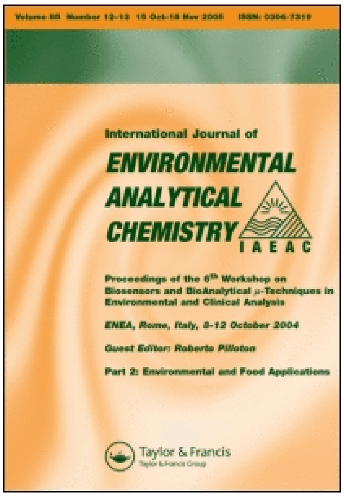

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Determination of cerium(III) ions in soil and sediment samples by Ce(III) PVC-based membrane electrode based on 2,5-dioxo-4-imidazolidinyl

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2,5-Dioxo-4-imidazolidinyl was used as an excellent sensing material in the preparation of a PVC membrane for a Ce(III)-selective sensor. The electrode shows a good selectivity for the Ce(III) ion with respect to most common cations including alkali, alkaline earth, transition, and heavy metal ions. The developed sensor exhibits a wide linear response with a slope of 19.6 ± 0.3 mV per decade over the concentration range of 1.0×10^{-6} to 1.0×10^{-1} M, while the illustrated detection limit is 5.7×10^{-7} M of Ce(III) ions. Moreover, it is concluded that the sensor response is pH-independent in the range of 3.1–9.8. The applications of the recommended electrode include the determination of concentration of Ce(III) ions in soil and sediment samples, validation with CRM's, and the Ce(III) ion potentiometric titration with EDTA as an indicator electrode.

Keywords: cerium; 2,5-dioxo-4-imidazolidinyl; PVC membrane; potentiometry

1. Introduction

Cerium(III) is traditionally referred to as one of the 'rare earths'. However, in reality, it is more plentiful in the earth's crust than many other elements. It is also the most widely distributed among the 'rare earths', averaging 22 mg kg^{-1} in the earth crust [1–3].

From a nutritional and a toxicological point of view, the detection and evaluation of rare earth elements in some biological materials have recently received an increasing attention. Also, owing to the extensive cerium application in metallurgical and functional material areas, the development of rapid and sensitive analysis methods for the determination of cerium is urgently required.

Many analytical techniques such as neutron activation analysis by Suc [4], inductively coupled plasma atomic emission spectrometry, and inductively coupled plasma mass spectrometry (ICP-MS) [5–7], even conventional spectroscopy and fluorimetric methods [8–11], are powerful tools for the quantification of cerium. Furthermore, there are several electrochemical methods [12–17].

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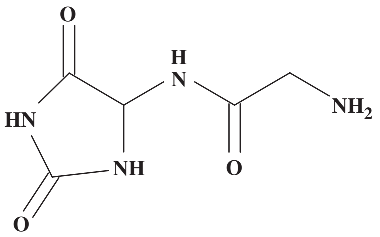

Figure 1. DI structure.

In this research, a greatly selective and sensitive solvent polymeric membrane electrode (PME) for Ce(III) ion is reported, based on the 2,5-dioxo-4-imidazolidinyl (DI) (Figure 1).

2. Experimental

2.1 *Reagents*

Reagent grades of dibutyl phthalate (DBP), *o*-nitrophenyloctyl ether (NPOE), nitrobenzene (NB), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF), and high-relative-molecular-weight PVC were purchased from Merck and Aldrich, and used as received. However, 2,5-dioxo-4-imidazolidinyl, being used as received, was purchased from Fluka. Finally, the cerium chloride and the nitrate and chloride salts of the other cations (all from Merck and Aldrich) were of the highest available purity and were used without any further purification, except for vacuum drying over P_2O_5. Triply distilled deionized water was used during the experimental measurements.

