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Sensitive and Selective Potentiometric Sensor Based on Carbon Paste Electrode for Determining Cerium(III) Ions in Soil and Water Samples; Simplex Lattice Mixture Design Application

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Abstract- The present paper describes the fabrication of a new potentiometric sensor to determine Cerium(III) ion based on a carbon paste electrode (CPE) as an indicator electrode. Four components, including N,N-bis(salicylidene)-1,3-propanediamine as the ionophore, graphite powder, ionic liquid ([HMIM][PF_6]) as the binder, and carboxyl functionalized MWCNTs as the modifier, was used to fabricate the CPE. The percentage of each CPE component was optimized using a simplex lattice mixture design, including 20 experimental runs. The optimum amount of ionophore, graphite powder, ionic liquid, and carboxyl functionalized MWCNTs was 0.1409, 0.5405, 0.2000, and 0.1186, respectively. The fabricated CPE with an optimum composite showed the Nernstian response in terms of 19.77 slope (mV/decade) and response time (<8 s) for the Ce(III) ion determination in the concentration range of 1.0×10^{-8}-1.0×10^{-3} M with a proper detection limit (5.17×10^{-9} M). Besides, the potentiometric response of the sensor was constant in the pH range of 4-9. The sensor was successfully utilized to determine the endpoint of the Ce(III) ion titration with a standard solution of EDTA as a titrant. Also, the sensor was applied to analyze soil and real water samples with recoveries between 90.7-104.2% and RSDs lower than 3.94%. The advantages of the sensor include simple fabrication, low cost, easy operation, wide linear range, short response time, high lifetime, and suitable selectivity.

Keywords- Carbon paste electrode; Potentiometric sensor; Cerium(III) ion; Simplex lattice mixture design; Multi-Walled Carbon nanotubes

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1. INTRODUCTION

Cerium is a metallic grey metal that belongs to the lanthanides group. The element is utilized in various fields in agriculture, microelectronic, therapeutic application, catalysis, glass, nuclear energy, luminescence, ceramic, metallurgy, and magnetism [1,2]. Due to the high applications of cerium, its determination in real samples, including environmental, biological, and agricultural samples, is necessary to investigate its effect on the environment and human and animal health. Several methods were presented to determine Ce(III) ions, such as fluorometric [2-4], voltammetric [5,6], and spectrophotometric methods [7,8]. These methods showed excellent sensitivity for determining Ce(III) ions. However, these methods require different instruments, sample preparation approaches, consumption of different reagents, and average analysis cost. Therefore, researchers have greatly interested in introducing new low-cost methods without requiring sophisticated tools with low analysis time to determine Ce(III) ions. Among them, a potentiometric sensor is a suitable device for determining metal ions, especially in liquid-phase samples [9,10].

The potentiometric sensor has various advantages in determining metal ions, including wide linear range, low cost, simple preparation and application, short analysis time, suitable reusability, high selectivity, and proper sensitivity with the possibility of long-term storage for reuse to measure metal ions [10]. The potentiometric sensor consists of indicator and reference electrodes to measure an analyte, and the indicator electrode plays a critical role in selective and sensitive determining metal ions [11,12]. Carbon paste electrode (CPE) as an indicator electrode has been widely selected in preparing the potentiometric sensor for measuring various metal ions due to its high benefits, including low cost, simple preparation, high chemical and thermal stability, long lifetime, short response time, and wide potential window [13]. CPE composite usually consists of four components, graphite powder, binder, ionophore, and a suitable nanoparticle or nanocomposite as a modifier. Its properties and ability depend highly on the type of binder, nanomaterial, and ionophore and their ratio in the CPE composite [14].

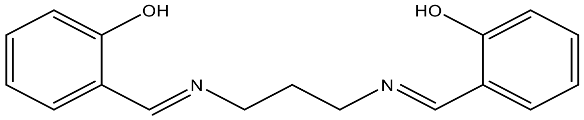
Carbon nanotubes (CNTs) are a nano-allotrope of carbon, divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [15-17]. MWCNTs are usually more widely used than SWCNTs because they are easier to prepare and less expensive. These nanomaterials displayed a high electrocatalytic effect, electron transfer rate, and high availability, leading to many applications in cell membranes and chemical and biochemical sensors [18-20]. In CPE, CNTs enhance the linearity of the sensor toward the analyte and decrease the sensor response time [21].

Binder is another component in the CPE composite. Mineral oils such as paraffin oil are the traditional binder in CPE. The mineral oils as a CPE binder have suitable properties such as low volatility and water solubility, high thermal and mechanical stability, and high viscosity [22]. The low conductivity of mineral oils and differences in their compounds produced in different refineries reduce their use in CPE composite [23,24]. Ionic liquids (ILs) have been considered a CPE binder to reduce the inherent limitations of mineral oils by improving the CPE conductivity [25,26].

