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ORIGINAL PAPER

Highly selective and sensitive Th^{4+}-PVC-based membrane sensor based on 2-(diphenylphosphorothioyl)-*N*′,*N*′-diphenylacetamide

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Abstract A Th^{4+} ion-selective membrane sensor was fabricated from poly (vinyl chloride) (PVC) matrix membrane containing 2-(diphenylphosphorothioyl)-*N*′,*N*′-diphenyl acetamide (DPTD) as a neutral carrier, potassium tetrakis (*p*-chlorophenyl) borate (KTpClPB) as anionic excluder and *o*-nitrophenyloctyl ether (NPOE) as a plasticizing solvent mediator. The effects of the membrane composition, pH and additive anionic influence on the response properties were investigated. The sensor, comprising 30% PVC, 63% solvent mediator, 4% ionophore and 3% anionic additive demonstrates the best potentiometric response characteristics. It displays Nernstian behavior (15.2 ± 0.5 mV per decade) over the concentration range 1.0×10^{-2}–1.0×10^{-6} M. The detection limit of the electrode is 6.3×10^{-7} M (~140 ng/ml). The response time of the electrode is 30 s .The sensor can be used in the pH range 3.0–9.0 for about 6 weeks. The membrane sensor was used as an indicator electrode in the potentiometric titration of Th^{4+} ions with EDTA. It was successfully applied to the determination of thorium ions in binary mixture.

Keywords Thorium · Ion-selective electrode · PVC membrane · 2-(diphenyl phosphorothioyl)-*N*′,*N*′-diphenyl acetamide (DPTD) · Potentiometry

1 Introduction

Thorium is a naturally occurring, slightly radioactive metal and has many applications such as an alloying element in magnesium, imparting high strength and creep resistance at elevated temperatures. Thorium is used to coat tungsten wire used in electronic equipment and has been used in gas tungsten arc welding electrodes and heat-resistant ceramics. The oxide is used to control the grain size of tungsten used for electric lamps and is used for high-temperature laboratory crucibles. Thorium oxide added to glass helps create glasses of a high refractive index and with low dispersion. Consequently, they find application in high quality lenses for cameras and scientific instruments. Uranium–thorium age dating has been used to date hominid fossils. One of the important application of thorium is used it as a fertile material for producing nuclear fuel. In particular, the proposed energy amplifier reactor design would employ thorium. Since thorium is more abundant than uranium, some designs of nuclear reactor incorporate thorium in their nuclear fuel cycle [1].

Many techniques have been used for determination of thorium including Titrimetric [2], Radiometric [3], Spectrophotometric [4–6], Fluorometric [7], Volumetric [8], Gravimetric [9] determination, ion exchange

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chromatography [10], isotope dilution mass spectrometry [11], epithermal neutron activation analysis [12] and Inductively Coupled Plasma Mass Spectrometry [13].

Potentiometric sensors can offer an inexpensive and convenient method of analysis of rare-earth ions in solution, provided that the acceptable sensitivity and selectivity are achieved.

There have been many studies on ion-selective electrodes for transition and heavy metal ions [14]. Among these metal ions, some attention has been paid to the development of lanthanide electrodes [15–36].

In this work we report a Th(IV) membrane sensor based on 2-(diphenyl phosphorothioyl)-*N′*,*N′*-diphenyl acetamide (DPTD) with a good Nernstian response over a relatively wide working range. Since the hydration energy of the Th^{4+} ions is very high (–5,815 kJ mol^{-1}) [37], the DPTD shows a high selectivity towards Th^{4+} ions.

2 Experimental

2.1 Reagents

Reagent grade dibutyl phthalate (DBP), banzylacetate (BA), *o*-nitrophenyloctyl ether (NPOE), acetophenone (AP), high relative molecular weight Poly (vinyl chloride) (PVC), potassium tetrakis (*p*-chlorophenyl) borate (KTpClPB) and tetrahydrofurane (THF) were purchased from Aldrich and used as received. The chloride and nitrate salts of the cations used (from Merck and Aldrich) were all of the highest purity available and used without further purification except for vacuum drying over P_2O_5. Doubly distilled deionized water was used throughout. 2-(diphenylphosphorothioyl)-*N′*,*N′*-diphenyl acetamide or DPTD (Fig. 1) was synthesized as described elsewhere [38].

