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Determination of Strontium Ion in Depilatory Powder, Toothpaste, and Raticide Samples using a Novel and Highly Sensitive Potentiometric Sensor Coupled with a Central Composite Design

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Abstract- The strontium ion, in water-soluble forms, is one of the major pollutant in drinking water. Therefore, a simple, rapid, selective, and sensitive potentiometric carbon paste electrode was developed to measure strontium ion in real samples with complex matrices. To prepare the potentiometric sensor, a synthetic ligand ((E)-4-(((2-amino-4-chlorophenyl)imino)methyl)-5-(hydroxymethyl)-2-methyl pyridine-3-ol) as an efficient ionophore and an ionic liquid (1-Butyl-3-methylimidazolium hexafluorophosphate) as a suitable binder were dispersed in a mixture of graphite powder and graphene oxide. The composition of the sensor was optimized using a central composite design (full factorial) to reduce the number of experimental runs and investigate interactions between effective factors. The proposed sensor showed a Nernstian behavior in the linear concentration range of 1×10^{-8} to 1.0×10^{-1} M with a low detection limit (1.59×10^{-9} M) and suitable relative standard division (1.01 %). The proposed sensor can be well applied in the pH range of 3.00-9.50 for the analyte determination. Moreover, the proposed electrode as an indicator electrode was successfully used to measure the Sr(II) concentration in the depilatory powder, toothpaste, and raticide samples.

Keywords- Strontium determination; Potentiometric sensor; Central composite design; Depilatory powder sample; Toothpaste sample; Raticide sample

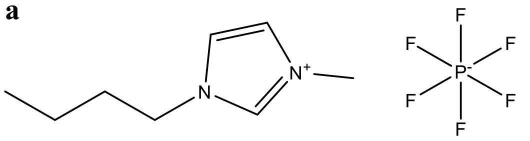
1. INTRODUCTION

Room-temperature ionic liquids (RTILs) are generally organic salts with a melting point lower than 100 ˚C. Due to their unique features such as non-flammable, chemical and thermal stability, non-volatile, eco-friendly, and recyclable, they are suitable candidates for many applications in various research topics [1-5]. Moreover, new and unique RTILs with the specific physical and chemical properties can also be prepared by changing the type of its cation or anion for each specific application [6-8]. In the preparation of electrochemical sensors, ILs are a great choice because of their excellent properties, including non-flammability, high ionic conductivity, wide electrochemical window, and thermal stability of them [5, 9-13].

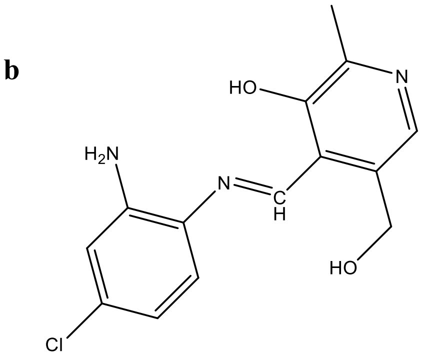
Graphene is one of the two-dimensional carbon nanomaterials that is composed of layers separated by a shallow thickness [14]. Graphene oxide (GO) has a similar structure of graphene sheet with a large number of oxygen functional groups, such as hydroxyls and carboxyls, alcohols, and epoxides, which is usually prepared from graphite oxidation with potassium permanganate in the presence of concentrated sulfuric acid [15, 16]. Suitable structure and properties of GO such as superior electrical conductivity, sizeable potential window, excellent mechanical flexibility, low charge-transfer resistance, large surface area, fast electron transfer rate, high thermal and chemical stability, and excellent electrochemical activity enhances its application for electrochemical sensors [15, 17-21]. Also, the presence of oxygen functional groups on the GO sheets can be active in electrochemical performance by increasing/ decreasing the electron transfer rate or adsorbing/desorbing analytes on the electrode surface [18, 22-24].

The potentiometric method is a non-destructive, sensitive, rapid, and simple analytical method for precise determination of metal ions in real samples. Potentiometric carbon paste electrodes (CPEs) is very attractive for analyte determination due to their advantages such as easy renewability of the surface, simplicity of the preparation, chemical inertness, high response stability, robustness, and no internal electrolyte solution [25-30]. The traditional CPEs usually prepared from dispersing graphite powder into a binder (nonconductive mineral oil) [31-35]. The most important features of a binder for mechanical linking the individual graphite particles in CPEs are high viscosity, very low solubility in sample solutions, low volatility, and immiscibility with organic solvents [36-39]. A limitation in the use of mineral oils as binders is that its constituent substance is not entirely fixable because it obtained from various petroleum refining and crude oil processing, and some of the uncertain components in it may have unpredictable effects in analyte determination [27]. Also, the other disadvantage of mineral oils is their low conductive that reducing the electrochemical capability of CPEs [40-45]. The use of a ligand in the work electrode composition can enhance the mass transfer of an analyte to the electrode surface by appropriate interaction with analyte [46-48]. Also, the electrode's potential varies with the change in the analyte structure in a sample solution, in particular by the formation of the complex. Therefore, the selection of a suitable ligand can influence the electrode selectivity and efficiency for analyte determination. Recently, the synthesis of a new ligand with high selectivity toward the analyte is a fascinating trend in CPEs [49-51].