2.2 *Electrode preparation*

Completely blending 32 mg of powdered PVC, 60.5 mg of NPOE, and 2.5 mg of NaTPB in 5 mL of THF was the first step for the PVC membrane construction. The second step involved the addition of 5 mg of DI. After thoroughly mixing the resulting mixture, it was transferred into a 2-cm-diameter glass dish. A Pyrex tube (5 mm i.d.) was dipped into the mixture for about 5 s, so that a non-transparent membrane (about 0.3 mm in thickness) was formed. The tube was then removed from the mixture, kept at room temperature for about 12 h, and filled with an internal filling solution (1.0×10^{-3} M $CeCl_3$). Finally, the electrode was conditioned by soaking in a 1.0×10^{-2} M $CeCl_3$ solution for 24 h [18–22]. As an internal reference electrode, a silver/silver chloride electrode was used.

For a comparative study, a membrane containing no active component was also prepared. The ratio of different membrane ingredients, the equilibrating solution concentration, and the contact time consisted of the optimised parameters to provide membranes, which result in reproducible, noiseless and stable potentials.

2.3 *Emf measurements*

The equipment for the emf (electromotive force) measurements consisted of (1) an Ag–AgCl/internal solution (1.0×10^{-3} M $CeCl_3$)/PVC membrane/test solution/

$Hg–Hg_2Cl_2$, KCl (satd.) (Orion reference cell electrode) and (2) a Corning ion analyser with a 250 pH/mV meter (Metrohm Swiss Made).

The potential measurements were performed at 25.0°C.

3. Results and discussion

3.1 *DI complexation with some common metal ions in acetonitrile*

In primary experiments, the DI interaction (with four nitrogen and three oxygen donor atoms) with a number of metal ions was investigated in acetonitrile solution by the conductometric method. The associated results showed that, in all cases, the ligand-to-cation molar ratio was 1. The formation constants (K_f) of the resulting 1 : 1 complexes were evaluated by fitting the molar conductance–mole ratio data by computer to appropriate equations [21, 23–26]. The results showed that the following sequences for the stability of the resulting 1 : 1 complexes: $Ce^{3+} \gg La^{3+} > Sm^{3+} > Nd^{3+} \sim Dy^{3+} > Cr^{3+} > Na^{+} \sim K^{+} \sim Ca^{2+} \sim Mg^{2+} \sim Co^{2+} \sim Zn^{2+} \sim Ni^{2+} \sim Cd^{2+}$. It can be seen that the DI could be used as an excellent ion carrier in the preparation of a Ce(III)-selective membrane sensor.

3.2 *Sensor potential response based on the DI*

In the next experiments, the DI was used as a neutral ion carrier to prepare a number of membrane sensors for common metal ions. Their potential responses were measured, and the corresponding resulting data are listed in Figure 2(a) and (b). As can be seen, the DI-based membrane displays a Nernstian response to the concentration of Ce(III) ions in a wide concentration range.

3.3 *Membrane composition effect*

Several important features of the PVC membranes, such as the properties of the plasticizer, the plasticizer/PVC ratio, the nature and amount of ionophore, and especially the nature and amount of the additives used are reported to influence the sensitivity and selectivity of the ion-selective electrodes significantly [27–32]. Thus, different aspects of the preparation of a Ce^{3+}-selective membrane based on DI were optimised, and the results are given in Table 1. Since the nature of the plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules, and the state of ligand [27–32], it was expected to play a key role in determining the selectivity, working concentration range, and response time of the membrane electrode. Among the three different solvent mediators tested, we found that in the construction of the cerium membrane sensor, NPOE is superior with respect to DBP and NB. The data in Table 1 revealed that the membrane prepared with a plasticizer/PVC ratio about 2.0 was suitable and showed the best performance. As can be seen from Table 1, the optimum amount of ionophore (DI) was 5% (No. 11).

In general, the presence of lipophilic anions in cation-selective membranes based on neutral carrier not only diminishes the ohmic resistance and enhances the response behaviour and selectivity but also, in cases where the extraction capability is poor, increases the sensitivity of the membrane electrodes [28, 33–36]. However, the membranes with the composition of 32% PVC, 5% DI, 2.5% NaTPB and 60.5% NPOE exhibit a Nernstian potential response.