2.2 Electrode preparation

The general procedure to prepare the PVC membrane involved the thorough mixing of 30 mg of powdered PVC, 63 mg of NPOE and 3 mg of the additive KTpClPB in 2 ml of THF. To this mixture, 4 mg of ionophore DPTD were added 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 the internal filling solution (1.0×10^{-3} M $ThCl_4$). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M $ThCl_4$ solution. A Silver/Silver chloride coated wire was used as an internal reference electrode [35, 36].

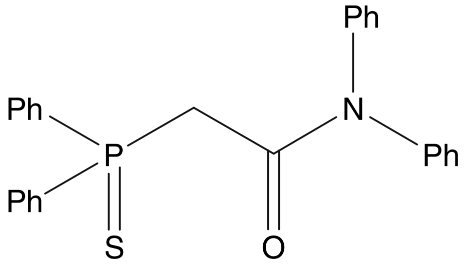

Fig. 1 Structure of DPTD

2.3 EMF measurements

All EMF measurements were carried out with the following assembly; Ag–AgCl/internal solution (1.0×10^{-3} M $ThCl_4$)/PVC Membrane/test solution/Ag–AgCl, KCl (satd.)

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

3 Results and discussions

Theoretical investigations have been carried out to understand better the fundamental interaction between metal ions and neutral molecules and their relationship to molecular recognition. Computational models capable of reliably predicting ligand selectivity in a variety of cations have been shown to be valuable tools for the advancement of practical work [39–42]. In order to have a clear picture about the selectivity of ligand for various metal ions, we investigated its binding to Ca^{2+}, Mg^{2+}, Eu^{3+}, La^{3+}, Zn^{2+}, Pb^{2+}, Cu^{2+}, K^{+}, Na^{+} and Th^{4+} ions using the Extended Hückel semi-empirical calculations. Because the system contains (Th^{4+}) ions which have not been assigned any basis function in ab initio calculation, extended Hückel semi-empirical calculations have been used. The influence of the nature, size and charge of metal ions on the complexation reaction with the neutral ligand is explained on the basis of the calculation of gas-phase binding energies.

The binding energy of the uncomplexed ligand and its complexes with Th^{4+}, and other metal ions were carried out using Hyper Chem software (Version 6.01) [43]. The binding energy (ΔE) was calculated using Eq. 1:

$$\Delta E = \Delta E_{\text{complex}} - (\Delta E_{\text{ligand}} - \Delta E_{\text{cation}}) \qquad (1)$$

where $\Delta E_{\text{complex}}$, ΔE_{ligand} and ΔE_{cation} are the total energies of the complex, uncomplexed ligand and metal ion, respectively. Table 1 summarizes the theoretical data relating the stability of the ligand compelexes with Ca^{2+}, Mg^{2+}, Eu^{3+}, La^{3+}, Zn^{2+}, Pb^{2+}, Cu^{2+}, K^{+}, Na^{+} and Th^{4+} ions.

Table 1 Interaction energy between metal ions and DPTD

Compounds	Interaction energy (kJ mol^{-1})
Th^{4+}-ligand	–12,929.16
Na^{+}-ligand	–845.16
Mg^{2+}-ligand	–421.71
Pb^{2+}-ligand	–5,768.87
Ce^{3+}-ligand	–3,059.72
La^{3+}-ligand	–0.391
Nd^{3+}-ligand	–7,790.79
Ac^{3+}-ligand	–1,232.51
Pr^{3+}-ligand	–5,342.54

Table 1 reveals that the cation binding energy with DPTD shows a pronounced dependence on the nature of the metal ions used. As can be seen from the Table 1, interaction energy between Th^{4+} and DPTD, are not very high due to the high hydration energy of the Th^{4+} ions. However, the high affinity of the ionophore towards Th^{4+} ions causes such high selectivity.

Thus, based on results from the ab initio calculations it seems that the proposed ionophore maybe can be used as a suitable ionophore in preparation of a thorium ion-selective membrane electrode. The optimized structures of the ionophore and its Th^{4+} complex are shown in Fig. 2a and b.