The ionophore is the critical component in the CPE composite. The selectivity and affinity of the CPE toward the analyte depended on the type and strength of the interactions between the ionophore and the analyte [12,27]. The structure and functional groups of the ionophore play an essential role in interacting with the analyte selectively [13]. In other words, the steric hindrance and the type of functional groups in an ionophore determine the type and strength of these interactions at the CPE surface [28].

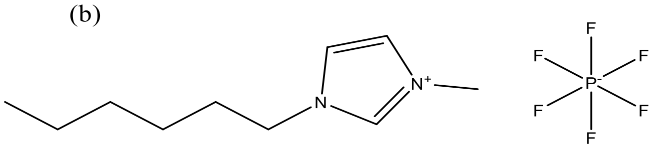
This research presents a new and sensitive potentiometric sensor to determine Ce (III) ions using a modified CPE as an indicator electrode and a calomel electrode as a reference electrode. The Ce (III) ion determination was performed based on the potentiometric titration in which the standard solution of EDTA was selected as a titrant. N, N-Bis (salicyliden)-1,3-propanediamine (BPDA) as selective ionophore and 1-Hexyl-3-methyl-imidazolium-hexafluorophosphate [HIMIM][PF_6] as a binder were chosen in preparing the CPE. The chemical structures of the ionophore and binder are presented in Figure 1. The CPE composite was optimized using an experimental design method [29].

(a)



N, N-Bis (salicyliden)-1, 3-propandiamine

(b)



1-Hexyl-3-methyl-imidazolium-hexafluorophosphate

Figure 1. Chemical structure of ionophore (a) and binder (b)

2. EXPERIMENTAL

2.1. Chemicals and reagents

The nitrate salts of all cations and the reagent grade Graphite powder, N, N-Bis (salicyliden)-1, 3-propanediamine (BPDA), were purchased from Merck (Germany). 1-Hexyl-3-methyl-imidazolium-hexafluorophosphate [HIMIM][PF_6] was obtained from Green Chemicals Co. (Iran). Carboxyl functionalized multi-walled carbon nanotubes (MWCNTs-COOH) were purchased from the Iranian Nanomaterials Pioneers Company. Deionized water was used in all experiments.

2.2. Instruments

The potentiometric sensor for determining Ce(III) ions was the electrochemical cell containing a saturated calomel electrode (Azar Electrode, Iran) as the reference electrode, the modified CPE as the indicator electrode, and a corning ion analyzer 250 pH/mV meters. The Schematic installation of the sensor is as follows:

Carbon Paste Electrode | sample solution |Hg- Hg_2Cl_2, KCl (sat'd).

All experiments and the potential measurements were performed at 25.0±0.5 °C.

2.3. Carbon paste electrode preparation

The intended amount of BPDA as an ionophore, graphite powder, [HIMIM][PF_6] as a binder and carboxyl functionalized MWCNTs was thoroughly mixed to form a homogeneous paste. The mixture was transferred into a glass tube with an inner diameter of 5 mm and a length of 3 cm. The paste was carefully packed into the tube to prevent the formation of air gaps in the CPE and impede the heightened electrical resistance of the electrode. A copper wire was inserted into the paste from the end of the glass tube to create an electrical connection. A soft abrasive paper was used to polish the working surface of the electrode. Finally, the CPE was immersed in a 1.0×10^{-3} mol L^{-1} of $Ce(NO_3)_3.6H_2O$ solution for 24 h under stirring to condition the electrode.

3. RESULTS AND DISCUSSION

3.1. Potential response of the electrode

After preparing the CPE, several species, including La(III), Nd(III), Gd(III), Sm(III) and UO_2(II) ions, were selected, and the ability of the prepared sensor to measure them was evaluated. For this purpose, the standard solution of each ion was prepared in the concentration range of 1.0×10^{-2}-1.0×10^{-7} M in deionized water. The curve of the sensor potential versus the logarithm of the ion concentration was plotted to determine the Nernstian slope and determination coefficient (Table 1). The results show that the obtained slope for the Ce(III) ion determination is close to the theoretical slope value (19.7 mV $decad^{-1}$). In contrast, the slope for other ions significantly differs from the theoretical slope value. Therefore, the sensor was selected to determine Ce(III) ion after optimizing the CPE composite.

Table 1. The slope and R^2 for the determination of various species using the sensor

Species	**UO_2(II)**	**La(III)**	**Nd(III)**	**Gd(III)**	**Sm(III)**	**Ce(III)**
Slope (mV $decad^{-1}$)	13.40	16.28	29.27	12.58	13.20	19.50
R^2	0.993	0.986	0.971	0.953	0.994	0.937

3.2. Optimization of CPEs

The percentage of the CPE composite, including four components, should be optimized to achieve a proper Nernstian response and high selectivity and sensitivity of the sensor for determining Ce(III) ions. Therefore, an experimental design strategy was used to optimize the amount of four components in the CPE to reduce the number of experimental runs, time, and cost [30,31]. For this purpose, a simplex lattice mixture design containing 20 runs was utilized to optimize four CPE components, including carboxyl functionalized MWCNTs, graphite powder, [HIMIM][PF$_6$], and BPDA. The independent factors and their level are presented in Table 2. Besides, the design and the dependent factor (the CPE slope) for each run are shown in Table 3. Each CPE in Table 3 was prepared and used to determine Ce(III) ions in the concentration range of 1.0×10^{-2}-1.0×10^{-9} M. Each run was performed in triplicate under the same conditions [32,33].

