Talanta 81 (2010) 1681–1687

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Optimization of a new polymeric chromium (III) membrane electrode based on methyl violet by using experimental design

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ARTICLE INFO

Article history:
Received 11 November 2009
Received in revised form 10 March 2010
Accepted 12 March 2010
Available online 19 March 2010

Keywords:
PVC membrane electrode
Chromium (III) ion
PVC membrane
Optimization
Plackett–Burman
Box–Behnken response surface

ABSTRACT

Plackett–Burman and Box–Behnken designs were applied as experimental design strategies to screen and optimize the influence of membrane ingredients on the electrode performance. A new poly(vinyl chloride) membrane sensor for Cr(III) based on methyl violet as an ionophore was planned. The major variables to find a model for achieving the best Nernstian slope as response were: PVC, plasticizers, methyl violet, KpClTPB, pH, conditioning time and internal solution concentration. Plackett–Burman design was used to screen the main factors and Box–Behnken response surface was led to find a model for optimizing the response. The optimized membrane electrode shows a Nernstian slope for chromium (III) ions over a wide linear range from 1.99×10^{-6} to 3.16×10^{-2} mol L^{-1} and a slope of 19.5 ± 0.1 mV decade^{-1} of activity. It would be successfully applied in the pH range from 3.5 to 6.5 with detection limit of 1.77×10^{-6} mol L^{-1} (0.092 mg L^{-1}). The response time of the sensor is about 8 s and the membrane can be used for more than 6 weeks without any deviation. The relative standard deviations (R.S.D.) for six replicate the measurements of 1.0×10^{-4} and 1.0×10^{-3} mol L^{-1} of Cr(III) were 3.2 and 3%, respectively. The electrode revealed comparatively good selectivity with respect to many cations including alkali earth, transition and heavy metal ions. The electrode was successfully used as an indicator in the potentiometric titration of Cr(III) with EDTA and was also applied to the direct determination chromium (III) content of spiked water and soil samples.

1. Introduction

In recent decades, many intensive studies on the design and synthesis of highly selective ionophore molecules for ion-selective electrodes (ISEs) have been reported [1]. These efforts might be due to several advantages of membrane selective electrodes such as fast response, high selectivity and sensitivity, good precision, simplicity, low cost and wide linearity range. In spite of successful progresses in the design of highly selective ionophore for various metal ions, there are only a limited number of reports about the selective electrode for chromium (III) [2–10]. Chromium is considerably distributed in many biological, industrial and environmental systems as a pollutant. It also enters water supply through industrial wastes and causes carcinogenic effect, epigastria pain, nausea, vomiting, severe diarrhea and hemorrhage [10]. Due to increasing industrial use of chromium and its serious hazardous effect on human health, the activity measurement of Cr(III) in aqueous systems is thus of vital importance from the environmental and analytical points of view. Ionophore-based PVC membrane electrodes are well-established analytical tools which are routinely used to measure the activity of different ions in complex biological and environmental samples. The key ingredient of such plasticized PVC membranes is the incorporated ionophore, which defines the selectivity of the electrodes via selective complex formation with the cations of interest [11].

The parameters that affect the performance of a polymeric membrane electrode are usually PVC, plasticizers, methyl violet (ionophore), pH value, conditioning time and internal solution concentration. It is expected that successful sensing the analyte with an electrode depends on the selection of suitable electrode composition and operation conditions. Therefore, determining the operating parameters at which the response reaches optimum value is the main approach. Due to several advantages of multivariate optimization over univariate (one-at-a-time), it was carried out for optimizing membrane ingredients. One-at-a-time method requires greater amounts of reagent and time to be accomplished. In addition, possible interactions among variables are not considered. In contrast, the multivariate optimization methodology considers the possible interactions and is also faster, more effective and economical. Simultaneous optimization of several variables is also possible in this approach [12–15]. Among the experimental design methodologies, Plackett–Burman employs a design which

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doi:10.1016/j.talanta.2010.03.012

Table 1
Factors and levels used in the experimental Plackett–Burman design.

Factors	Low (−1)	High (+1)
pH	3	5
Internal solution (mol L^{-1})	0.001	0.01
PVC (mg)	32.5	37
Ionophore (mg)	0.6	1.1
Additive (mg)	0.6	1.6
DBP (mg)	59.3	65.8
Time condition (h)	17	28

allows testing the largest number of effective factors with the least number of observations. Also Box–Behnken design as a response surface was useful in modeling and optimizing the effective parameters on the electrode performance. The application of response surface methodology in optimizing the polymeric PVC membrane is quite sparse [16–20].