In the study, a novel and sensitive CPEs as a potentiometric sensor was constructed to determine strontium ion in real samples. GO, IL (*1-Butyl-3-methylimidazolium* hexafluorophosphate) and a synthetic ligand ((E)-4-(((2-amino-4-chlorophenyl)imino) methyl)-5-(hydroxymethyl)-2-methyl pyridine-3-ol) [52] were added into the CPEs composition to increase the electrochemical capability and selectivity of CPEs for determination of the analyte. Chemical structures of IL and ligand are shown in Fig. 1.



1-Butyl-3-methylimidazolium hexafluorophosphate



(*E*)-4-(((2-amino-4-chlorophenyl)imino)methyl)-
5-(hydroxymethyl)-2-methylpyridin-3-ol

Fig. 1. Chemical structures of used IL (a) and ligand (b) in the sensor

Optimization of the CPEs compositions was carried out using an experimental design to reduce cost and number of trial runs and obtain large quantities of information [53]. Valid parameters in the determination of the analyte with CPEs were also investigated and optimized with one variable at a time. Finally, the potentiometric sensor was applied for the measurement of the analyte in depilatory powder, toothpaste, and raticide samples.

2. EXPERIMENTAL

2.1. Chemical and instrumentation

Ionic liquid (1 -Butyl-3-methylimidazolium hexafluorophosphate) and graphite powder were obtained from Merck (Darmstadt, Germany) and were analytical grade. GO with characteristic; >99% purity and 3.4–7 nm, 6–10 layers were bought from Research Institute of the US Nanomaterials, Inc. The synthetic ligand ((E)-4-(((2-amino-4-chlorophenyl)imino) methyl)-5-(hydroxymethyl)-2-methyl pyridine-3-ol) was sensitized base on the previous paper [52]. Other used chemicals such as $Ni(NO_3)_2.7H_2O$, $Zn(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$, $Cd(NO_3)_2.4H_2O$, $Bi(NO_3)_2.5H_2O$, NaOH, MoO_2, $SbCl_3$, were obtained from Merck (Darmstadt, Germany). A stock solution of Sr(II) (1.0×10^{-1} M) was prepared by dissolving 2.1163 g of $Sr(NO_3)_2$, (Merck, Germany) in 100 mL of distilled water. Working sample solutions were prepared daily by appropriate dilution of the stock solution of Sr(II) with distilled water.

A pH/mV meter (Metrohm-780, Switzerland) was applied for adjusting the pH of the sample solution and measuring electrode potential. In the procedure, an Ag/AgCl (Azar electrode, Iran) as the reference electrode and the proposed electrode as the indicator electrode were utilized for potentiometric determination of Sr(II) in the sample solution. To compare the obtained results from the proposed sensor, ICP-OES (Spectro Arcos, model 76004555, Germany) was applied to determine the Sr(II) ion in the real samples.

2.2. Preparation of CPE

To prepare CPE, different amounts of graphite powder, G0, ligand, and the *ionic liquid* were mixed for 30 min at room temperature until an utterly uniform mixture was obtained. The resulting mixture was thoroughly packed into a tip of the polypropylene syringe barrel with an internal diameter of 2.8 mm and a length of 3.0 cm as the electrode body. The created package is carefully investigated to prevent the presence of air gaps and increase the electrode resistance. A copper wire was carefully placed into the mixture inside the barrel for creating an electrical contact. The outer surface of CPE was smoothed with soft paper. The old electrode surface was removed and replaced with the carbon paste to the preparation of the new electrode surface. The CPE sensor was finally conditioned in an aqueous solution of Sr(II) (1.0×10^{-3} mol L^{-1}) for 24 h at room temperature.

3. RESULTS AND DISCUSSION

3.1. Optimization of electrode composition

An experimental design was applied to optimize the structure of the CPE. For the purpose, a central composite design (CCD) was generated including 30 experimental runs (30 basic runs and 5 center points) to determine the percentage of four compounds (ligand, graphite powder, GO, and IL) present in the CPE electrode. The experimental runs were randomly carried out for removing the uncontrolled variable effects [53]. The selected symbols for graphite powder, GO, ligand, and IL are A, B, C, and D, respectively. Symbol and level of each component, experimental runs were represented in Table 1 and 2.