Table 2. The selected components of CPE in the optimization step

Component	Name	Type	Minimum	Maximum	Mean	Std. Dev.
A	Graphite powder	Mixture	0.5	0.6	0.5262	0.0334
B	BPDA	Mixture	0.1	0.2	0.1263	0.0334
C	MWCNT-COOH	Mixture	0.1	0.2	0.1237	0.0334
D	[HIMIM][PF$_6$]	Mixture	0.2	0.3	0.2238	0.0334

The slope of each prepared CPE was calculated by plotting the mean of potential versus the logarithm of the Ce (III) ion concentration. The results were investigated by analysis of variance (ANOVA) at a 95 % confidence interval using the p-value of factors (Table S1). The presented model to investigate the CPE components is significant because its p-value is lower than 0.05 at a 95 % confidence interval and the p-value of lack of fits (LOF) is higher than 0.05 (the parameter is nonsignificant). The linear maxing of the CPE components is a significant factor due to a lower p-value than 0.05. Besides, the meaningful interactions of the CPE components included interaction between graphite powder and BPDA (AB), graphite powder and MWCNT-COOH (AC), BPDA and MWCNT-COOH (BC), and MWCNT-COOH and [HIMIM][PF$_6$] (CD). Two other interactions (AD and BD) have non-meaningful effects on the sensor slope.

A quadratic equation was presented to describe the effects of the CPE components or their interactions on the sensor slope as follows:

$$\text{Slope} = 17.2938 * A + 21.1317 * B + 18.677 * C + 18.9338 * D + 2.1183 * AB + 6.83961 * AC + 1.50015 * AD - 3.77336 * BC + 1.36718 * BD - 6.48077 * CD$$

The amount of R^2, adjusted R^2, and predicted R^2 are shown in Table S2.

Table 3. The simplex lattice mixture design for optimizing the CPE composite

Standard run	**Run**	**A**	**C**	**B**	**D**	**Slope (mV decad^{-1})**	**R^2**	**Linear range (M)**
3	1	0.5	0.2	0.1	0.2	18.87	0.9782	10^{-2}-10^{-6}
10	2	0.5	0.15	0.1	0.25	17.26	0.9641	10^{-2}-10^{-7}
7	3	0.55	0.1	0.1	0.25	18.59	0.9597	10^{-3}-10^{-7}
1	4	0.6	0.1	0.1	0.2	17.15	0.9714	10^{-3}-10^{-7}
17	5	0.5	0.1	0.2	0.2	21.25	0.9547	10^{-3}-10^{-7}
14	6	0.5125	0.1125	0.1125	0.2625	18.71	0.9547	10^{-3}-10^{-7}
5	7	0.55	0.1	0.15	0.2	19.75	0.9614	10^{-2}-10^{-6}
16	8	0.6	0.1	0.1	0.2	17.43	0.9433	10^{-2}-10^{-6}
13	9	0.5125	0.1625	0.1125	0.2125	18.62	0.9567	10^{-2}-10^{-6}
12	10	0.5125	0.1125	0.1625	0.2125	20.04	0.9746	10^{-3}-10^{-7}
18	11	0.5	0.2	0.1	0.2	18.45	0.9659	10^{-2}-10^{-6}
9	12	0.5	0.1	0.15	0.25	20.45	0.9567	10^{-2}-10^{-6}
2	13	0.5	0.1	0.2	0.2	20.98	0.9767	10^{-2}-10^{-6}
6	14	0.55	0.15	0.1	0.2	19.79	0.9726	10^{-2}-10^{-7}
8	15	0.5	0.15	0.15	0.2	19.03	0.9875	10^{-2}-10^{-6}
20	16	0.55	0.1	0.15	0.2	19.83	0.9923	10^{-2}-10^{-7}
15	17	0.525	0.125	0.125	0.225	18.97	0.9613	10^{-3}-10^{-7}
19	18	0.5	0.1	0.1	0.3	18.81	0.9654	10^{-3}-10^{-7}
11	19	0.5625	0.1125	0.1125	0.2125	18.69	0.9681	10^{-2}-10^{-6}
4	20	0.5	0.1	0.1	0.3	19.03	0.9839	10^{-3}-10^{-7}

Their high amounts indicated that the model fitted well with the results to describe the relationship between the CPE components or their interaction with the sensor slope.

