Ho³⁺ Ion Selective Microelectrode: An Asymmetric PVC Membrane Sensor

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A Ho³⁺ microelectrode, an asymmetric PVC membrane sensor was prepared based on N-(1-thien-**2-**ylmethylene)-1,3-benzothiazol-2-amine (TBA) for the first time. TBA shows a good selectivity and sensitivity towards Ho³⁺ ions, in respect with other tested cations. The $\log K_f$ of complexation between Ho³⁺ and TBA which was calculated by spectroscopic method was 5.23±0.27. The proposed Ho³⁺ microsensor exhibits a nice Nernstian response of 19.4±0.2 mV/decade of holmium concentration in a wide linear range of 1.0×10^{-8}-1.0×10^{-3} M and a detection limit of 1.0×10^{-8} M. It can be used in the pH range of 3.0-8.0.

1. INTRODUCTION

Nowadays, the interest in lanthanoids in probing biochemical reactions arises because they can be used as probes to unravel the interactions between Ca^{2+} and biologically important molecules. The lanthanoids have similar ionic radii to calcium, but by virtue of possessing a higher charge, they exhibit a high affinity for the Ca^{2+} sites on biological molecules and a stronger binding to water molecule [1-3].

Thus, because of the increasing industrial use of lanthanum compounds as well as their enhanced discharge and its useful and harmful biological activity, monitoring of trace amount of holumium has been of a recent increasing concern. There are some main methods for trace amount monitoring of holmium ion in solution including X-ray fluorescence spectrometry, ICP-AES, spectrophotometry, isotope dilution mass spectrometry, neutron activation analysis. These methods are

either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories [4-7].

Potentiometric electrodes, offer several advantages such as fast and ease of preparations and procedures, simple instrumentations, relatively fast responses, very low detection limit, wide dynamic ranges, reasonable selectivity and low costs. This has led to increasing the number of available sensors and microsensors over the last few years [8-12].

Although the neutral carrier-type ISEs have been successfully used for monitoring of different metal ions including the alkali, alkaline-earth, transition, and some other heavy metal ions [13-15], there is not any report on the development of microsensor for holmium ions based on different ionophores.

Potentiometric membrane sensors, according to their construction, are categorized into two important groups: symmetrical ion-selective electrodes, and asymmetrical ion-selective electrodes. Symmetrical ion-selective electrodes are classical electrodes in which the ion-selective membrane is placed between two solutions. In an asymmetrical ion selective electrode, one side of the membrane is in contact with a solid phase while the other is exposed to the measured solution. Similar to the rest of the chemical sensors, a potentiometric micro-sensor comprises two basic parts; a transducer and an ion-sensitive receptor layer [13-16].

In addition, the miniaturization of the working electrode for the in vivo or in vitro determination of the analyte, or for using the flow injection system has recently become an interesting field of research. Asymmetric sensors exhibit several other attractive possibilities including; exploration of macroscopic domains, detection in micro flow system, time-resolved probing of processes in the single cells and analyses of very small sample volume [16].

In this work, N-(1-thien-2-ylmethylene)-1,3-benzothiazol-2-amine (TBA) which is previously used in construction of symmetric ion sensor [17] was applied in construction of a highly selective and sensitive Ho^{3+} ion selective microelectrode, an asymmetric potentiometric ones for fast monitoring of trace amounts of Ho^{3+} ions in aqueous solutions.

