Iranian Journal of Analytical Chemistry
Volume 3, Issue 2, September 2016 (96-104)

مجله ایرانی شیمی تجزیه
دوره ۳، شماره ۲، مهر ماه ۱۳۹۵ (۱۰۴-۹۶)

بهینه‌سازی الکترود یون‌گزین سرب با استفاده از روش طرح ترکیب مرکزی و مطالعه رفتار آن با اسپکتروسکوپی امپدانس الکتروشیمیایی

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تاریخ دریافت: ۱۹ مهر ۱۳۹۵ **تاریخ پذیرش:** ۲۵ مهر ۱۳۹۵

Optimization of Lead-Selective Membrane Electrode Using Central Composite Experimental Design, and Study of Its Behavior with Electrochemical Impedance Spectroscopy

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Received: 10 October 2016 **Accepted:** 16 October 2016

چکیده

در این کار روش سطح پاسخ همراه با روش طرح ترکیب مرکزی برای شبیه‌سازی و بهینه‌سازی اثر برخی متغیرها (مقادیر پلی‌وینیل‌کلرید، یونوفر، افزودنی و نرم‌کننده) بر عملکرد الکترود یون‌گزین سرب استفاده شده است. شیب ۲۹/۱ میلی‌ولت در مقادیر بهینه از پلی‌وینیل‌کلرید (۰/۰۲۸۳ گرم)، یونوفر(۰/۰۰۷۴ گرم)، افزودنی (۰/۰۰۲ گرم) و نرم کننده (۰/۰۶۰ گرم) به دست آمد. محدوده خطی غلظت $۱/۰×۱۰^{-۵}$–$۱/۰×۱۰^{-۱}$ مولار با روش پتانسیومتری برای سرب بدست آمد. تکنیک اسپکتروسکوپی امپدانس الکتروشیمیایی برای ارزیابی مکانیسم پاسخ الکترود بکار برده شد. نتایج بدست آمده از اسپکتروسکوپی امپدانس الکتروشیمیایی محدوده خطی غلظتی از $۱/۰ ×۱۰^{-۶}$ تا $۱/۰×۱۰^{-۱}$ مولار را نشان می‌دهد. همچنین در مقایسه با روش پتانسیومتری محدوده pH بدست آمده از ۳ تا ۵/۵ به مقدار ۲/۵ تا ۶/۰ افزایش پیدا کرد.

واژه‌های کلیدی

الکترود یون‌گزین؛ غشا پلی‌وینیل‌کلرید؛ یونوفر؛ روش سطح پاسخ؛ طرح ترکیب مرکزی.

Abstract

In this work, response surface methodology in conjunction with central composite design for modeling and optimization of the influence of some process variables (polyvinyl chloride (F_1), ionophore (F_2), additive (F_3) and plasticizer (F_4) amounts), on the performance of polyvinyl chloride membrane lead (II) ion-selective electrode is discussed. The slope of 29.1 ± 0.1 mV at the optimal amounts of polyvinyl chloride (0.0283 g), ionophore (0.0074 g), additive (0.002 g) and plasticizer (0.060 g) has been achieved. The electrode exhibited a linear potential response to lead (II) in the concentration range of 1.0×10^{-5} mol L^{-1} to 1.0×10^{-1} mol L^{-1} over pH range of 3.0 - 5.5. Greatly, the alternating current impedance technique was applied to investigate the response mechanism of the electrode. The results were obtained from electrochemical impedance spectroscopy shows a linear concentrations range of 1.0×10^{-6} mol L^{-1} to 1.0×10^{-1} mol L^{-1} and in comparison with potentiometry, the pH range increased to 2.5 − 6.0.

Keywords

Ion-Selective Electrode; Polyvinyl Chloride Membrane; Ionophore; Response Surface Methodology; Central Composite Design.

1. INTRODUCTION

Heavy metals present in industrial effluents remain as alarming pollutants due to their nondestructive nature, toxicity, bioaccumulation

