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Fabrication of a Ho^{3+}-PVC membrane sensor based on *N*-phenyl-2-(thiophen-2-ylmethylene)hydrazinecarbothioamide for determination of holmium ions

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Abstract

In this research, a new poly(vinyl chloride) (PVC) membrane sensor for Ho^{3+} ion based on *N*-phenyl-2-(thiophen-2-ylmethylene)hydrazinecarbothioamide (PHC) as an ionophore was prepared. This sensor demonstrated good selectivity and sensitivity towards the holmium ion in comparison with variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The effect of membrane composition and pH on the response properties of the electrode was investigated. In detail, the suggested sensor exhibited a Nernstian behavior (with a slope of 20.4 ± 0.3 mV decade^{-1}) in the range of 1.0×10^{-6} to 1.0×10^{-2} mol/L with a detection limit of 6.2×10^{-7} mol/L. The response time was relatively quick in the whole concentration range (~5 s). The sensor usage was found to be at least 10 weeks in a pH range of 3.3–10.9. It was successfully applied in determination of fluoride ions in mouth wash preparations.

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

Holmium 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 studied to produce catalysts and to polish glass [1]. The available methods for low-level determination of rare-earth ions in solution include spectrophotometry, ICP-MS and ICP-AES. Isotope dilution mass spectrometry, 7 neutron activation analysis, X-ray fluorescence spectrometry, *etc*., are also used in some laboratories. These methods are either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories.

Potentiometric detection based on ion-selective electrodes (ISEs) offer the advantages of speed and ease of preparation and procedures, relatively fast response, reasonable selectivity thorough judicious choice of the membrane active materials, wide linear dynamic range, and low cost [2].

In recent years, a number of potentiometric PVC membrane ion-selective electrodes were reported for some ions [3–12]. There have been some reports of ion-selective holmium electrodes in the literature [13–16]. The aim of this research is the fabrication of a greatly selective and sensitive Ho^{3+} membrane sensor, based on *N*-phenyl-2-(thiophen-2-ylmethylene)hydrazinecarbothioamide (PHC) (Fig. 1) as a suitable ionophore for the potentiometric measurement of the Ho^{3+} ion amounts for a certain concentration range.

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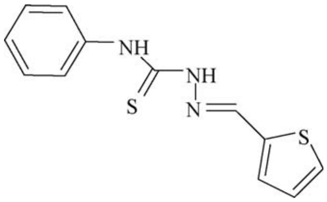

Fig. 1. The PHC structure.

Reagent grade benzyl acetate (BA), nitrobenzene (NB), dibutyl phthalate (DBP), acetophenone (AP), high relative molecular weight PVC, sodium tetraphenyl borate (NaTPB), tetrahydrofurane (THF) and chloride and nitrate salts of the cations used were purchased from Merck and Aldrich and used as received. Triply distilled deionized water was used through out.

The procedure for the preparation of *N*-phenyl-2-(thiophen-2-ylmethylene)hydrazinecarbothioamide: The thiophen 2-carbaldehyde (1 mmol, 0.112 g) was solved in hot ethanol, after that the *N*-phenylhydrazine-carbothioamide (1 mmol, 0.167 g) and catalytic amount of acetic acid were added to the solution of thiophen2-carbaldehyde. The mixture of reaction was refluxed for 1 h. Then the solid product was crystallized in acetone and ethanol (1:1).

To prepare the electrodes 30 mg of powdered PVC, 66 mg of NB and 2 mg of additive NaTPB were dissolved in 3 mL of THF, and 2 mg of PHC was added to the resulting solution. 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 $HoCl_3$), 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 $Ho(NO_3)_3$ solution [17–25]. A silver/silver chloride coated wire was used as an internal reference electrode.

All the electromotive force (emf) measurements were carried out with the following cell assembly; Ag/AgCl | internal solution, (1×10^{-3} mol/L $HoCl_3$) | PVC membrane | test solution | Hg_2Cl_2, KCl (saturated). A corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 ± 0.1 °C. The activities were calculated according to the Debye–Huckel procedure [26].

