

Cerium(III) Ion-Selective Electrodes Based on 1,4,7-Trithiacyclononane

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Novel plasticized polymeric membrane (PPME) and coated platinum wire (CPWE) electrodes based on 1,4,7-trithiacyclononane and oleic acid, as a good lipophilic additive for highly selective determination of Ce^{3+} ions, have been developed. The electrodes exhibit a Nernstian slope of 19.4 mV/decade (for both electrodes) over a wide Ce^{3+} ion concentration range, from 5.0×10^{-6} - 5.0×10^{-2} M and 1.0×10^{-7} - 1.0×10^{-2} M for PPME and CPWE, respectively. The limits of detection were 3.5×10^{-6} and 8.0×10^{-8} M for PPME and CPWE, respectively. The electrodes possess a fast response time of 15 s, can be used for at least 3 months without observing any deviation, and can be used in a pH range of 5.0-8.0. The proposed electrodes could reveal excellent selectivity for Ce^{3+} over a wide variety of alkali, alkaline earth, some transitions, and heavy metal ions. The practical utility of the electrodes has been demonstrated by their use as indicator electrodes in the potentiometric titration of Ce^{3+} ions with EDTA and vice versa, and in the determination of fluoride ions in some mouthwash preparations.

Key Words: Cerium(III)-selective electrode, coated platinum wire electrode, plasticized polymeric membrane electrode.

Introduction

Among the various analytical techniques available, the use of ion-selective membrane electrodes is a well-established routine analytical technique. Good 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.¹⁻³

Crown ethers have been widely used as suitable neutral carriers for the construction of membrane-selective electrodes for alkali and alkaline earth cations.⁴⁻⁷ Meanwhile, the substitution of some oxygen atoms

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of crown ethers by nitrogen and or sulfur atoms results in complexation properties that are intermediate between those of ordinary crown ethers (with a strong tendency for alkali and alkaline earth cations) and those of all-nitrogen and all-sulfur macrocyclic ligands (with a strong tendency for transition and heavy metal ions).^{8,9} In this respect, macrocyclic polythiaethers have received considerable attention, due to their unique properties as carriers for some transition and heavy metal ions.^{10–14} In recent years, Shamsipur and co-workers used some thia-substituted crown ethers as neutral carriers in the construction of ISEs for heavy and transition metal ions.^{15–21}

Cerium is industrially important and is used in nuclear reactors, in alloys with nickel and chromium, in microwave devices, lasers, masers, and television sets. Cerium is also used in agriculture, forestry, and animal husbandry, and much attention is now being paid to the study of cerium in the environment. Inhalation exposure of cerium in humans has been known to cause sensitivity to heat, itching, and an increased awareness of odor and taste. The increasing industrial use of cerium and reports of cerium toxicity make it essential to have analytical procedures suitable for monitoring cerium in the environment.²²

In this work, we report highly selective and sensitive coated platinum wire (CPWE) and plasticized polymeric membrane electrodes (PPME) for Ce(III) ions based on 1,4,7-trithiacyclononane (trithia-9-crown-3, TT9C3) as an excellent neutral ionophore. The structure of the ionophore is shown in Figure 1.

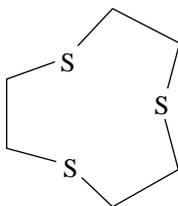


Figure 1. Structure of 1,4,7-trithiacyclononane (TT9C3).

Experimental

Materials and apparatus

Analytical reagent grade dibutyl phthalate (DBP), benzyl acetate (BA), *o*-nitrophenyl octyl ether (*o*-NPOE), oleic acid (OA), tetrahydrofuran (THF), and high relative molecular weight PVC (all from Merck) were used as received. 1,4,7-Trithiacyclononane (from Fluka) was used with the highest purity. All solutions of metal ions included cerous chloride heptahydrate and were prepared from analytical reagents with doubly distilled water.

All potentiometric and pH measurements were carried out at 25 °C using a Metrohm Model 624 pH/ion meter. A double-junction saturated Calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solution was used in the junction with the proposed electrodes.