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*Corresponding Author: mazloum@yazd.ac.ir and subsequent biomagnifications [1]. Lead is one out of four metals that have the most damaging effects on human health. It is a widespread used toxic metal that has caused extensive environmental contamination and health problems in many parts of the world. The World Health Organization (WHO) stated a legal limit of 50 ppb for lead in 1995 [2], which is decreased to 10 ppb in 2010. It can enter the human body through uptake of food (65%), water (20%) and air (15%). As a result; the need for reducing the use and releases of lead to reduce environmental and occupational exposures, particularly for children and women at child-bearing ages. Accordingly, several instrumental methods including graphite furnace atomic absorption, inductively coupled plasma mass spectroscopy, voltammetery and choronoamperometry have been developed for lead detection [3]. Potentiometric sensors (e.g. ion selective electrodes) are alternative suitable tool for accurate, reproducible and selective metal ion determination. Ideally, potentiometric sensors detect the ion activity in the sample [4]. Liquid-membrane electrodes, based on a polymeric membrane impregnated with water-immiscible liquid substances, are widely used for direct potentiometric measurements of several polyvalent cations (e.g. Cu^{+2}, Pb^{+2} and Zn^{+2}) and anions (e.g. SCN^-, Sal^- and SO_4^{-2}) [5–7].

It is known that the nature and amount of the additive strongly influence the response of the ion-selective sensors, such as reducing the matrix resistance, improving the response behavior and selectivity and in some cases, where the extraction capability is poor, increase the sensitivity of the sensors. For ionophores that operate via a charged carrier mechanism, the addition of small amounts of negative site in the membrane will improve the selectivity of electrode [8].

The parameters which influence electrode response significantly are the quantity of polyvinyl chloride (PVC), ionophore, additive and plasticizer. Improving the performance of a system, a process, or a product and increasing the yield of the process without increasing the cost and obtaining the maximum benefit from it, is important. The method used for this purpose is optimization. Applications of response surface methodology (RSM) [9] in the optimization of analytical procedures are today largely diffused and consolidated principally [10-11]. This technique has several advantages over one-variable-at-a-time method including a reduced number of experiments, time consuming, cost-effective, and possibility of evaluating interactions among variables and generation of large amounts of information from a small number of experiments [12]. In order to use this methodology in experimental optimization, selecting an experimental design to fit a relevant mathematical function, and to estimate the quality of the fitted model is essential. Here, a central composite experimental design (CCD) was applied.

Electrochemical impedance spectroscopy (EIS) is a powerful, informative and nondestructive tool for the electrical characterization of sensor membranes [13-14].

The great advantage of impedance measurements over other techniques commonly used in electrochemistry is that high quality results can be achieved using signals of very low amplitude which only cause very small perturbations to the system under study [15-16]. In most electrochemical methods, studying electrode reactions, takes place through creating a large perturbations by imposing potential sweeps, potential steps, or current steps on the system. In this case, the electrode drives to a condition far from equilibrium and the response, which is usually a transient signal, observes. Using an alternating signal of small magnitude creates a perturbation at steady state in system which has many advantages, as; high-precision measurements, ability to treat the response theoretically by linearized current-potential characteristics, and measurement over a wide time or frequency range. Nowadays, electrochemical impedance spectroscopy applied as a powerful tool for studying the mechanisms of electrochemical reactions, measuring the dielectric and transport properties of materials, exploring the properties of porous electrodes, and investigating passive surfaces [17–20].

The main objective of this work was to achieve the best Nernstian slope at optimum conditions consisting of the amount of PVC, ionophore, additive, and plasticizer. Therefore, the second order central composite design was employed to determine the optimum value of factors (amount of PVC, ionophore, additive and plasticizer) which affect the lead electrode response. After obtaining the optimum values, the electrode with the best Nernstian slope was fabricated and the response mechanism of the proposed electrode was explored by potentiometry and EIS.

2. EXPERIMENTAL

2.1. Apparatus

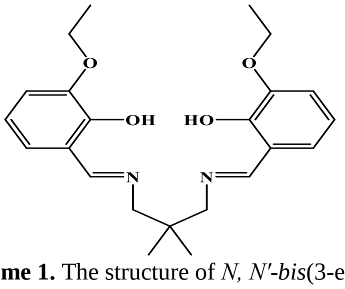
Potentiometric measurements were done using a Metrohm 480 pH/mV meter. EIS data were obtained using PGSTAT 302 Autolab (Eco Chemie B.V., Utrecht, Netherlands) potentiostat/galvanostat controllers with FRA software. The electrochemical cell was assembled using a conventional three-electrode system: an Ag/AgCl electrode (Metrohm Co., Netherlands) as reference electrode, the lead-selective electrode as working electrode, and a platinum electrode (Azar Electrode, Iran) as counter electrode.

