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Lanthanide Recognition: A Ho^{3+} Potentiometric Membrane Sensor

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Ion-selective electrodes based on impregnated polymeric membranes now are used routinely for the monitoring of a wide variety of anions and cations. In this work, complexation of a macrocycle compound, derivative of diazatetrathia-18-crown-6 containing the 4,5-dithio-1,3-dithiole-2-thione unit, with some mono, di and trivalent metal ions was investigated by conductometric method. Since macrocycle was able to form a selective complex with Ho^{3+} ion (K_f=5.13± 0.22), it was applied as a sensing material in construction of a Ho^{3+} potentiometric membrane sensor. The response of proposed sensor was Nernstian across the concentration range of 1.0×10^{-6}-1.0×10^{-2} mol L^{-1}, while its response time was fast (~10s). The sensor potential response was not affected by the pH changes over the pH range of 4.5-9.0. The accuracy of the recommended electrode was tested by a Holmium ICP/DCP standard solution.

Keywords: Holmium; Ion-selective electrode; Potentiometric membrane; Sensor

1. INTRODUCTION

Holmium compounds have specialized uses in ceramic, glass and phosphor lamps. It is also used in nuclear reactors to keep the atomic chain reactions from running out of control. There is a growing trend in the uses of this element, due to the fact that it is studied to produce catalysts and to polish glass. The bioaccumulation of the holmium ions in the body can be a threat to the liver. Nowadays, it is known that holmium causes damages to the cell membranes of the water animals with negative effects on the reproduction and the nervous systems. For this reason, the analysis of this element is greatly important.

For these, and many more applications, Ho ion must be determined precisely and accurately at trace levels. Conventional methods of Ho ion analysis have included neutron activation analysis, ICP-

MS, ICP-AES and isotope dilution mass spectrometry [1-7]. These are elaborate and time consuming methods and involve sophisticated equipment that might not be available in most analytical laboratories.

The increase use of ion sensors in the fields of environmental, agricultural and medicinal analysis is stimulating analytical chemists to develop new sensors for fast, accurate, reproducible and selective determination of various ions [8-20].

The primary conductance study for complexation, showed the tendency of the derivative of diazatetrathia-18-crown-6 containing the 4,5-dithio-1,3-dithiole-2-thione unit (ATCD) (Fig. 1) toward selective complexation with Ho^{3+} ions, one of the lanthanide members. Thus, this ionophore was used as a sensing material in construction of Ho^{3+} membrane sensor.

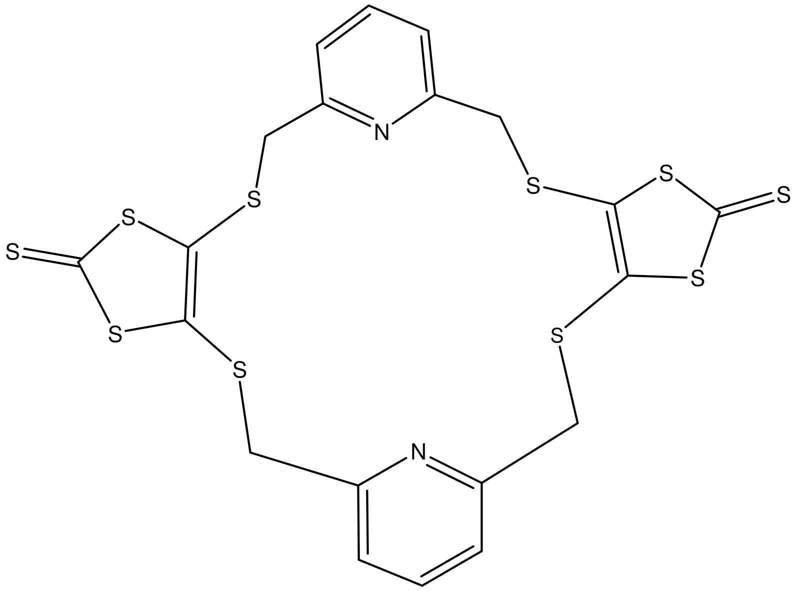

Figure 1. The structure of the ionophore diazatetrathia-18-crown-6 derivative (ATCD)

2. EXPERIMENTAL PART

2.1. Apparatus

The glass cell, where the Ho^{3+} ion-selective electrode was placed, consisted of an R684 model Analion Ag/AgCl double junction reference electrode as the internal reference electrode and a double-junction saturated calomel electrode (SCE, Philips). The cell chamber was filled with an ammonium nitrate solution and both electrodes were connected to a Corning ion analyzer with a 250 pH/mV meter with ±0.1 mV precision.