2. EXPERIMENTAL PART

2.1. Reagents

Sodium tetraphenyl borate (NaTPB), PVC of high relative molecular weight, *o*-nitrophenyloctyl ether (NPOE), benzyl acetate (BA), tetrahydrofuran (THF), chloride and nitrate salts of cations were of the highest purity available (from Merck and Aldrich), and were used without further purification. All aqueous solutions were prepared with deionized distilled water. The pH of all solutions, were adjusted with dilute nitric acid and sodium hydroxide. The ionophore TBA (Fig. 1) was synthesized as described elsewhere [17].
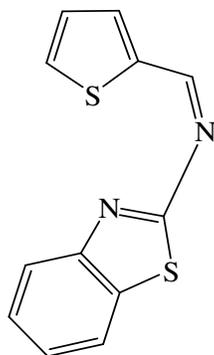
Figure 1. The chemical structure of the used ionophore TBA

2.2. Apparatus

Potentials were measured with a Corning ion analyzer Model 250-pH/mV meter. The pH of the sample solutions was monitored simultaneously with a conventional glass pH electrode. Spectroscopic measurements were carried on a PERKIN-ELMER Lambda 2 UV-Vis. Spectrophotometer with 1 cm quartz cells.
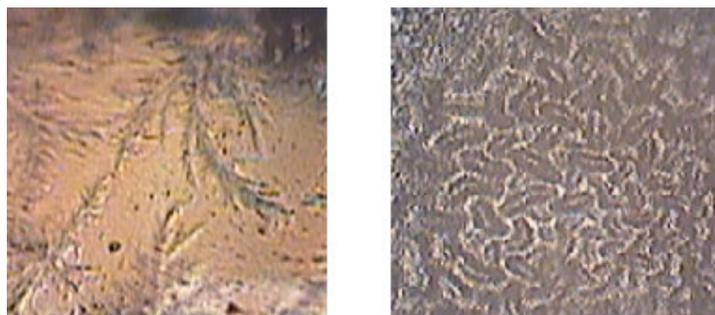
Figure 2. Surface of the microelectrode before (A) and after conditioning (B) with Ho^{3+} solution

2.3. Electrode preparation

To prepare the PVC membrane, we used dipping method [13-16], after thoroughly mixing 20 mg of powdered PVC, 72 mg of BA, 2 mg of additive NaTPB, and 6 mg of TBA and 3 ml of THF, the resulting mixture was transferred into a glass dish with a 2 cm in diameter. The solvent was slowly evaporated until a relative oily concentrated was obtained. The gold electrode was prepared by sealing gold micro-wire (Good fellow Metals Ltd., UK) into a soft glass capillary. The capillary was then cut perpendicular to its length to expose the gold wire. Electrical contact was made using silver epoxy (Johnson Matthey Ltd., UK). Before each experiment the electrode surface was polished for 1 min, using extra fine carborundum paper and then for 10 min with 0.3 µm alumina, sonicated in distilled water and dried in air. The polished gold electrode was dipped into the membrane solution mentioned above and the solvent was evaporated. A membrane was formed on the gold surface and the electrode

was allowed to set overnight. The electrode was finally conditioned for 48 h by soaking in a 1.0×10^{-3} M of $HoCl_3$. The surface of conditioned and unconditioned of the Ho^{3+} microsensors is shown in Fig. 2 [16].

2.4. Electromotive force Measurement

All emf measurements were carried out with the following assembly:

Ag/AgCl, KC1 (satd.) | sample solution | PVC membrane | gold surface of microelectrode

In all measurements, the ionic strength of the solutions was maintained by using 10^{-4} M of sodium chloride.

3. RESULTS AND DISCUSSION

Recently, a number of neutral ion carriers, containing nitrogen, oxygen or sulfur donor atoms, have been used in construction of selective and sensitive lanthanide metal ions [18-26]. Due to the existence of nitrogen and oxygen donor atoms in the semi cavity of TBA, its interaction with some cation using spectroscopic method was studied and the results showed that TBA has special interaction with Ho^{3+} ions, as shown in Fig. 3, in comparison with other tested cations and may be acts as a suitable ion carrier in fabrication of Ho^{3+} microsensor. The substantial decrease in the absorbance at a certain wavelength of the ligand solution, after adding the ion solution stepwise, may give a new adsorption peak at another wavelength, which is related to complex formation. At the same time, the effects of the other ions on the spectrum of the carrier were also investigated. When a metal ion, M, reacts with a ligand, L, to form a 1:1 complex, the formation constant is given as equation (1); Using mass balance equations and the observed absorbance given:

$$K_f = \frac{[ML]}{[M][L]} \tag{1}$$

$$C_M = [M] + [ML] \tag{2}$$

$$C_L = [L] + [ML] \tag{3}$$

$$A_{obs} = \varepsilon_L[L] + \varepsilon_{ML}[ML] = \frac{A_o}{C_L}[L] + \varepsilon_{ML}[ML] \tag{4}$$

