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# Application of an orthogonal design to optimization of Indigo Carmine Bromate reaction for the kinetic spectrophotometric determination of Vanadium (IV) 

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#### Abstract

A highly selective and sensitive method was presented for the determination of V (IV), based on its catalytic effected on the oxidation reaction of Indigo Carmin by bromate. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of Indigo Carmin at 612 nm , between 0.5 to 3 min (the fixed time method). Three-level orthogonal array design (OAD) was used as a chemometric approach to optimize the reaction and study the effect of various factors on recovery of extraction. Factors such as IC concentration ( M ); $\mathrm{KBrO}_{3}$ concentration (M); pH and temperature ( ${ }^{\circ} \mathrm{C}$ ) were obtained.


Key words: orthogonal design, optimization of Indigo Carmine Bromate reaction ,kinetic spectrophotometric determination, Vanadium (IV).

## Introduction

Chemometric optimization methods have been applied in all branches of analytical chemistry and many strategies are available, such as the sequential simplex method [1], factorial design [2], simulated annealing [3], retention mapping [4], computer simulation [5] and multi-criteria design making [6]. Experimental design, as an effective and efficient optimization strategy has found widespread application in all branches of analytical chemistry. Statistically, orthogonal array design has been developed for many years [7-12].
To study the effect of various factors on the recovery of the technique and to optimize them in the minimum number of experiments, three-level orthogonal array design (OAD) was used as a chemometric approach
[13], [14]. OAD, which is in fact a saturated fractional factorial design, maintains the merits of factorial design. On the other hand, the number of experiments performed by OAD increases arithmetically instead of geometrically, thus keeping the merits of simplex optimization. In other words, the use of OAD can reduce the number of experiments without affecting the quality of results. The theory and methodology of OAD as a chemometric method for the optimization of analytical procedures has been described in detail elsewhere $[15,16]$. In this paper catalytic effect of V $(\mathrm{V})$ on the oxidation of Indigo carmine by bromide was considered. The effects of the Factors such as IC concentration (M); $\mathrm{KBrO}_{3}$ concentration (M); pH and temperature (o C) were studied by a three-level OAD with an $\mathrm{OA}_{27}\left(3^{13}\right)$ matrix.

## Experimental

## Reagents

All reagents were of analytical-reagent grade and triply distilled water was used throughout. A 1000
to 50 mL . Solutions of $\mathrm{pH} 1,3$ were prepared by adding 0.1 M nitric acid (Merck) to sodium acetate (Merck). Solution of pH 5 was prepared by adding 0.1 M acetic acid ( pH 4 ) to sodium acetate (Merck). 0.022 M solution of potassium bromate was prepared by dissolving 0.3304 gr of $\mathrm{KBrO}_{3}$ (Merck) in water, in a 100 mL volumetric flask.

## Apparatus

A UV-Visible spectrophotometer (Jenway 3605) was used. The change in absorbance by time was displayed on the screen. pH was adjusted by a Jenway 6310 pH meter. A micropit ( $1000 \mu$ l Eppendorf) was used for taking different volumes in $\mu \mathrm{l}$ limit.

## General procedure

The catalytic reaction was monitored specto photometrically by measuring the change in absorbance of the reaction mixture at 612 nm . The solutions were prepared in $1 \mathrm{~cm}, 4 \mathrm{~mL}$ glass cell. Four variables were considered in this work: volume of Indigo carmine (A), volume of Bromate (B), $\mathrm{pH}(\mathrm{C}$ ), temperature (D) 1.5 mL of buffer solution was added to a sample solution containing a $\mu \mathrm{L}$ of IC and $\mathrm{B} \mu \mathrm{L}$ of bromate. The solution was diluted to 3 mL by addition of appropriate amount of water. For different experimental trials, the variables were varied with the level setting shown in table 6 (experimental trial Nos. $1,2,5,9$ is in table 2). The cell was inserted in the cell compartment of the spectrophotometer. A mechanical stirrer was used to mix the solution in the cell. After 10 seconds $300 \mu \mathrm{~L}$ of vanadium (IV) was added to the cell by a variable $1000 \mu \mathrm{~L}$ sampler and the variation of absorbance versus time was measured during a three minutes interval.

## Experimental Design

## Matrix Construction

A three-level orthogonal array design, denoted by $\mathrm{OA}_{25}{ }^{+}\left(3^{\mathrm{S}}\right)$, is a $(2 \mathrm{~S}+1) \times \mathrm{S}$ matrix, where $S$ is the number of the columns, which corresponds to the factors, $2 \mathrm{~S}+1$ is the number of the rows, which corresponds to the experimental trails. $\mathrm{OA}_{27}\left(3^{13}\right)$ matrice, which are frequently used three-level orthogonal array matrices, is displayed in Table 1 .It can be seen that each of thirteen columns is varied over three level settings, each level setting repeats nine times, and thus a total of $3 \times 9=27$ experimental trials are necessary for each column. Tables 1 demonstrate
$\mu \mathrm{g} / \mathrm{mL}$ stock solution of Vanadium (IV) was prepared by dissolving of 0.3907 gr of $\mathrm{VOSO}_{4}, 2 \mathrm{H}_{2} \mathrm{O}$ salt (Merck) in 100 mL of distilled water. Stock solution of IC $\left(1 \times 10^{-3} \mathrm{M}\right)$ was prepared by dissolving 0.0233 gr of recrystalized IC (Merck) in distilled water and diluting that, in any two columns, the horizontal combination of any two level numbers appears the same number of times.