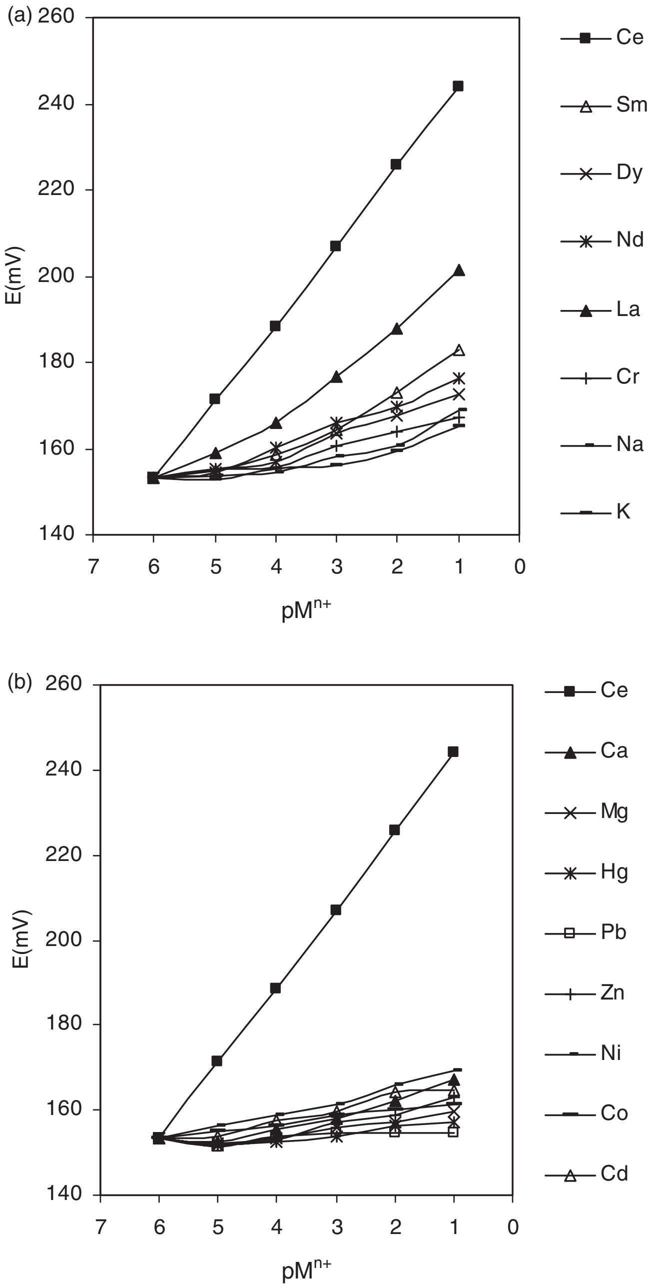

Figure 2. Potential responses of various ion-selective electrodes based on DI.

3.4 *Dynamic response time*

Dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time of the proposed sensor was recorded by changing the Ce(III) concentration in a series of solutions (1.0×10^{-1} to 1.0×10^{-6} M). The resulting data show

Table 1. Optimization of membrane ingredients (wt. %).

Membrane	PVC	Plasticizer	DI	NaTPB	Slope (mV/decade)	Dynamic linear range (mol L^{-1})
1	32	NPOE, 68	0	0	2.4 ± 0.3	3.8×10^{-2} to 1.5×10^{-3}
2	32	NPOE, 67	0	1	5.3 ± 0.4	3.0×10^{-2} to 1.3×10^{-3}
3	32	NPOE, 66.5	0	1.5	6.8 ± 0.3	6.5×10^{-1} to 1.0×10^{-3}
4	32	NPOE, 66	0	2	7.6 ± 0.5	5.0×10^{-1} to 1.0×10^{-3}
5	32	NPOE, 65.5	0	2.5	8.0 ± 0.4	5.0×10^{-1} to 1.0×10^{-3}
6	32	NPOE, 65	0	3	7.7 ± 0.5	5.0×10^{-1} to 1.0×10^{-3}
7	32	NPOE, 64.5	1	2.5	12.4 ± 0.7	1.0×10^{-1} to 1.0×10^{-4}
8	32	NPOE, 63.5	2	2.5	15.2 ± 0.6	1.0×10^{-1} to 2.4×10^{-5}
9	32	NPOE, 62.5	3	2.5	16.8 ± 0.4	1.0×10^{-1} to 1.0×10^{-6}
10	32	NPOE, 61.5	4	2.5	18.6 ± 0.3	1.0×10^{-1} to 1.0×10^{-6}
11	32	NPOE, 60.5	5	2.5	19.6 ± 0.3	1.0×10^{-1} to 1.0×10^{-6}
12	32	NPOE, 59.5	6	2.5	18.5 ± 0.2	1.0×10^{-1} to 1.0×10^{-6}
13	32	NB, 60.5	5	2.5	17.1 ± 0.3	1.0×10^{-1} to 1.0×10^{-6}
13	32	DBP, 60.5	5	2.5	16.6 ± 0.5	1.0×10^{-1} to 1.0×10^{-6}

