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Influence of Metal Ions as Interfering Species on Potentiometric Behavior of Tb(III) Ion-Selective Electrode

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ABSTRACT

A new terbium(III) sensor based on 1, 3-Diaminopropane-N,N,N',N'-tetraacetic acid as a suitable ionophore is described. The electrode comprises 3% ionophore, 30% PVC, 65% NB and 2% NaTPB. The sensor has a linear dynamic range of 1.0×10^{-8} to 1.0×10^{-2} M with a Nernstian slope of 19.8 ± 0.4 mV per decade and a detection limit of 8.4×10^{-9} M. In this study, potentiometric selectivity coefficients, describing the preference of the membrane for terbium ions relative to an interfering ion, were determined by the matched potential method (MPM). The proposed sensor shows a very good selectivity towards a large number of cations, such as Yb(III), Gd(III), Eu(III), Ho(III), Tm(III), Fe(III), Na(I), K(I), Ca(II), Mg(II), Zn(II), Co(II), Cd(II), Ni(II) and Pb(II) in comparison with former ones. It was used as an indicator electrode in the potentiometric titration of Tb(III) ions with EDTA. The sensor was applied to the determination of Tb(III) ions concentration in water samples solutions.

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

INTRODUCTION

Terbium oxide and other rare earth oxides are used in making of the optical glasses, in the preparation of glass fibers for optical purposes, in gasoline-cracking catalysts, polishing compounds, carbon arcs, and in the iron and steel industries to remove sulfur, carbon, and other electronegative elements from iron and steel [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, 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 sensors have shown to be very effective tools for analysis of a wide variety of cations, anions, and molecules. They are very simple, inexpensive, and capable of producing reliable responses in a wide concentration range [2-25]. In spite of successful progress in the design of highly selective ionophores for various metal ions, there are only a limited number of reports on the development of selective ionophores for terbium [26–28]. In this work a Tb(III) membrane sensor based on 1, 3-Diaminopropane-N,N,N',N'-tetraacetic acid was constructed and the effect of interfering ions was evaluated on the sensor.

EXPERIMENTAL SECTION

Reagent grade dibutyl phthalate (DBP), benzyl acetate (BA), nitrobenzene (NB), acetophenone (AP), high relative molecular weight Poly vinyl chloride (PVC), sodium tetraphenylborate (NaTPB), and tetrahydrofuran (THF) were purchased from Aldrich and used as received. The 1, 3-Diaminopropane-N,N,N',N'-tetraacetic acid, 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 except for vacuum drying over P₂O₅. Doubly distilled de-ionized water was used throughout the experiment.

The viscous solution that was used for the formation of the membrane was prepared [25–27] by mixing 30 mg of powdered PVC, 65 mg of NB and 2 mg of additive NaTPB in 5 mL of THF and 3 mg of ionophore. The resulting, low-viscosity mixture was thoroughly mixed and transferred into a glass dish of 2 cm in diameter and then, its solvent was slowly evaporated to gain an oily concentrated mixture. Consequently, the membrane was formed on the tip of a Pyrex tube (3–5mm o.d.) and by dipping the tube into the mixture for about 5 s, so that a transparent membrane of about 0.3mm thickness was formed. Before being filled with an internal filling solution (1.0×10⁻³ M TbCl₃), the tube was pulled out and given enough time to dry at room temperature for about 12 h. The final step was to condition the electrode for 24 h, by soaking in a 1.0×10⁻³ M TbCl₃ solution. A silver–silver chloride electrode was used as an internal reference electrode.

The cell assembly, used for all measurements:

Ag–AgCl | 1.0×10⁻³ M TbCl₃ | PVC membrane: test solution | Hg–Hg₂Cl₂, 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.

RESULTS AND DISCUSSION

To investigate the possible ions towards which the ionophore is selective preliminary experiments were carried out in which this carrier was used in the construction of membrane sensors for some metal ions. The curves of the best potential responses of the resulting membranes versus the concentration of each ion showed that among the lanthanide, transition and representative ions tested, Tb(III) showed the highest Nernstian response.

As with many carrier-modified membrane electrodes, the total potentiometric response of the electrode towards terbium is dependent on the concentration of the ionophore and NaTPB incorporated within the membrane [29-33]. Thus, different aspects of membrane preparation

based on ionophore were optimized. Using 3% of ionophore and 2% NaTPB in the membrane electrode displays Nernstian slope towards terbium. However, the best performance was obtained with 30% PVC, 2% NaTPB, 3% ionophore and 65% NB.