Where C and ε values are the analytical concentration and molar absorptivities of the species indicated, and A is the absorbance of the ligand in the absence of metal ion. The mass balance equations can be solved in order to obtain an equation for the free ligand concentration, [L], as:

$$K_f[L]^2 + (1 + K_f(C_M - C_L))[L] - C_L = 0 \tag{5}$$

For the evaluation of the formation constant from absorbance-mole ratio data, again the non-linear least-squares curve-fitting program KINFIT was used. The formation-constant values (K_f) of the resulting 1:1 complexes were reported was calculated 5.23±0.27 [27].
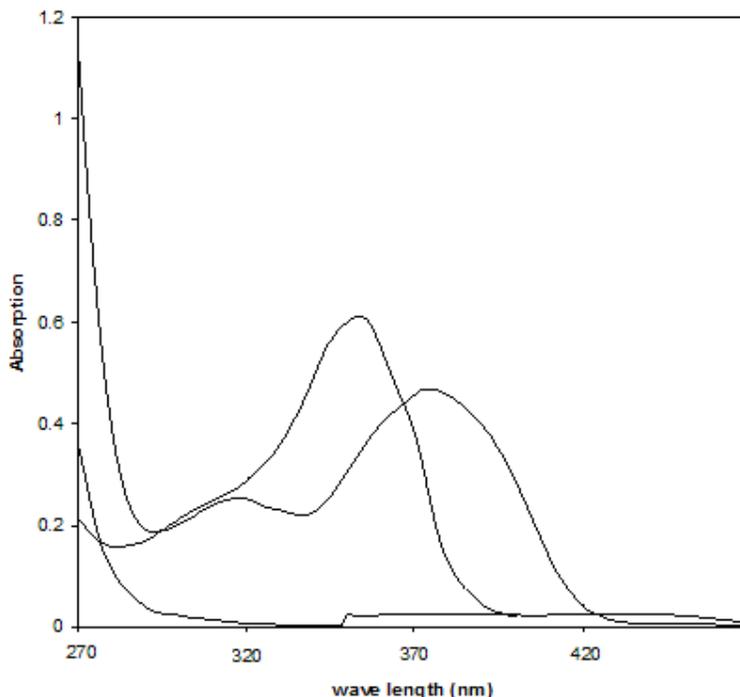
Figure 3. UV-Vis. spectrum for complexation study. A: ligand spectrum (10^{-5} M); B: the complex spectrum after adding 30 µl 10^{-3} M Ho^{3+}; C: Ho^{3+} ion spectrum

3.1. Membrane composition

It is well understood the sensitivity and selectivity of a potentiometric PVC membrane electrode is significantly related to the composition of the membrane, the nature of the solvent mediators and additives used [28-30]. In this study the effects of the nature and amount of the plasticizer, the amount of PVC, and the additive on the potential response of the proposed Ho^{3+} microsensor were investigated, and the results are given in Table 1. These data show that between two plasticizers used, BA and *o*-NPOE, BA with lower polarity than *o*-NPOE acts as better solvent mediator.

The data in Table 1 shows the optimum amount of the ion carrier is 6% (No. 2), while the slope of the resulting emf *vs.* log Ho^{3+} concentration plot is about two-thirds of the expected Nernstian value. However, addition of 2% NaTPB (No. 6) will increase the sensitivity of the microsensor response to a great extent. The fact that the presence of lipophilic anions in the composition of cationic-selective membrane microelectrodes, 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 [31-33].