Electrode preparation and measurement of electrode potentials

The membranes were prepared by dissolving optimized amounts of PVC, plasticizer, OA, and ionophore in the ratio of 30:49:15:6, respectively, in 5 mL of THF. The mixture was shaken vigorously and the clear solution was poured into a glass dish 5 cm in diameter. The solvent was allowed to evaporate at room temperature, until an oily concentrated mixture was obtained. For preparation of the PPME, a Pyrex tube

(5 mm o.d.) was dipped into the mixture for 5 s so that a nontransparent membrane of ~ 0.3 -mm thickness was formed. The tube was then filled with internal filling solution (1.0×10^{-3} M CeCl_3). The electrode was finally conditioned for 12 h by soaking in 1.0×10^{-2} M CeCl_3 . A silver/silver chloride electrode was used as an internal reference electrode.

To prepare the CPWE, platinum wire about 3 cm long and 1 mm in diameter with a spherical head sealed into the end of a glass tube and soldered onto a shielded cable was used. This wire was dipped into the membrane solution 4 times and the solvent was evaporated each time at room temperature. After 3 h, a membrane was formed on the platinum surface. Then, the electrodes were rinsed with water and finally conditioned for 36 h by soaking in a 1.0×10^{-2} M solution of CeCl_3 .

The potential measurements with PPME and CPWE were carried out with the following cell assemblies: the

$\text{Ag-AgCl/KCl (3 M)/internal solution } 1.0 \times 10^{-3} \text{ M CeCl}_3/\text{PVC membrane/test solution // Hg-Hg}_2\text{Cl}_2, \text{KCl (satd) (PPME)}$

$\text{Hg-Hg}_2\text{Cl}_2, \text{KCl (satd) // test solution/PVC membrane/Pt (CPWE)}$

Activities were calculated according to the Debye-Hückel procedure.²³

Fluoride ion determination in pharmaceutical samples

Some 0.2 mL of sodium fluoride mouthwash solution (2.0%) was diluted to 50.0 mL and the pH was adjusted to 7.0 (using a concentrated NaOH solution). The resulting solution was titrated with a 0.10 M solution of cerium(III) solution using the proposed CPWE as an indicator electrode.

Two sodium fluoride tablets (1.0 mg/tablet) were placed in a 100-mL beaker, 25 mL of water was added, and the solution was mixed thoroughly. The undissolved components were separated on filter paper and the clear filtrate was titrated with a 0.10 M solution of cerium(III) using the proposed CPWE as an indicator electrode.

Results and Discussion

Crown ethers and specific thiocrown ethers, due to sufficient insolubility in water, were expected to act as suitable ion carriers in the ISEs with PVC membrane.²⁴ Trithia-9-crown-3, among thiocrown ethers, has a low molecular weight and flexible structure. Moreover, the presence of 3 donating sulfur atoms in the structure causes this compound to show selectivity to transition and heavy metal ions of proper size and charge.¹⁰⁻¹⁴; therefore, in preliminary experiments it was used as a neutral carrier to prepare PPMEs for a variety of transition and heavy metal ions. The potential responses of some of the most sensitive electrodes for solutions containing each cation separately are shown in Figure 2, which shows that this sensor had the most sensitive response to Ce^{3+} among the different cations tested. Thus, TT9C3 can be selected as a suitable ionophore for the preparation of ISEs for determining cerium(III) ions in the presence of other metal ions. This behavior of the membrane electrode can be due to selectivity of the ionophore against Ce^{3+} in comparison to other cations and the rapid exchange kinetics of the complex of TT9C3- Ce^{3+} .²⁵

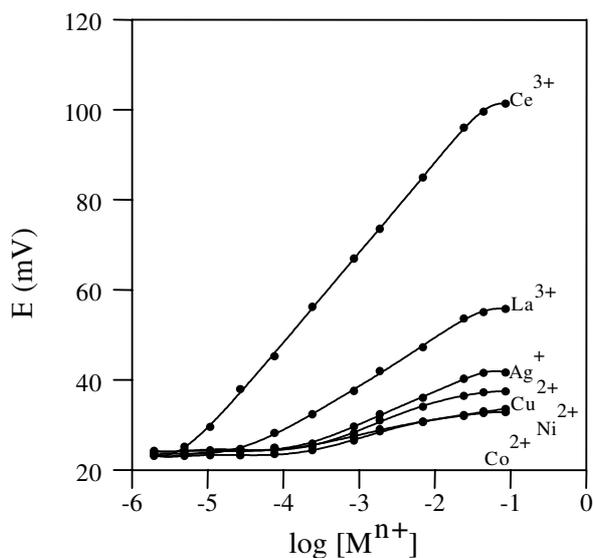


Figure 2. Potential response of various PPMEs based on TT9C3. Conditions: membrane ingredients: 30% PVC, 49% BA, 6% TT9C3, and 15% OA. Each electrode was conditioned in 1.0×10^{-2} M concentration of the corresponding cation for 12 h. A 1.0×10^{-3} M concentration of each cation was used as the inner solution for the corresponding electrode.