Table 1. Symbols and levels of factors selected for the central composite design

Factor	Name	Units	Type	Low Actual	Mean	High Actual
A	Graphite	w/w%	Numeric	57.50	60.00	62.50
B	GO	w/w%	Numeric	9.00	10.00	11.00
C	Ligand	w/w%	Numeric	7.50	10.00	12.50
D	IL	w/w%	Numeric	18.00	20.00	22.00

Table 2. Experimental runs for the central composite design

Standard order	Run	Block	A	B	C	D	Response (Slope)
21	1	Block 1	60.00	10.00	5.00	20.00	20.75
2	2	Block 1	62.50	9.00	7.50	18.00	18.25
29	3	Block 1	60.00	10.00	10.00	20.00	29.54
23	4	Block 1	60.00	10.00	10.00	16.00	17.00
30	5	Block 1	60.00	10.00	10.00	20.00	30.00
24	6	Block 1	60.00	10.00	10.00	24.00	28.60
8	7	Block 1	62.50	11.00	12.50	18.00	22.18
27	8	Block 1	60.00	10.00	10.00	20.00	30.00
5	9	Block 1	57.50	9.00	12.50	18.00	23.10
3	10	Block 1	57.50	11.00	7.50	18.00	19.23
6	11	Block 1	62.50	9.00	12.50	18.00	22.85
10	12	Block 1	62.50	9.00	7.50	22.00	24.73
15	13	Block 1	57.50	11.00	12.50	22.00	28.15
12	14	Block 1	62.50	11.00	7.50	22.00	26.00
11	15	Block 1	57.50	11.00	7.50	22.00	25.75
9	16	Block 1	57.50	9.00	7.50	22.00	25.88
4	17	Block 1	62.50	11.00	7.50	18.00	18.88
13	18	Block 1	57.50	9.00	12.50	22.00	29.58
25	19	Block 1	60.00	10.00	10.00	20.00	30.00
18	20	Block 1	65.00	10.00	10.00	20.00	24.50
26	21	Block 1	60.00	10.00	10.00	20.00	30.00
22	22	Block 1	60.00	10.00	15.00	20.00	27.75
19	23	Block 1	60.00	8.00	10.00	20.00	24.20
28	24	Block 1	60.00	10.00	10.00	20.00	30.00
7	25	Block 1	57.50	11.00	12.50	18.00	21.03
1	26	Block 1	57.50	9.00	7.50	18.00	20.00
20	27	Block 1	60.00	12.00	10.00	20.00	23.40
16	28	Block 1	62.50	11.00	12.50	22.00	29.90
14	29	Block 1	62.50	9.00	12.50	22.00	28.93
17	30	Block 1	55.00	10.00	10.00	20.00	24.50

Each experimental run was repeated three times, and the average of the results was selected as a response. An analysis of variance (one-way ANOVA) with a 95% probability was applied to evaluate the effect of the percentage of each compound on the CPE response for the determination of the analyte (Table 3). P-value is essential data to exam the significance of the factors and the model provided by the ANOVA test.

According to Table3, the amount of graphite powder in the CPE composition is not a significant factor, and the other main factors are significant. Also, the interaction between the amount of graphite and IL (AD) and the interaction between the amount of ligand and IL (CD) are two non-significant variables. Other factors and their interactions display a significant effect on the CPE composition. However, a factor is a significant variable in the design when its p-value is lower than α-level (0.05at 95% confidence level) [54]. Therefore, the suggested model is the significance because its p-value (< 0.0001) is lower than 0.05. Another parameter to evaluate the excellent fitting of the model with the responses in the ANOVA Table is Lack of Fit (LOF). When the p-value of LOF was more significant than the α-level (this parameter is not an important variable), then this suggests that the proposed model is well fitted to the responses.

Table 3. The obtained ANOVA from the central composite design

Source	Sum of Squares	df	Mean Square	F-Value	p-value
Model	495.5164	14	35.39403	301.7108	< 0.0001
A-Graphit	70.04167	1	70.04167	597.0591	0.5601
B-Nano	0.601667	1	0.601667	5.128812	0.0388
C-Ligand	0.041667	1	0.041667	0.355181	< 0.0001
D-Ionic Liquid	244.4817	1	244.4817	2084.045	< 0.0001
AB	1.1025	1	1.1025	9.398087	0.0078
AC	1.5625	1	1.5625	13.31928	0.0024
AD	0.1225	1	0.1225	1.044232	0.3230
BC	2.7225	1	2.7225	23.20752	0.0002
BD	0.7921	1	0.7921	6.752131	0.0202
CD	0.1225	1	0.1225	1.044232	0.3230
A^2	52.77258	1	52.77258	449.8515	< 0.0001
B^2	61.68	1	61.68	525.7814	< 0.0001
C^2	48.124	1	48.124	410.2255	< 0.0001
D^2	83.96	1	83.96	715.7038	< 0.0001
Residual	1.759667	15	0.117311		
Lack of Fit	1.583333	10	0.158333	4.489603	0.0556
Pure Error	0.176333	5	0.035267		
Cor Total	497.276	29			

According to Table 3, the p-value of LOF for the proposed model is 0.0556 indicating the model is adequately fitted with the responses. Also, a large amount of R-squared (0.9965), and in particular adjusted R-squared (0.9932), can also confirm that the model is well fitted to the responses. The obtained result showed that the predicted R-squared (0.9811) obtained for the model is high, and therefore, the model can well predict the responses for the changes in the significant factors without experimenting.

