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Highly Selective and Sensitive Coated-Wire Yttrium (III) Cation Selective Electrode Based on Kryptofix-22DD

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An yttrium (III) cation selective electrode based on kryptofix-22DD (1,10-didecyl-1,10-diaza-18-crown-6) incorporated into a polyvinylchloride (PVC) membrane has been developed. The optimized membrane incorporating dibutylphtalate (DBP) as plasticizer, kryptofix-22DD and palmitic acid as a new component in a highly selective and sensitive coated wire electrode (CWE) for yttrium (III) cation was directly coated on the surface of a platinum wire electrode. The selective electrode showed more effective performance than other yttrium (III) cation PVC based sensors. The electrode exhibits a Nernstian slope (18.89 ± 0.43 mv.decade^{-1}) in a wide linear concentration range of 1.0×10^{-8}–1.0×10^{-1} M. The detection limit of electrode is 2.15×10^{-9} M. The effects of the *p*H and possible interfering ions were investigated and the optimized conditions for electrode were evaluated. The electrode was applied as an indicator electrode for potentiometric titration of yttrium (III) cation in solutions. Determination of fluoride ion in tap water, mouthwash and toothpaste gave results that compare favorably with those obtained by the fluoride ion selective electrode.

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The most important use of yttrium is in making phosphors, such as in the red phosphors in colour TV tubes and in LEDs.[1] Other uses include the production of electrodes, electronic filters, lasers, superconductors, computer monitors, trichromatic fluorescent lights, temperature sensors, X-ray intensifying screens and various medical applications and also as traces in various materials to enhance their properties. Yttrium is an important element used in atomic reactors for control rods. It is also used in manufacturing of glass, ceramics and in microwave communication equipments. It is used for the production of labeled monoclonal antibodies for tumor therapy studies.[2,3]

Several reagents are reported for the spectrophotometric determination of yttrium (III) cation, but they are not sensitive and not free from interferences.[4–12] The solvent extraction techniques for the extraction of this metal cation are scarce.[13] Yttrium (III) cation can not be determined by direct atomic absorption or plasma atomic emission methods, since the ionization causes low response and it is reduced by the presence of mineral acids.[14] Also the flame spectrometric determination of yttrium is not sensitive.[15]

Ion-selective electrodes (ISEs) possess many advantages over traditional methods of analysis and provide accurate, reproducible, fast, and regular selective determination of various ionic species. In addition, ion-selective electrodes allow non-destructive, on-line monitoring of particular ions in a small volume of sample without any pretreatment. Because of these merits, the use of ISEs is increasing day by day in medicinal, environmental, agricultural, and industrial fields.[16–18]

Macrocyclic ligands have been widely used as suitable neutral carriers for the construction of membrane selective electrodes especially for alkali and alkaline earth metal cations.[19–22]

The ligands for use as ionophore in an yttrium ion-selective sensor should ideally fulfill certain conditions. They should be selective for yttrium (III) cation over other metal ions; they should have rapid exchange kinetics and should be sufficiently lipophilic to prevent leaching of the ligand into the solutions surrounding the membrane sensor. Cryptands are macrocyclic molecules with several oxyethylene chains linked to two ammonium groups and an internal cavity of spherical shape well suited to encapsulate the cations.

In the present paper, we introduce a new ion selective electrode based on the incorporation of kryptofix-22DD (Fig. 1) with higher concentration range and lower detection limit for determination of yttrium (III) cation than that of pervious reported. The developed electrode shows a good potentiometric response versus yttrium (III) cation in solutions.

Experimental

Reagents and standard solutions.—Kryptofix-22DD(Aldrich), tetrahydrofuran(THF) and ethylacetate(EtOAc) (Merck), copper(II) nitrate (BDH), zinc (II)nitrate (Merck), silver(I) nitrate (Merck), cadmium(II) nitrate(Riedel),lead(II) nitrate(BDH),chromium(III) nitrate(BDH), calcium nitrate(Merck), sodium nitrate(BDH), strontium (II)nitrate (Riedel), magnesium(II) nitrate (Merck), potassium nitrate (Merck), lithium nitrate (Riedel), nickel (II)nitrate (Riedel), aluminum(III) nitrate (Riedel), were used without further purification.