The potential response of the microelectrode 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 microelectrodes falls to very low values of 3.2 mV/decade, indicating that the sensitivity of the microsensor is major due to the complexing behavior of TBA.

Table 1. PVC membrane composition ingredients

Membrane	PVC (%wt.)	Plasticizer (%wt.)	TBA (%wt.)	Additive (%wt.)	Slope (mV/decade)
1	20	BA, 75	5	-	10.2±0.3
2	20	BA, 74	6	-	12.3±0.3
3	20	BA, 73	7	-	11.6±0.4
4	20	NPOE, 74	6	-	10.3±0.2
5	20	BA, 73	6	1	17.4±0.5
6	20	BA, 72	6	2	19.4±0.2
7	20	BA, 78	-	2	4.4±0.3

$$y = 19.403x + 120.74$$
$$R^2 = 0.9988$$
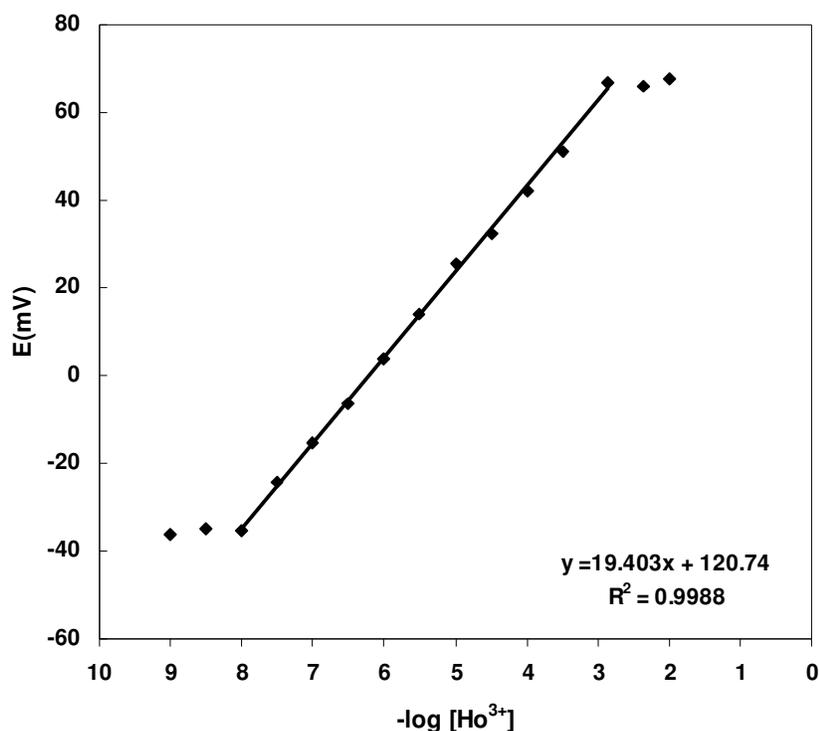
Figure 4. The calibration curve of the Ho^{3+} membrane microsensor based on TBA

3.2. Response characterization of the microsensor

The critical response characteristics of the Ho^{3+} microsensor were assessed according to IUPAC recommendations [34]. The potential response of the membrane at varying activity of Ho^{3+} ions (Fig. 4) indicates a rectilinear range from 1.0×10^{-8}-1.0×10^{-3} M. The slopes of the calibration curves were 19.4 ± 0.2 mV/decade of Ho^{3+} activity. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 1.0×10^{-8} M. The standard deviation of 10 replicate potential measurements for the proposed electrode is ±0.2. The potential drift within 5 minutes after each measurement is ±0.3 mV.