that the plasticized membrane sensor reaches its equilibrium responses in a fast time (<10 s) in the whole concentration range.

3.5 *Calibration curves and statistical data*

The potential response of the suggested DI-based sensor (composition no. 11) at varying cerium ion concentrations demonstrated a linear response to the cerium ion concentration in the range 1.0×10^{-6} to 1.0×10^{-1} M. The calibration graph slope was 19.6 ± 0.3 mV per decade for the cerium ion concentration. The detection limit of the sensor, as determined from the intersection of the two extrapolated segments of the calibration graph, was 5.7×10^{-7} M, while the standard deviation of eight replicate measurements was ±0.6 mV. The suggested PVC-based membrane sensor could be used for at least 10 weeks (1 h per day and then washed and dried). After this time, the electrode slope decreased (from 19.6 to 17.8 mV per decade).

3.6 *pH effect*

The potential electrode response was considered in the pH range of 2.0–12.0 (the pH was adjusted with the use of concentrated NaOH or HCl), and the results are shown in Figure 3. Clearly, the potential response of the sensor remains constant in the pH range of 3.1–9.8. At pH values lower than 3.1, a potential increase was observed. This increase was caused by the membrane response to hydronium ion (protonation of nitrogen atoms in acidic media). At pH values higher than 9.8, a potential decrease, due to the insoluble cerium hydroxide formation, was observed.

3.7 *Sensor selectivity*

The influence of the interfering ions on the response behaviour of any ion-selective sensor is usually described in terms of selectivity coefficients, K_{sel}. In this work, selectivity coefficients were determined by the matched potential method (MPM) [37–42].

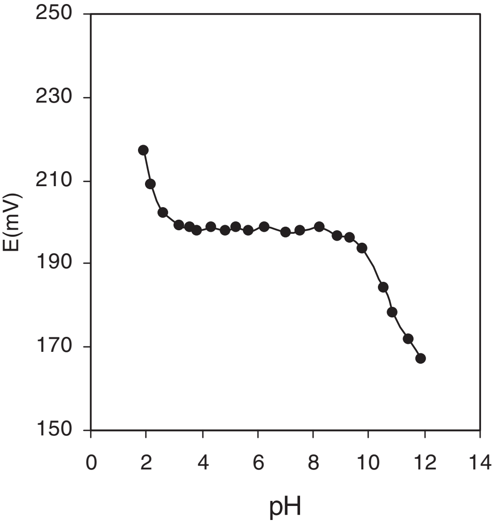

Figure 3. pH effect of the test solution on the potential response of the cerium sensor.

Table 2. Selectivity coefficients of various interfering ions (*B*) calculated by the match potential method.

Interfering ion (*B*)	Selectivity coefficients
Sm^{3+}	1.0×10^{-3}
Cr^{3+}	6.2×10^{-4}
Nd^{3+}	9.4×10^{-4}
Dy^{3+}	8.4×10^{-4}
La^{3+}	8.6×10^{-3}
Al^{3+}	5.3×10^{-4}
Na^{+}	4.7×10^{-4}
K^{+}	4.2×10^{-4}
Mg^{2+}	5.6×10^{-4}
Ca^{2+}	7.7×10^{-4}
Zn^{2+}	6.2×10^{-4}
Ni^{2+}	8.0×10^{-4}
Co^{2+}	6.5×10^{-4}
Cd^{2+}	7.6×10^{-4}
Hg^{2+}	3.2×10^{-4}
Pb^{2+}	2.6×10^{-4}

According to this method, a specified activity (concentration) of primary ions (A, 1.0×10^{-3} M of cerium ions) is added to a reference solution (1.0×10^{-6} M of cerium ions), and the potential is measured. In a separate experiment, interfering ions (B, 1.0×10^{-1} M) are added to an identical reference solution, until the measured potential matches that obtained before the addition of primary ions. The matched potential method selectivity coefficient, K_{MPM}, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K_{MPM} = a_A/a_B$.