In the next experiment, the interactions between ion-carrier (DPTD) and a number of cations were investigated conductometrically. To the best of our knowledge there is no report on the stability of DPTD complexes with different cations. Thus, the complexation of DPTD with a number of common cations was conductometrically investigated in an acetonitrile solution at 25 ± 0.05 °C, in order to obtain information about the stability and selectivity of the resulting complexes. About 15 ml of 1.0×10^{-4} M of each cation solution were 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, both the starting solution and the titrant had the same cation concentration. Then, a known amount of the DPTD (1.0×10^{-2} M) solution was added in a stepwise manner using a calibrated micropipette. The solution conductance was measured after each addition. The DPTD addition was continued until the desired DPTD-to-cation mole ratio was achieved.

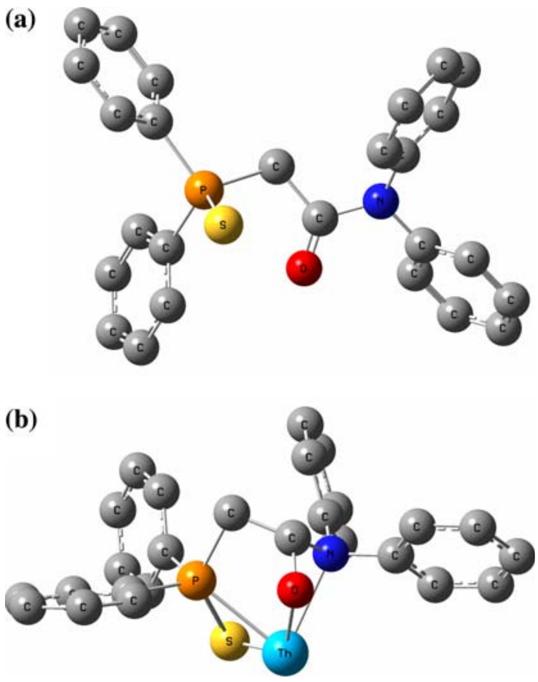

Fig. 2 Optimal conformation of ionophore before (**a**) and after (**b**) complexation with Th^{4+}

The results show that the ligand to cation mole ratio is 1.0 in all cases. The complex formation constants, K_f, were evaluated by computer fitting of the molar conductance/mole ratio data with appropriate equations [44, 45]. These results are summarized in Table 2. The stability constant of the Th4^{+}–DPTD complex is higher than that of other cations–DPTD complexes tested. Consequently, DPTD may be used as a suitable selective ionophore in the construction of a Th^{4+} ion-selective membrane electrode.

Therefore, in the next experiments DPTD was used as a neutral carrier for the preparation of PVC-membrane electrodes for a number of metal ions, including alkali, alkaline earth, transition and heavy metal ions. While the slopes of the linear parts of the EMF sensor responses for all the other shown cations are much lower than those expected by the Nernst equation, the resulting Th^{4+} potential response presents Nernstian behavior.

It is well known that some important features of PVC-based membranes, such as the nature and amount of the ionophore, the plasticizer properties, the plasticizer/PVC ratio and, particularly, the nature of the additives used,

Table 2 Formation constant of Th^{4+}–DPTD complexes

Cation	Log K_f
Th^{4+}	4.47 ± 0.11
Ce^{3+}	2.33 ± 0.11
La^{3+}	2.36 ± 0.10
Zn^{2+}	2.32 ± 0.10
Sr^{2+}	<2
Cu^{2+}	2.45 ± 0.13
Ca^{2+}	<2
Na^{+}	2.56 ± 0.19
Mg^{2+}	<2
Cr^{3+}	2.57 ± 0.10
Fe^{3+}	2.46 ± 0.17

Table 3 The optimization of the membrane ingredients

No.	PVC%	Plasticizer%	Ionophore%	Additive%	Slope (mV decade^{-1})
A	30	67, NPOE	3	–	9.70 ± 0.3
B	30	66, NPOE	4	–	10.6 ± 0.2
C	30	65, NPOE	5	–	10.3 ± 0.5
D	30	64, NPOE	4	2	14.1 ± 0.3
E	30	63, NPOE	4	3	15.2 ± 0.5
F	30	63, AP	4	3	13.1 ± 0.2
G	30	63, DBP	4	3	11.2 ± 0.4
H	30	63, BA	4	3	11.2 ± 0.3
I	30	67, NPOE	–	3	2.3 ± 0.4

