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Potentiometric Determination of La(III) Using Chitosan Modified Carbon Paste Electrode with An experimental Design

Negar Rajabi[a], Mahboubeh Masrournia[a,*], Mohamadreza Abedi[b]

[a] Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

[b] Department of Applied Chemistry, Quchan Branch, Islamic Azad University, Quchan, Iran

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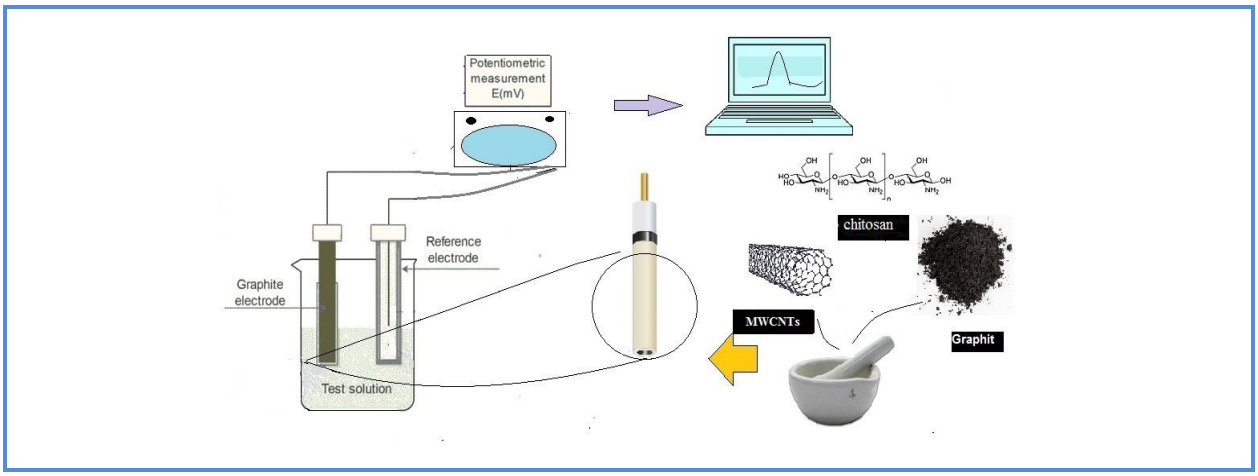
ABSTRACT

In this work, *D*-optimal mixture design was applied as an experimental design to screen and optimize the effect of the composition of a carbon paste on its performance. In this study, chitosan was offered as a ligand for the determination of La(III) with the carbon paste electrode. In the fabricated sensor, the greatest nernstian slope was achieved on the optimized mixture composition by experimental design: 60.00% w/w powder graphite, 1.53% w/w multi-walled carbon nanotubes (MWCNTs), 29.79% w/w paraffin oil, and 8.68% w/w chitosan. MWCNT was used for increasing the electrode response to La(III). The quadratic fitting pattern based on *D*-optimal model was used to find the desirability functions of the suggested design to assess the cross-interferences and the interactions between the factors. The fabricated sensor for determining the La(III) ions demonstrated a maximum nernstian slope equal to 19.70 mV.decade^{-1} along a linear range from 1.0×10^{-6} to 1.0×10^{-2} mol/L^{-1} and detection limit of 10^{-6} mol/L^{-1}. The designed sensor was successfully tested in the pH range of 2-9 with suitable selectivity, fast response time (about 30 s) and long lifetime (over 2 months) was obtained without any deviation. The offered electrode was used successfully as an indicator in the potentiometric titration of La(III) with EDTA.

*Corresponding author: E-mail: mah.masrour@gmail.com, Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran, Tel: 09153981685

Graphical Abstract



Introduction

Lanthanum is a significant expensive element that has been utilized in many industries such as optometry, ceramic, cracking catalysts of petrol, polishing and steel industries for removing carbon and electronegative elements such as sulfur. The quantity analysis of La in trace amounts is very important as it is used in the region of industrial and medicinal applications [1].