A CPWE with the same membrane composition as the PPME was used for investigation of the behavior of the sensor to the tested metal ions (Figure 3). The similar results obtained showed that the sensor had better selectivity for Ce^{3+} ions. Thus, based on the preliminary results of the experiments, TT9C3 can be used as a suitable ionophore for Ce^{3+} -selective electrodes as PPME and/or CPWE.

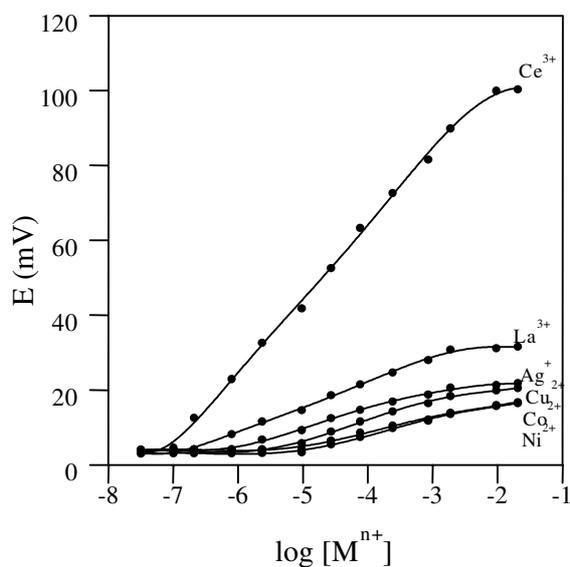


Figure 3. Potential response of various CPWEs based on TT9C3. Conditions: membrane ingredients: 30% PVC, 49% BA, 6% TT9C3, and 15% OA. Each electrode was conditioned in 1.0×10^{-2} M concentration of the corresponding cation for 36 h.

It is well known that the sensitivity, dynamic range, and detection limit of a membrane electrode significantly depends on the membrane ingredients and the nature of the plasticizer and additives used.^{15–21,26–30} Thus, the influences of membrane composition, nature and amount of solvent mediator, and amount of additives, such as OA or sodium tetraphenylborate, on the potential response of the proposed sensor were investigated and the obtained results are given in Table 1.

Table 1. Optimization of membrane ingredients.

No.	Composition (wt%)				Slope (mV/decade)
	PVC	Plasticizer	TT9C3	OA	
1	35	DBP-62	3	-	8.8
2	34	o-NPOE-63	3	-	7.2
3	35	BA-62	3	-	10.3
4	30	DBP-57	3	10	13.8
5	30	o-NPOE-58	3	9	11.1
6	30	BA-57	3	10	15.6
7	30	BA-50	4	16	17.1
8	30	BA-49	6	15	19.4
9	30	BA-44	6	20	18.9
10	31	BA-45	8	16	17.7
11	31	BA-53	-	16	-

Based on investigations of the polymeric films, the plasticizer/PVC ratio (w/w) of ~ 1.6 shows the optimum physical properties and ensured high enough mobilities of their constituents.^{19,31,32} As such, this ratio was used as an optimum value in the construction of the membrane electrode.

It should be noted that the nature of the solvent mediator influences the dielectric constant of the membrane phase, the mobility of ionophore molecules, and the state of ligands, and is therefore expected to play an important role in determining the ISE characteristics.^{31–33} In order to investigate the effect of the plasticizer on the characteristics of the proposed sensor, 3 sets of membranes of similar composition (nos. 1, 2, and 3, and nos. 4, 5, and 6) (Table 1), but with different plasticizers (DBP, o-NPOE, and BA) were prepared and tested. As seen from Table 1, among the 3 different plasticizers used, the use of BA in the series gave a response slope larger than that of the others. Thus, BA was used as a suitable solvent mediator for the construction of a Ce^{3+} -selective electrode.