For the conductivity measurements, a Metrohm 660 conductivity meter and a black platinum dip-type conductivity cell (with a 0.83 cm^{-1} cell constant) were used.

2.2. Reagents and materials

Reagent grade dibutyl phthalate (DBP)**,** nitrobenzene (NB), benzyl acetate (BA), high relative molecular weight polyvinyl chloride (PVC), sodium tetraphenyl borate (NaTPB), and tetrahydrofurane (THF) were purchased from Merck and used as received. The acetic acid, furan-2-carboxylic acid hydrazide, pyridine-2-carbaldehyde, chloride and nitrate salts of the cations used (from Merck and Aldrich) were all of the highest purity available and used without any further purification. The macrocycle compound was synthesized as described elsewhere [21]. Triply distilled deionized water was used throughout.

2.3. Electrode Preparation

The general procedure to prepare the PVC membrane was as follow: Different amounts of the ionophore along with appropriate amounts of PVC, plasticizer and additive were dissolved in tetrahydrofuran (THF), and the solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A pyrex tube (3-5 mm o.d.) was dipped into the mixture for about 10 s so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 10 h. The tube was then filled with an internal filling solution (1.0×10^{-3} mol L^{-1} $HoCl_3$). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} $Ho(NO_3)_3$ solution.

2.4. Emf Measurements

The following cell was assembled for the conduction of the emf (electromotive force) measurements; Ag–AgCl | internal solution, 1.0×10^{-3} mol L^{-1} $HoCl_3$ | PVC membrane | sample solution | $Hg–Hg_2Cl_2$, KC1 (satd.)

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 ± 0.1 °C.

3. RESULTS AND DISCUSSION

3.1. Complexation Study

Complexation can actually be defined as an interaction between a donor (ligand) and an acceptor (substrate). The characteristics of a ligand and the substrate are important in molecular recognition, because the selective bonding between the ligand and the substrate originates from the information stored in the ligand and is read out by the substrate. This characteristic information helps define the stability, selectivity, reactivity and transport of the complexes [8,10].

For this purpose, the ATCD interaction with numerous metal ions was monitored conductometrically in an acetonitrile solution [22-26].

Conductivity measurements can be useful tools to investigate the complexation. In all measurements, the cell should be thermostated at the temperature of 25.0 ºC, using a Phywe immersion thermostat. In typical experiments, 25 mL of an ion solution (1.0×10^{-4} mol L^{-1}) are placed in a water-jacketed cell, equipped with a magnetic stirrer and connected to the thermostat, circulating water at the desired temperature. In order to keep the electrolyte concentration constant during the titration, it should be noted that both the starting solution and the titrant have the same ion concentration. Then, a known amount of an ionophore or a ligand (1.0×10^{-2} mol L^{-1}) solution is added in a stepwise manner, using a calibrated micropipette. The conductance of the solution is measured after each addition.

The ligand addition is continued until the desired ionophore-to-ion mole ratio is achieved. The 1:1 binding of the cations with the ionophore can be expressed by the following equilibrium:

$$\mathrm{M}^{n+} + \mathrm{L} \underset{\longleftarrow}{\xrightarrow{Kf}} \mathrm{ML}^{n+} \tag{1}$$