There are a number of approaches for low level determination of La(III) ions in solutions such as neutron activation analysis, spectrophotometry, inductively coupled plasma atomic emission spectrometry (ICP-AES) [2]. Chitosan (CTS) is a biopolymer (non-toxic polysaccharide) with plentiful amino and hydroxyl groups, constructed of linearly linked-glucosamine units derived from chitin (*N*-acetyl-*d* glucosamine) through a deacetylation reaction. Chitosan can be used for fabrication of electrochemical sensors due to its attractive property-including, good water permeability, vast mechanical stability, and partly cheap, that can effectively adsorb metal ions and various organic compounds in solution [3-5]. Multi-walled carbon nanotubes (MWCNT) inclusive multiple concentric graphite cylinders of increasing diameter of 2–100 nm [6]. Carbon nanotubes (CNTs) have been the topic of plenty research in different sciences such as chemistry and physics and materials areas due to mechanical, electronic, and chemical properties and their new structural [7]. The potentiometric sensors with significant sensitivity, reproducibility, portability, simple renewal of surface and no requirement of internal solution, lower ohmic resistance rather than other instrumentations analysis procedure have been as a cheap and simple analytical procedure [8-12]. Extensive ranges of applications in the field of clinical, industrial and agricultural analysis have discovered [13-21].

In this work, for the first time, we used chitosan as a ligand in the composition of carbon paste electrode for intermediate elements. Optimization of the conditions by experimental design may decrease the number of experiments and reduction of cost. Also, investigate the effective interaction of parameters with together and their effects on slope.

Experimental

Reagent and methods

The graphite powder with M=12.01 gr/mol^{-1} (Merck) along with the paraffin oil (Aldrich, USA) was of high purity, chitosan from Nano Rad Bahan Gilan company was used for the preparation of the carbon pastes. The multi-walled carbon nanotubes (MWCNTs) with 20–30 nm diameters were purchased from us research nanomaterial's, Inc. All analytical reagent chemicals and de-ionized water were used for preparing all aqueous solutions. A stock solution of 1.0×10^{-2} M La(III) was prepared by dissolving of 0.3426 g La $(NO_3)_3.6\ H_2O$ (Merck) at water. Working solutions prepared by convenient dilution of the stock solution daily at 25 ◦C. The other nitrate salts (Merck) solutions were prepared from their stock standard solution of 0.01 M, freshly.

Instrumentation

The pH/mV meter (Metrohm-780, Switzerland) was performed for adjusting pH and potentiometric measurements by utilizing of proposed sensor (CPE) as indicator electrode in conjunction with an Ag/AgCl (Azar electrode, Iran) reference electrode. ICP-OES instrument spectro arcos system (model 76004555, France) of HORIBA Jobin Yvon company was used. All measurements were performed on a computer with 8 GB memory and an intel pentium 73.07 GHz CPU and design-expert (Stat-Ease 7.0.0, USA) were used for experimental design, statistical calculations in this work. The surface of electrode was equilibrated in 0.001 M La(III) solution for 24 hours. All electromotive force (EMF) computations were carried out with the following cell assembly: Ag, AgCl(s), KCl (3M)||sample solution| carbon paste electrode. The potentials were measured by various the concentrations of La(III) in the range of 1.0×10^{-9} to 1.0×10^{-2} mol/L^{-1}. Calibration graph was drawn by plotting the amounts of potential (E) versus the logarithm of the lanthanum ion concentration.

Preparation of carbon paste electrode

The ingredients of membrane containing; chitosan, graphite powder and MWCNTs with various and certain amounts were mixed together and then appropriate amount of paraffin using of a syringe was added to the mixture and blended well for 20 min. The resulting mixture was transferred into a

metal tube that was placed a copper wire at the end of it to establish electrical contact. The paste was packed in the tube tip carefully to avoid penetration of air, increasing the electrode refractory. Before each measurement, theouter surface of the electrode was smoothed with softpaper until produced a new surface of electrode. The sensor was finally conditioned in a 1.0×10^{-3} mol/L^{-1} La(III) solution for 24 h.