In this study, for the first time, we have applied statistical design of experiment for optimization of a Cr(III)-selective membrane electrode which is based on methyl violet. The ultimate aim of this new inspection was to verify the main factors and their interaction effects, and modeling the slope of calibration curve as analytical response. Therefore the effects of main factors such as PVC, plasticizer and pH were investigated and optimized.

2. Experimental

2.1. Apparatus

All potential measurements were carried out with the following assembly:

Ag–AgCl|3.0 mol L^{-1} KCl|internal solution, 0.0099 mol L^{-1} $Cr(NO_3)_3$ mol L^{-1})|PVC membrane|test solution|external reference electrode SCE.

A Metrohm ion analyzer pH/mV meter was used for the potential measurements at 25.0 ± 0.1 °C. Activities were calculated according to Debye–Hückel procedure [21]. A PerkinsElmer 3280 atomic absorption spectrophotometer was used for determination of Cr(III) in real samples too.

2.2. Reagents

Reagent-grade dioctyl phthalate (DOP), 2-nitrophenyl octyl ether (NPOE), dimethylsebacate (DMS), tetrahydrofuran (THF), potassium tetrakis (4-chlorophenyl) borate (KpClTPB) and high relative molecular weight PVC were purchased from Fluka Chemical Company. Methyl violet and dibutyl phthalate (DBP) were from Merck Chemical Company and they were used as received. Reagent-grade nitrate salts of all cations (all from Merck) were of the highest purity available and were used without further purification except for vacuum drying. Doubly distilled and deionized water was used throughout.

2.3. Electrode preparation

According to experimental design strategy the PVC membrane was prepared in two steps: at first for screening the main factor, the amounts of membrane ingredients (PVC, DBP, methyl violet, KpClTPB) were chosen as they were listed at Table 1 through mixing in a usual manner which was reported earlier [22]. For the optimization step, the membranes were planned according to Table 3. At last, the PVC membrane was a mixture of 62.8 mg of plasticizer DBP, 33.4 mg of powdered PVC, 1.1 mg of methyl violet and 1.1 mg of KpClTPB. In all runs the mixtures were dissolved in 5 mL of THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The THF content of the mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (4–5 mm diameter on the top) was dipped into the oily mixture for about 10 s so that a non-transparent membrane of about 0.3 mm thickness was formed. Then, the tube was pulled out from the mixture and was placed at room temperature for about 1 h. The tube was then filled with internal filled solution (0.0099 mol L^{-1} chromium (III) nitrate) and was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} solution of $Cr(NO_3)_3$. A silver/silver chloride electrode was used as an internal reference electrode.

Table 2
Regression coefficient and their significances for response of the Plackett–Burman design.

Term	Effect	Coeff.	Standard error	*T*	*P*-value
Constant	–	13.439	0.4831	27.82	0.000
pH	9.603	9.801	0.5597	17.51	0.000
Internal solution (mol L^{-1})	2.863	1.431	0.4758	3.01	0.017
PVC (mg)	−2.363	−1.181	0.4758	−2.48	0.038
Ionophore (mg)	−2.288	−1.144	0.4758	−2.40	0.043
Additive (mg)	1.487	0.744	0.4758	1.56	0.157
DBP (mg)	0.038	0.019	0.4758	0.04	0.970
Time condition (h)	−1.063	−0.531	0.4758	−1.12	0.297

2.4. Experimental designs strategy

Experimental designs strategy was applied in two stages: (i) screening the significant factors to prepare membrane electrode using Plackett–Burman design and (ii) optimizing the significant factors by using a Box–Behnken response surface design (RSM). The results were analyzed using MINITAB 14 for windows.

3. Results and discussion

3.1. Screening of significant factors using Plackett–Burman design

Plackett–Burman design was used as a screening method in order to select the factors that have influence on preparation of membrane. Plackett–Burman design is practical especially when investigator faces a large number of factors. The Plackett–Burman is a two factorial design (−1 for a low level and 1 for a high level), which identifies the critical factors required for desired slope of membrane by screening n variables in $n+1$ experiments [12–14]. Initially, we selected seven factors while they were potentially affecting the membrane response (Table 1). Eight trials were performed in duplicate and the mean of response were listed. Regression coefficients and their significances for the response of Plackett–Burman were illustrated in Table 2. The factors which were significant at 5% level ($P<0.05$) from the regression analysis (Fig. 1) were considered to have greater impact on the response of ion-selective electrode and were further optimized [12–14]. Table 2 and Fig. 1 showed that the factors such as pH of solution, internal solution concentration, the amount of PVC and ionophore were statistically significant.

3.2. Optimization using response surface methodology

The levels of significant factors and interaction effects between them which influence the membrane response were analyzed and optimized by Box–Behnken design (BBD). The number of experiments (N) required for development of BBD is defined as:

$$N = 2k(k-1) + C_0$$

where k is the number of factors and C_0 is the number of central points [17–19].