In order to check the suitability of PHC as an ion carrier for Ho^{3+} and other metal ions, 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 respective potential responses of the most sensitive ion-selective based on PHC clearly showed that only the Ho^{3+} ion illustrated a strong response (with a slope of 20.4 ± 0.3 mV decade^{-1}) to the PVC-based membrane sensors in comparison with the other tested cations.

t is well established that some important features of the PVC-based membranes, such as the nature and amount of the ionophore, the properties of the plasticizer, the plasticizer/PVC ratio and, especially, the nature of the additives used, significantly influence the sensitivity and selectivity of the ion-selective electrodes [2,27,28]. Thus, different aspects of the membrane preparation based on PHC for Ho^{3+} ion were optimized and the results are summarized in Table 1.

The data given in Table 1 revealed that in the absence of a proper additive, the sensitivity of the PVC membrane based on PHC is quite low (no. 7 with a slope of 10.7 ± 0.4 mV decade^{-1}). However, the presence of 2% of NaTPB as a suitable lipophilic additive will improve the sensitivity of the Ho^{3+} sensor considerably (no. 3 with slope 20.4 ± 0.3 mV decade^{-1}). As can be seen, membrane number 3 with a PVC:NB:PHC:NaTPB percent ratio of 30:66:2:2 resulted in Nernstian behavior of the membrane electrode over a wide concentration range. It is reported that the sensitivity, selectivity, and measuring range of ion-selective membranes are affected by the nature and amount of plasticizer used. This is due to the influence of the plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules, and the state of the ligands [2,29,30]. As can be seen from Table 1, among the four different plasticizers used, NB results in the best sensitivity. Moreover, some 2% of the ionophore PHC was chosen as the optimum amount of ionophore in the PVC membrane (no. 3).

Membrane no. 3 exhibits a wide working concentration range of 1.0×10^{-6} to 1.0×10^{-2} mol/L with a detection limit of 6.2×10^{-7} mol/L Ho^{3+}, and a Nernstian slope of 20.4 ± 0.3 mV decade^{-1}. The proposed sensor usage lasted for at least 10 weeks (using 1 h per day and then washing and drying it). After 10 weeks, the electrode slope diminished (from 20.4 to 18.2 mV decade^{-1}).

Table 1
Optimization of the membrane ingredients.

Electrode No.	Composition (wt%), PVC 30%						Slope (mV $decade^{-1}$)	Concentration range (mol/L)
	PHC	NaTPB	NB	DBP	BA	AP		
1	2	2	0	0	0	66	17.8 ± 0.4	1.0×10^{-6} to 5.0×10^{-2}
2	2	2	0	66	0	0	18.5 ± 0.6	1.0×10^{-6} to 1.0×10^{-2}
3	2	2	66	0	0	0	20.4 ± 0.3	1.0×10^{-6} to 1.0×10^{-2}
4	2	2	0	0	66	0	18.5 ± 0.5	1.0×10^{-6} to 1.0×10^{-2}
5	1	2	67	0	0	0	17.5 ± 0.5	1.0×10^{-6} to 1.0×10^{-2}
6	3	2	65	0	0	0	18.2 ± 0.3	1.0×10^{-6} to 1.0×10^{-2}
7	2	0	68	0	0	0	10.7 ± 0.4	1.0×10^{-6} to 1.0×10^{-2}
8	2	1	67	0	0	0	14.6 ± 0.6	1.0×10^{-6} to 1.0×10^{-2}
9	2	3	65	0	0	0	21.3 ± 0.5	1.0×10^{-6} to 1.0×10^{-2}

The influence of pH on the response of the membrane sensor was studied in a 1.0×10^{-3} mol/L Ho^{3+} solution over a pH range of 2.0–12.0. In the pH range of 3.3–10.9, the potential did not change with changing pH, indicating the applicability of this sensor in this pH range.

Dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded by changing the holmium ion concentration in solution in the range of 1.0×10^{-6} to 1.0×10^{-2} mol/L. The electrode reaches quickly (~5 s) its equilibrium response within the whole concentration range.

Selectivity, which describes an ion-selective electrode specificity toward the target ion in the presence of interfering ions, is the most important characteristic of these devices. The potentiometric selectivity coefficients of the Ho^{3+} sensor were evaluated by the matched potential method (MPM) [31,32]. The MPM selectivity coefficient is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{MPM} = \Delta a_A/a_B$. The resulting values of the selectivity coefficients are given in Table 2.

Table 2
Comparison of selectivity coefficients, detection limit, response time and linearity range of the developed Ho^{3+} sensor and the formerly mentioned Ho^{3+} ion-selective electrodes.