Since the presence of lipophilic anionic sites in cation-selective membrane electrodes not only reduces ohmic resistance and improves response behavior and selectivity, it also, in cases where the extraction capability of the ionophore is poor, enhances the sensitivity of the membrane electrode. Moreover, lipophilic additives may catalyze the exchange kinetics at the sample-membrane interface.^{19,31,34–36} The data sets (Table 1) for nos. 1, 2, and 3 show that, in the absence of a lipophilic additive, the sensitivity of the proposed sensor is quite low. Accordingly, in order to improve the sensitivity of the electrode, the influence of OA as a lipophilic additive was studied.^{17,19,37,38} Comparison of the data for nos. 3, 6, and 7 (Table 1) revealed that, with the addition of OA and increasing it to 16% of the membrane composition, the sensitivity of the PVC membrane electrode increased and the slope of calibration curve increased from 10.3 to 17.1 mV/decade. OA with a fraction of 16 wt% contributed significantly to the dielectric constant of the membrane, in addition to the plasticizer.

The amount of ionophore TT9C3 was also found to affect the sensitivity of membrane electrodes (nos. 7 and 8). The sensitivity of the electrode response increased with increasing ionophore content until

the value of 6 wt% was reached (no. 8). It is interesting to note that, in membrane 8, the molar ratio of the ligand to OA was $\sim 1:2$, which implies that OA is not only primarily a phase transfer catalyst, but also contributes to the complexation mechanism.³⁹ Moreover, the membrane composition of nos. 9 and 10 (Table 1) revealed an increasing wt% of OA > 15% and ionophore > 6% , and decreased sensitivity of the electrodes. As a result, among the different compositions studied, the membrane incorporating 30% PVC, 49% BA, 6% TT9C3, and 15% OA exhibited the best response characteristics with a nice Nernstian slope of 19.4 mV/decade. Hence, this composition was used to study various operation parameters of the electrode.

In order to investigate the role of TT9C3 as an ionophore, the membrane composition no. 11 was prepared and the EMF of the electrode was measured in a wide dynamic range of Ce^{3+} . The obtained slope (0 mV/decade) revealed that in the absence of TT9C3, the electrode did not show sensitivity for cerium(III) ions.

The influence of the concentration of internal solution in the PPME on its potential response was studied. Three concentrations (1.0×10^{-4} , 1.0×10^{-3} , and 1.0×10^{-2} M of Ce^{3+}) were used and the calibration curves (EMF vs. pCe^{3+}) for each concentration were obtained. It was found that the change in cerium(III) concentration of the internal solution did not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting Nernstian plots. For smooth functioning of the system, a concentration of 1.0×10^{-3} M Ce^{3+} was used as the internal solution.

The optimum equilibration times in 1.0×10^{-2} M of Ce^{3+} for the PPME and CPWE were 12 and 36 h, respectively, after which time they generated stable potentials when placed in contact with Ce^{3+} solutions. The dynamic range and detection limit of both cerium(III) ion-selective electrodes were assessed according to IUPAC recommendations.⁴⁰ The potential responses of the PPME and CPWE at various concentrations of cerium(III) ions showed a linear range of 5.0×10^{-6} - 5.0×10^{-2} M for PPME (slope: 19.37 ± 0.40 mV/decade; regression coefficient: 0.9991) and from 1.0×10^{-7} to 1.0×10^{-2} M for CPWE (slope: 19.41 ± 0.48 mV/decade; regression coefficient: 0.9981). The limit of detection, as determined from the intersection of the 2 extrapolated segments of the calibration graphs, was 3.5×10^{-6} M for PPME and 8.0×10^{-8} M for CPWE. The wider range and lower detection limit for CPWE in comparison to PPME may have been due to higher electrical conductivity of the platinum wire in CPWE versus an internal 1.0×10^{-3} M CeCl_3 solution in the case of PPME.

The time required for the electrodes to reach a potential response within ± 1 mV of the final equilibrium value following successive immersions in a series of Ce^{3+} solutions, each having 10-fold difference in concentration, was studied. The static response time of the electrodes was ~ 15 s over the entire concentration range. Such a fast response time was most probably due to the fast exchange kinetics of complexation-decomplexation of Ce^{3+} with TT9C3 at the test solution-membrane interface. The lifetime of PPME and CPWE obtained was 3 and 4 months, respectively, without any measurable change in slope, detection limit, or linear range of both electrodes. It should be noted that the reuse of the dried electrode required further conditioning.