The corresponding equilibrium constant, K_f, is given by

$$K_f = \frac{[\mathrm{ML}^{n+}]}{[\mathrm{M}^{n+}][\mathrm{L}]} \times \frac{f_{(\mathrm{ML}^{n+})}}{f_{(\mathrm{M}^{n+})} f_{(\mathrm{L})}} \tag{2}$$

where, $[\mathrm{ML}^{n+}]$, $[\mathrm{M}^{n+}]$, [L] and f represent the equilibrium molar concentration of the complexes, the free cation, the free ionophore and the activity coefficient of the indicated species, respectively. Under the diluted conditions, the activity coefficient of the unchanged ligand $f_{(L)}$ can be reasonably assumed to be unity. The use of the Debye–Hückel limiting law of the 1:1 electrolytes [26] leads to the conclusion that $f_{(M^{n+})} \approx f_{(ML^{n+})}$, so the activity coefficient in Eq. (2) is canceled out. Therefore, the complex formation constant in terms of the molar conductance can be expressed as:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \tag{3}$$

where

$$K_f = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})} \tag{4}$$

where, Λ_M is the molar conductance of the cation before the addition of the ionophore; Λ_ML is the molar conductance of the complexes, Λ_obs the molar conductance of the solution during titration, C_L the analytical concentration of the added ionophore and C_M the analytical concentration of the cation salt. The complex formation constant, $K_\mathrm{f,}$ and the molar conductance of the complex, Λ_ML, were obtained by computer fitting the Eqs. (3) and (4) to the molar conductance-mole ratio data, using the nonlinear least-squares program KINFIT [27].

Table 1. Stability constants of the M^{n+}- ATCD complexes

Ion	Log K_f	Ion	Log K_f
Na^+	<2.0	Nd^{3+}	2.21 ± 0.32
K^+	<2.0	Sm^{3+}	<2.0
Mg^{2+}	<2.0	Eu^{3+}	2.35 ± 0.23
Ca^{+2}	2.10 ± 0.13	Gd^{3+}	3.31 ± 0.24
Co^{+2}	2.23 ± 0.31	Tb^{3+}	2.44 ± 0.24
Pb^{+2}	2.10 ± 0.23	Dy^{3+}	2.65 ± 0.31
Fe^{3+}	<2.0	Ho^{3+}	5.13 ± 0.22
Cu^{2+}	2.21 ± 0.14	Er^{3+}	2.14 ± 0.35
La^{3+}	3.92 ± 0.22	Tm^{3+}	3.42 ± 0.16
Ce^{3+}	2.80 ± 0.25	Yb^{3+}	3.22 ± 0.21
Pr^{3+}	2.65 ± 0.12	Lu^{3+}	3.85 ± 0.16

In this experiment, the ligand-to-cation mole ratio was equal to 1 in all cases. Then, the formation-constant values (K_f) of the resulting 1:1 complexes were evaluated (Table 1). From Table 1, it was concluded that ATCD was an appropriate ion carrier for the Ho^{3+} membrane sensor design. Thus, the macrocycle ATCD was applied as a suitable ionophore in construction of Ho^{3+} ion-selective electrode.

3.2. Membrane composition effect on the potential response of the sensor

Because the degree of sensitivity and selectivity for a certain ionophore is greatly related to the membrane ingredients, the influence of membrane composition on the potential responses of the Ho^{3+} sensor was inspected [28-32]. In this study, different membrane compositions, as shown in Table 2, were tested. As can be seen, the membrane with the composition of 30% PVC, 5% ATCD, 2% NaTPB and 63% BA (no. 4) was the optimum one in the development of this sensor. This membrane composition was selected after many considerations.

The high Ho^{3+} ion extraction into the liquid membrane was a result of the elevated ionophore tendency to form a selective complex with the Ho^{3+} ions. From Table 2, it was obvious that in the absence of ionophore and with the presence of other components (no. 8), the response of the recommended electrode was low (slope of 4.23±0.2 mV per decade).

The second factor which helps Ho^{3+} to extract from an aqueous solution to the membrane as an organic phase is a plasticizer. After the evaluation of three solvent mediators (NB, BA and DBP), it was observed that BA is more effective solvent mediator than the other ones. Thus, BA was chosen to be employed in the sensor construction.

The presence of lipophilic anions in a cation-selective membrane was also considered. Actually, the presence of such anions in a cation-selective membrane, which is based on a neutral carrier, decreases the ohmic resistance and improves the response behaviour and selectivity.

Furthermore, when the extraction capability is poor, it increases the membrane electrode sensitivity [33,34]. Here, a NaTPB addition of 2% as additive led to the slope increase of the potential sensor response from the sub-Nernstian value of 16.51± 0.4 mV per decade (no. 2) to the Nernstian value of 19.97 ± 0.3 mV per decade (no. 4).