significantly influence the sensitivity and the selectivity of the ion-selective electrodes [46, 47]. As a consequence, different aspects of membrane preparation based on DPTD were optimized. The results are given in Table 3. Solvent polymeric membrane ion-selective electrodes are usually based on a matrix of the solvent mediator/PVC ratio about 2. Polymeric films with such a plasticizer/PVC ratio will result in the optimum physical properties and sufficiently high mobility of their constituents. In this study, a plasticizer/PVC ratio of about 2.0 was found to be the most suitable. It is reported that the selectivity and working concentration range of the membrane sensor are affected by the nature and amount of plasticizer used. This is due to the plasticizer influence on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of the ionophore [48]. As seen from Table 3, among four different plasticizers used, NPOE demonstrates the best sensitivity. This is because of the ability of NPOE to extract Th^{4+} ions with high hydration energy from aqueous solution to the organic membrane phase. Moreover, 4% of the ionophore DPTD was chosen as the optimum amount in the PVC membrane (no. B).

It has been demonstrated that the presence of the lipophilic negatively charged additives improves the potentiometric behavior of certain selective electrodes not only by reducing the ohmic resistance and improving the response behavior and selectivity, but also, in cases where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the membrane electrode [49, 50]. The data given in Table 3 show that in the absence of a suitable additive, the sensitivity of the PVC membrane based on DPTD is low (no. B with slope of 10.6 mV per decade). However, the presence of 3% KTpClPB as a suitable lipophilic additive improves the sensitivity of the Th^{4+} sensor considerably (no. *E* with slope of 15.2 mV per decade).

The optimum equilibration time for the membrane electrode in the presence of 1.0×10^{-3} M $ThCl_4$ was 24 h, after which it had stable potentials in contact with thorium solutions. The electrode shows a linear response to the Th^{4+} ion activity in the range 1.0×10^{-2}–1.0×10^{-6} M (Fig. 3). The calibration graph slope was 15.2 ± 0.5 mV per decade (for eight measurements). The detection limit, as determined from the intersection of the two extrapolated segments of the calibration graph, was 6.3×10^{-7} M.

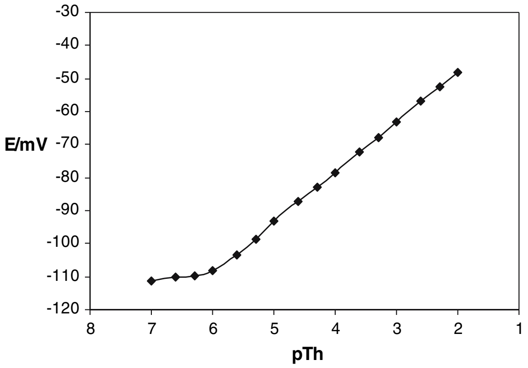

Fig. 3 Calibration curve of the Th^{4+} sensor of membrane. The standard deviation of 8 replicates is ±0.5

The pH influence of the test solution (1.0×10^{-4} M) on the potential response of the membrane sensor was tested in the pH range 2.0–6.0. The corresponding results are summarized in Fig. 4. The potential remains constant over a pH range 3.0–5.0, beyond which it changes considerably. The observed drift at higher pH may be due to the formation of some soluble and insoluble hydroxy complexes of Th^{4+} ions. The observed increase in potential at lower pH than 3.0 indicates that the protonated ionophore possesses a poor response to the Th^{4+} ions and a strong response to H_3O^+ ions in solution. It is well known that cations with more than two charges such as Fe^{3+}, Al^{3+}, lanthanide ions and actinides (Th^{4+}) in the various pH and concentrations form many different kinds of complexes including the hydroxyl group.

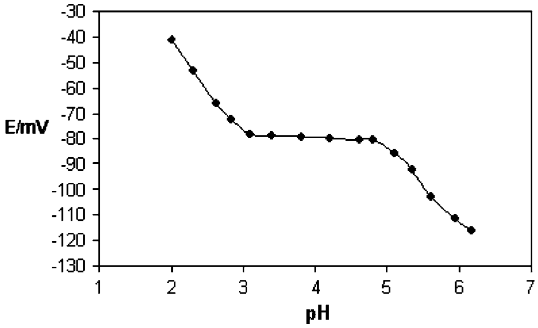

Fig. 4 Effect of the pH of test solution (1.0×10^{-4} M) on the potential response of the Th^{4+} ion-selective electrode

For analytical applications the dynamic response time is an important factor for any ion-selective electrode. In this research the practical response time was recorded by changing the Th^{4+} concentration in solution over a range 1.0×10^{-2}–1.0×10^{-6} M. Figure 5 shows the results.