The predicted R^2 of the equation is 0.8978 and indicates that the equation can be applied to predict the sensor slope for different amounts of the CPE components. According to the equation, BPDA (B) as an ionophore in the CPE composite has the highest positive effect on the sensor slope due to the highest coefficient. The amount of graphite powder (A) has the lowest impact. Also, two significant interactions (BC and CD) have negative effects, while two other meaningful interactions (AB and AC) positively affect the CPE slope. The simultaneous effects of three factors on the slope are shown in contour plates (Figure 2). The slope changes are the most in Figure 2a, which shows that the slope was increased by reducing the amount of graphite powder (A) and increasing the amounts of BPDA (B) and MWCNT-COOH (C). By replacing each of these factors with the amount of [HIMIM][PF_6] (D), the slope changes decrease (Figure 2b, c, and d) and indicate that the effect of the amount of [HIMIM][PF_6] and its interactions with other CPE components is minimal.

The optimum amounts of the CPE components were calculated using the target value of the CPE slope (19.7 mV decade^{-1}). The optimum amount of graphite powder, BPDA, MWCNT-COOH, and [HIMIM][PF_6] to prepare CPE was 0.5405, 0.1409, 0.1186, and 0.2000, respectively (Table S3).

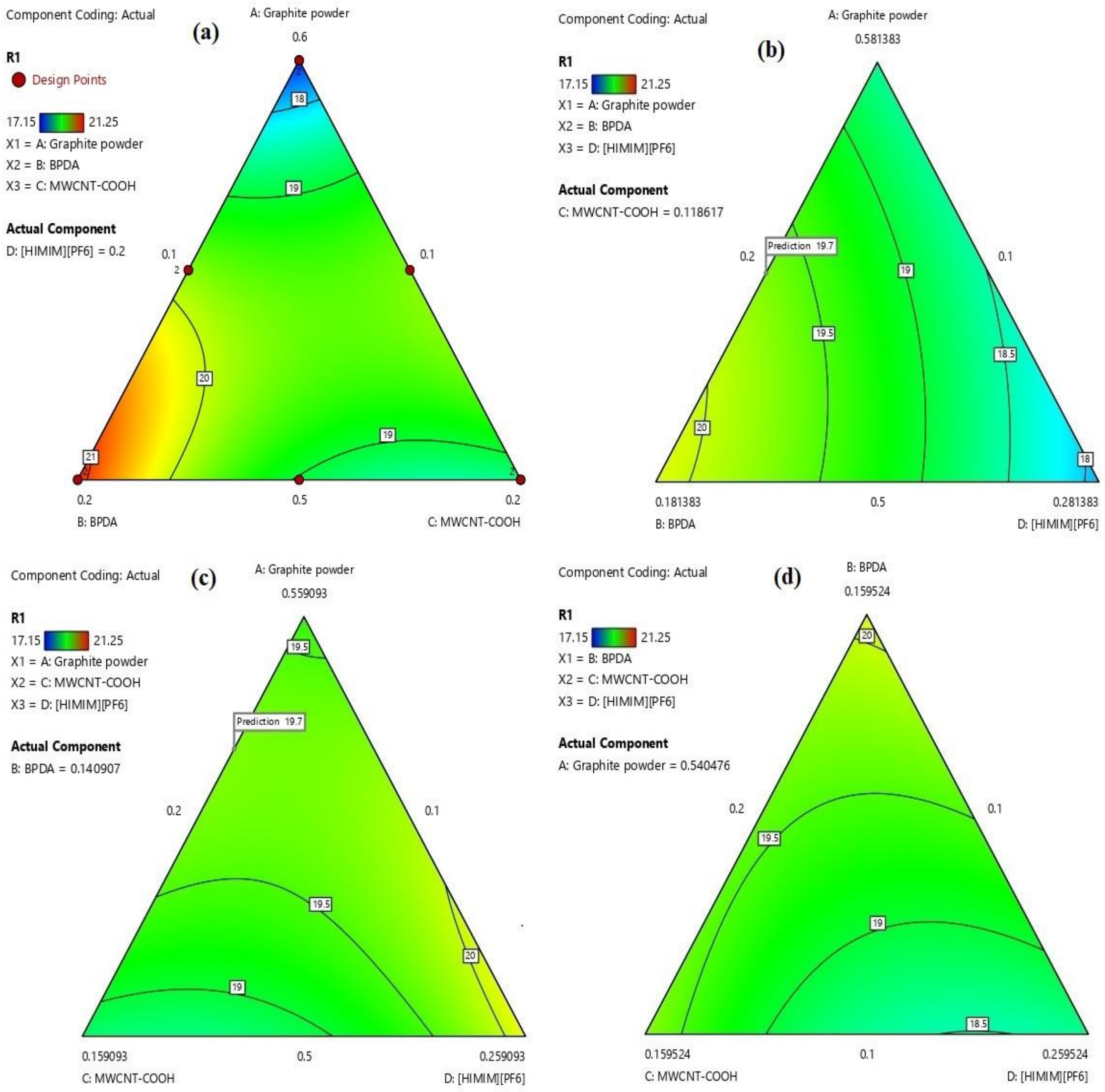


Figure 2. Contour plates for investigating the simultaneous effects of three factors on the slope

3.3. Calibration graph

The linearity of the sensor to determine Ce(III) ion was obtained by plotting the calibration curve. The potential of the sensor was determined in the standard solution of Ce(III) ion in the concentration range of 1.0×10^{-2}-1.0×10^{-10} M. The calibration curve based on triplicate measurements was presented in Figure 3, indicating that the sensor has a linear response from 1.0×10^{-3} to 1.0×10^{-8} M with a proper slope of 19.77 mV decade^{-1}. The detection limit is defined as the Ce(III) ion concentration obtained from the extrapolation of the linear region of the standard plot to the baseline potential. The detection limit of the sensor for the Ce(III) ion determination was 5.1×10^{-9} M.