Table 2 . The optimization of the membrane ingredients

Membrane No.	**Composition (%)**				**Slope (mV per decade)**
	PVC (%wt.)	Plasticizer (%wt.)	ionophore (%wt.)	Additive (%wt.)	
1	30	BA, 66	4	-----	12.32 ± 0.3
2	30	BA, 65	5	-----	16.51 ± 0.4
3	30	BA, 64	6	-----	15.78 ± 0.3
4	30	BA, 63	5	2 (NaTPB)	19.97 ± 0.3
5	30	BA, 62	5	3 (NaTPB)	19.15 ± 0.3
6	30	NB, 63	5	2 (NaTPB)	13.20 ± 0.2
7	30	DBP, 63	5	2 (NaTPB)	15.13 ± 0.2
8	30	BA, 68	0	2 (NaTPB)	4.23 ± 0.2

3.3. pH effect on the electrode response

In an approach to understanding the impact of pH on the electrode response, the potential was measured at two particular concentrations of the Ho^{3+} solution (1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1}) from the pH value of 2.0 up to 12.0 (concentrated NaOH or HCl solutions were employed for the pH adjustment). In agreement with the resulting data, the potential remained constant despite the pH change in the range of 4.5 to 9.0, indicating the applicability of this electrode in the specific pH range.

On the contrary, relatively noteworthy fluctuations in the potential *vs.* pH behavior took place below and above the formerly stated pH limits. In detail, the fluctuations above the pH value of 9.0 might be justified by the formation of the soluble and insoluble Ho^{3+} ion hydroxy complexes in the solution, such as $Ho(OH)^{2+}$, $Ho(OH)_2^+$ and $Ho(OH)_3$. On the other hand, the fluctuations below the pH value of 4.5 were attributed to the partial protonation of the employed ionophore.

3.4. Study of sensor properties

The properties of an ion-selective electrode are characterized by parameters like these : measuring range, detection limit, response time, selectivity, lifetime, accuracy.

3.4.1. Measuring range

The measuring range of an ion-selective electrode includes the linear part of the calibration graph as shown in Fig. 2. Measurements can be performed in this lower range, but it must be noted that more closely spaced calibration points are required for more precise determinations. For many electrodes the measuring range can extend from 1 molar down to 10^{-6} or even 10^{-7} molar concentrations. According to another definition, the measuring range of an ion-selective electrode is defined as the activity range between the upper and lower detection limits. The applicable measuring range of the proposed sensor is between 1×10^{-6} and 1×10^{-1} mol L^{-1}.

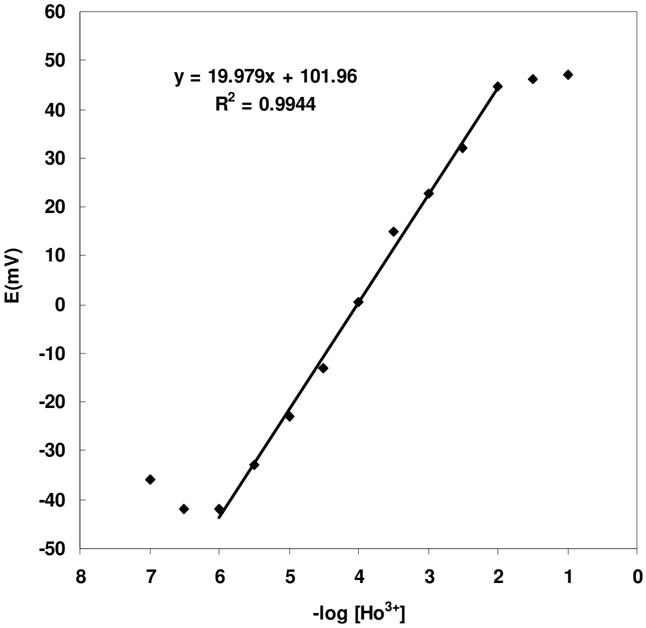

Figure 2. The calibration curve of the Ho^{3+} membrane sensor based on ATCD (membrane no. 4).