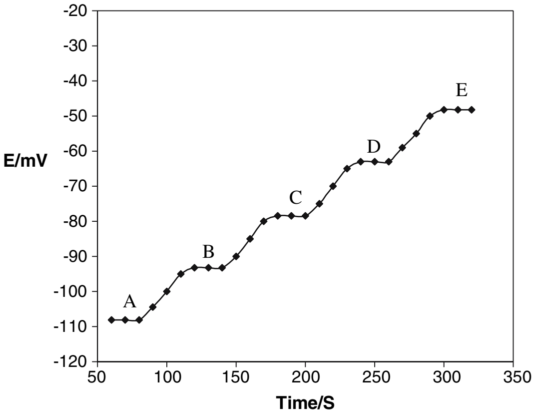

Fig. 5 Dynamic response time of the electrode for step changes in the concentration of Th^{4+} solution; (A) 1.0×10^{-6} M, (B) 1.0×10^{-5} M, (C) 1.0×10^{-4} M, (D) 1.0×10^{-3} M, (E) 1.0×10^{-2} M

Eventually, the response time of the electrode was 30 s in the whole concentration range.

Potentiometric selectivity coefficients describing the membrane preference towards an interfering ion were determined by the separation solution method (SSM) and match potential method (MPM) [51, 52]. According to the MPM method, a specified activity (concentration) of primary ions (A, 1.0×10^{-3} M of Th^{4+} ions) is added to a reference solution (1.0×10^{-6} M of Th^{4+} ions) and the potential is measured. In a separate experiment, interfering ions (B, 1.0×10^{-2} M) are successively added to an identical reference solution until the measured potential matches that obtained before the primary ion addition. The matched potential method selectivity coefficient, K_{MPM}, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K_{\mathrm{MPM}} = a_{\mathrm{A}}/a_{\mathrm{B}}$.

In the separation solution method (SSM), the concentrations of a cell comprising an ion-selective electrode and a reference electrode (ISE cell), are adjusted using two separate solutions; one containing the ion A (but no B) of a_{A} activity and the other containing the ion B (but no A) of activity as high as required to achieve the same measured cell voltage. From any pair of the a_{A} and a_{B} activities giving the same cell voltage, the value of may be calculated from the equation $K_{\mathrm{SSM}} = a_{\mathrm{A}}/a^{Z_{\mathrm{A}}/Z_{\mathrm{B}}}$.

The resulting values are given in Table 4. Obviously, for all the diverse ions used, the selectivity coefficients are in the order of 3.4×10^{-3} or smaller for both methods, indicating they would not significantly disturb the Th^{4+} ion-selective electrode function.

The lifetime of the Th^{4+} membrane sensor was tested over a period of 10 weeks. During this period, the electrodes were in daily use over an extended period of time (1 h per day), and the results are provided in Table 5. According to Table 5, after 6 weeks a very slight gradual decrease and increase in the slopes and detection limit were observed, respectively. This is caused by the leakage of the ionophore from the membrane to the solution.

Table 4 The selectivity coefficients of various interfering cations for Th^{4+} membrane sensor

Cation	K_{SSM}	K_{MPM}
Na^{+}	4.2×10^{-4}	4.5×10^{-4}
K^{+}	4.7×10^{-4}	4.4×10^{-4}
Mg^{2+}	2.3×10^{-4}	2.5×10^{-4}
Ca^{2+}	3.7×10^{-4}	3.5×10^{-4}
La^{3+}	5.4×10^{-4}	5.3×10^{-4}
Eu^{3+}	8.6×10^{-4}	8.7×10^{-4}
Zn^{2+}	2.9×10^{-4}	2.6×10^{-4}
Pb^{2+}	2.3×10^{-4}	2.7×10^{-4}
Cu^{2+}	3.7×10^{-3}	3.4×10^{-3}
Lu^{3+}	5.8×10^{-4}	5.6×10^{-4}
Ag^{+}	8.0×10^{-4}	8.2×10^{-4}

Table 6 compares the detection limit, linear range and response time of the proposed Th^{4+} sensor with those of the best previously reported thorium membrane electrodes.