3.4. Effect of pH

The pH effect on the sensor response was investigated in the range of 1-13 for the Ce(III) ion determination at two concentrations of 1.0×10^{-3} and 1.0×10^{-4} M (Figure 4). The potential of the sensor was constant in the pH ranges of 6-10 and 5-10 for the Ce(III) ion concentrations of 1.0×10^{-3} and 1.0×10^{-4} M, respectively. Therefore, the sensor can measure Ce(III) ions in the sample solution in these pH ranges without significant changes in the potential of the sensor. A reduction in the sensor potential at pH higher than 10 is attributed to forming the precipitation of $Ce(OH)_3$ ($K_{sp}=1.6\times10^{-20}$) in the solution. At pHs below 6 (or 5), a competition between hydronium ions and Ce(III) ions for interaction with the ionophore in the CPE composite occurred, leading to significant changes in the potential of the sensor. In other words, protonation of the amine or hydroxyl groups in the CPE ionophore prevents the proper interaction of free electron-ion pairs in these functional groups with the Ce(III) ion, which increases the sensor potential [34].

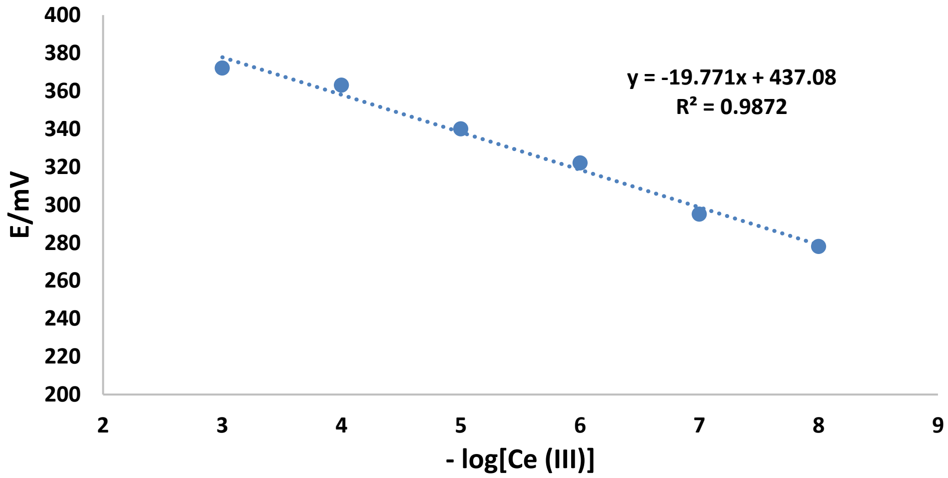


Figure 3. Calibration curve for determining the Ce(III) ion using the sensor

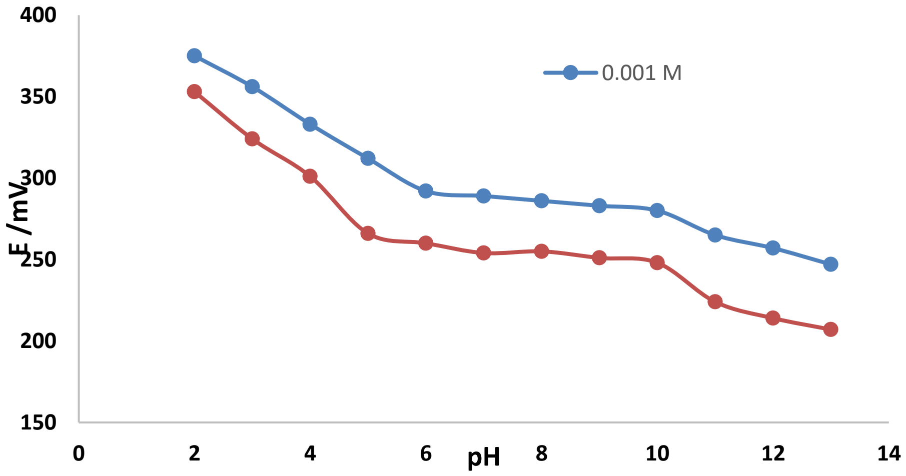


Figure 4. Effect of the pH on the potential response of the sensor

3.5. Dynamic Response time

The response time of a sensor is the primary practical factor in determining an analyte. In the practical application of sensors, the analysis time is modified by reducing the response time of the sensor. It is crucial when the number of samples to analyze is high. The response time is defined as the time required for the potential of the electrode immersed in the analyte solution to reach 90% of its final value [35]. Therefore, the dynamic response time of the sensor was investigated for different concentrations of the Ce(III) ions in the range of 1.0×10^{-3}-1.0×10^{-8} M. The sensor displayed a proper response time lower than 8 s for the Ce(III) ion determination (Figure 5).