Experimental designs strategy (the mixture design)

The experimental design is a remarkable program that investigate the influence of the factors on fabrication of the membrane. In this project, the optimization process was conducted based on the mixture design using the *D*-optimal model. With use of four membrane components as dependents factors namely; the powder graphite (A), ligand (B), MWCNTs (C) and paraffin oil (D) , For each of the four variable (a high level and a low level) were considered that listed in Table 1. The whole content of the blended powder was 100% w/w. In order to access to this state, the assembled of the upper amount for each factor plus the lower amount for the left over factors must not be bigger than 0.1 g, it means 100 percent in our work [22]. So, for paraffin oil, MWCNTs , ligand and graphite powder the lower levels were 25.00, 0.000 and 0,600 and the upper levels were 30.00, 3.000, 15.00 and 70.00 percent, respectively. The manner variable is not a section of blend, although it can influence on the mixture properties when the levels are variable [23]. The first step in the optimization procedure was to select and investigate an appropriate design. To achieve the best slope, a random mixture design with various design of matrix was used.

Table 1. Design constraints

Constraint	Low	High
A: Graphite powder	60.00	70.00
B: Ligand	0.000	15.00
C: MWCNTs	0.000	3.000
D: Praffine oil	25.00	30.00

Results and discussion

After analyzing the responses, the optimal amount of each factor was suggested by the design-expert (Stat-Ease 7.0.0, USA) software. Preparation of the modifier sensor with use of certain value; 60.00% w/w powder graphite, 1.53% w/w multi-walled carbon nanotubes (MWCNTs), 29.79% w/w g paraffin oil and 8.68% w/w chitosan was performed and obtained the same appropriate slope.

Calibration curve

The modified sensor has opportune measuring range between 1.0×10^{-6} and 1.0×10^{-2} mol/L^{-1} (as shown in Figure 1). The detection limit of an ion selective electrode can be calculate by extrapolated

the linear parts of the ion selective calibration curve [24]. In this project the detection limit of the modified CPE calculated with this approach that estimated 10^{-6} mol/L^{-1}.

The following optimization model manufactured from adjusting a mathematical equation to the experimental data acquired from the particular experimental design for the mixtures, the terminal equation in terms of real ingredient offered can be written [24-26]. In this work, the quadratic model has been used as explained in equation 1.

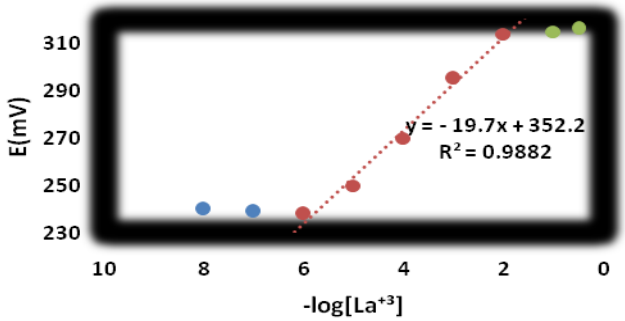


Figure 1. Calibration curve for La(III) carbon paste electrode based on chitosan

$$Y = -47.94\,A - 604.65\,B - 37653.39\,C - 1115.51\,D - 589.08\,AB + 36686.89\,AC + 1711.78\,AD + 37528.96\,BC + 5334.22\,BD + 45972.7\,CD \quad \text{Eq. (1)}$$

In this equation, Y is the predicted value for slope, A: graphite powder, B: ligand, C: MWCNTs and D: praffine oil according upper equation, factor A in the equation has a negative effective on slope or tuple factor such as CD has a positive effective. In the mixture design, the quantity of each ingredient of a system act as a changeable (mixture changeable), dependent of the others. The interaction of the parameters affect was checked using the analysis of variances (ANOVA). The quality of the equation which has been written as a model was shown by the collaboration of designation (R^2, adjusted R^2). R^2 of 0.9481 and adjusted R^2 of 0.9013 showed a good relationship between experimental data and fitted pattern and high potential of pattern in prediction of slope. The analysis of variance [partial sum of squares] show a combination of effective parameters. The using of analysis of variance explains interaction effects of the variables on the slope also evaluate the significance of each factors and interaction terms.