The experimental conditions and the resulting values are summarised in Table 2. For all diverse ions, the selectivity coefficients of the electrode are in the order of 8.6×10^{-3}

Table 3. Comparison of the selectivity coefficients, linearity range, detection limit, pH range, and response time of the proposed Ce(III) sensor and the previously reported Ce(III) PVC-membrane sensors.

		References			
	Properties	This work	[12]	[13]	[17]
	Detection limit (M)	5.7×10^{-7}	7.6×10^{-6}	3.0×10^{-5}	1.8×10^{-6}
	pH range	3.1–9.8	3.5–10.0	5.0–8.0	4.1–7.3
	Slope (mV per decade)	19.6 ± 0.3	19.4 ± 0.3	19.4 ± 0.4	19.6 ± 1.0
	Linear range (M)	1.0×10^{-6} to 1.0×10^{-1}	1.0×10^{-5} to 1.0×10^{-1}	5.0×10^{-5} to 1.0×10^{-1}	2.0×10^{-6} to 2.0×10^{-2}
	Response time (s)	<10	<15	<15	~13
	Sm^{3+}	−3.00	−2.89	–	–
log K_{MPM}	Cr^{3+}	−3.21	–	–	–
	Nd^{3+}	−3.03	−3.10	–	–
	Dy^{3+}	−3.08	−3.11	–	–
	La^{3+}	−2.07	−3.00	−1.30	−2.52
	Na^{+}	−3.33	−2.58	−2.62	−6.0
	K^{+}	−3.38	−2.30	−2.20	–
	Mg^{2+}	−3.25	−2.55	−2.51	−6.0
	Ca^{2+}	−3.11	−3.24	−1.66	−6.0
	Zn^{2+}	−3.21	−3.00	−1.20	−6.0
	Ni^{2+}	−3.10	−2.34	−1.88	–
	Co^{2+}	−3.19	−2.51	−1.49	−4.55
	Cd^{2+}	−3.12	−2.74	−1.15	−3.68
	Hg^{2+}	−3.49	–	−4.00	−2.77
	Pb^{2+}	−3.59	−2.32	−1.96	−2.59

or less, indicating that they would not significantly disturb the function of the Ce(III) selective membrane sensor. It is also worth noticing that the response of the Ce(III) sensor was found to be insensitive to the nature of the tested anions.

Table 3 compares the selectivity coefficients of the Ce(III) sensor with those of the best previous Ce(III) electrodes reported in the literature by other researchers [12, 13, 17]. Clearly, the selectivity coefficient of the electrode for all tried cations is superior in respect of the coefficients of the best previously reported cerium sensors.

3.8 *Analytical application*

3.8.1 *Ce(III) determination in soils and sediments*

First, a sample (1 g) was weighed into a PTFE beaker. Then, 5 mL of 70% $HClO_4$ and 10 mL of 48% HF were added, and this sample was heated in a sand bath to incipient dryness. Acid attack with $HClO_4$ and HF $(1+2)$ followed and was repeated three times to complete the digestion of the silicate matrix. Then, the samples were transferred into flasks and diluted with 5 mL of 5% NaOH and distilled water to 50 mL (pH ~5) [43].

In addition, the potential measurements of these solutions were performed using the recommended Ce(III) sensor and its calibration curve (1.0×10^{-6} to 1.0×10^{-1} M), being obtained after measuring a series of cerium ion standard solutions. Then, the cerium ion concentration in the samples was determined, by conducting triplicate measurements with

Table 4. Determination of cerium in soil samples by the proposed Ce(III)-selective membrane sensor and Arsenazo method (results are based on triplicate measurements).