2.2. Reagents

High relative molecular weight PVC (polyvinyl chloride), dioctyl phthalate (DOP), dibuthyl phthalate (DBP), tetrahydrofuran (THF), nitrate salts of all the cations, and all other chemicals were purchased from Merck. Sodium tetraphenylborate (NaTPB) were used as received from Aldrich. The Schiff base ligand N, N′-bis (3-etoxy salicyliden)-2, 2-dimethyl-1, 3-propane diamine was used as the ionophore. Doubly distilled water was used for preparing all solutions. The pH adjustments were made with dilute nitric acid and sodium hydroxide solutions as required.

2.3. Synthesis of ionophore

The ligand was synthesized by adding 3-ethoxy-salicylaldehyde (4 mmol) to a solution of 2,2-dimethyl-1,3-propanediamine (2.0 mmol) in ethanol (20 ml). The mixture was refluxed with stirring for half an hour. The resultant yellow solution was filtered. Yellow single crystals of the ligand were recrystallized from ethanol by slow evaporation of the solvents at room temperature over several days [21]. The structure of ionophore was given in Scheme 1.



Scheme 1. The structure of *N, N′-bis*(3-etoxy salicyliden)-2,2-dimethyl-1,3-propane diamine.

2.4. Electrode preparation

To obtain the best conditions in the preparation of the electrode, we optimized the ratio of PVC, ionophore, additive and plasticizer. The optimum conditions obtained, are: PVC (0.0283 g), ionophore (0.0074 g), additive (0.002 g) and plasticizer (0.060 g). The mixture of ionophore, plasticizer and additive were dissolved in minimum amount of THF. Also, PVC was dissolved in THF, separately and was added to the mixture. By stirring the mixture, THF was evaporated and an oily liquid was obtained. Then a polymeric tube with 2 mm diameter was dipped into the solution for 10s and left it for 4h for drying. Finally, the electrode was conditioned by soaking in 1.0 × 10^{-2} mol L^{-1} Pb^{2+} solution for 4h (1.0 × 10^{-2} mol L^{-1} Pb^{2+} solution was used for internal filling solution).

2.5. Potentiometric measurements

After conditioning the membrane electrode, the potentiometric measurements were carried out with the following cell assembly:

Ag, AgCl | KCl (satd.) || sample solution | PVC membrane | 0.01 M $Pb(NO_3)_2$ | SCE

All measurements were carried out while sample solution stirred.

2.6. Impedance measurements

Impedance measurements were undertaken in three electrode cell, equipped with an Ag/AgCl electrode as reference electrode, the lead-selective electrode as working electrode, and a platinum electrode as counter electrode. All measurements were done while sample solution was quite static. During an impedance measurement, a frequency response analyzer (FRA) is used to impose a small amplitude AC signal to the system. The response of the electrode is analyzed by the FRA to determine the impedance of the electrode at that particular frequency.

EIS spectra were collected at the open circuit potential (OCP) using an AC amplitude of 30 mV through a frequency domain from 40 KHz to100 Hz with 40 frequency points. The EIS spectra were fitted to the Randles circuit [22]. Data analysis for the impedance measurements were performed using the Z-View 2.1 software.

2.7. Design of experiment using central composite design

A four-factor, five levels central composite design was applied to determine the optimum value of factors which affect the lead electrode response. The range of values of each of the four independent variables (i.e. PVC (F1), ionophore (F2), additive (F3) and plasticizer (F4)) was defined as shown in Table 1. Furthermore, Table 2 shows the experimental design matrix derived from CCD.

Table 1. Independent variable and their levels for CCD.

Factor	Name	Factor Level				
		-2 (Low)	-1	0	+1	+2 (High)
F_1	PVC (mg)	28	31	34	37	40
F_2	Ionophore (mg)	2	3.5	5	6.5	8
F_3	NaTPB (mg)	2	3.5	5	6.5	8
F_4	DOP (mg)	60	62	64	66	68

Table 2. Central composite design consisting of experiments for the study of four experimental factors in coded levels with experimental results.