The influence of pH of the test solution (1.0×10^{-4} M CeCl_3) on the EMF measurements of both electrodes was studied over the pH range of 2.0-10.0 (Figure 4). The pH was adjusted by introducing small drops of 0.1 M solutions of hydrochloric acid or sodium hydroxide. As seen from Figure 4, the potential remained constant from pH 5.0 to 8.0, beyond which drift in potential was observed. The observed drift at low pH could have been due to the membrane sensor response to hydrogen ions. At pH > 8.0, the formation

of some hydroxy complexes of Ce^{3+} in solution caused drift in potential.

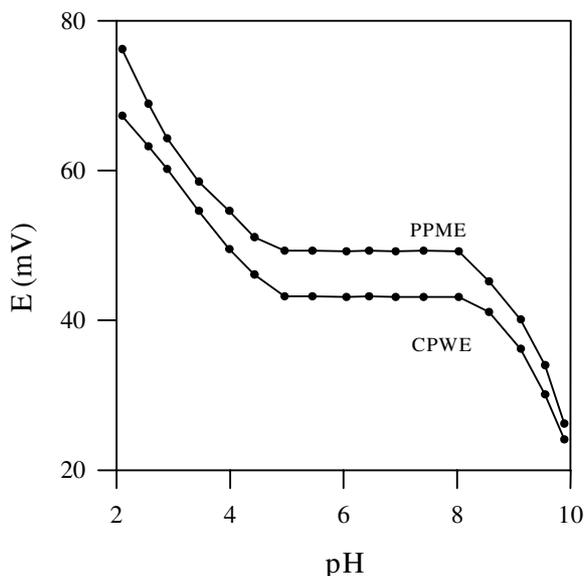


Figure 4. Effect of the pH of the test solution on the potential response of the PPME and CPWE at a cerium(III) concentration of 1.0×10^{-4} M.

The influence of interfering ions on the response behavior of ISEs is usually described in terms of selectivity coefficients, $K_{A,B}^{Pot}$. The matched potential method (MPM) was used for determination of selectivity coefficients.^{41,42} 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 MPM selectivity coefficients, $K_{A,B}^{MPM}$, are then given by the resulting ratio of primary ions to interfering ion activity (concentration), $K_{A,B}^{MPM} = a_A/a_B$. The experimental conditions employed and the resulting values for CPWE and PPME for cerium(III)-selective electrodes are summarized in Table 2. The obtained values for both electrodes showed that, for all diverse ions used, the selectivity coefficients were in the order 10^{-2} or less, indicating they would not significantly disturb the functioning of the Ce^{3+} ISE. It is expected that metal ions, such as Ag^+ and Hg^{2+} , based on soft-soft interaction, show a considerable tendency toward the ionophores bearing sulfur atoms (as donor atoms) in their structure, but a small interfering effect of these ions on the functioning of the proposed Ce^{3+} ISE, most probably due to larger ionic size and lower charge density of interfering ions as compared to Ce^{3+} ions. Additionally, although the trend of the selectivity coefficients observed by both electrodes were more or less the same, these values for CPWE were slightly smaller than the corresponding values for PPME. This is actually one of the great advantages of the coated electrodes.^{43–45}

In order to investigate the proposed Ce^{3+} ISEs, they were used in the determination of fluoride ions in real samples and in end-point detection of a titration Ce(III) ion solution with EDTA and vice versa. The PPME was used as an indicator electrode in the titration of cerium(III) ions with EDTA and vice versa at a buffered solution in pH 7.0. The resulting curves are shown in Figure 5. As seen, the amount of Ce^{3+} in solution can be accurately determined with the electrode and the forward and reverse potentiometric

titration showed a common point for the end of titration. Additionally, the amount of fluoride ions in 2 different pharmaceutical samples was determined with a coated platinum wire electrode by titration of prepared solutions by CeCl_3 . The results of triplicate measurements are given in Table 3. As seen, there is satisfactory agreement between the declared fluoride content and the determined values.

Table 2. Selectivity coefficients ($K_{A,B}^{pot}$) of various interfering ions for PPME and CPWE.