	Ref. [13]	Ref. [14]	Ref. [15]	Ref. [16]	This work
Linearity range (mol/L)	1.0×10^{-5} to 1.0×10^{-2}	1.0×10^{-6} to 1.0×10^{-2}	1.0×10^{-5} to 1.0×10^{-2}	2.0×10^{-5} to 1.0×10^{-2}	1.0×10^{-6} to 1.0×10^{-2}
Detection limit (mol/L)	7.0×10^{-6}	8.5×10^{-7}	8.0×10^{-6}	5.0×10^{-6}	6.2×10^{-7}
Response time (s)	<15	<15	~5	~5	~5
Selectivity coefficients	MPM	MPM	MPM	MPM	MPM
K^+	7.0×10^{-3}	6.7×10^{-4}	7.0×10^{-3}	3.0×10^{-3}	8.3×10^{-4}
Na^+	4.0×10^{-2}	5.9×10^{-4}	6.5×10^{-3}	3.0×10^{-3}	2.2×10^{-4}
Ca^{2+}	8.5×10^{-3}	3.3×10^{-3}	3.2×10^{-3}	1.2×10^{-3}	3.2×10^{-3}
Pb^{2+}	4.5×10^{-2}	7.4×10^{-3}	6.7×10^{-3}	7.5×10^{-3}	3.8×10^{-3}
Co^{2+}	–	7.5×10^{-4}	–	–	2.7×10^{-3}
Ni^{2+}	–	8.5×10^{-4}	–	–	4.2×10^{-4}
Cr^{3+}	–	–	–	–	9.4×10^{-4}
Fe^{3+}	–	–	–	–	5.4×10^{-3}
La^{3+}	1.0×10^{-2}	8.7×10^{-4}	1.3×10^{-3}	3.0×10^{-3}	7.2×10^{-3}
Sm^{3+}	3.0×10^{-2}	5.3×10^{-3}	3.2×10^{-2}	3.0×10^{-2}	3.3×10^{-4}
Er^{3+}	4.0×10^{-3}	–	3.5×10^{-2}	3.0×10^{-3}	3.6×10^{-4}
Pr^{3+}	2.0×10^{-2}	–	3.0×10^{-3}	3.5×10^{-3}	2.8×10^{-4}
Eu^{3+}	–	–	–	–	5.6×10^{-4}
Tm^{3+}	6.5×10^{-3}	–	2.0×10^{-3}	1.5×10^{-3}	4.2×10^{-4}
Gd^{3+}	4.0×10^{-2}	6.4×10^{-3}	–	–	2.1×10^{-4}
Dy^{3+}	7.0×10^{-2}	8.2×10^{-3}	5.0×10^{-2}	1.7×10^{-2}	2.7×10^{-4}
Yb^{3+}	–	4.2×10^{-3}	–	–	8.6×10^{-4}

Table 3
Determination of fluoride ions in mouth wash solutions.

Sample	Labeled (mg/mL)	Found ISE[a] (mg/mL)
Sodium fluoride mouth wash solution (Aquafresh, Brentford, U.K.)	1.35	(1.38 ± 0.05)[b]
Sodium fluoride mouth wash solution (Eurodont, DuroDont GmbH)	1.45	(1.47 ± 0.04)

[a] Suggested Ho^{3+} sensor.
[b] Results are based on three measurements.

The data given in this table present that the selectivity coefficients of the proposed Ho^{3+} membrane sensor for all the trivalent ions tested are 7.2×10^{-3} or smaller, whereas for all the mono and divalent ions the selectivity coefficients are in the order of 3.8×10^{-3} or smaller, which seems to indicate negligible interferences in the performance of the electrode assembly. Also, Table 2 summarizes and compares the linearity range, detection limit, response time and selectivity coefficient values of the presented sensor with those of the best previous Ho^{3+} electrodes, reported in the literature by other researchers [13–16]. As it is seen, the sensor not only in the case of detection limit, but also in the case of selectivity coefficients is superior to the previously reported Ho^{3+} ion-selective membrane electrode.

Furthermore, the electrode was used in the potentiometric determination of fluoride ions in two mouthwash samples. 1.0 g of each sample was taken and diluted with distilled water in a 100 mL flask and titrated with a Ho^{3+} solution (1.0×10^{-3} mol/L) and the results of triplicate measurements are summarized in Table 3. There is a satisfactory agreement among the declared fluoride content and the determined values by the sensor.

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