3.4.2. Detection limit

By extrapolating the linear parts of the ion-selective calibration curve, the detection limit of an ion-selective electrode can be calculated. In practice, detection limits for the most selective electrodes are in the range of 10^{-5}–10^{-6} mol L^{-1}. However, recent studies have shown that even sub-nM detection limits can be obtained for these devices by different methods such as application of metal buffers to eliminate the contamination of very dilute solutions, using cation-exchange resin in the internal solution of ISEs to keep the primary ion activity at a constant low level, using liphophilic particles such as silica-gel 100 C18-reversed phase into the sensing membrane, using sandwich membranes, and so on [35-40].

In this work the detection limit of the proposed membrane sensor was 6.3×10^{-7} mol L^{-1} which was calculated by extrapolating the two segments of the calibration curve (Fig. 2).

In comparison with other reported Ho^{3+} membrane sensors, Table 3 [42-44], the proposed sensor is superior to the previously reported ones in selectivity coefficients, linearity range, Nernstian slope, and detection limit.

Table 3. Comparison of the selectivity coefficients, linearity range, detection limit and response time of the proposed Ho^{3+} sensor and the previous reported ones

Properties	Ref. 39	Ref. 40	Ref. 41	Ref. 42	This work
Detection limit (M)	8.0×10^{-6}	7.0×10^{-6}	5.0×10^{-5}	8.5×10^{-7}	6.3×10^{-7}
Linear Range (M)	$1\times10^{-5}-1\times10^{-2}$	$1\times10^{-5}-1\times10^{-2}$	$2\times10^{-5}-1\times10^{-2}$	$1\times10^{-6}-1\times10^{-2}$	$1\times10^{-6}-1\times10^{-2}$
Response Time (s)	~5	15	~5	15	~10
Slope (mV per decade)	19.60 ± 0.2	19.7 0± 0.2	19.50 ± 0.3	19.70 ± 0.3	19.97 ± 0.3
$\log K_{sel} > -2$	Na^+, Pb^{2+}, Dy^{3+}, Nd^{3+}, Er^{3+}	Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Pb^{2+}, Dy^{3+}, La^{3+}, Lu^{3+}	Pb^{2+}, Cu^{2+}, Nd^{3+}	Pb^{2+}, Tb^{3+}	La^{3+}

3.4.3. Response time

The response time of an electrode is evaluated by measuring the average time required to achieve a potential within ±0.1 mV of the final steady-state potential, upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. It is notable that the experimental conditions-like the stirring or flow rate, the ionic concentration and composition of the test solution, the concentration and composition of the solution to which the electrode was exposed before experiment measurement was performed, any previous usages or preconditioning of the electrode, and the testing temperature have an effort on the experimental response time of a sensor [45].

In this work, less than 10s response time was obtained for the proposed electrode when contacting different Ho^{3+} solutions from 1.0×10^{-3} to 1.0×10^{-1} mol L^{-1}, and about 15s in low concentration solutions, which is due to the effect of analyte concentration on the response time of ion selective electrode.

3.4.4. Selectivity

Selectivity, which describes an ion-selective electrode's 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) and separated solution method (SSM) [46].

The resulting values of the selectivity coefficients are given in Table 4. As can be seen from Table 4, for the all mono and bivalent metal ions and trivalent lanthanide ions tested, the selectivity coefficients are about 10^{-3}, which seems to indicate negligible interferences in the performance of the electrode assembly.

Also, there is a good correspondence between the formation constants and the selectivity coefficients order, because the selectivity of an ion-selective sensor is mainly related to the stability of the complex between ion and ionophore.