3.6. Lifetime

The sensor lifetime is determined by evaluating the Nernst slope changes in the analyte measurement in consecutive weeks [10]. A sensor can be used for a period of time when its slope does not change significantly compared to the theoretical slope of the sensor. The lifetime of the sensor was investigated using three prepared sensors. For this purpose, the potential of the sensor was measured weekly for Ce(III) ions in the concentration range of 1.0×10^{-3}-1.0×10^{-9} M for ten weeks to calculate the slope of the sensor. After each use, the sensor was washed with deionized water and stored at room temperature for reuse for the following week. The results dominated that the Nernstian slope of the sensor decreased from 19.77 to 15.4 mV decade^{-1} for ten weeks (Table S4). Therefore, the sensor can use to determine Ce(III) ions for eight weeks without significant change in its Nernstian slope.

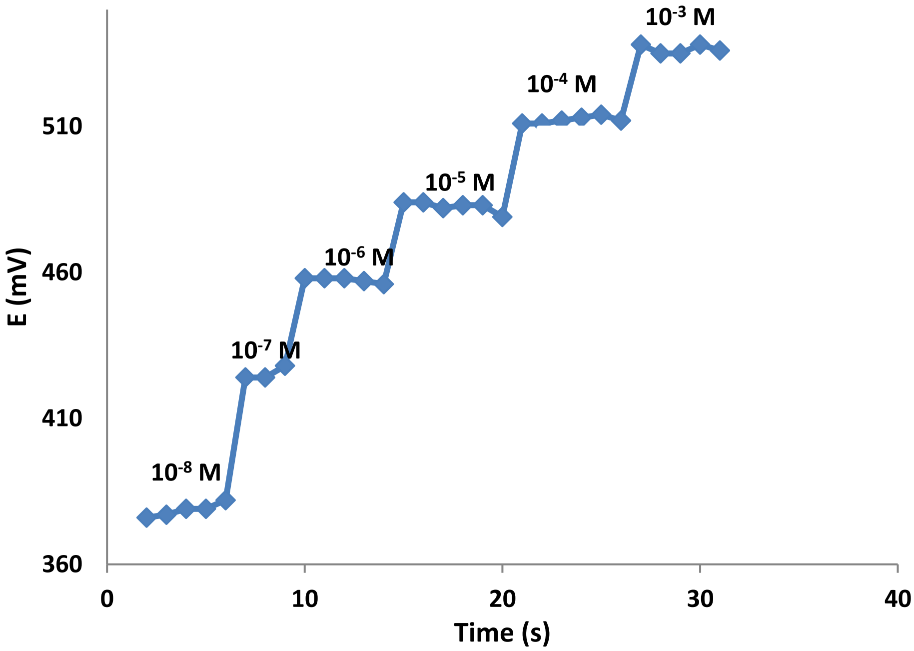


Figure 5. Dynamic response time of the sensor for the Ce(III) ion determination

3.7. Selectivity

The presence of interfering species in real samples usually causes adverse effects on analyte measurements. Therefore, the selectivity of a sensor is a critical property of its application in the analysis of real examples. In this research, the selectivity coefficients were determined by the matched potential method (MPM). According to the procedure, a solution of primary ion (Ce(III) ion) (1.0×10^{-7} M) was added to the reference solution of primary ion (1.5×10^{-7} M), and its potential was determined using the sensor. Then, an interfering ion (x) with various concentrations was added to the reference solution of the primary ion (1.5×10^{-7} M) step by step until its potential became equal to the potential of the first solution. The MPM selectivity coefficient (K_{MPM}) was calculated using the following equation:

$$K_{MPM} = \frac{a_{Ce(III)ion}}{a_x}$$

where $a_{Ce(III)\ ion}$ and a_x are the activity of Ce(III) ion and interfering ion, respectively [36]. The results are summarized in Table S5, which shows that the interference of alkali, alkaline earth, transition, heavy metal, and lanthanide ions was nonsignificant.

3.8. Analytical application

The fabricated sensor was applied to detect the endpoint of titration Ce (III) ion with the standard solution of EDTA as a titrant. The standard solution of EDTA with a concentration of 1.0×10^{-3} M was utilized to titrate 25.0 mL of a standard solution of Ce(III) ion (1.0×10^{-4} M). The potential values decrease with adding EDTA solution under stirring because of the formation of Ce(III) ion-EDTA complex and reduction of the Ce(III) ion concentration in the sample solution. The obtained curve displayed a sharp change in potential at EDTA volumes close to the titration endpoint, confirming that the carve is appropriate to determine the Ce (III) ion concentration using the endpoint of the titration. The relevant results are demonstrated in Figure 6.