CCD can provide a mathematical equation to display the relationship between the significant factors and the obtained responses. For the purpose, several models such as linear, special cubic, and quadratic models can be applied. In the study, a quadratic model was used to describe this relationship because the model can express the relationship of responses to linear terms and binary interaction terms. The obtained mathematical equation is as follows Eq.1:

$$\text{Slope}=29.92+1.71A-0.16B-0.042C+3.19D-0.26AB+0.31AC+0.41BC$$
$$+0.22BD-1.39A^{2}-1.50B^{2}-1.32C^{2}-1.75D^{2}$$ **Eq. (1)**

The equation (Eq. 1) and results in Table 4 showed that the percentage of IL (D) in the sensor is the most important factor with a positive effect on the response because its regression coefficient value in the equation is the highest. The percentage of IL and ligand are the following important variables with a positive effect on the response, respectively. All interactions between two different factors (quadratics regression coefficients) have a high and positive effect on the response except for the interaction between the percentages of GO and ligand (BC) that has a negative effect. Due to the highest regression coefficient value for the interaction between the percentage of graphite powder and GO (AB), the interaction has the highest effect on the response with a positive effect in comparison with other interaction between two different factors. The results also display that the interactions between the same factors are more effective variables than the interactions between different factors because their regression coefficient values are higher the quadratics regression coefficient values. Also, all interactions between the same factors have negative effects on the responses. Several typical graphs of the simultaneous effects of the two variables on the response are shown in Fig. 2.

Table 4. The estimated coefficients of the quadratic model for the determination of Sr(II)

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	29.92333	1	0.139828	29.6253	30.22137	
A-Graphit	1.708333	1	0.069914	1.559315	1.857351	1
B-Nano	-0.15833	1	0.069914	-0.30735	-0.00932	1
C-Ligand	-0.04167	1	0.069914	-0.19068	0.107351	1
D-Ionic Liquid	3.191667	1	0.069914	3.042649	3.340685	1
AB	-0.2625	1	0.085627	-0.44501	-0.07999	1
AC	0.3125	1	0.085627	0.129991	0.495009	1
AD	0.0875	1	0.085627	-0.09501	0.270009	1
BC	0.4125	1	0.085627	0.229991	0.595009	1
BD	0.2225	1	0.085627	0.039991	0.405009	1
CD	0.0875	1	0.085627	-0.09501	0.270009	1
A^2	-1.38708	1	0065399	-1.52648	-1.24769	1.05
B^2	-1.49958	1	0.065399	-1.63898	-1.36019	1.05
C^2	-1.32458	1	0.065399	-1.46398	-1.18519	1.05
D^2	-1.74958	1	0.065399	-1.88898	-1.61019	1.05

In each graph, the simultaneous changes of the two factors on the response are examined, while the other two factors are in the central point value. According to Fig. 2A, the response was increased with an increasing the amount of IL and GO up to 20.41 and 10.50, respectively, and was decreased afterward. Besides, a dramatically increase in the response was displayed by the simultaneous increasing the amount of Ligand (up to 10.58) and GO (up to 10.50), while a slight increase in the electrode response was presented by the simultaneous increasing the amount of Ligand (up to 10.58) and IL (up to 20.41). However, the response was reduced for more amount of these factors (Fig. 2B and C). Optimization of the percentage of each compound in the sensor was determined using the proposed model in the design. A target response (Slope 29.55) was chosen as the goal. Therefore, the optimal percentage of each compound in the sensor was selected: graphite powder, 59.30%; GO, 10.50%; ligand, 10.58%; IL, 20.41%. Moreover, indicating that the desired response (slope) can be well achieved using the optimal percentage of each compound obtained in the model.