Run NO.	Coded level of variables				Response
	F_1	F_2	F_3	F_4	Slope / mV
1	0	-2	0	0	12
2	0	0	2	0	10
3	1	1	1	-1	12.6
4	-1	1	1	-1	25.5
5	-1	-1	-1	1	18.1
6	0	0	0	0	18.6
7	-1	-1	1	-1	21.1
8	1	1	-1	-1	15.9
9	0	0	0	-2	10.5
10	-1	-1	1	1	17
11	-1	1	-1	1	34.4
12	0	2	0	0	30.8
13	1	1	-1	1	29.7
14	1	-1	1	1	12.7
15	1	-1	-1	1	20.8
16	0	0	-2	0	16
17	-2	0	0	0	29
18	1	1	1	1	12.4
19	-1	-1	-1	-1	10
20	1	-1	-1	-1	7.2
21	-1	1	1	1	23.5
22	2	0	0	0	22.7
23	-1	1	-1	-1	25.9
24	0	0	0	0	17.5
25	0	0	0	0	16.5
26	1	-1	1	-1	20.56
27	0	0	0	2	19.77

The total number of design points is $N = 2^f + 2f + n_0$, including the 2^f factorial points, 2f star (axial) points at β distance ($\beta = 2^{f/4}$) from the center, and n_0 replicates at the center; where f is the number of independent variables. Here, the total number of experiments for the four independent variables is:

$$2^4 + (2 \times 4) + 3 = 27.$$

After obtaining data associated with each experimental point of a chosen design, it is customary to fit a mathematical equation to investigate the relationship between response and process variables. By RSM, a quadratic polynomial equation was used to predict the response. A second degree polynomial equation was obtained to estimate the response as a function of variables:

$$\text{Response} = b_0 + b_1F_1 + b_2F_2 + b_3F_3 + b_4F_4 + b_5F_1^2 + b_6F_2^2 + b_7F_3^2 + b_8F_4^2 + b_9F_1F_2 + b_{10}F_1F_3 + b_{11}F_1F_4 + b_{12}F_2F_3 + b_{13}F_2F_4 + b_{14}F_3F_4 \quad (1)$$

Where F_1, F_2, F_3 and F_4 are independent variables, b_0 the intercept coefficient, b_1, b_2, b_3, b_4 the linear terms, b_5, b_6, b_7, b_8 the squared terms, b_9, b_{10}, b_{11}, b_{12}, b_{13}, b_{14} represent the interaction terms. To evaluating the coefficients of the model, MLR which is a multiple regression technique, was used. The adequacy and significance of the model was justified through analysis of variance (ANOVA). The significant factors can be ranked by determining the probability level that F-statistic calculated from the data is less than %5. Generally, the fisher's $F_{\text{statistics}}$-value with low probability P-value indicates high significance of regression model. P-value represents the probability of incorrectly rejecting the null hypothesis and ranges from 0 to 1. A commonly used value is 0.05. If the P-value of a test statistic is less than 0.05, the null hypothesis is rejected.

In order to confirm the goodness of fit model, coefficient R^2 was determined, and three replicates at the center of design were used for investigation of error sum of square.

3. RESULT AND DISCUSSION

3.1. Study of ionophore and Pb^{2+} interaction

To gain an understanding of the interaction mechanism between ionophore and Pb^{2+} ion, UV-Vis spectroscopy and EIS were used. The Schiff base ligand N, N′-bis (3-etoxy salicyliden)-2, 2-dimethyl-1, 3-propane diamine was used as the ionophore. The structure of ionophore was given in Scheme 1.

The UV-Vis spectra of ionophore and the mixture solution of ionophore and Pb^{2+} ion were shown in Fig. 1 (A). The spectra of the ionophore show the absorption bands at 520 nm. In the presence of Pb^{2+} ion shift of about 15 nm in the peaks and decreasing in height was observed. It was suggested that the size of the complex increases on interaction of Pb^{2+} ion with the carrier. Therefore, a shift in the peaks wavelength and decreasing in height in the mixed ionophore and Pb^{2+} anion spectrum confirms the interaction of this ion with the desired complex. Impedance spectra of membrane with and without ionophore were shown in Fig. 1 (B). These measurements were carried out on the electrode with and without ionophore, and 1.0×10^{-2} mol L^{-1} solution of lead nitrate as the internal solution of the electrode.