The proposed microsensor is an asymmetrical sensor without any internal reference electrode and internal solution. The main problem of the symmetric ion selective liquid membrane electrodes is the leaking of the internal solution to the outer surface of the membrane, causing changes in the surface potential. Therefore, the detection limit of this kind of electrode is about 10^{-6} M. In the case of asymmetric sensors, the wire coated and the graphite coated detection limit is about 10^{-8}-10^{-11} M (on the grounds that there is no leaking of the internal solution). Due to the high tendency of the asymmetric microsensor to the low Ho^{3+} concentration, the selectivity will be drastically improved.

3.3. pH effect on the potential response

The influence of pH on the response of the Ho^{3+} microsensor for a 1.0×10^{-5} M Ho^{3+} solution, was evaluated over a pH range of 2.0 to 12.0, and the results show that in the pH range of 3.8 to 8.0, the potential does not change with changing pH that indicates the applicability of this microsensor in the mentioned pH range. The observed drift at the higher pH values of this range could be due to the formation of insoluble $Ho(OH)_3$ or other soluble hydroxy complexes of Ho^{3+} ion in the solution. In acidic solutions having pH values of less than the minimum of this range, the nitrogen donor atoms of ionophore used could be protonated to some extent, which results in improper functioning of the microsensor to the Ho^{3+} ion concentration.

3.4. Selectivity

Selectivity is one of the most important factors for any ion selective electrode. In this work, matched potential method (MPM) [35-37] was used for determination of selectivity coefficients of the proposed Ho^{3+} microelectrode. According to MPM method, the specified activity (concentration) of the primary ion (A, 1.0×10^{-4} M of Ho^{3+} ion) is added to a reference solution (1.0×10^{-8} M) and, afterwards, the potential is measured. In a separation experiment, the interfering ions (B, 1.0×10^{-8}-1.0×10^{-3} M) are added to an identical reference solution until the measured potential matches that obtained before by adding the primary ions. Fig. 5 shows the potential responses of various cation selective microelectrodes based on TBA.
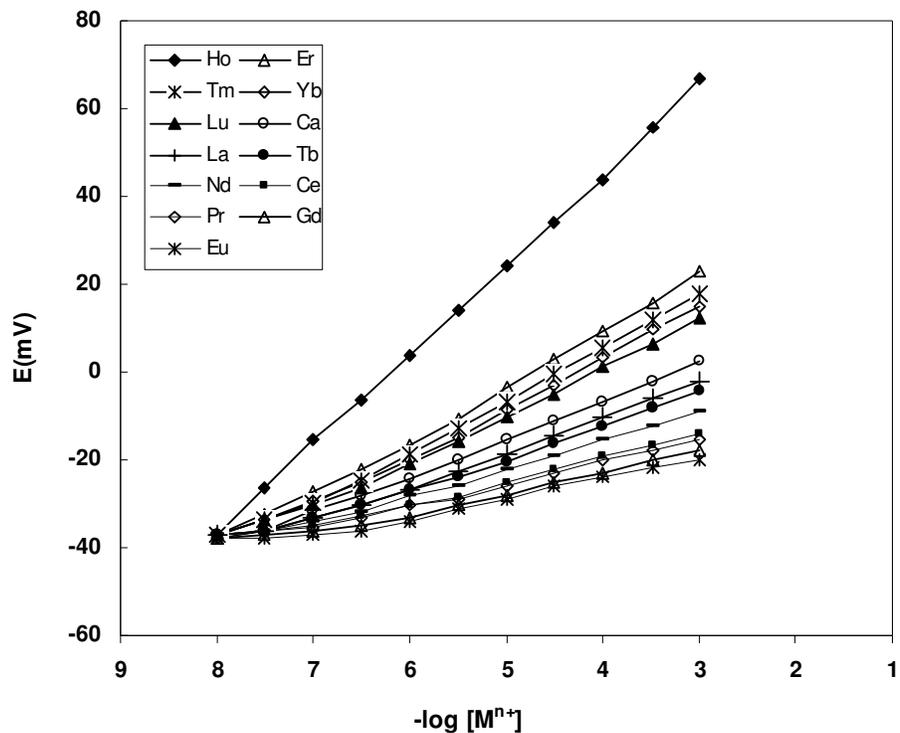
Figure 5. The potential responses of various cation selective microelectrodes based on TBA