Polyvinylchloride (PVC) powder, dioctylphetalate (DOP) and dibutylphetalate(DBP) were purchased from Fluka. All reagents were used in high purity (>99%). All metal-ion solutions were prepared in doubly distilled water and solutions of different concentrations were made by diluting 0.1 M stock solutions.

Potential measurement and calibration.—A coated-Pt wire electrode containing kryptofix-22DD was used as an indicator electrode. All emf measurements were performed at ambient temperature (25 ± 1°C) using a potentiometer model PHM-632 (Metrohm, Swiss) having ±0.01 mv accuracy with respect to an Ag/AgCl reference electrode. The pH of the solutions was measured by a conventional glass pH electrode.

The following cell was used for emf measurements:

Pt electrode| PVC membrane |test solution || Ag, AgCl, KCl (saturated)

The performance of the ion selective electrode was investigated by measuring its potential in Y(III) cation solutions prepared in the concentration range (1×10^{-10})–(1×10^{-1}) M by serial dilution at constant *p*H. The solutions were stirred and potential readings recorded when they reached to a steady state value. The data were plotted as observed potential versus the logarithm of the Y (III) concentration. The characteristic properties of the optimized coated membrane were studied. The calibration curve of Y (III) cation is shown in Fig. 2. Over the wide concentration range from 1.0×10^{-8} to 1.0×10^{-1} M of the cation, the electrode potential response was

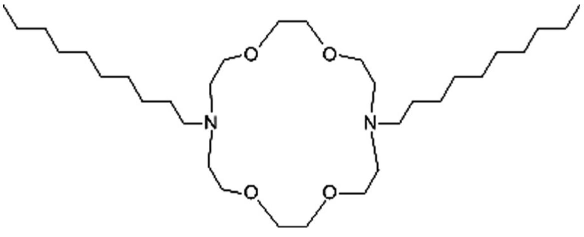

Figure 1. Kryptofix-22 DD structure.

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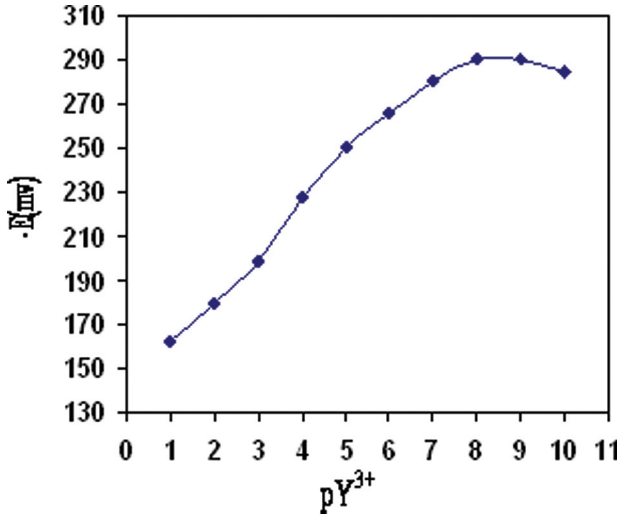

Figure 2. (Color online) Calibration curve for yttrium (III) cation selective electrode.

linear with the logarithm of Y (III) cation concentration. The slope of the calibration curve was found to be 18.89 ± 0.43 mv.decade^{-1}.

The potentiometric titration of Y (III) cation solution was carried out with a fluoride ion solution using the coated-wire electrode as the indicator electrode in conjunction with Ag/AgCl reference electrode. The potentiometric selectivity coefficients ($K_{Y,\ M}$), were determined according to the mixed solution method (MSM).

Electrode preparation.—A mixture of 2 wt % ionophore, 30 wt % PVC and 62 wt % dibutylphethalate and 6 wt % palmitic acid with total weight of 100 mg was dissolved in 0.7 ml of tetrahydrofurane in a glass beaker. A Pt-wire, about 0.5 cm length with 2 mm diameter sealed into the end of a glass and soldered onto a shielded cable, was coated by dipping it in to the membrane solution in THF. A thin layer of membrane was coated on platinum wire surface. The membrane on the wire was allowed to dry in air for overnight. The electrode was finally conditioned for 3 h in a 0.01 M yttrium (III) nitrate solution