The sensor was also used to determine the Ce(III) ion concentration in the presence of two or three ions. The Ce(III) ion concentration and other ions were 1.5×10^{-7} and 1.0×10^{-7} M, respectively. The recovery (%) was calculated based on the ratio of the Ce(III) ion concentration determined by the sensor in the presence of other ions to its initial concentration. Each experiment was repeated three times to calculate the recovery. The obtained recoveries are presented in Table S6, indicating that the recoveries are in the range of 90-108%.

Several real samples, including two soil samples, river water and well water samples, were analyzed using the sensor. The soil samples were obtained from farmland on the outskirts of Mashhad (Iran). The samples were grounded to prepare soft powders. The soil samples (2.0 g) were poured into a beaker, followed by adding 20.0 mL of a solution containing concentrated HNO_3 (5.0 mL) and HCl (15.0 mL). The mixture was heated to near drying. The procedure was repeated two times. The resulting was dissolved in 10.0 mL of HNO_3 (0.1 M), and its pH was adjusted to 6.0 using NaOH solution (0.2 M) before diluting it to 100.0 mL with distilled water. Spiked soil samples were prepared by adding the appropriate amount of $Ce(NO_3)_3.6H_2O$, in which the final spiked concentrations of Ce(III) ions were 40 and 80 mg Kg^{-1}. River water and well water samples were obtained from the Mayan river (Torqabeh-Shandiz, Iran) and a well on the outskirts of Mashhad (Iran).

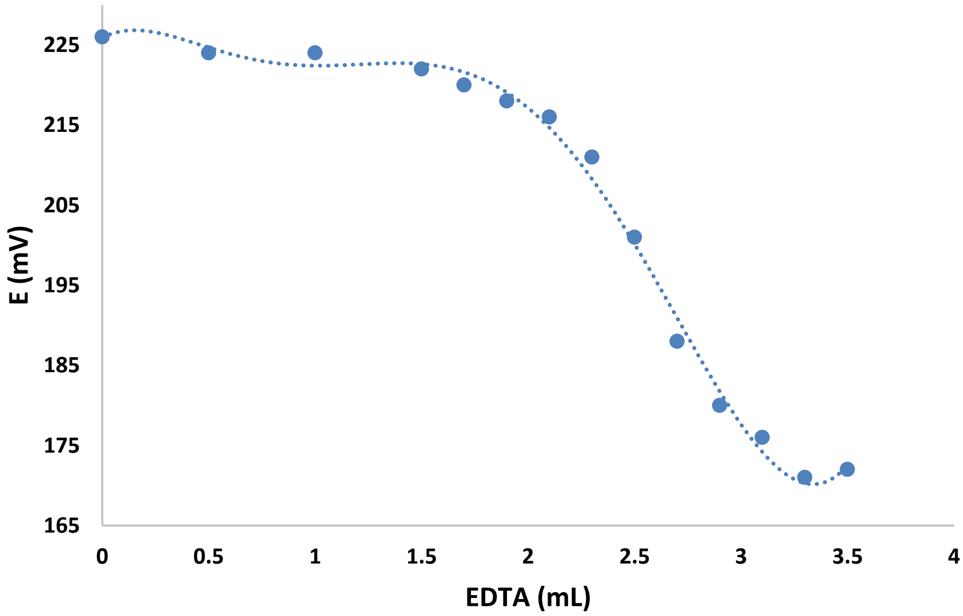


Figure 6. Potentiometric titration curve of Ce(III) ions (25.0 mL, 1.0×10^{-4} M) with a standard solution of EDTA (1.0×10^{-3} M) as a titrant

Table 4. Analysis of real soil and water samples

Sample	Spike	Found ± S	Recovery (%)
Soil^1	0 (mg Kg^{-1})	12.7 ± 0.5	----
	40 (mg Kg^{-1})	48.2 ± 1.2	91.5
	80 (mg Kg^{-1})	87.4 ± 1.8	94.3
Soil^2	0 (mg Kg^{-1})	26.1 ± 0.8	---
	40 (mg Kg^{-1})	60.9 ± 1.5	92.1
	80 (mg Kg^{-1})	110.6 ±1.9	104.2
River water	0 (µg L^{-1})	18.4 ± 0.7	----
	40 (µg L^{-1})	53.0 ± 1.2	90.7
	80 (µg L^{-1})	92.1 ±1.6	93.6
Well water	0 (µg L^{-1})	19.7 ± 0.7	----
	40 (µg L^{-1})	54.4 ± 1.3	91.1
	80 (µg L^{-1})	93.1 ± 1.5	93.4

All water samples were analyzed without any sample preparation strategy and spiked with a standard solution of Ce(III) ions. The final spiked concentrations of Ce(III) ions in the real samples were 40 and 80 mg L^{-1}. The obtained recoveries for the Ce(III) determination were between 90.7-104.2, with relative standard deviations lower than 3.94 % (Table 4). Therefore, the sensor is suitable for the Ce (III) ion determination with acceptable recoveries.