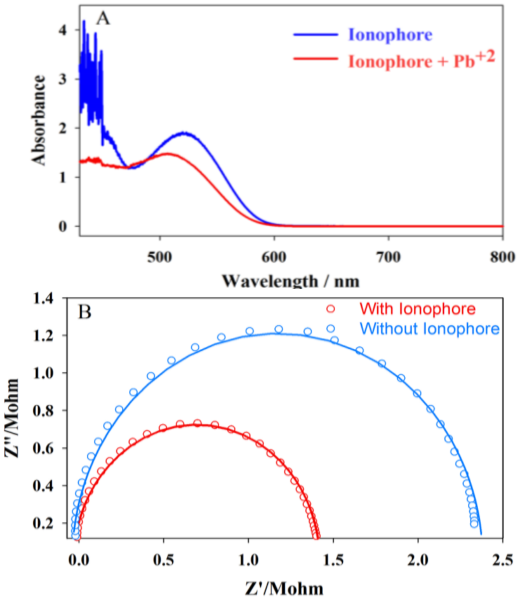


Fig. 1. (A) The UV/VIS absorption spectra of the ionophore 1.0×10^{-4} mol L^{-1} and mixture solution of ionophore 1.0×10^{-4} mol L^{-1} and $Pb(NO_3)_2$ 1.0×10^{-4} mol L^{-1}. (B) Complex plan plots of the membrane with and without ionophore. (Points and lines indicate the experimental and fitting data, respectively).

The results indicate that charge transfer resistance in presence of ionophore (1.449 Mohm) is smaller than its absence (2.420 Mohm), because the presence of ionophore increases electrical conductivity and hence the charge transfer resistance decreases. This explanation confirms the results obtained from the UV−vis studies.

3.2. Central composite experimental design

The Nernstian slope of 29.58 mV/decade was studied as response in order to optimize four independent variables, namely the amounts of PVC (polyvinyl chloride) (F_1), ionophore (F_2), DOP (dioctyl phthalate) as plasticizer (F_3) and NaTPB (Sodium tetraphenylborate) as additive (F_4). The results obtained from the CCD (see section 2.7.) were fitted to Equation 2 using Minitab.v.16 software. Empirical relationship between response and operational variables is the following:

$$\text{Slope} = 17.5333 - 1.1717 F_1 + 1.8758 F_2 - 0.5967 F_3 + 1.0079 F_4 + 0.5349 F_1^2 + 0.2568 F_2^2 - 0.2682 F_3^2 - 0.1347 F_4^2 - 0.5275 F_1F_2 - 0.2194 F_1F_3 + 0.1381 F_1F_4 - 0.7369 F_2F_3 + 0.1619 F_2F_4 - 0.9088 F_3F_4 \qquad (2)$$

The effects having P-values less than 0.05 indicate that the corresponding terms are significant. The adequacy of a regression model is sometimes assessed in terms of the proportion of variability in the response variable that is explained by the model. This proportion, which is the ratio of the model sum of squares to the sum of squares total, is called the coefficient of multiple determination, or the R^2-value. The model adequacy was tested by R^2, adjusted-R^2, predicted-R^2 and prediction error sum of squares (PRESS). A good model will have a predicted R^2 close to one and a low PRESS [23]. The values of R^2, adjusted-R^2 and predicted-R^2 are respectively 96.66%, 92.76% and 81.34%. The R^2 value of 96.66% which is closer to the unity indicates a satisfactory adjustment of the quadratic model to the experimental data and the correlation is best suited for predicting. The predicted responses were plotted versus the experimental one (Fig. 2) which presents the predicted values are very close to experimental results and the residual values are low.

Also Table 3 shows the analysis of variance (ANOVA) for equation 2. The fitted model was presented that the F_1, F_2, F_3, F_4, F_1^2, F_2^2, F_3^2, F_1F_2, F_2F_3, F_3F_4 affect the response of the electrode significantly.

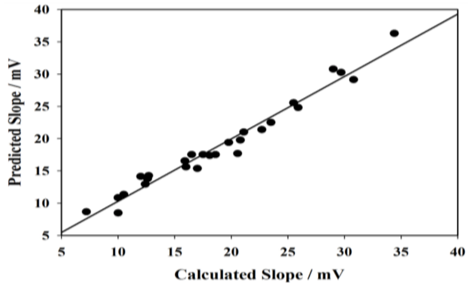


Fig. 2 Relation between experimental and predicted slope values using Equation 2.

Residual sum of squares (SSR) is the residual variation which measures the variation which cannot be explained by the regression line. When replicate measurements are available SSR can be separated into (a) a component which measures the variation due to pure experimental uncertainty (pure error sum of squares, SS_{PE}) and (b) a component which measures the variation of the group means, $\hat{y}_i$, about the regression line (sum of squares due to lack-of-fit, SS_{LOF}) [24]. All this can be arranged in an ANOVA table (Table 3) in which the mean squares, MS, are as always obtained by dividing the sums of squares, SS, by their corresponding degrees of freedom (DF).