Results and Discussion

In preliminary experiments, the complexation of kryptofix-22DD with yttrium (III) cation was investigated. We use a conductometric titration and the changes of molar conductivity (Λ_m) versus the ligand to the cation molar ratio ($[L]_t/[M]_t$) and stability constant for complexation of kryptofix-22DD with yttrium(III) cation in EtOAc was studied. As is shown in Fig. 3, the stoichiometry of the complex formed between yttrium(III) cation and this macrocyclic ligand is 1:1. The experimental procedure is as follows: a solution of metal salt (1×10^{-4} M) was placed in a titration cell, thermostated at 25°C, and the conductance of solution was measured. Then a step-by-step increase of the crown ether solution prepard in the same solvent (2×10^{-3} M) was carried out by a rapid transfer to the titration cell using a microburette and the conductance of the solution in the cell was measured after each transfer at 25°C.

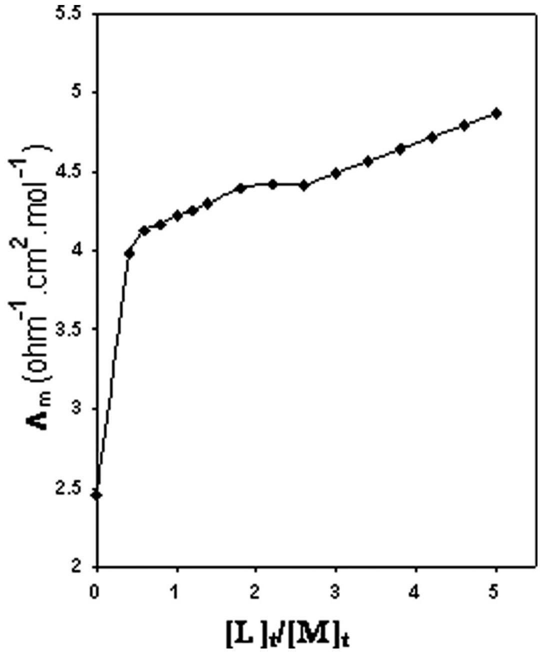

Figure 3. Molar conductance-mole ratio plots for [Y-Kryptofix-22DD]$^{3+}$ complex in EtOAc.

The conductance measurements were performed using a digital AMEL conductivity apparatus, model 60, in a water bath thermostated at a constant temperature which maintained within ± 0.03°C.The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. The cell constant was 0.73 cm^{-1}.

The stability constant of (kryptofix-22DD.Y)$^{3+}$ complex at 25°C was calculated from changes of the molar conductance as a function of ligand/cation molar ratios using a GENPLOT computer program.[23] The details of calculation of the stability constants of complexes by conductometric method have been described in refrence.[24] The

Table I. Optimization of membrane ingredients.

Membrane		Composition (wt %)				
	PVC	Plasticizer	Kryptofix22	Additive	Slope (mV/decade)	Linear range (log C_x)
1	30	62(DOP)	5	3(graphite powder)	10.26 ± 1.42	−7 to −2
2	30	61(DBP)	2	7(graphite powder)	16.97 ± 1.7	−9 to−5
3	30	63(DBP)	2	5(graphite powder)	9.86 ± 1.55	−9 to−6
4	30	61.5(DBP)	5	3.5(OA)	12.20 ± 1.31	−5 to −1
5	30	62(DBP)	2	6(OA)	8.73 ± 1.1	−5 to −2
6	30	62(DBP)	2	6(PA)	18.89 ± 0.43	−8 to −1
7	30	64(DBP)	2	4(PA)	13.95 ± 2	−8 to −1
8	30	61(DBP)	2	7(PA)	13.70 ± 0.97	−8 to −1
9	30	61.5(DBP)	5	3.5(PA)	10.92 ± 2	−8 to −1
10	30	60(DBP)	4	6(PA)	10.67 ± 0.6	−8 to −1
11	30	62(DBP)	2	6(OA)	8.73 ± 1.1	−5 to −2
12	30	62(DBP)	2	6(Triton X-100)	16.67 ± 5	−9 to −6
13	30	62(NB)	2	6(PA)	29.03 ± 4	−4 to −1
14	30	62(DOP)	2	6(PA)	12.05 ± 2	−4 to −1