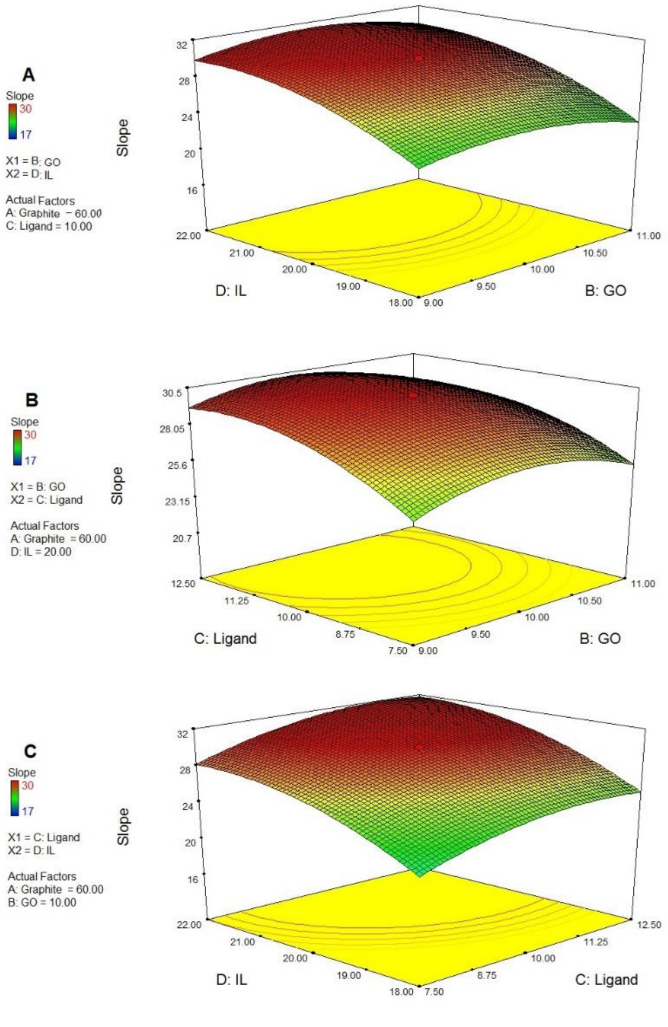


Fig. 2. 3D graphs of the simultaneous effects of the two variables on the response

3.2. Effect of pH on CPE electrode response

The pH of sample solution was changed in the range of 2-12 by addition of HNO_3 (0.1 M) or NaOH (0.1 M) while the electrode potential was measured for 1.00×10^{-3} M of Sr(II) solution to study the pH effect on the electrode response. The results are presented in Fig. 3, indicating the electrode potential remained constant in the pH range of 3–9.5. Therefore, the electrode worked well in the pH range without any interference of H^+ and OH^- ion. However, a decrease in the electrode potential at pH>10 can be due to form an insoluble complex between Sr(II) ion and hydroxyl ion in the sample solution such as $Sr(OH)^+$ and $Sr(OH)_2$ and reduce interaction between the formation complex and the ionophore. Based on the obtained results, the electrode can be applied to determine Sr(II) ion in an extensive range of pH.

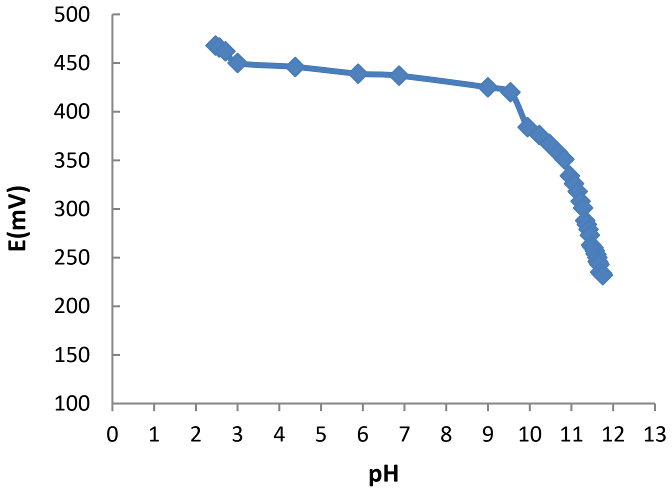


Fig. 3. Effect of pH on the electrode potential for the determination of the Sr(II) ion

3.3. Response time and Lifetime of the CPE electrode

The response time of the potentiometric electrode is an essential parameter in its practical application for the determination of the analyte. The practical response time is defined as the necessary time to achieve 90% of the final steady potential value of the sensor that immersed successively in the sample solution with a 10-fold difference in analyte concentration [26]. Therefore, The practical response time for the CPE sensor was studied by changing the Sr(II) concentration in the range of 1.00×10^{-8} to 1.00×10^{-1} M, and the results were presented in Fig. 4. According to the obtained results in Fig. 4, the practical response time of about 10 S was obtained to determine the Sr(II) ion indicating the sensor reaches the equilibrium value in a short time, and its response rate is very high in the analyte measurements.

Another important parameter that plays a fundamental role in the potentiometric sensor application for the determination of Sr(II) is the sensor lifetime. The sensor lifetime is defined as the time between the electrode membrane preparation and the change in at least one of the properties of the electrode potential response. For the purpose, the modified CPE was used to measure the standard solutions of analyte weekly over 2 months. After each use of the electrode, it was washed with deionized water and dried and stored at room temperature. The results showed that no significant change in the electrode performance was observed and the electrode potential was stable for 8 weeks. A slight decrease in the electrode potential occurred after eight weeks and as a result, a decrease was observed in the sensor slope, indicating the lifetime of the electrode was more than 8 weeks.

