectivity of the membrane electrode for Ho(III) ions over other cations used most probably arises from the strong tendency of the carrier molecule for Ho(III) ions.

Table 2. Selectivity coefficients of various interfering cations for the membrane with the optimum composition

Ion	$K_{\text{Sel,MPM}}$	$K_{\text{Sel,SSM}}$	Ion	$K_{\text{Sel,MPM}}$	$K_{\text{Sel,SSM}}$
Dy^{3+}	5.0×10^{-2}	3.5×10^{-2}	La^{3+}	1.3×10^{-3}	1.1×10^{-3}
Nd^{3+}	8.1×10^{-3}	8.0×10^{-3}	Ca^{2+}	3.2×10^{-3}	1.7×10^{-3}
Tm^{3+}	2.0×10^{-3}	5.0×10^{-3}	Mg^{2+}	3.3×10^{-3}	1.8×10^{-3}
Sm^{3+}	3.2×10^{-2}	1.7×10^{-2}	Na^+	6.5×10^{-3}	3.9×10^{-3}
Pr^{3+}	3.0×10^{-3}	1.2×10^{-3}	K^+	7.0×10^{-3}	4.5×10^{-3}
Ho^{3+}	6.2×10^{-3}	3.5×10^{-3}	Cu^{2+}	1.7×10^{-3}	1.2×10^{-3}
Er^{3+}	3.5×10^{-2}	3.0×10^{-2}	Pb^{2+}	6.7×10^{-3}	2.9×10^{-3}

Table 3. The lifetime behavior of the Ho^{3+} membrane sensor

Period	Slope / (mV decade^{-1})	Limit of Detection
14 days	19.6 ± 0.2	8.0×10^{-6}
1 month	19.1 ± 0.3	8.0×10^{-6}
1.5 months	18.8 ± 0.3	9.0×10^{-6}
2 months	18.3 ± 0.2	1.0×10^{-5}
2.5 months	18.0 ± 0.4	1.5×10^{-5}
3 months	17.6 ± 0.3	2.5×10^{-5}
3.5 months	17.3 ± 0.2	4.0×10^{-5}
4 months	17.1 ± 0.4	5.0×10^{-5}

The dynamic response time of the sensor, being another very important parameter in the evaluation of a sensor, was studied by varying the concentration of a solution from $1.0 \times 10^{-5} \text{ mol L}^{-1}$ to $1.0 \times 10^{-2} \text{ mol L}^{-1}$ and recording the times needed for the sensor to reach $\pm 1 \text{ mV}$ of its equilibrium potential (Figure 5). The response time of the sensor was found to be about 5 seconds.

The proposed Ho(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 $1.0 \times 10^{-4} \text{ mol L}^{-1}$ of Ho(III) solution with $1.0 \times 10^{-2} \text{ mol L}^{-1}$ of standard EDTA, and *vice-versa*. The resulting titration curve is shown in Figure 6. As can be seen from Figure 6, the amount of Ho(III) ions, and EDTA, can be determined with good accuracy.

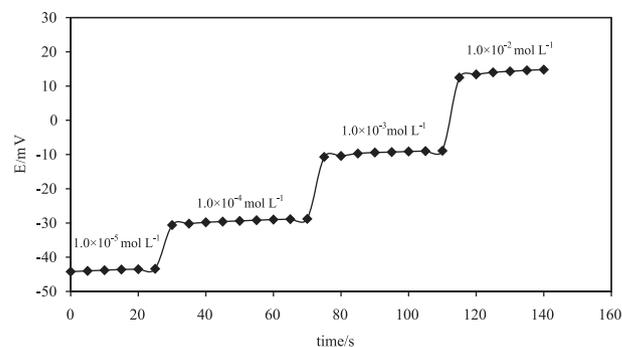


Figure 5. Dynamic response time of the electrode for step changes in the concentration of Ho(III) solution.

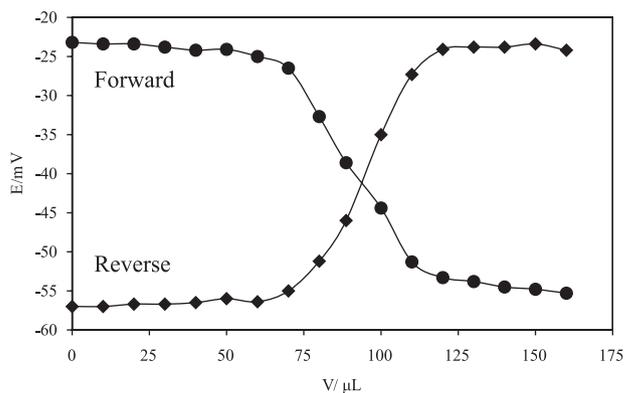


Figure 6. Potentiometric titration curve of 25 mL of a $1.0 \times 10^{-4} \text{ mol L}^{-1}$ Ho(III) solution, with a $1.0 \times 10^{-4} \text{ mol L}^{-1}$ EDTA and *vice-versa*, using the proposed membrane sensor as an indicator electrode.

The proposed Ho(III) membrane sensor was also successfully used to the determination of fluoride ion in three different pharmaceutical samples, and the results of triplicate measurements are given in Table 4. As can be seen from Table 4, there is a good agreement between the declared fluoride content and the determined values.

Table 4. The results of the determination of fluoride in mouth wash solution samples

Sample ^a	Labeled / (%)	Found / (%)
1	2.0	2.03 ± 0.04
2	0.2	0.22 ± 0.03
3	1.0	0.97 ± 0.04

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Conclusions

The results obtained from the above-mentioned study revealed that a potentiometric PVC-based membrane sensor based on H_2BPB functions as an excellent Ho(III) selective membrane sensor and can be used for the determination of this ion in the presence of considerable concentrations of common interfering ions. Applicable pH range, lower detection limit, and potentiometric

selectivity coefficients of the proposed sensor make it a superior device both compared to other methods used for the determinations of this ion.

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