The model *F*-value of 20.28 implies the model is significant. There is only a 0.01% chance that a "model *F*-Value" this large could occur due to noise. Values of "Prob>F" less than 0.0500 indicate model terms are significant. In this case linear mixture components, AC, BC, BD, CD are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. So the parametteres AB, BC, BD, CD are suitable for have a good slope, the value of relative standard deviations (RSD) was obtained from

4 repetitions (different extractions with different sensing phases) was 0.43.

The results obtained by the analysis variance showed that *P*-value for lack-of-fit (0.876) was not significant (P>0.05) and regression was meaningful. In this case, fitting was very well (R^2 = 94.81%) and only (5.190%) of entire variance was not described by the model. The high value of adjusted regression coefficient (R^2=90.13%) also indicated high significance of the proposed model and a good relationship between experimental data and fitted pattern and high potential of pattern in prediction of slope. The residuals also had to be examined for normal distribution which demonstrate the interaction between examined factors. The entity of interaction means that factors may affect the response interactively and not independently. So their blended effect is greater or less than that of anticipated for the direct excess of the effects [27].

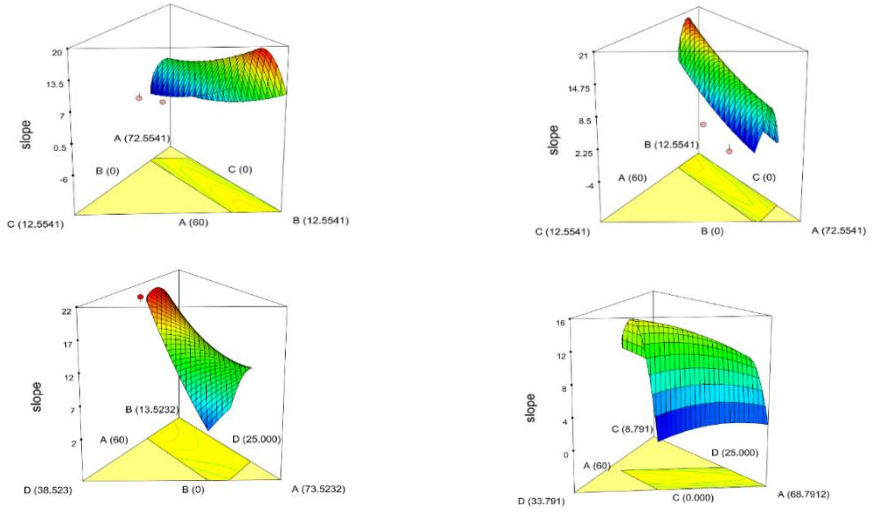


Figure2. Interaction plots between the effective parameters; (a) interaction between of graphite powder and MWCNTs (AC), (b) interaction between of ligand and MWCNTs (BC), (c) interaction between of ligand and paraffin oil (BD), (d) interaction between of MWCNTs and paraffin oil (CD) on the slope of the electrode membrane

Figure 2a. depicts the response surface obtained by plotting amount of graphite powder versus MWCNTs amount. The slope improved with the 60.00% w/w of graphite powder and 1.43% w/w MWCNTs. Figure 2b. determine a significant positive interaction between ligand and MWCNTs amount, indicating that higher amount of ligand and MWCNTs are optimal for the find appropriate slope. In fact, the addition of ligand to the composition until amount 9.07% w/w cause to improve the slope. As seen in Figure 2c, the higher slope was obtained at interaction between ligand and paraffin oil. Figure2d. shows an interaction between MWCNTs and paraffin oil, according to the overall conclusion of the optimization study, the following experimental conditions were suggested

by software: graphite powder, 60.00% w/w; ligand, 8.68% w/w; CNT, 1.53% w/w and paraffin oil, 29.79% w/w.