Thus, four screened significant factors pH (X_1), concentration of internal solution (X_2), PVC amount (X_3) and the amount of

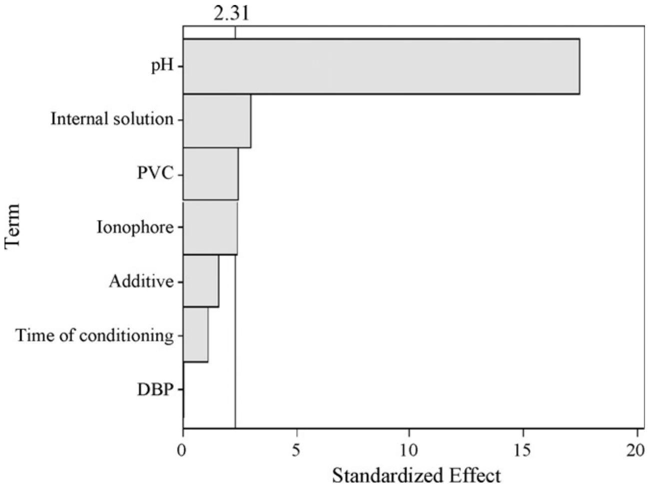

Fig. 1. Pareto chart of standardized effects for the Plackett–Burman design (the vertical line define the 95% confidence interval).

Table 3
Factors and levels used in the Box–Behnken design.

Independent variable	Symbol	Coded level		
		−1	0	1
pH	X_1	3	4	5
Internal solution (mol L^{-1})	X_2	0.001	0.0055	0.01
PVC (mg)	X_3	32.5	34.75	37
Ionophore (mg)	X_4	0.6	0.85	1.1

ionophore (X_4) were designed in a matrix shown in Table 3 and runs at 27 trials (3 center points) which were presented in Table 4. These factors were chosen in three levels of −1, 0, and +1 for low, middle and high values, respectively (Table 3).

Table 4
Box–Behnken design matrixes.

Trial number	X_1 pH	X_2 internal solution	X_3 PVC	X_4 ionophore	Response (slope/mV)	R^2
1	0	1	1	0	−22.40	0.9835
2	0	0	−1	−1	−26.15	0.9834
3	−1	1	0	0	−7.90	0.9544
4	−1	−1	0	0	−7.00	0.9315
5	0	0	0	0	−36.94	0.9918
6	1	0	0	1	−30.12	0.9926
7	−1	0	1	0	−3.20	0.9970
8	−1	0	−1	0	−8.46	0.9170
9	1	0	1	0	−25.78	0.9911
10	0	0	−1	1	−24.40	0.9903
11	−1	0	0	−1	−9.38	0.9797
12	0	−1	−1	0	−27.98	0.9801
13	−1	0	0	1	−11.26	0.9816
14	0	0	0	0	−31.80	0.9903
15	0	1	−1	0	−24.22	0.9645
16	0	0	1	−1	−34.82	0.9430
17	0	1	0	−1	−26.01	0.9284
18	1	0	−1	0	−11.00	0.9852
19	0	−1	1	0	−24.03	0.9822
20	0	0	0	0	−34.50	0.9960
21	0	−1	0	1	−30.09	0.9871
22	0	1	0	1	−34.78	0.9881
23	1	−1	0	0	−31.10	0.9860
24	0	−1	0	−1	−45.75	0.9713
25	1	0	0	−1	−32.25	0.9815
26	0	0	1	1	−25.45	0.9833
27	1	1	0	0	−20.05	0.9870

Table 5
Analysis of variance for suggested second-order model.

Source	DF	Seq SS	Adj SS	Adj MS	*F*	*P*
Regression	14	2933.94	2933.94	209.567	21.06	0.000
Residual error	12	119.43	119.43	9.953		
Lack-of-fit	10	106.21	106.21	10.621	1.61	0.444
Pure error	2	13.22	13.22	6.611		
Total	26	3053.38				

For statistical calculations, the relation between the coded values and real values are described:

$$X_i = \frac{A_i - A_0}{\Delta A_i}$$

X_i is a coded value of variable, A_i is the real value of variable, A_0 is the real value of A_i at the center point and ΔA_i is the step change of variable.

One of the main advantages of Box–Behnken design matrix is that it does not contain combinations for which all factors are simultaneously at their highest or lowest levels. So this design is useful to avoid experiments performed under extreme conditions [17–19].