The lack-of-fit test is a one-sided test that is performed by comparing the ratio $F = MS_{LOF}/MS_{PE}$ with the F-distribution at corresponding degrees of freedom and assess the fit of the model. If the P-value is less than selected P-level (0.05), evidence exists that the model does not accurately fit the data and may need to add terms or transform data to more accurately model the data. In this study the proposed model accurately fits the data (Table 3).

Table 3. ANOVA for response surface quadratic model (response: Nernstian slope).

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	1260.36	1260.36	90.026	24.78	0.000
Linear	4	601.29	601.29	150.323	41.38	0.000
F_1	1	131.79	131.79	131.789	36.27	0.000
F_2	1	337.80	337.80	337.800	92.98	0.000
F_3	1	34.18	34.18	34.177	9.41	0.010
F_4	1	97.53	97.53	97.526	26.84	0.000
Square	4	213.50	213.50	53.376	14.69	0.000
$F_1 * F_1$	1	135.80	97.68	97.679	26.89	0.000
$F_2 * F_2$	1	52.36	22.51	22.514	6.20	0.028
$F_3 * F_3$	1	19.14	24.55	24.548	6.76	0.023
$F_4 * F_4$	1	6.20	6.20	6.197	1.71	0.216
Interaction	6	445.56	445.56	74.260	20.44	0.000
$F_1 * F_2$	1	71.23	71.23	71.234	19.61	0.001
$F_1 * F_3$	1	12.32	12.32	12.320	3.39	0.090
$F_1 * F_4$	1	4.88	4.88	4.884	1.34	0.269
$F_2 * F_3$	1	139.00	139.00	139.004	38.26	0.000
$F_2 * F_4$	1	6.71	6.71	6.708	1.85	0.199
$F_3 * F_4$	1	211.41	211.41	211.412	58.19	0.000
Residual Error	12	43.60	43.60	3.633	-	-
Lack-of-Fit	10	41.39	41.39	4.139	3.75	0.229
Pure Error	2	2.21	2.21	1.103	-	-
Total	26	1303.9	-	-	-	-

3.3. Response surface and determination of optimal conditions

RSM was used to obtain the factors values that optimize the response function. To illustrate the effects of the independent variables and interactive effects on the response, response surface plots were employed. The response surface plot is the theoretical 3-dimensional plot showing the relationship between the response and the independent variables. 3-D graphs were drawn by considering pair-wise combination of four factors, while keeping the others at the central (0) levels. In order to calculate the optimal points, the first derivative of the mathematical function, which describes the response surface, was equaled to zero.

3.4. The influence of concentration of internal solution

The effect of the concentration of internal solution (1.0 × 10^{-2} mol L^{-1}, 1.0 × 10^{-4} mol L^{-1}, 1.0 × 10^{-5} mol L^{-1} and 1.0 × 10^{-6} mol L^{-1} $Pb(NO)_3$) on the sensor response was investigated. The potentiometric results as shown in Fig. 3 (A) demonstrate that the concentration of internal solution doesn't cause any considerable effect on Nernstian slope and linear range of electrode response. The electrode exhibited a linear potential response to lead (II) in the concentration range of 1.0 × 10^{-5} mol L^{-1} to 1.0 × 10^{-1} mol L^{-1} with the slope of 29.1 mV.

To investigate the influence of the concentration of internal solution on the electrode impedance spectra, the measurements were carried out for concentration of 1.0 × 10^{-4} mol L^{-1}, 1.0 × 10^{-5} mol L^{-1}, and 1.0 × 10^{-6} mol L^{-1} lead nitrate.