Table 2. Selectivity coefficients of various interfering ions for Ho^{3+} microsensor

Ion	Log K_{MPM}	Ion	Log K_{MPM}
Na^+	-3.3	Nd^{3+}	-3.4
K^+	-3.3	Sm^{3+}	-3.3
Mg^{2+}	-3.2	Eu^{3+}	-3.6
Ca^{+2}	-3.0	Gd^{3+}	-3.3
Co^{+2}	-3.6	Tb^{3+}	-3.1
Pb^{+2}	-3.6	Dy^{3+}	-2.7
Fe^{3+}	-3.7	Er^{3+}	-2.5
La^{3+}	-3.1	Tm^{3+}	-2.5
Ce^{3+}	-3.2	Yb^{3+}	-2.3
Pr^{3+}	-3.4	Lu^{3+}	-2.7

The matched potential method selectivity coefficient, K_{MPM}, is then given by the resulting primary ion to the interfering ion activity (concentration) ratio. The selectivity coefficient, $K_{A,B}^{Pot}$, is determined as;

$$K_{A,B}^{Pot} = \Delta a_A / a_B$$

Where $\Delta a = a_A' - a_A$, a_A is the initial primary ion activity and a_A' is the activity of A in the presence of the interfering ion, a_B.

The resulting selectivity coefficients are given in Table 2. As it can be seen, the proposed Ho^{3+} microsensor is highly selective with respect to the most of cations.

3.5. Response time

The dynamic response time of the microelectrode, being another very important parameter in the evaluation of a microelectrode, was studied by varying the concentration of a solution from 1.0×10^{-8} M to 1.0×10^{-3} M and recording the times needed for the microelectrode to reach ± 1 mV of its equilibrium potential. The response time of the microelectrode was found to be about 10 seconds in the whole concentrations. This is highly likely due to the fast complexation-decomplexation exchange kinetics of Ho^{3+} ion with the TBA at the test solution-membrane interface. To evaluate the microsensor reversibility, a similar procedure in the opposite direction was adopted. The measurements were performed in the sequence of high-to-low sample concentrations. The results showed that the potentiometric response of the sensor is reversible, although the time needed to reach the equilibrium values was longer than that for the low-to-high sample concentration procedure.

3.6. Lifetime

The lifetime of the microsensor, which is a measure of microsensor durability, was also considered in a 10 weeks period. During this period the microsensor was used for at least 2 hours a day, and 5 days a week. After each usage it was washed completely and dried. After nine weeks only a relatively slight changes in the microsensor slope and detection limit from 19.4 ± 0.2 and 1.0×10^{-8} M to 17.8 ± 0.4 mV/decade and 1.0×10^{-7} M of Ho^{3+} ion.

3.7. Analytical Application

The proposed Ho^{3+} microelectrode was found to work well under laboratory conditions. It was applied as an indicator electrode for the titration of 25.0 mL of 1.0×10^{-5} M of Ho^{3+} solution with 1.0×10^{-3} M of standard EDTA, and the resulting titration curve is shown in Fig. 6. As it can be seen from Fig. 6, the amount of Ho^{3+} ions can be determined with good accuracy.