The multiple regression analysis on the resulted response led to the following second-order polynomial equation which explains the relation of electrode response (slope/mV) with significant factors and interactions:

$$\begin{aligned} Y = {} & -34.413 - 8.591\,X_1 + 2.549X_2 - 1.122X_3 + 1.521X_4 \\ & +15.168X_1^2 + 2.192X_2^2 + 7.619X_3^2 - 1.45X_4^2 + 2.987X_1X_2 \\ & -5.01X_1X_3 + 1.00X_1X_4 - 0.532X_2X_3 \\ & -6.107X_2X_4 + 1.905X_3X_4 \end{aligned}$$

While Y is the predicted value of response electrode, X_1, X_2, X_3 and X_4 are the coded values of pH, internal solution concentration, PVC and ionophore amounts, respectively. The adequacy of the model was checked using the analysis of variances (ANOVA) which was tested using Fisher's statistical analysis and the results are shown in Table 5. The model *F* value of 21.06 implies that the model is significant. There was no chance that a model *F* value could occur due to noise because the *P*-value of model was 0.0000, which also confirmed the high significance of model. The smaller is *P*-value, the bigger is the significance of the corresponding factors [12–14]. The results obtained by the analysis variance showed that *P*-value for lack-of-fit (0.444) was not significant ($P > 0.05$) and regression was meaningful (Table 5). Goodness-of-fit for this model was also evaluated by the coefficient of determination (R^2) which denotes better correlation between the observed and predicted values. In this case, fitting was very well ($R^2 = 96.1\%$) and only (3.9%) of total variance was not explained by the model. The high value of adjusted regression coefficient ($R^2 = 91.5\%$) also indicated high significance of the proposed model. The residuals also had to be examined for normal distribution. Anderson–Darling test is a powerful statistical means which generates normal probability plot and performs a hypothesis test to examine whether the observations follow a normal distribution. The *P*-value of test ($0.394 > 0.05$) shows that the null hypothesis cannot be rejected and it is concluded that residuals follow the normal distribution. Fig. 2a–f illustrated the interaction between investigated factors. The existence of interaction means that factors may affect the response interactively and not independently. So their combined effect is greater or less than that of expected for the straight addition of the effects [23,24].