The influence of interfering ions on the response behavior of ion-selective membrane electrodes is usually described in terms of selectivity coefficients, $K_{A,B}^{Pot}$. In this work, matched potential method (MPM) was used for calculation of selectivity coefficient [34-36]. According to the MPM, a specified activity (concentration) of primary ions (A) is added to a reference solution and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution, until the measured potential matches the one obtained before by adding primary ions. The selectivity coefficient, $K_{A,B}^{Pot}$, is determined as: $K^{MPM} = a_A/a_B$. The resulting values are shown in Table 1. As it is seen, for all alkali and alkaline earth metal ions used, the selectivity coefficients are smaller than 5.5×10^{-4} and in the case of transition metal ions, the selectivity coefficients are in the order of 4.7×10^{-3} or smaller that indicating they would not significantly disturb the functioning of the Tb^{3+} sensor. Table 2 compared the performance characteristics of the proposed sensor with those of the best previously reported terbium sensors. It is immediately obvious, not only the working concentration range and detection limit of proposed sensor, but also its selectivity coefficients are superior to those reported for the terbium ion-selective membrane electrodes [26-28].

The Tb^{3+} -sensor was used for the determination of the concentration of Tb^{3+} ions tap water and river water samples and the results of triplicate measurements are summarized in Table 3. As it is seen, the recoveries of the Tb^{3+} ions in all samples are acceptable.

The proposed Tb^{3+} ion-selective electrodes were found to work well under the laboratory conditions. The proposed sensor was successfully applied as an indicator electrode in the titration of Tb^{3+} (1.0×10^{-4} M) with 25 mL of EDTA solution (1.0×10^{-2} M). The resulting titration curve is shown in Figure 1, from which it is clear that the titration end point is sharp and the amount of Tb^{3+} ions in solution can be accurately determined with the electrode

Table 1: Selectivity coefficients of various interfering ions

Interfering ion (B)	Selectivity coefficient ($K_{Tb,B}$)
Yb^{3+}	8.5×10^{-4}
Eu^{3+}	6.2×10^{-4}
Gd^{3+}	4.7×10^{-3}
Ho^{3+}	3.3×10^{-3}
Tm^{3+}	3.4×10^{-3}
Fe^{3+}	2.9×10^{-3}
Na^+	4.2×10^{-4}
K^+	5.5×10^{-4}
Ca^{2+}	3.8×10^{-4}
Mg^{2+}	5.1×10^{-4}
Zn^{2+}	4.2×10^{-3}
Co^{2+}	3.8×10^{-3}
Cd^{2+}	2.6×10^{-3}
Ni^{2+}	2.5×10^{-3}
Pb^{2+}	6.8×10^{-4}

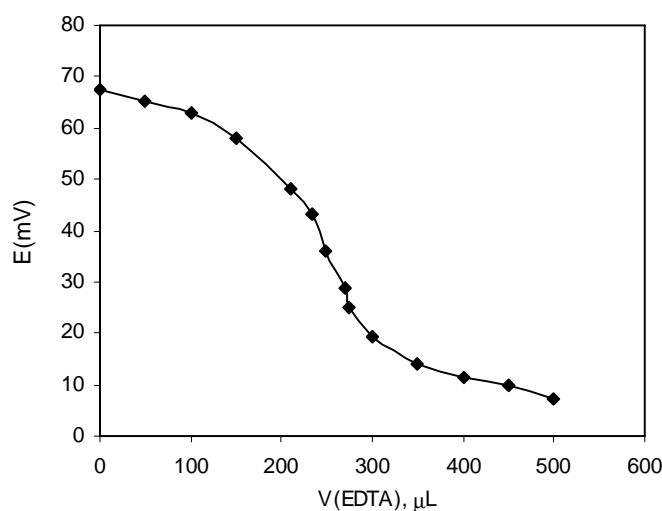
Table 2: Comparison of different Tb(III) electrodes

Parameter	Ref. 26	Ref. 27	Ref. 28	This work
LR (M)	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^{-8} - 1.0×10^{-2}
DL (M)	8.0×10^{-7}	8.6×10^{-7}	7.0×10^{-6}	8.4×10^{-9}
Response time (s)	~10	15	<20	~5
pH range	3.5-8.0	3.8-8.2	3.5-7.7	2.1-9.5
Slope (mV/decade)	19.7	19.4	19.8	19.8
Log $K_{sel} > 2$	Gd	Gd	Ce, La, Dy, Yb, Sm	-

Table 3: Determination of Tb³⁺ ions in water samples solutions using the Tb³⁺-sensor

Sample	Tb ³⁺ added (mg/mL)	Found (mg/mL)	Recovery (%)
River water	0.25	(0.27 ^a ± 0.03)	108
	0.5	(0.54 ± 0.02)	108
Tap water	0.25	(0.29 ± 0.04)	116
	0.5	(0.55 ± 0.03)	110

^a. Results are based on three measurements

**Figure 1. Potential titration curve of 25.0 mL from a 1.0×10^{-4} M Tb³⁺ solution with 1.0×10^{-2} M of EDTA.**

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