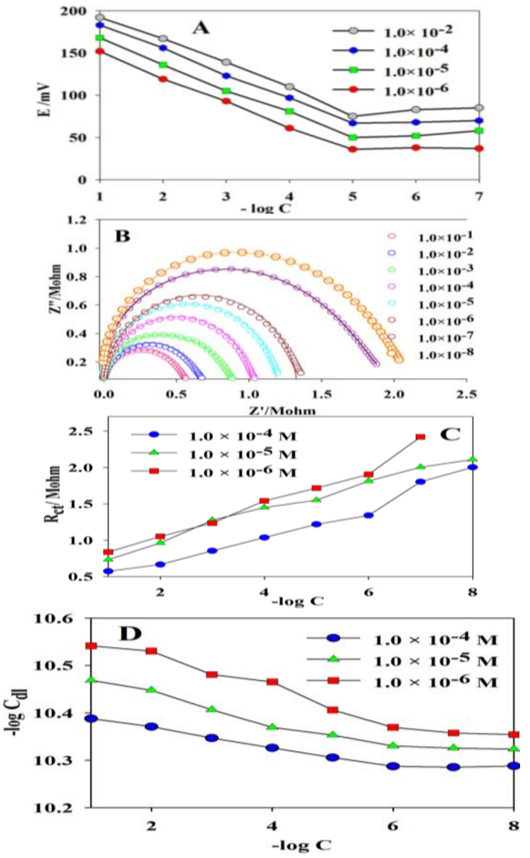


Fig. 3. (A) The effect of the concentration of the internal solution of the Pb^{+2} selective electrodes on the potential response of the electrode. (B) Complex plan plots of the electrode with an internal solution of 1.0 × 10^{-4} mol L^{-1}, $Pb(NO)_3$. (C) The influence of the internal solution concentration on R_{ct}. (D) The influence of the internal solution concentration on C_{dl}.

The obtained results indicate that the linear range becomes wider, namely a linear range from 1.0 × 10^{-1} to 1.0 × 10^{-6} mol L^{-1} was obtained. And with the concentration of 1.0 × 10^{-4} mol L^{-1} $Pb(NO_3)_2$, the electrode has more regular behavior and R_{ct} decreases. Furthermore, the diagrams of the R_{ct} and −log C_{dl} versus the −logarithm of the $Pb(NO_3)_2$ concentration for different concentrations of the internal solution are presented in Figure 3 (B). As a result, the detection limit reduces to about 1.0 × 10^{-6} mol L^{-1}.

3.5. The influence of pH

The dependence of potential response of the electrode on the pH of test solutions has been examined in the pH range of 1.5 - 10.0 at two concentrations (1.0 × 10^{-2} and 1.0 × 10^{-4} mol L^{-1} Pb (II) solutions) with an internal solution concentration of 1.0 × 10^{-4} mol L^{-1}. The potential of the electrode was determined as a function of pH and the results presented in Figure 4 (A).

The potential is independent of pH over the range of 3.0 - 5.5. Outside this range, considerable potential changes were seen. At pH higher than 5.5, the change of potential may be related to lead hydroxide formation, and at pH lower than 3.0, the potential deviation is due to the response of electrode to hydrogen ions.

Also, the effect of pH on the response of the sensor was investigated using EIS, at two concentrations (1.0 × 10^{-2} and 1.0 × 10^{-4} mol L^{-1} Pb (II) solutions). For example, the Nyquist plots related to 1.0 × 10^{-4} mol L^{-1} Pb (II) are given in Figure 4 (B), which implies that over a wide pH range any considerable change observes in the impedance spectra. In order to more study, R_{ct} and –Log C_{dl} versus pH changes were plotted in Figure 4 (C and D), which indicates the possibility of Pb^{+2} ions measurement over a pH range of 2.5 - 6.0.

3.6. Selectivity of the electrode

Selectivity is clearly one of the most important characteristic of a sensor as it often determines whether a reliable measurement in target sample is possible [25]. The selectivity coefficients (K_{ij}) for a variety of cations were tested using the separate solution method (SSM) and fixed interference method (FIM). The selectivity coefficients toward lead (II) are presented in Table 4. Results show a good selectivity of the prepared ISEs over most ions tested. It was found that Cu^{2+} and Zn^{2+} cause a little interference.

In this study, the newly PVC-based lead ion-selective electrode was prepared, and in order to optimize the membrane components, a central composite experimental design was employed.