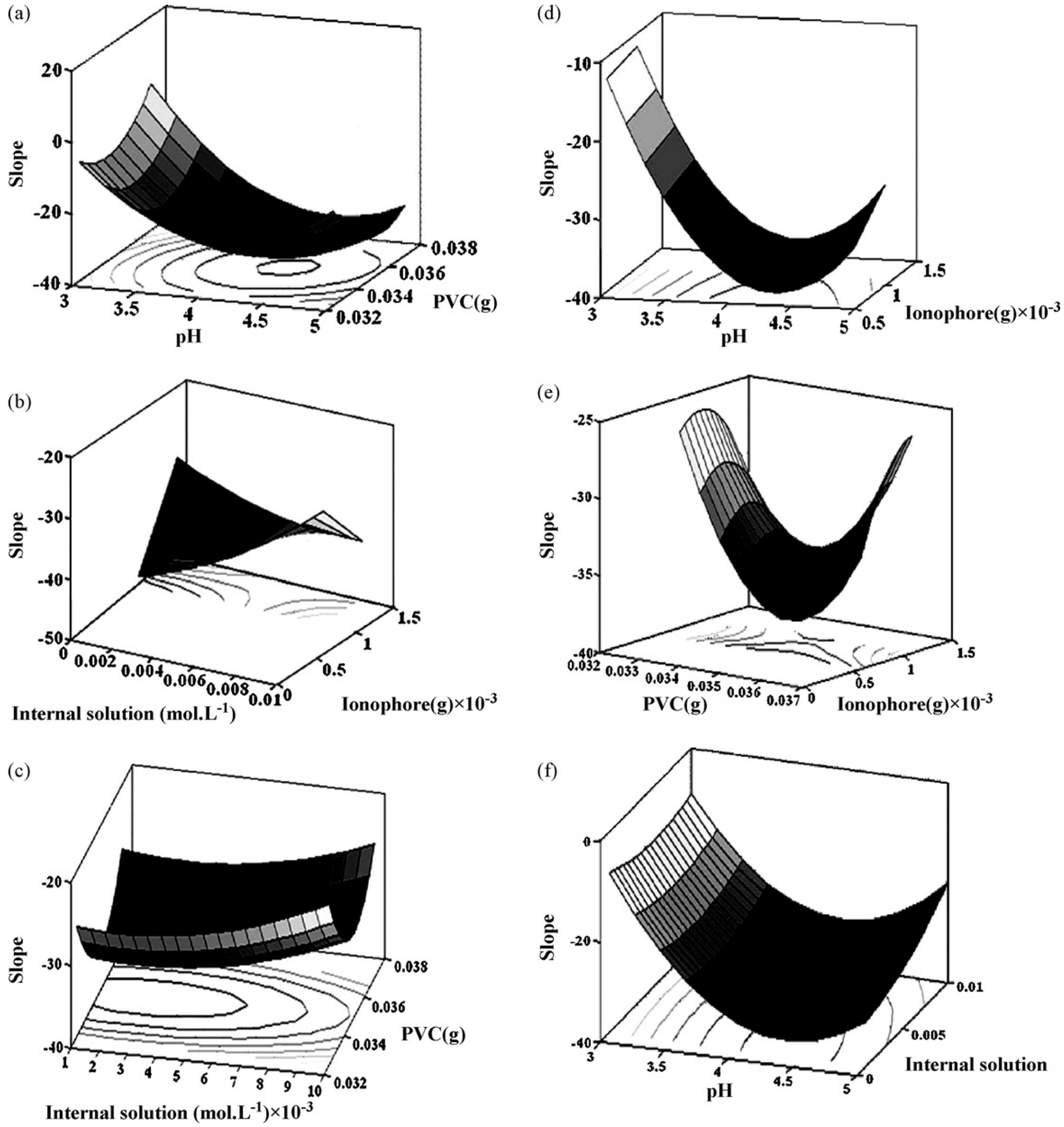

Fig. 2. (a–f) Response surface plots showing the effective parameters; pH, PVC, internal solution concentration and ionophore amounts as well as their mutual effect on the slope of electrode membrane while other parameters was kept constant at middle level (zero level).

3.3. Determination of optimal conditions

The basic strategy for RSM had four steps: procedures to move into the optimum region, behavior of the response in the optimum region, estimation of the optimal condition and verification. The visualization of the predicted model equation can also be obtained by response surface plots. The response surfaces were also drawn (Fig. 2a–f) as three-dimensional plots of two factors while the others were kept constant. Usually the constant variable is chosen at its middle level (zero point). It is possible to find the optimum region through visual inspection of the surfaces and also the interactions between factors are shown clearly: pH × PVC, pH × internal solution, pH × ionophore, PVC × ionophore and PVC × internal solution and internal solution × ionophore [15,25,26]. It is evident that the interactions between the pH and PVC, internal solution and ionophore were significant. The results also show that PVC amount has a moderate interaction effect with internal solution.

According to criteria for finding the optimum conditions [19,25], the best experimental values were obtained for every parameter by using toolbox in MAPLE. The optimum value for electrode response (19.5 mV decade^{-1}) was obtained when the pH, PVC, internal solution, methyl violet, DBP, KpClTPB and time conditioning were 5, 33.4 mg (34%), 0.0099 mol L^{-1}, 1.1 mg (1.1%), 62.8 mg (64%), 1.1 mg (1.1%) and 24 h, respectively.

3.4. Validation of the models

The statistical model was examined with respect to all four significant factors within the design space. A random set of six experimental combinations was used for validation of the statistical model. The results of analysis indicated that the experimental values were in good agreement with the predicted ones (Table 6).

3.5. Emf response characteristics and pH effect

The PVC-based membrane of methyl violet generates stable potentials when it is placed in contact with Cr(III) solutions. The critical response characteristics of Cr(III) selective elec-

Table 6
Model validation experiments.

pH	Internal solution	PVC	Ionophore	Predicted[a] response	Observed[a] response
5	0.001	0.0325	0.00085	−18.16	−16.08
4	0.01	0.0325	0.00085	−20.5	−18.2
5	0.01	0.035	0.0007	−19.45	−20.4
5	0.001	0.034	0.0099	−27.12	−30.6
3	0.001	0.034	0.0099	−7.5	−9.8

[a] Slope of calibration curve (mV decade^{-1}).

trodes were assessed according to IUPAC recommendations [27]. The potentiometric response of the membrane at varying activity of Cr(III) indicates a rectilinear range from 1.99×10^{-6} to 3.16×10^{-2} mol L^{-1} (Fig. 3). The slopes of the calibration curves were 19.5 ± 0.1 mV decade^{-1} of chromium (III) concentration. The limit of detection, as determined from the intersection of two extrapolated segments of calibration plot was 1.77×10^{-6} mol L^{-1} (0.092 mg L^{-1}) [28,29].

The pH dependence of the membrane electrode was examined by adjusting the pH of measured solution (Cr(III) with the concentration of 1.0×10^{-4} mol L^{-1}) with 1 mol L^{-1} nitric acid and sodium hydroxide. It is immediately obvious that the potential stays constant from pH 3.5 to 6.5, beyond which sharp decreases in potential are observed (Fig. 4). Below pH 3.5, the protonation of carrier is possible which can result in the loss of its complexing ability with chromium ions. Above pH 6.5, the observed increase in potential may be due to interference of OH^- ions and hydrolysis of Cr(III).