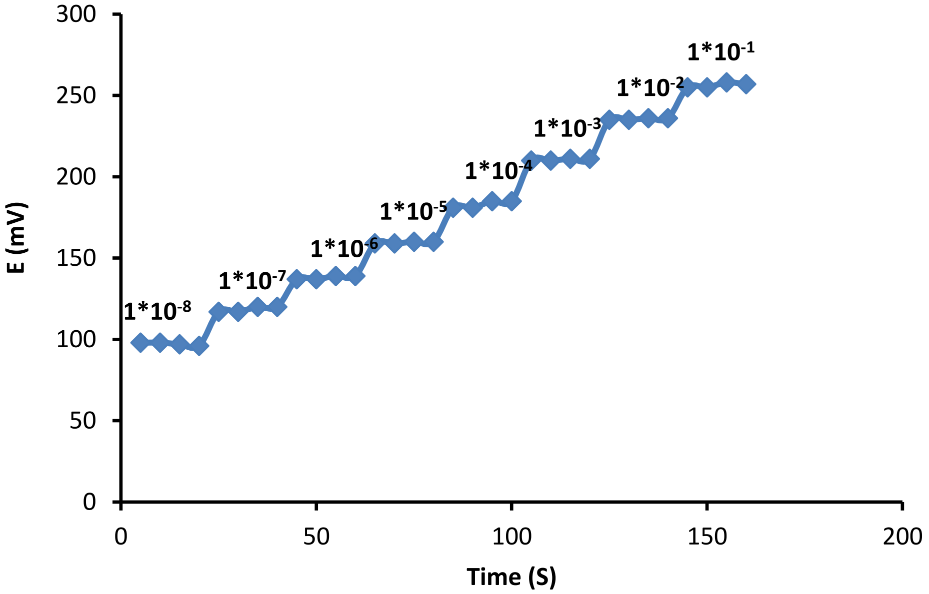


Fig. 4. Response time of the proposed sensor for the determination of the Sr(II) ion

3.4. Limit of detection and linear dynamic range

The linear dynamic range of the proposed electrode was evaluated by the determination of Sr(II) in different concentrations of the analyte under the optimum conditions. The electrode response was linear in the concentration range of 1×10^{-8}–1.00×10^{-1} M for determination of Sr(II) with a calibration equation of y= -29.80 x + 480 and R^2= 0.98, within the Nernstian slope of -29.80±0.3 mV $decade^{-1}$ at 25±1 °C (Fig. 5).

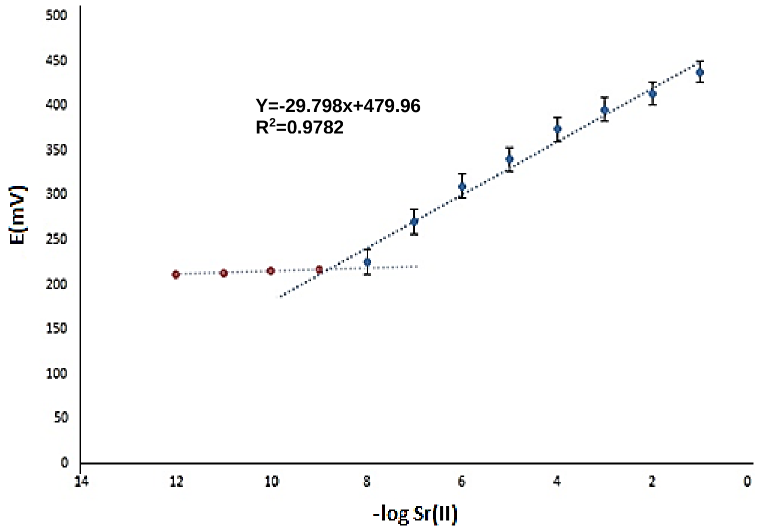


Fig. 5. Calibration curve of the proposed sensor for the determination of the Sr(II) ion

Therefore, the suggested sensor represents a near-Nernstian behavior for the determination of the analyte. The detection limit of the recommended sensor was obtained from the calibration curve extrapolation and was 1.16×10^{-9} M.

3.5. Repeatability and Reproducibility

To determine the repeatability of the sensor, a standard solution of Sr(II) (1.0×10^{-3} M) was measured for three repetitions with the proposed sensor under the optimum conditions, and the relative standard deviation (RSD) was calculated to be 1.01%. The reproducibly of the sensor was studied by preparation of several sensors (three) with the optimal composition. The preparation sensors were used to measure the concentration of Sr(II) (1.0×10^{-3} M), and the average of the slope was obtained to be 29.52 ± 0.3 mV decade^{-1} (Fig. 6).