The Ho(III) microsensor was also used for determination of Ho(III) content of some holmium alloys samples. 0.1 g of holmium alloys ($Ho_2Co_{14}Fe_3$ and $HoFe_{11.4}Ta_{0.6}$) powder (from Sigma-Aldrich) was weighed carefully and transfer to a 50-mL beaker and 10 mL of HCl (10 %) was added. The solution was stirred and heated (50 ℃). Then, the pH was adjusted to 5.0 with ammoniac and the

solution was filtered. The filtered solution was transferred to a 250-mL volumetric flask. Then, 25 mL of acetate buffer was added and the solution was made up to volume by distilled water. By using calibration method, the holmium content of 10 mL of this solution was measured with the proposed microsensor. The results which are compared with inductive coupled plasma atomic emission spectroscopy (ICP-AES) were shown in Table 3. Considering Table 3, there is a satisfactory agreement between the results obtained from the proposed sensor and ICP method. At 95% confidence level the calculated t-value did not exceed the theoretical t-value indicating no significant difference between the proposed methods and the reference method.
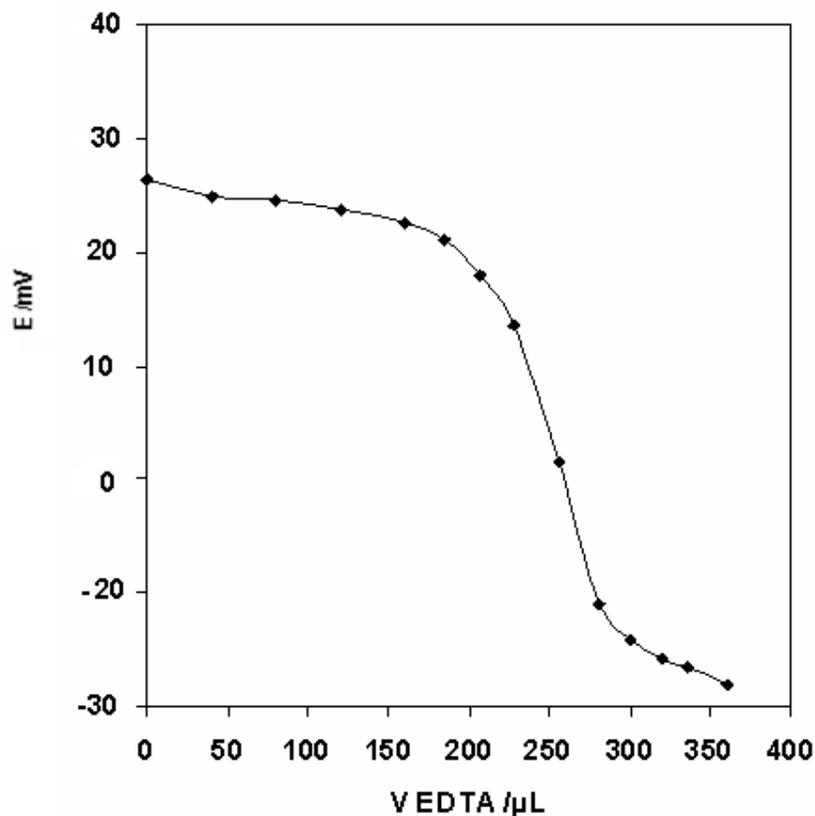
Figure 6. Potentiometric titration curve of 25.0 mL of a 1.0×10^{-5} M Ho^{3+} solution, with a 1.0×10^{-3} M EDTA using the proposed microelectrode as an indicator electrode

Table 3. Analysis of the holmium alloys

Sample	The proposed method*	ICP-AES*	t-test
			(P=0.05; $t_{theoritical}$=2.20)
$Ho_2Co_{14}Fe_3$	97.3±2.1 ppm	95.5±0.3 ppm	$t_{experimental}$= 2.15
$HoFe_{11.4}Ta_{0.6}$	72.7±2.3 ppm	70.7±0.4 ppm	$t_{experimental}$= 2.09

* The results are based on 6 replicates measurements.

4. CONCLUSIONS

The results obtained from the above mentioned study revealed that a potentiometric PVC-based membrane microsensor based on TBA functions as an excellent Ho^{3+} selective membrane microsensor 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 asymmetric sensors make it a very good device used for the determinations of Ho^{3+} ion in micro flow system or probing of processes in biological research or analyses of very small sample volume.

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