3.6. Plasticizer effect

Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands, it is expected to play an important role in determining the ion-selective characteristics [30]. Thus, four membranes with similar composition (i.e. 33.4 mg PVC, 62.8 mg plasticizer, 1.1 mg ionophore and 1.1 mg KpClTPB at pH 5, condition time; 24 h, concentration of internal solution = 0.99×10^{-2} mol L^{-1}), but with four different plasticizers having various dielectric constant over the range from 4 to 24 were prepared and tested. Membrane with DBS as plasticizer $\varepsilon = 4$, showed lowest linear ranges from ca. pCr = 4.7 to 1.7 with super Nernstian slopes of 31.5 ($R^2 = 0.999$) mV decade^{-1} (Fig. 3). The application of NPOE and DOP as plasticizers showed linear ranges from ca. pCr = 5.4 to 1.7 and pCr = 5.1 to 1.9 with super Nernstian slopes of 36.3 ($R^2 = 0.998$) and 26.1 ($R^2 = 0.998$) mV decade^{-1}, respectively. As can be seen, among the four different plasticizers used, DBP has the widest linear range ca. pCr = 5.7 to 1.5 with a good Nernstian slope of 19.5 ($R^2 = 0.998$) mV decade^{-1}.

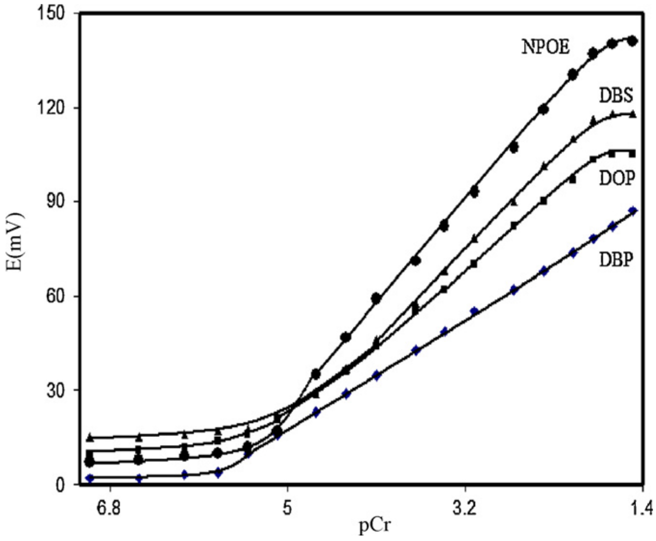

Fig. 3. Effect of different plasticizers on the potential response of the Cr(III) ion-selective electrode.

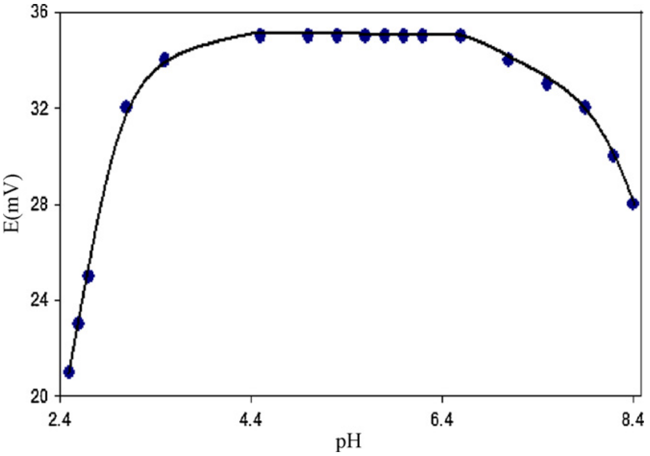

Fig. 4. Effect of pH of test solution on the potential response of the Cr(III) ion-selective electrode.

3.7. Selectivity coefficients evaluation

The usefulness of ion-selective electrodes depends largely on their selectivity over the present ions. It is perhaps the most important electrode characteristic which defines the extent to which it may be successfully employed. This is usually expressed in terms of potentiometric selectivity coefficient ($K_{A,B}^{Pot}$). However, the methods based on the Nicolasky–Eiseman equation for determining the potentiometric selectivity coefficient (e.g., the fixed interference method and the mixed solution method) suffer from some limitations in terms of values for ions of unequal charges, non-Nernstian behavior of interfering ions and the activity dependence of values [28,31,32].

Thus, in this work, the recommended matched potential method (MPM) which is totally independent of the Nicolsky–Eiseman equation was used to overcome the above mentioned difficulties [28,33]. According to MPM, the selectivity coefficient is defined as the activity ratio of the primary ion and the interfering ion that gives the

Table 7
Selectivity coefficient of various interfering cations.