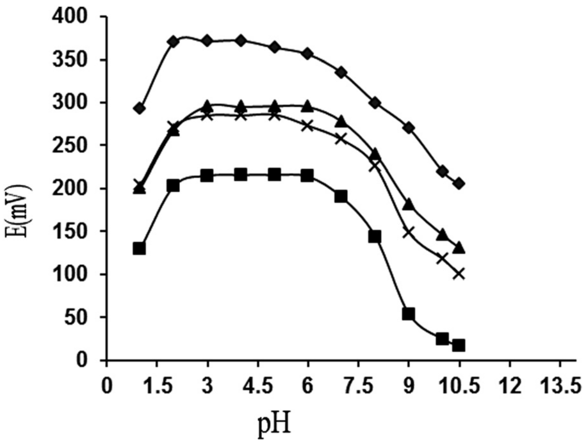

Figure 4. Effect of *p*H of the test solution on the potential response of the yttrium (III) cation selective electrode, at yttrium (III) cation concentration (◆ = 1.0×10^{-3} M) and three same electrode for 1.0×10^{-4} M (■ = electrode 1, ▲ = electrode 2, × = electrode 3).

results show that this ligand forms a stable 1:1 complex with Y^{3+} cation (log $K_f = 5.13 \pm 0.67$) in solution. Due to the existence of two donating nitrogen atoms in the kryptofix 22-DD ring, it is expected that according to the hard and soft acid–base concept, yttrium (III) cation as a soft acid, can form a stable complex with the nitrogen donor atoms as a relatively soft base.

By considering the high enough liophilicity of the ligand and its suitable complexation with yttrium (III) cation, it was tested as a potential ionophore for construction of a new membrane sensor for this metal cation.

Influence of the membrane composition.—It is well known that the sensitivity, linear dynamic range, and selectivity of the ISEs depend not only on the nature of the carrier used, but also significantly on the membrane composition and the properties of the additives employed.[25,26] Thus, the influence of the membrane composition, the nature and amount of the plasticizer, and lipophilic additives on the potential response of the membrane was investigated. The results are given in Table I. Several membranes were prepared with different compositions. The best response was observed with the membrane composed of the following ingredients: 30% PVC, 62% DBP, 2% ionophore and 6% palmitic acid.

The influence of the plasticizer type and its concentration on the characteristics of the yttrium (III) cation selective electrodes was investigated by using three plasticizers with different polarities including DBP, DOP and NB. The plasticizer/PVC weight ratios of ca. 2 produced a maximum sensitivity for all of the plasticizers. The electrodes containing DBP generally showed a better potentiometric response, i.e. better sensitivity and linearity for the calibration plots. It seems that among the plasticizers used in this study, DBP provides more appropriate conditions for incorporation of the yttrium (III) cation into the membrane. Therefore, we used DBP as a suitable plasticizer for further studies.

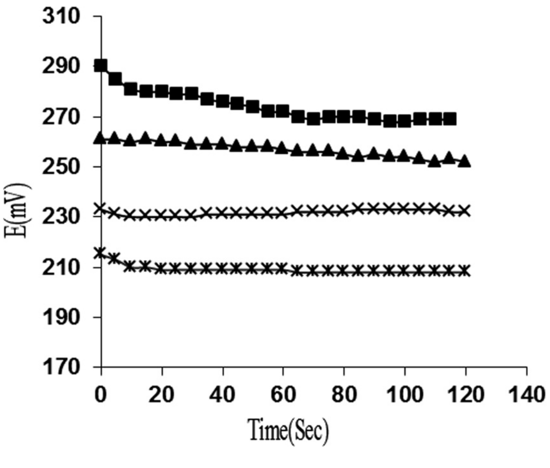

Figure 5. The response time curve of the yttrium (III) cation selective electrode (* = 1.0×10^{-1} M, × = 1.0×10^{-2} M, ▲ = 1.0×10^{-3} M, ■ = 1.0×10^{-4} M).