Effect of pH on electrodes performance

The effect of pH on the response electrode was studied at two La(III) concentrations of 1.0×10^{-2} and 1.0×10^{-6} mol/L^{-1} La(III) in the range of 2.0–12.0. The pH adjusting performed by the addition nitric acid 0.1 mol/L^{-1} or sodium hydroxide 0.1 mol/L^{-1} solutions. The potential over the pH range of 2–9 remains fixed which can be taken as the working pH range of the sensor without any interference of H^+ or OH^- in this range (Figure 3). The formation of insoluble precipitation of La(III) ion with hydroxide ion by increasing the pH cause to decrease of the sensor response in the pH above 9. During all experiments, the combination of the electrode was fixed based on the optimized amounts.

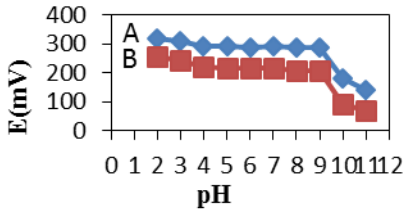


Figure 3. The influence of pH on the potential response of the optimized La(III) selective electrode in two concentration: A:1.0 $\times10^{-2}$ and B:1.0×10^{-5} mol/L^{-1}

Response time and life time

Response time of an electrode depends on the kind and interference, when all measurements are made under the identical experimental condition [28]. Access to a fixed potential for designate the response time of the sensor do by measuring the change of potentials to time in varying concentrations of solution over the range 1.0×10^{-6} M–1.0×10^{-2}mol/L^{-1}. The sensors attain to equilibrium in about 30 s as shown in Figure 6. in the ordering investigation of reversibility of the sensor two concentrations of 1.0×10^{-2} and 1.0×10^{-4} mol/L^{-1} solution changed sequentially and determined potentials. The results are designate that the potentiometric responses of the sensor are reversible. These observations indicate no memory effect on the electrode response. The lifetime of the modified sensor was investigated by the potentiometric response to La(III) ion in standard lanthanum nitrate solutions. After the conditioning stage the sensor was measured several times during a period of 2 month, no remarkable shift was observed in the performance of the electrode. This shows that the lifetime of the suggested sensor was about 2 months.

Potentiometric titration method

In the potentiometric titration of La(III) with EDTA the modified sensor was used as an indicator electrode. 2.5 mL of 1.0×10^{-3} mol/L^{-1} La $(NO_3)_3$ solution with buffer 6 reached to 25 mL (preserved at pH 6.0) was titrated against 1.0×10^{-2} mol/L^{-1} EDTA solution. This sensor can be used for the determination of La(III) potentiometrically and titration curve obtained from drawing potential versus volume of titrant during titration that showed in Figure 4.

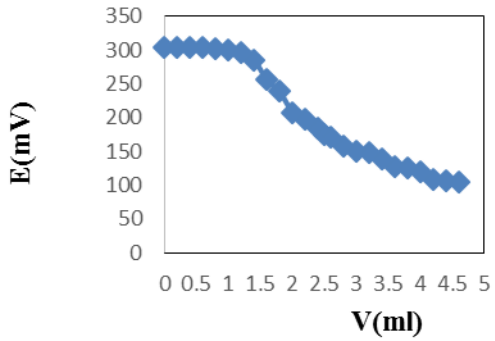


Figure 4. The potentiometric titration plot of (1.0×10^{-3} mol/L^{-1}) La(III) solution (25 mL) with EDTA (1.0×10^{-2} mol/L^{-1})

Selectivity coefficient

For any ion-sensitive sensor the main characteristics is its reply to the main ion in the presence of foreign ions available in the solution, which is presented in term of the potentiometric selectivity coefficients. For this work, the selectivity coefficient of the sensors with regard to various cationic species (M^{n+}) was assessment by using of the matched potential procedure (MPM) [29]. The selectivity coefficient (K_{MPM}) is shown in Table 2. It is obvious from Table 2 that the fabricated sensor is selective for La(III) over many cations.