The proposed Th^{4+} ion-selective electrodes were found to work well under laboratory conditions. The proposed sensor was successfully applied as an indicator electrode in titration of 25 ml Th^{4+} (1.0×10^{-4} M) with EDTA solution (1.0×10^{-2} M). The resulting titration curve is shown in Fig. 6. As can be seen the end point of titration is sharp and the amount of Th^{4+} ions in solution can be accurately determined using the electrode. It was found to be equal to $(1.1 \pm 0.1) \times 10^{-4}$ M.

Owing to the good selectivity of the Th^{4+} sensor, it was used for the direct monitoring of the Th^{4+} ion concentration in binary mixtures. The results obtained are summarized in Table 7. The recovery of Th^{4+} ions in various binary mixtures is in the range of (100.2–102.3%).

Table 5 The lifetime of the Th^{4+} membrane sensor

Week	Slope (mV $decade^{-1}$)	DL (M)
First	15.2 ± 0.5	6.4×10^{-7}
Second	15.1 ± 0.2	6.2×10^{-7}
Third	15.3 ± 0.4	6.4×10^{-7}
Fourth	15.0 ± 0.3	6.2×10^{-7}
Fifth	14.9 ± 0.6	6.3×10^{-7}
Sixth	14.7 ± 0.5	5.3×10^{-7}
Seventh	13.2 ± 0.2	8.8×10^{-6}
Eighth	12.8 ± 0.4	5.4×10^{-6}
Ninth	12.5 ± 0.5	1.7×10^{-6}
Tenth	12.1 ± 0.3	8.3×10^{-5}

Table 6 Comparison of the selectivity coefficient of the best Th^{4+} sensors with the proposed sensor

Reference	DL (M)	LR (M)	RT
17	1.4×10^{-6}	1.0×10^{-1}–8.0×10^{-6}	15 s
21	1.6×10^{-6}	1.0×10^{-1}–5.0×10^{-6}	Fast
29	5.0×10^{-5}	1.0×10^{-1}–1.0×10^{-4}	–
This work	6.3×10^{-7}	1.0×10^{-2}–1.0×10^{-6}	30 s

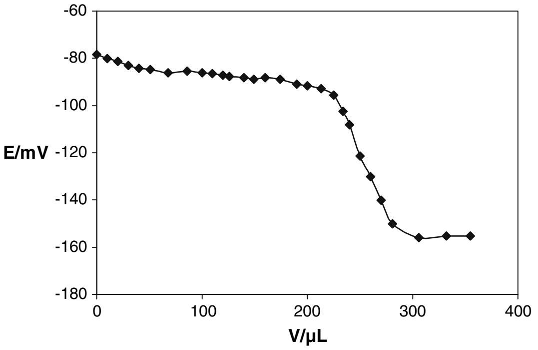

Fig. 6 Potentiometric titration curve of 25 ml of a 1.0×10^{-4} M Th^{4+} solution, with a 1.0×10^{-2} M EDTA, using the proposed membrane sensor as an indicator electrode

Table 7 Recovery from binary mixture

Th^{4+} (ppm)	Added cations (ppm)	Recovery (%)
23.2	10,000, Na^+	100.6
23.2	10,000, K^+	100.4
23.2	10,000, Mg^{2+}	100.9
23.2	10,000, Ca^{2+}	101.1
23.2	5,000, Pb^{2+}	102.2
23.2	5,000, Cu^{2+}	101.7
23.2	3,000, Ce^{3+}	102.3
23.2	3,000, La^{3+}	102.2
23.2	5,000, Cr^{3+}	101.7
23.2	5,000, Fe^{3+}	101.4

4 Conclusion

A potentiometric PVC-based membrane sensor based on DPTD functions as an excellent Th^{4+} selective sensor and can be used for the determination of this ion in the presence of considerable concentrations of common interfering ions. The applicable pH range, lower detection limit and potentiometric selectivity coefficients of the proposed sensor make it a superior device compared with other methods used for the determinations of this ion.

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