It was also observed that the potentiometric response of the electrode toward yttrium (III) cation depends on the concentration of the ionophore incorporated within the membrane. The amount of the ionophore about 2 wt % resulted in membranes for which the Nernstian slopes were more appropriate. Further addition of the ionophore concentration worsened the electrode response, most probably due to saturation of the membrane or due to some non-uniformity of the membrane. The potential response of the electrode was also investigated in presence of graphite powder, and lipophilic surfactants including oleic acid, triton X-100 and palmitic acid mediate. The results show that the slopes and the linear range become better in the presence of palmitic acid (a long-chain fatty acid) additive. It is known that the nature and the amount of lipophilic additive strongly influence the response of an ion-selective electrode. The presence of liophilic anion in cation-selective membrane electrodes, diminishes the ohmic resistance,[27] enhances the selectivity[28] and also increase the sensitivity of the electrode.

The palmitic acid has been used for construction of some potentiometric biosensors,[29] but in this work, we used it for the first time as a very suitable additive in PVC matrix of the ion selective membrane electrode. Palmitic acid is probably interposed between the matrix (62% DBP, 30% PVC) and kryptofix-22DD to facilitate more effective binding and it may also prevent that the active site of the ionophere to be located in deep position of the membrane.

Effect of pH.—The *p*H dependence of the potentials of the constructed ion selective electrodes was investigated by measuring their potential over a *p*H range of 1–10.5, where *p*H was adjusted with dilute HNO_3 and NaOH solutions. The effect of *p*H for four CWEs constructed at the same conditions is shown in Fig. 4. As it is obvious from this Figure, the response of the electrodes is independent from *p*H in the *p*H range of about 2.0–6.0 which can be taken as the working *p*H range of the proposed electrode. The significant change in the potential response which is observed above *p*H 6.0 could be due to the formation of some hydroxyl complexes of yttrium (III) cation which reduces the free cation concentration in the solution. The drift in the electrode potentials at *p*H values less than 2 may be due to the hydrolysis of Y^{3+} cation in solution.

Response time.—The response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded over a concentration range 10^{-4}–10^{-1} M of Y^{3+} cation and the changes of potential vs. time are shown in Fig. 5. As is

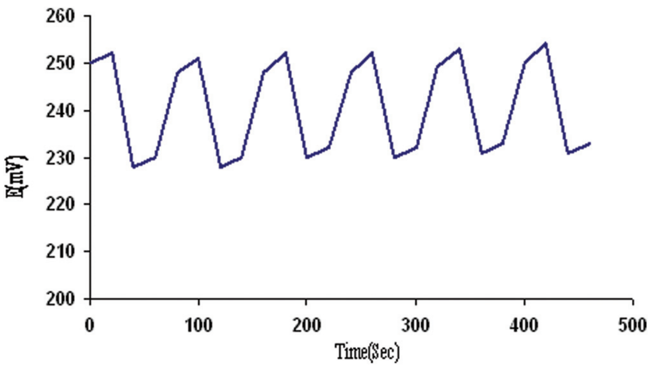

Figure 6. (Color online) Dynamic response characteristics of the yttrium (III) cation selective electrode for several high-to-low (10^{-2} to 10^{-3} M) sample cycles.

Table II. Selectivity coefficients of cationic interferences for yttrium-ISE.

M^{n+}	$K^{Pot}_{Y^{3+}}$
Na^+	2×10^{-2}
Cu^{2+}	1×10^{-2}
Zn^{2+}	1×10^{-2}
Sr^{2+}	3.5×10^{-3}
Ni^{2+}	4.9×10^{-2}
Cr^{3+}	8×10^{-6}
Ca^{2+}	1×10^{-5}
Li^+	4.8×10^{-3}
Pb^{2+}	5.6×10^{-2}
K^+	4×10^{-5}
Mg^{2+}	4×10^{-4}
Cd^{2+}	9×10^{-4}
Al^{3+}	2×10^{-2}

evident in this Figure, at the whole concentration range, the electrode reaches its equilibrium response in a very short time (∼15 s). This is most probably due to the fast exchange kinetics of complexation–decomplexation of Y^{3+} cation with the ion-carrier at the test solution–membrane interface.