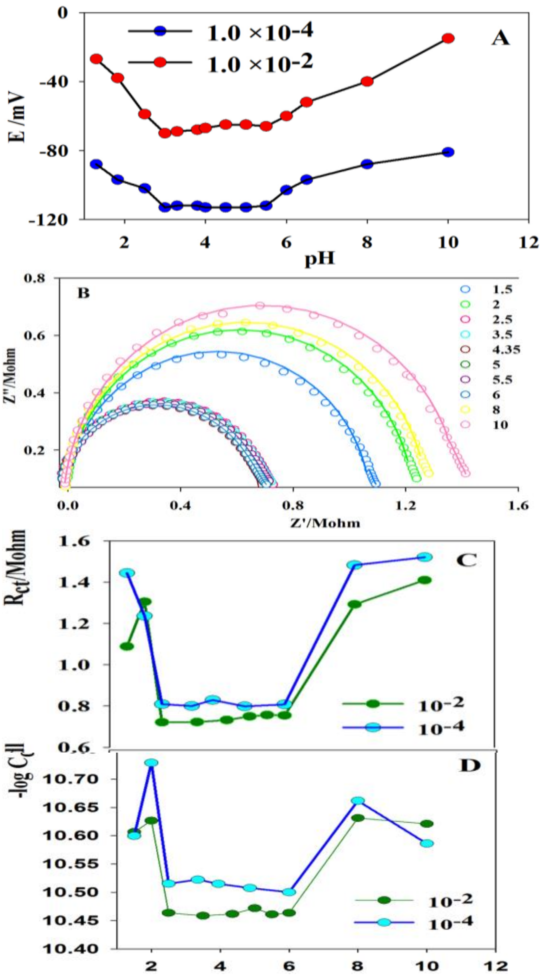


Fig. 4. (A) Effect of pH in response of Pb^{2+}- ISE at 1.0 × 10^{-2} and 1.0 × 10^{-4} mol L^{-1} $Pb(NO_3)_2$. (B) Complex plan plots of the Pb^{2+}- ISE at different pH values with an external solution concentration of 1.0 × 10^{-4} mol L^{-1} $Pb(NO_3)_2$. (C) The influence of the pH changes on the R_{ct}. (D) The influence of the pH changes on the C_{dl}.

Table 4. Selectivity coefficients for Pb (II) ion-selective electrode.

Interference ion	K^{pot} (FIM)	K^{pot} (SSM)
Co^{2+}	5.32 × 10^{-3}	5.49 × 10^{-3}
Cd^{2+}	3.65 × 10^{-3}	2.46 × 10^{-3}
Ni^{2+}	5.14 × 10^{-3}	7.19 × 10^{-3}
Cu^{2+}	1.56 × 10^{-2}	2.21 × 10^{-2}
Hg^{2+}	3.26 × 10^{-3}	4.16 × 10^{-3}
Zn^{2+}	2.78 × 10^{-2}	3.1 × 10^{-2}
Ag^{+}	2.25 × 10^{-3}	1.3 × 10^{-3}
Ca^{2+}	5.75 × 10^{-4}	4.32 × 10^{-4}
NH_4^{+}	4.25 × 10^{-4}	5.13 × 10^{-4}
K^{+}	3.22 × 10^{-4}	4.58 × 10^{-4}
Na^{+}	5.00 × 10^{-4}	5.78 × 10^{-4}

At optimum condition, the electrode showed the Nernstian slope of 29.1 mV in linear concentration range of 1.0 × 10^{-5} to 1.0 × 10^{-1} mol L^{-1}. Importantly, the performance of the electrode was explored using EIS technique. Compared with potentiometry, the impedimetric results showed an increase in linear concentration range (1.0×10^{-6} to 1.0×10^{-1} mol L^{-1}) and in the applied pH range (2.5 - 6.0). Characteristics of the different techniques used to measure the lead ion using the lead- membrane electrode are summarized in Table 5 [3,26,27].

Table 5. Comparison of the different techniques used to measure the lead ion by lead- membrane electrode.

Ref.	Methods	Nerstian slope (mV / decade)	Linear range (M)	pH range
[3]	Potentiometry	29.0 ± 0.2	8.0×10^{-8} to 1.0×10^{-2}	3.5 - 7
[26]	Potentiometry	25.79	1.0×10^{-6} to 0.1	5.0 - 7.2
[27]	Potentiometry[a] EIS[b]	29.5 ± 0.3	5.9×10^{-10} to 1.0×10^{-2}	2.5 - 6.5
Present work	Potentiometry	29.1 ± 0.1	1.0×10^{-5} to 1.0×10^{-1}	3.0 - 5.5
	EIS		1.0×10^{-6} to 1.0×10^{-1}	2.5 - 6.0

[a] Potentiometric measurements were carried out by a Carbon paste electrode.

[b] The EIS was used only for study of the response mechanism of the electrode.

4. CONCLUSION

In this study, the newly PVC-based lead ion-selective electrode was prepared, and in order to optimize the membrane components, a central composite experimental design was employed. At optimum condition, the electrode showed the Nernstian slope of 29.1 mV in linear concentration range of 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1}. Importantly, the performance of the electrode was explored using EIS technique. Compared with potentiometry, the impedimetric results showed an increase in linear concentration range (1.0×10^{-6} to 1.0×10^{-1} mol L^{-1}) and in the applied pH range (2.5-6.0).

ACKNOWLEDGMENTS

We gratefully acknowledge the support of this work by the Payame Noor University Research Council (center of Ardakan) and the Yazd University Research Council

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