K_B^A	Cation	K_B^A	Cation
Mn^{2+}	3.16×10^{-5}	Mg^{2+}	5.01×10^{-4}
Cd^{2+}	3.98×10^{-3}	Al^{3+}	1.0×10^{-1}
Ni^{2+}	1.25×10^{-3}	Cs^+	7.94×10^{-2}
Na^+	7.94×10^{-3}	Zn^{2+}	5.01×10^{-3}
Co^{2+}	1.99×10^{-3}	Tl^+	2.23×10^{-2}
Cu^{2+}	1.25×10^{-2}	K^+	6.3×10^{-3}
Sr^{2+}	2.7×10^{-3}	Ag^+	1.2×10^{-2}

Table 8

Comparison of selectivity coefficient of different Cr(III) sensor and their other figure of merits.

Parameter	Ref. [2]	Ref. [5]	Ref. [6]	Ref. [7]	Ref. [10]	This work
K_B^A						
Zn^{2+}	1.36×10^{-2}	6.80×10^{-3}	2.25×10^{-1}	1.3×10^{-2}	5.5×10^{-2}	5.00×10^{-3}
Mg^{2+}	7.90×10^{-3}	6.10×10^{-3}	2.38×10^{-2}	–	4.7×10^{-2}	5.01×10^{-4}
Na^{+}	1.23×10^{-1}	3.30×10^{-3}	1.80×10^{-1}	6.11×10^{-2}	2.2×10^{-1}	7.94×10^{-3}
Co^{2+}	1.79×10^{-2}	6.80×10^{-3}	–	5.59×10^{-4}	1.2×10^{-2}	1.99×10^{-3}
K^{+}	1.26×10^{-1}	2.40×10^{-3}	–	9.00×10^{-3}	3.1×10^{-2}	6.30×10^{-3}
Sr^{2+}	3.68×10^{-3}	4.20×10^{-3}	7.50×10^{-2}	–	9.8×10^{-3}	2.70×10^{-3}
Cd^{2+}	9.76×10^{-3}	-	6.80×10^{-3}	2.13×10^{-3}	2.2×10^{-1}	3.98×10^{-3}
pH range	3–6.5	2.7–6.5	3.0–6.5	3.8–5.5	2.8–5.1	3.5–6.5
Linear range	1.7×10^{-6} to 0.1	3.0×10^{-6} to 0.01	1.6×10^{-6} to 0.1	7.0×10^{-6} to 0.1	4.0×10^{-6} to 0.1	1.99×10^{-6} to 3.16×10^{-2}
D.L.	–	6.3×10^{-7}	–	7.0×10^{-6}	2.0×10^{-7}	1.77×10^{-6}
Response time	15	15	20	20	–	8

same potential change in a reference solution. Thus, one should measure the changed potential upon changing the primary ion activity, and then the interfering ion should be added to an identical reference solution until the same potential change is obtained.

The MPM selectivity coefficient is determined as: $K_{A,B}^{Pot} = \Delta A / a_B$, while $\Delta A = a'_A - a_A$, a_A is the initial primary ion activity, a'_A is the activity of A in the presence of interfering ion B and a_B is the interfering ion activity (Table 7) [28,34]. As can be seen, with the exception of Al(III), for all diverse ions used, selectivity coefficients of tested cations are in the order of 2.7×10^{-2} or smaller. It seems that these metal ion exert negligible disturbances on the functioning of Cr(III) membrane sensor. In Table 8, the response characteristics of the proposed Cr(III) sensor based on methyl violet with the corresponding values previously reported for five randomly taken chromium (III) ion-selective membrane electrodes based on different ionophores are compared [2,5–7,10]. It is apparent that the selectivity of the ionophore employed in this work is usually superior and sometimes similar to that of the most selective chromium (III) sensors prepared previously. In terms of shorter response time, lower detection limit, wider linear ranges and fully Nernstian response slope, however, the proposed electrode is superior to previously reported Cr^{3+} ion-selective electrodes. In addition to the advantageous mentioned above, the main goal of this study was multivariate optimization of sensor based on the experimental design.

3.8. *Response time and lifetime of proposed electrode*

The optimum conditioning time for the designed membrane was found to be 24 h, after that, stable potentials are generated in contact with Cr(III) solutions. For analytical applications, the response time of a membrane is an important factor. The average time required for the Cr(III) sensor to reach a potential within ±1 mV of the final equilibrium value after successive immersion of a series of chromium (III) solution, each having 10-fold difference in concentration was measured. The static response time in this way was less than 8 s, and the potentials stayed constant for 8 min, after that, only a very slow divergence within the resolution of the pH meter (±0.1 mV) was recorded.