In order to evaluate the reversibility of the electrode response, similar measurements were carried out in the sequence of high-to-low sample concentrations (10^{-2}–10^{-3} M) and the results are shown in Fig. 6. As is obvious in this Figure, the potentiometric response of the electrode is reversible.[30]

Potentiometric selectivity.—The selectivity is clearly one of the most important characteristics of a chemical sensor, This characteristic for the coated wire electrode, was measured in terms of potentiometric selectivity coefficient values ($K^{Pot}_{Y,M}$). A mixed solution method (MSM) was used,[31] and the selectivity coefficients, $K^{MSM}_{Y,M}$, were evaluated graphically from potential measurements of solutions containing a fixed concentration of Y^{3+} cation(1.0×10^{-3} M) and varying amounts of interfering ions (M^{n+}) according to the following equation

$$a_M^{3/n} K^{MSM}_{Y,M} = a_Y\{\exp(E_2 - E_1)2F/RT\} - a_Y$$

where a_Y is the activity of the Y^{3+} cation, a_M the activity of the interfering ion, M, with a charge of n, and E_1 is the potential measured when only Y^{3+} is present in solution, E_2 is the potential measured in the presence of both the Y^{3+} cation and the interfering ion, M^{n+}. The $K^{MSM}_{Y,M}$ values for ions can evaluated from the slop of graph of $a_Y^{3+}\{\exp(E_2 - E_1)2F/RT\} - a_Y^{3+}$ versus $a_M^{3/n}$. Selectivity parameter data for various ions are presented in Table III. The selectivity coefficient pattern clearly indicates that the electrode is selective to Y^{3+} cation over a number of other metal cations in solutions.

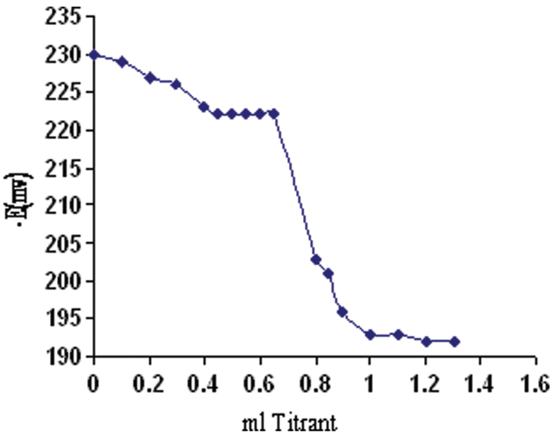

Figure 7. (Color online) Potentiometric titration curve for 25.0 ml of 1.0×10^{-4} M yttrium (III) cation solution with 0.01 M sodium fluoride.

Table III. Results of the determination of the fluoride ion in the different samples.

Sample	Fuoride electrode[a]	Found ISE[b]	Re[c]%
Sodium fluoride mouthwash solution	0.21 ± 0.05 (%)	0.214 ± 0.03 (%)	1.9
Sodium fluoride toothpaste	0.679 ± 0.02 (%)	0.685 ± 0.03 (%)	0.88
Sodium fluoride tap water	1.229 ± 0.03 (mgl^{-1})	1.357 ± 0.04 (mgl^{-1})	10

[a] Solid state fluoride electrode.
[b] Proposed yttrium (III) cation selective electrode.
[c] Relative error.

Analytical applications.—The present CWE was found to work well under laboratory conditions. A typical potentiometric titration curve for titration of yttrium (III) cation (25 ml of 1×10^{-4} M) with a solution of sodium flouride (0.01 M) is shown in Fig. 7. The end point of the titration and the concentration of yttrium (III) cation in solution can be determined potentiometrically by using this ion selective electrode. The present coated wire electrode has been successfully used for the determination of fluoride ion in aqueous solutions including tap water and in the pharmaceutical preparations such as mouthwash and toothpaste.In each case, the *p*H was adjusted to 5.0 (using a TISAB solution) and a successful titration was carried out. We also determined the fluoride ion concentration in a sample solution with a fluoride ion selective electrode as a reference method. The results are compared in Table III. As is evident in this Table there is a good agreement between the results obtained with these two ion selective electrodes.

Conclusion

The main advantages of this constructed yttrium (III) cation electrode are the simplicity of its preparation, short conditioning time, fast response time, wide dynamic range, low detection limit, low cost, Nernstian behavior and fairly good selectivity. Another major advantage of the present ptentiometric sensor, concerns its application. The electrode permits the direct measurement of the yttrium (III) cation in different real samples such as pharmaceutical products and water without prior separation steps.

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