Cation	^a PPME	^b CPWE
Li^+	3.1×10^{-4}	4.5×10^{-5}
Na^+	2.5×10^{-4}	4.4×10^{-5}
K^+	2.1×10^{-4}	3.2×10^{-5}
Cs^+	1.8×10^{-4}	1.2×10^{-5}
Mg^{2+}	3.8×10^{-4}	2.2×10^{-4}
Ca^{2+}	2.2×10^{-4}	1.5×10^{-4}
Sr^{2+}	1.9×10^{-4}	1.4×10^{-4}
Ba^{2+}	1.6×10^{-4}	1.3×10^{-4}
Co^{2+}	6.1×10^{-3}	1.1×10^{-3}
Ni^{2+}	6.4×10^{-3}	1.5×10^{-3}
Cu^{2+}	7.3×10^{-3}	2.9×10^{-3}
Zn^{2+}	4.8×10^{-3}	1.0×10^{-3}
Cd^{2+}	4.1×10^{-3}	2.8×10^{-3}
Pb^{2+}	3.0×10^{-3}	1.6×10^{-3}
Hg^{2+}	2.5×10^{-3}	1.5×10^{-3}
Ag^+	7.6×10^{-3}	7.0×10^{-3}
Tl^+	3.8×10^{-3}	3.4×10^{-3}
Al^{3+}	1.4×10^{-4}	1.1×10^{-4}
Fe^{3+}	2.2×10^{-3}	2.0×10^{-3}
La^{3+}	6.8×10^{-2}	6.1×10^{-2}

^aConditions: reference solution: 1.0×10^{-6} M CeCl_3 ; primary ions (A): 10^{-5} - 10^{-4} M Ce^{3+} ; interfering ions (B): 10^{-2} - 10^{-1} M.

^bConditions: reference solution: 5.0×10^{-8} M CeCl_3 ; primary ions (A): 10^{-7} - 10^{-6} M Ce^{3+} ; interfering ions (B): 10^{-3} - 10^{-2} M.

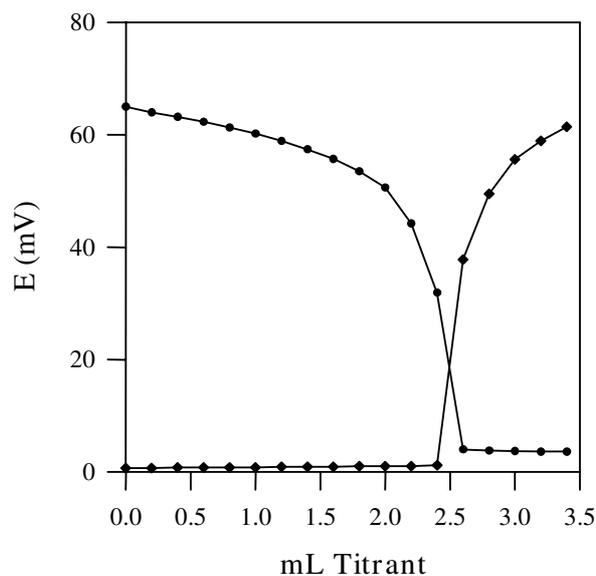


Figure 5. Potential titration curves for (●) 25.0 mL of 1.0×10^{-3} M Ce^{3+} ions with 0.01 M EDTA and (◆) 25.0 mL of 1.0×10^{-3} M EDTA with 0.01 M CeCl_3 in buffered solution of pH = 7.0.

Table 3. Determination of fluoride ions in real samples.

Sample	Labeled	Determined
Sodium fluoride mouthwash solution (Chimia Daru Co., Tehran, Iran)	2.0%	$2.02 \pm 0.02\%$
Sodium fluoride tables (Loghman Pharmaceutical Co., Tehran, Iran)	1.0 mg/tablet	0.996 ± 0.028 mg/tablet

Conclusion

The PVC membrane with composition of PVC, BA, OA, and 1,4,7-trithiacyclononane with the ratio of 30:49:15:6, respectively, was used for preparation of PVC PPME and CPWE electrodes. The electrodes were suitable for the determination of Ce^{3+} ions with regard to working concentration range, slope, pH range, response time, and selectivity over a number of cations. The electrodes exhibited good reproducibility over a useful lifetime of 3 months. Further, the electrodes could be used to determine Ce^{3+} ions both by direct potentiometry and titration.

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