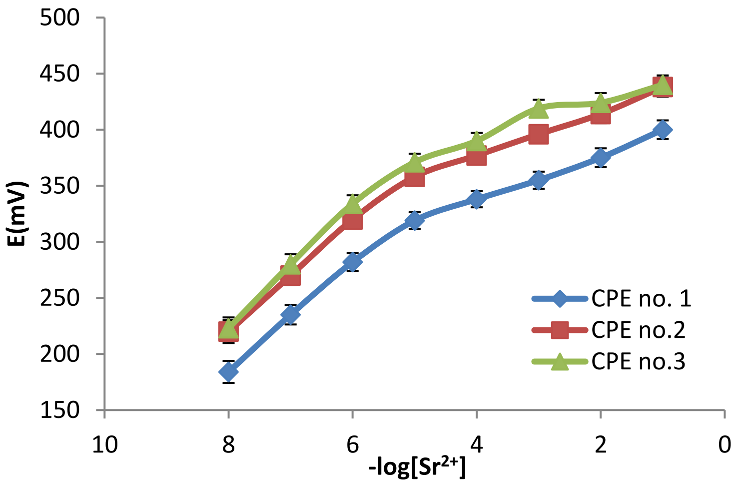


Fig. 6. The sensor reproducibly for the determination of the Sr(II) ion

3.6. Selectivity and interference studies

The electrode selectivity is a critical parameter, which indicates the ability of the electrode for the measurement of an analyte with high accuracy in the presence of interfering ions. The effects of various metal ions in the determination of Sr(II) with the proposed sensor was investigated under the optimum conditions. The selectivity coefficient was calculated using Matched potential (MPM) method. Based on this method, in the first stage, the determined concentration of the primary ion is added to the reference solution of Sr(II) (1.0×10^{-4} M), and the potential amount is determined. In the second stage, interfering ions (X) in the concentration range of 1.0×10^{-5} to 1.0×10^{-1} M are added to an identical reference solution step by step until the potential changes are comparable to the previous solution. K_{MPM} Sr(II), X will be counted as the following Eq. 2:

$$K_{Sr(II),x}^{MPM} = \frac{a_{Sr(II)}}{a_x} \qquad \textbf{Eq. (2)}$$

where $a_{Sr(II)}$ and a_x are the activity of Sr(II) and interfering ion, respectively. The obtained results were shown in Table 5, confirming the proposed sensor has high selectivity response to measure the Sr(II) concentration toward interfering metal ions.

Table 5. Selectivity coefficients of interfering ions on the proposed sensor for the determination of Sr(II)

Interfering ion (x)	$K_{Sr(II),x}^{MPM}$
Zn^{2+}	1.8×10^{-3}
Pb^{2+}	7.8×10^{-4}
Cd^{2+}	1.3×10^{-3}
Mg^{2+}	3.0×10^{-4}
Ni^{2+}	7.6×10^{-3}
K^{+}	5.2×10^{-3}
Al^{3+}	3.4×10^{-2}
Cr^{3+}	3.1×10^{-3}
Fe^{2+}	1.4×10^{-3}

3.7. Potentiometric titration method

The proposed sensor, as the indicator electrode was applied for the potentiometric titration of standard analyte solution with EDTA standard solution while an Ag/AgCl electrode, was selected as the reference electrode.

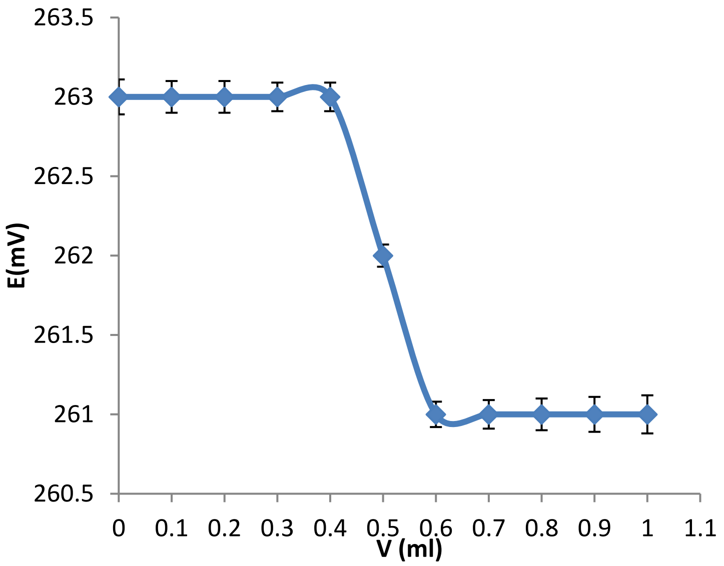


Fig. 7. The potentiometric titration curve of 5.0 mL 1.0×10^{-3} M of $Sr(NO_3)_2$ solution with standard EDTA solution (1.0×10^{-2} M)