Samples	Designed electrode (ppm)	Arsenazo method[44] (ppm)
1	37.1 ± 0.3	34.5 ± 0.2
2	33.5 ± 0.4	31.0 ± 0.3
3	67.6 ± 0.5	65.4 ± 0.3
4	48.2 ± 0.4	47.3 ± 0.2
5	72.9 ± 0.3	71.0 ± 0.2

Table 5. Results from the analysis of calcareous soil (ERM®-CC690) as a certified reference material.

Element	Certified values ($\mathrm{mg\,kg^{-1}}$)
Ce	49.1 ± 2.5
Dy	2.90 ± 0.28
Gd	3.2 ± 0.4
La	24.4 ± 1.7
Nd	19.1 ± 2.2
Sc	7.9 ± 0.9
Sm	3.5 ± 0.4
Tb	0.50 ± 0.07
Tm	0.232 ± 0.026
Yb	1.57 ± 0.19
Th	7.6 ± 0.8
U	1.90 ± 0.23

the same sensor. As is clear from Table 4, the results of this sensor were in agreement with that determined by the Arsenazo method [44].

3.8.2 *CRM validation*

Concerning the practical applicability of the newly designed sensor, it was utilised in the Ce(III) determination of the Calcareous soil (ERM®-CC690), as certified reference material (CRM). The CRM resulting data are depicted in Table 5. From this table, it is obvious that the Ce(III) concentration in the CRM was $49.1 \pm 2.5\,\mathrm{mg\,kg^{-1}}$. However, when the calibration method was employed, this concentration value relatively changed, being equal to $50.4 \pm 0.3\,\mathrm{mg\,kg^{-1}}$. After a comparison of the above data, it was concluded that the Ce(III) sensor could be used as an alternative for the Ce(III) ion determination in the presence of other rare earth elements.

3.8.3 *Titration with EDTA*

The recommended Ce(III) sensor was found to work well under laboratory conditions. It was successfully used as an indicator electrode in the titration of a 1.0×10^{-4} M of Ce(III) with a standard EDTA solution (1.0×10^{-2} M). The resulting titration curve is shown in Figure 4, where it can be noticed that the amount of Ce(III) ions in solution can be determined with the sensor.

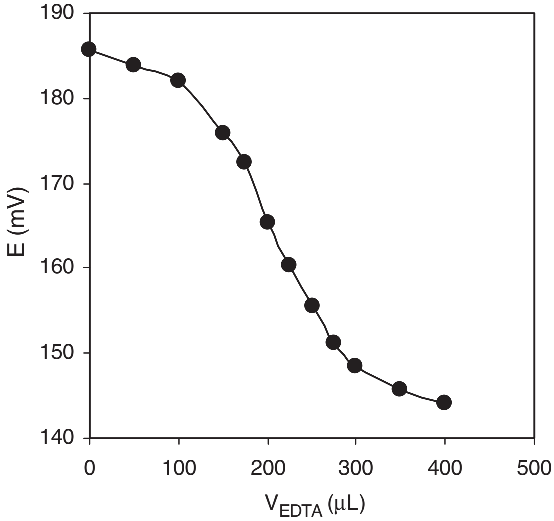

Figure 4. Potentiometric titration curve of 20.0 mL of 1.0×10^{-4} M solution of Ce^{3+} with 1.0×10^{-2} M of EDTA.

4. Conclusion

This work has demonstrated that ISEs based on 2,5-dioxo-4-imidazolidinyl with NPOE as the plasticizer exhibits cerium selectivity, with low interference from common alkali, alkaline earth, transition, and heavy metal ions. The proposed sensor shows the best response characteristics with Nernstian behaviour over the concentration range 1.0×10^{-6} to 1.0×10^{-1} M Ce^{3+} and a fast response time of <10 s. The sensor works well in a pH range of 3.1–9.8 and can be used successfully for the concentration of Ce(III) ions in soil and sediment samples and validation with CRMs. Thus, the membrane sensor is superior to existing sensors in terms of response time and detection limit. For actual analysis, the developed sensor exhibits a comparable performance in comparison with the best formerly reported cerium sensors, regarding other parameters such as slope, pH range, concentration range, and selectivity.

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