The lifetime of electrodes based on ionophore in solvent polymeric membranes depends on the distribution coefficient of the ionophore and plasticizer between the aqueous and membrane phases and also on how often it is used [2,35]. The sensor could be used for at least 6 weeks without any measurable divergence.

3.9. *Analytical application*

In order to assess the applicability of the proposed electrode, the electrode was successfully applied to the direct chromium (III) determination in soil samples and spiked water sample.

Table 9

Chromium content determination of final solutions of spiked sample of water (Nos. 1–3) and soil samples (Nos. 4 and 5)[a].

No.	Taken	Found	
		AAS	Proposed electrode
1	10 (mg L^{-1})	10 ± 0.1	11.20 ± 0.35
2	20 (mg L^{-1})	20 ± 0.1	18.70 ± 0.56
3	30 (mg L^{-1})	30 ± 0.1	28.40 ± 0.76
4		0.15 ± 0.01	0.17 ± 0.01
5		0.25 ± 0.01	0.25 ± 0.02

[a] The results are three replicate.

A 35 g of soil sample was extracted with 70 mL of solvent mixture (diethyl tetra amine penta acetic acid + calcium chloride + three ethanol amine) through shaking for 2 h. Then, the suspension was filtered with a Whatman No. 42 filter paper. The Cr(III) content of solutions was measured with both proposed sensor and atomic absorption spectrophotometer [36].

The electrode was also applied to the direct determination of chromium (III) in spiked water samples and compared with those atomic absorption spectrometric (AAS) measurements. The obtained results are shown in Table 9. The results are in good agreement with those obtained by AAS and clearly validated the accuracy of proposed sensor [37]. Statistical treatment shows no significant difference between two techniques at 95% confidence level. The relative standard deviations (R.S.D.) for six replicate measurements of 1.0×10^{-4} and 1.0×10^{-3} mol L^{-1} of Cr(III) were 3.2 and 3.0%, respectively[37]. This sensor was also used as an indicator successfully for the end point determination in the potentiometric titration

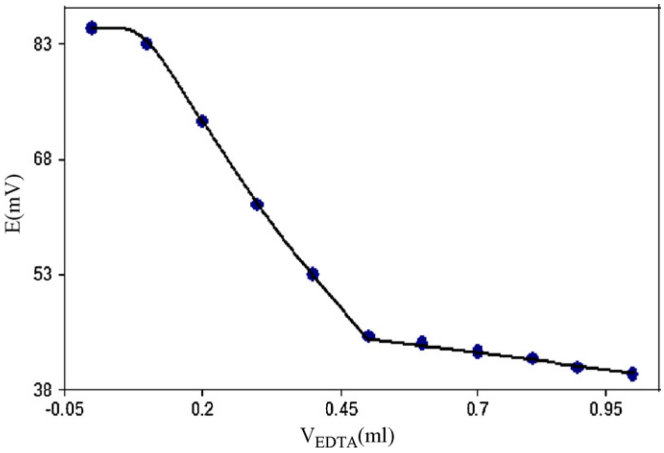

Fig. 5. Potentiometric titration plot of 50.0 mL of 1.0×10^{-4} mol L^{-1} solution of Cr(III) with 1.0×10^{-2} mol L^{-1} EDTA solution (thermostated at 50 °C), using the proposed sensor as indicator electrode.

of Cr(III) against EDTA solution. A 50 mL of 1.0×10^{-4} mol L^{-1} solution of Cr(III) was titrated against 1.0×10^{-2} mol L^{-1} EDTA solution. Due to slow kinetic of Cr(III) reaction with EDTA [38], titration cell was thermostated temperature of 50 ± 0.1 °C, using Huber thermostated. The resulting titration curve is shown in Fig. 5. As seen, the amount of chromium (III) ions can be accurately determined with the electrode.

4. Conclusion

To the best of our knowledge, there are currently no reports on optimization of the chromium (III) selective electrode by statistical experimental design (RSM).

Plackett–Burman design offers good and fast screening procedure and mathematically computes the significance of a large number of factors in one experiment which is time saving and maintains convincing information on each component. Applying Box–Behnken design to optimize the selected factors for preparation electrode is an efficient method which tests the effect of factors' interaction.

The optimized formulation of the membrane resulted in a linear concentration range of 1.99×10^{-6} to 3.16×10^{-2} with a slope of 19.5 ± 0.1 mV decade^{-1} and a limit of detection of 1.77×10^{-6} mol L^{-1}. The sensor works well in a pH range of 3.5–6.5. It could be used as an indicator electrode in the potentiometric titration of Cr(III) ions with EDTA. It exhibits good reproducibility (RDS = 3.2% for six measurements of 1.0×10^{-4} mol L^{-1}) and fast response time (<8 s). It also can be used for more than 6 weeks in aqueous medium.

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