3.9. Comparison with other electrodes

The performance of the prepared CPE was compared with other ion-selective electrodes for measuring Ce(III) ions. The type of ionophores, the electrode composite, and other conditions were summarized in Table 5.

Table 5. Ion-selective electrodes for the Ce (III) ion determination

Ionophore	Electrode composition	Electrode characterization	Ref.
1,3,5-trithiane	PVC: 32 % Plasticizer (Benzyl acetate):45 % Ionophore: 5% Additive (Oleic acid): 18%	LR[1]: 1.0×10^{-5}-1.0×10^{-1}M Slope: 19.40 mV/decade DL[2]: 3.0×10^{-5} pH:5-8 RT[3]: <15s	[37]
N, N-bis [2-salicylideneamine) ethyl] ethane-1, 2-diamine	PVC: 150 Plasticizer (o-NPOE)[4]: 250 Ionophore: 6.5 mg Additive (Oleic acid): 20	LR: 1.41×10^{-7}-1.0×10^{-2}M Slope: 20.0 mV/decade DL: 8.91×10^{-8} pH:3.0-8.0 RT: <10	[38]
2,5-Dioxo-4-imidazolidinyl	PVC:32% Plasticizer (o-NPOE): 60.5 % Ionophore: 5 % Additive (NaTPB[5]): 2.5 %	LR: 1.0×10^{-6}-1.0×10^{-1}M Slope: 19.6 mV/decade DL: 5.7×10^{-7} pH:3.1-9.8 RT: <10 s	[39]
N-[(2-hydroxyphenyl) methylidene]-2-furohydrazide	MWCNTs:15% Graphite:44% Ionophore:16% Binder [bmim][BF_4]: 25%	LR: 8.0×10^{-7}-1.0×10^{-1}M Slope:19.9 mV/decade DL:3.60×10^{-7} pH:3.5-9 RT:10s	[40]
Dibenzo-24-crown-8	PVC:33% Plasticizer: o-NPOE 62.5% Ionophore:4.5%	LR: 1.0×10^{-5}-1.0×10^{-1}M Slope: 19.0 mV/decade DL: 3.0×10^{-5} pH:4-10 RT: 20s	[41]
N, N-Bis (salicyliden)-1, 3-propanediamine	MWCNTs:11.86% Graphite:54.05% Ionophore:14.09% Binder[HMIM][PF_6]: 20%	LR: 1.0×10^{-8}-1.0×10^{-3}M Slope: 19.77mV/decade DL: 5.7×10^{-9} pH:4-9 RT: <8s	This work

[1] Linear range, [2] Detection limit, [3] Response time, [4] *O*-nitrophenyloctyl ether, [5] Sodium tetraphenylborate

The sensor showed a lower LOD and response time than other electrodes. The linear range of the sensor was also about six orders of magnitude, which is wider than most electrodes. Besides, the sensor can be used in the suitable pH range for the Ce(III) ion determination. Other advantages of the sensor are simple preparation and operation, low cost, long lifetime, and excellent selectivity toward Ce(III) ions.

4. CONCLUSION

This project designed a new potentiometric sensor for measuring Ce(III) ions. A CPE was prepared as the indicator electrode based on four components, including N, N-Bis (salicyliden)-1, 3-propanediamine as the ionophore, graphite powder, [HMIM][PF_6] as the binder, and carboxyl functionalized MWCNTs as the modifier. The CPE composite was optimized using a simplex lattice mixture design, including 20 experimental runs. Under optimization of the CPE composite, the values of the ionophore, graphite powder, binder, and modifier were 0.1409, 0.5405, 0.2000, and 0.1186, respectively. The fabricated sensor provides a suitable detection limit (5.7×10^{-9} M), short response time (<8 s), long lifetime (8 weeks), wide linearity (1.0×10^{-8}-1.0×10^{-3} M), and proper detection limit (5-10) for the Ce(III) ion determination with a Nernstian slope of 19.77 mV decade^{-1}. The sensor was used to determine the endpoint of potentiometric titration of Ce(III) ions with a standard solution of EDTA as the titrant, which shows an appropriate titration curve for determining Ce(III) ions. The analysis of real samples, such as soil and real water samples, indicated that the sensor has the responsible ability to determine Ce(III) ions in real samples with a complex matrix with adequate recoveries and RSDs. The advantages of the sensor to determine Ce(III) ions include simple preparation and operation, low cost, long lifetime, low LOD, wide linear range, low response time, and excellent selectivity toward Ce(III) ions. The use of new synthetic ionospheres, nanoparticles or nanocomposites based on graphene and graphene oxide as modifiers and other ionic liquids as binders in the CPE fabrication can be considered for future studies to improve selectivity, linear range, and detection limit.

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Declarations of interest

The authors declare no conflict of interest in this reported work.

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