Table 2. Selectivity coefficient values for La(III) selective carbon paste based on chitosan

Ion	K_{MPM}	Ion	K_{MPM}
Cu^{2+}	9.4×10^{-4}	Fe^{3+}	1.3×10^{-4}
As^{3+}	8.3×10^{-4}	Na^{+}	1.2×10^{-4}
Ni^{2+}	7.0×10^{-4}	k^{+}	1.1×10^{-4}
Fe^{2+}	5.8×10^{-4}	Co^{2+}	6.1×10^{-3}
Zn^{2+}	4.4×10^{-4}	Gd^{3+}	4.3×10^{-3}
Ca^{2+}	2.9×10^{-4}	pb^{3+}	2.7×10^{-3}
Mg^{2+}	1.5×10^{-4}	Cd^{2+}	1.4×10^{-3}

The electrode shows comparable selectivity, stability, working concentration range, slope and response time (<30 s) in comparison to the other La(III) selective electrodes reported in literature (Table 3).

Table 3. General performance characteristics of some lanthanoid ion sensors based on various ionophores

Ionophore	Dynamic range (M)	Slope (mVdecade^{-1})	Response	pH range	Reference
1,3,5-trithiacyclohexane	8.0×10^{-6} to 5×10^{-2}	Nernstian	~10 s	5-8	[28]
1-phenyl-3-methyl-4-octadecanoyl-5-pyrazolone	$\sim 10^{-6}$ to 10^{-2}	Nearly Nernstian	NM	5.5	[29]
1-phenyl-3-methyl-4-acyl-5-pyrazolone	10^{-6} to 10^{-5} to 10^{-2}	Nernstian	NM	5.5	[30]
Dinonylnaphthalene sulfonic acid	10^{-1} to 10^{-4}	20.0	5 min	4–5	[31]
Tetra phenyl ester of imidodiphosphoric acid	10^{-4}	18.5	NM	5	[32]
Monoaza-12-crown-4	3.16×10^{-5} to 1×10^{-1}	20.5 ± 1.0	<15 s	3-7	[12]
Chitosan	1×10^{-2} to 1×10^{-6}	19.70	<30 s	3-8	This study

Real sample analysis

To evaluation the analytical applicability of the proposed sensor for real samples, an attempt was made to determine lanthanum ions in water samples, tap water and Zoshk river water samples gathered from the local points around Mashhad. The different amounts of lanthanum ions were spiked to the sample and then analyzed by the ICP method. The results from ICP presented in Table 4.

Table 4. Comparison of recovery values between CPE and ICP methods for determination of the La(III) ions in the various water

Sample	Added/ppm	Foundby ICP/ppm	Found by CPE/ppm	Recovery% ICP	Recovery% CPE
Zoshk river water (1)	- 2.00×10^{-4}	0.00 1.90×10^{-4}	0.00 2.15×10^{-4}	- 95.00	- 107.5
	5.00×10^{-5}	5.10×10^{-5}	4.80×10^{-5}	102.0	96.00
Tap water (2)	- 2.00×10^{-4}	0.00 1.97×10^{-4}	0.00 1.80×10^{-4}	- 98.50	- 90.00
	5.00×10^{-5}	4.90×10^{-5}	5.30×10^{-5}	98.00	106.0

Conclusions

In this research study, the optimized combination of the chitosan modified sensor acquired as; powder graphite: ligand: MWCNT: paraffin oil as (% w/w) with 60.00: 8.6^{7}: 1.5^{3}: 29.79, respectively. The design-expert software decreased the number of experiments and saved the time and expense. Also this design investigated the interaction of the factors on each other that it's not possible in one variable at the time method of optimization. The fabricated sensor revealeda wide linear range from 1.0×10^{-6} to 1.0×10^{-2} mol/L^{-1} with a slope of 19.70 Mv/decade for La(III) with quick response time (30 s), vast pH range from 3 to 8, high selectivity and low detection limit for

lanthanum that can be used for over 2 months. Furthermore, this sensor applied as an indicator electrode in potentiometric titration of La(III) ions with EDTA successfully. Finally this method compared with ICP method and gained the acceptable recoveries in environmental water samples.

Acknowledgments

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Conflict of Interest

We have no conflicts of interest to disclose.

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