Table 4. The selectivity coefficients of various interfering cations for the membrane

Ion	Log K_{MPM}	Log K_{SSM}
Na^+	-3.5	-3.6
K^+	-3.7	-3.7
Mg^{2+}	-3.3	-3.5
Ca^{+2}	-3.0	-3.1
Co^{+2}	-3.5	-3.7
Pb^{+2}	-3.5	-3.5
Fe^{3+}	-3.9	-3.8
La^{3+}	-1.8	-2.0
Ce^{3+}	-3.6	-3.7
Pr^{3+}	-3.3	-3.3
Nd^{3+}	-3.0	-3.1
Sm^{3+}	-3.5	-3.4
Eu^{3+}	-3.6	-3.5
Gd^{3+}	-2.5	-2.7
Tb^{3+}	-3.4	-3.4
Dy^{3+}	-2.9	-3.0
Er^{3+}	-3.5	-3.6
Tm^{3+}	-3.1	-3.0
Yb^{3+}	-2.3	-2.2
Lu^{3+}	-2.2	-2.3

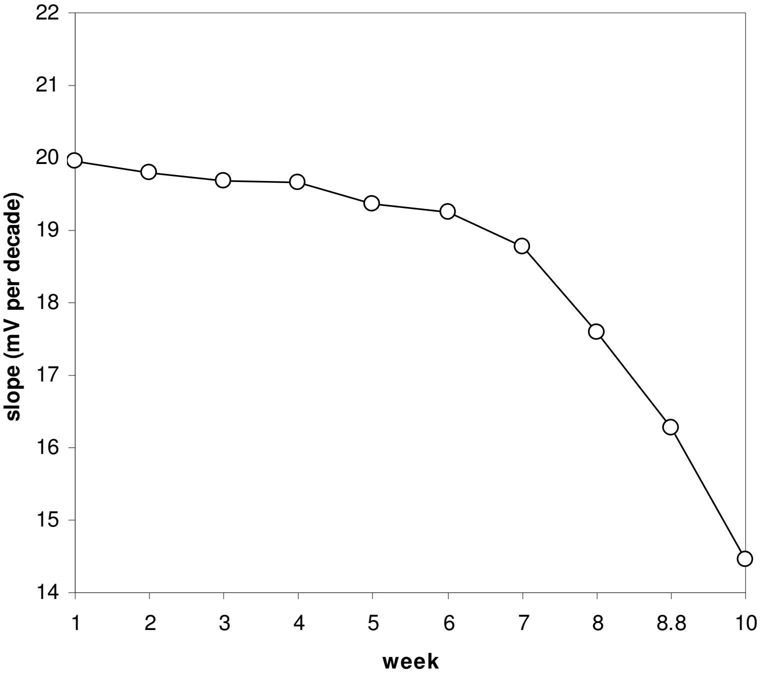

Figure 3. The lifetime of the Ho^{3+} membrane sensor (membrane no. 4)

3.4.5. Lifetime

The average lifetime for most of the reported ion-selective sensors is in the range of 4–10 weeks. After this time the slope of the sensor will decrease, and the detection limit will increase. The sensors were tested for 10 weeks, during which time the electrodes were used extensively (one hour per day). Fig. 3 shows the changes in the slope and detection limits of a sensor with time. The proposed sensors can be used for seven weeks. First, there is a slight gradual decrease in the slopes (from 19.97 to 18.77 mV per decade) and, second, an increase in the detection limit (from 6.3×10^{-7} mol L^{-1} to 7.0×10^{-6} mol L^{-1}). It is well established that the loss of plasticizer, carrier, or ionic site from the polymeric film due to leaching into the sample is a primary reason for the limited lifetimes of the sensors [47].

3.4.6. Accuracy

To evaluate the accuracy of the proposed sensor, the sensor was successfully applied to direct monitoring of Ho^{3+} in Holmium ICP/DCP standard solution (10,000 mg/mL Ho in 3 wt. % HNO_3) as a certified reference material. The results showed that recovery of Ho^{3+} ions is very good (102.3%-104.2%). These experimental data revealed that the proposed electrode performed a trustworthy detection of the Ho^{3+} ions.

4. CONCLUSIONS

In line with the resulting data of this study, the ion-selective electrode constructed by the ATCD showed a better performance than the formerly described methodologies in the linear concentration range, detection limit, and selectivity coefficients. The proposed sensor exhibited a fast response time, a lower detection limit of 6.3×10^{-7} ml L^{-1} and pH independent potential responses across the range of 4.5–9.0. Its selectivity towards the holmium ions was not influenced by the presence of the common alkali, alkaline earth, or transition and heavy metal ions, since the interference of these substances was low. For the assessment of the electrode performance, a Holmium ICP/DCP standard solution as a certified reference material (CRM) was used.

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