For the purpose, (5.0 mL, 1.0×10^{-3} M) titrated with standard EDTA solution (1.0×10^{-2} M). The titration curve was represented in Fig. 7. The concentration of the free analyte in the solution decreases due to the formation of the complex with the EDTA solution with adding the titrant to the analyte solution, which, as a result, reduces the electrode potential. These potential changes are severe around the equivalence point, which indicates the successful behavior of the sensor in determining the Sr(II) ion in the potentiometric titration method. Also, a good the endpoint break was obtained in the curve which can be applied well to determine the endpoint volume and the analyte concentration.

3.8. Real sample analysis

Depilatory powder (Royder, Shghayegh Talaee Chehelsoton Co., Esfahan, Iran), raticide sample (roeodfin cebo fresco no 200A), and toothpaste (Crest, American multinational Procter & Gamble) as real samples were purchased from a drugstore in Mashhad, Iran. The depilatory powder was disintegrated to a fine homogeneous powder in a mortar. The powder (0.100 g) was weighed accurately and dissolved of hydrochloric acid. The resulting solution was transferred into a volumetric flask and diluted to *100.*0 *ml* with distilled water. The raticide sample (0.100g) and the toothpaste sample (0.500g) were individually dissolved in 35.0 mL of a solution of HCl and HNO_3 (3:1 V/V) and diluted to 100.0 ml with distilled water, respectively.

All obtained solutions were spiked at two concentrations of Sr(II) standard solution (1.0 and 4.0 mg L^{-1}) before analysis. The resulting solutions were titrated with EDTA (0.1 M) for determination of Sr(II) ion. Each experiment was repeated three times to obtain the response. Besides, all real samples were analyzed to determine the Sr(II) content with inductively coupled plasma (ICP) method. The obtained results are presented in Table 6. Comparison of ICP and sensor results showed that the results do not display significantly different and so the proposed sensor can be successfully used to the determination of Sr(II) in the real sample with a meager price and a suitable relative standard deviation (RSD) of less than 5.5%.

Table 6. Determination of Sr(II) ions in the real samples (n=3)

Sample	**Added (mg L^{-1})**	**CPE sensor**		**ICP**	
		Found (mg L^{-1})	Recovery%	Found (mg L^{-1})	Recovery%
Depilatory powder	0.0	22.7±0.9	----	22.6±0.9	----
	1.0	22.7±0.8	95.7%	23.6±0.9	100%
	4.0	28.7±0.9	100%	28.6±2.3	107%
Crest toothpaste	0.0	$(1.8\pm0.2)*10^{-2}$	---	$(1.6\pm0.1)*10^{-2}$	---
	$2.5*10^{-2}$	$(0.4.2\pm0.3)*10^{-2}$	100%	$(4.1\pm0.1)*10^{-2}$	100%
	$6.5*10^{-2}$	$(8.5\pm0.5)*10^{-2}$	101%	$(8.2\pm0.1)*10^{-2}$	101%
Raticide	0.0	$(0.6\pm0.3)*10^{-2}$	---	$(0.6\pm0.1)*10^{-2}$	---
	$3.7*10^{-2}$	$(4.2\pm0.2)*10^{-2}$	97.6%	$(4.2\pm0.1)*10^{-2}$	97.6%
	$8.0*10^{-2}$	$(8.5\pm0.2)*10^{-2}$	98.8%	$(8.7\pm0.2)*10^{-2}$	101%

4. CONCLUSION

A modified CPE as a novel and sensitive indicator electrode was developed to measure the concentration of Sr(II). For this purpose, a synthetic ligand ((E)-4-(((2-amino-4-chlorophenyl)imino)methyl)-5-(hydroxymethyl)-2-methyl pyridine-3-ol) as an efficient ionophore, an ionic liquid (1-Butyl-3-methylimidazolium hexafluorophosphate) as a suitable binder, graphene oxide, and graphite powder was used as electrode compositions for preparing the electrode. The central composite design was generated to optimize the percentage of electrode compositions. The proposed electrode showed constant and quantitative potential in the pH range of 3–9.50. Also, the electrode response was linear in the concentration range of 1×10^{-8}–1.0×10^{-1} M for determination of Sr(II) with a calibration equation of y=-29.80 x+480and R^2=0.98 at 25±1 °C. Use of IL and synthetic ligand in the electrode composition have enhanced the selectivity and stability of the electrode for the determination of the analyte. A low detection limit (1.59×10^{-9} M) and suitable relative standard division (1.01 %) was obtained. Finally, the suggested method was successfully used to measure the Sr(II) ion for the depilatory powder, toothpaste, and raticide samples with high recovery (> 97.6).

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