In Table 1 when the nine rows for a column are at level 1 , for any other columns, three of nine rows are at level 1 , three at level 2 , and three at level 3. Similar cases can be seen when this column is at other two level settings. The above features of the $\mathrm{OA}_{25}{ }^{+}\left(3^{\mathrm{S}}\right)$ matrix provide the orthogonality among all the $S$ columns. This can be proved by the following statistical method.
(i) For a three-level factorial design, a quadratic regression model representing a response surface can be expressed as:

$$
\begin{equation*}
y=\beta_{o}+\sum_{X=A}^{X} \beta_{X} \phi_{X}+\sum_{X \neq X^{\prime}=A}^{X} \beta_{X X} \phi_{X} \phi_{X^{\prime}}+\sum_{X \neq A}^{X} \beta_{X X} \phi_{X}^{2}+\varepsilon \tag{1}
\end{equation*}
$$

Where

$$
\begin{equation*}
\phi_{X}=\frac{Z_{X}-\bar{Z}_{X}}{H_{X}} \tag{2}
\end{equation*}
$$

In eqn. (2), suppose that

$$
\begin{equation*}
H_{X}=Z_{X 2}-Z_{X 1}=Z_{X 3}-Z_{X 2} \tag{3}
\end{equation*}
$$

Then

$$
\begin{equation*}
\bar{Z}_{X}=\frac{Z_{X 1}+Z_{X 2}+Z_{X 3}}{3}=Z_{X 2} \tag{4}
\end{equation*}
$$

Substituting eqns. (3) and (4) into eqn. (2) will lead to

$$
\begin{equation*}
\phi_{x 1}=-1 ; \quad \phi_{x 2}=0 ; \quad \phi_{x 3}=1 ; \tag{5}
\end{equation*}
$$

And

$$
\begin{equation*}
\sum_{K=1}^{3} \phi_{X K}=0 ; \quad \sum_{K=1}^{3} \phi_{X K}^{2}=2 \tag{6}
\end{equation*}
$$

(ii) Suppose all the thirteen columns in the $\mathrm{OA}_{27}\left(3^{13}\right)$ matrix are assigned an independent parameter, namely $\mathrm{A}, \mathrm{B}, \ldots$, and M , respectively, and no interactions exist between parameters; then the third term in eq. (1) can be neglected, hence eqn. (1) can be rewritten as

$$
\begin{equation*}
y=\beta_{o}+\sum_{X=A}^{M} \beta_{X} \phi_{X}+\sum_{X=A}^{M} \beta_{X X} \phi_{X}^{2}+\varepsilon \tag{7}
\end{equation*}
$$

Moreover, suppose that
$E_{X}=\beta_{X} \phi_{X}+\beta_{X X} \phi_{X}^{2}$
Where,
$\beta_{X}=\frac{1}{2}\left(r_{X 3}-r_{X 1}\right)$

Table (1) The $\mathrm{OA}_{27}\left(\mathbf{3}^{13}\right)$ matrix associated with the analytical results of determination of Vanadium (IV)


* The basic column are shown in bold
$\oplus$ Polynomial values excluding $\beta_{0}$ term
+ Polynomial values including $\beta_{0}$ term
+ Polynomial values including $\beta_{0}$ term
$\beta_{X X}=\frac{1}{2}\left\{\left(r_{X 3}-r_{X 2}\right)-\left(r_{X 2}-r_{X 1}\right)\right\}$
Then, according to eqns. (7) and (8) the response, $y_{i}$, for each experimental trial in the $\mathrm{OA}_{27}\left(3^{13}\right)$ matrix can be described as follows:
$y_{i}=\beta_{0}+E_{\text {IK }}+E_{\text {gK }}+E_{C K}+E_{\text {ok }}+E_{\text {EK }}+E_{\text {FK }}+E_{\text {GK }}+E_{\text {YKK }}+E_{\text {KK }}+E_{\text {JK }}+E_{\text {KK }}+E_{\text {LK }}+E_{\text {UK }}$

Where K represents the level setting numbers which are varied with the intersections in the $\mathrm{OA}_{27}\left(3^{13}\right)$ matrix. The statistical error $\left(\varepsilon_{i}\right)$ is an independent random variable from an $\mathrm{N}\left(\begin{array}{ll}0 & 0^{2}\end{array}\right)$ distribution. Therefore,

$$
\begin{equation*}
\frac{1}{I} \sum_{i=1}^{1} \varepsilon_{i} \cong 0 ; \quad \frac{1}{L} \sum_{l=1}^{L} \varepsilon_{l} \cong 0 ; \tag{12}
\end{equation*}
$$

From eqns. (5), (8), (9) and (10), it is clear that the effect of the factor X at each level in only dependent on the level means for this factor at different levels and independent of the effect for any other factors. Hence, the orthogonality has been proven.

Note that from eqn. (10) it is convenient to judge whether second-order effects are present or absent. If for a factor X the difference of the level mean between level 2 and level $1\left(r_{x 2}-r_{x 1}\right)$ is not significantly different from that between level 3 and level $2\left(r_{x 3}-r_{x 2}\right)$, then the second-order effect of the factor X can be neglected.

Table (2) Triangular table associated with OA27(313) matrix

| Column no.$1$ |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|  | 3 | 2 | 2 | 6 | 5 | 5 | 9 | 8 | 8 | 12 | 11 | 11 |
|  | 4 | 4 | 3 | 7 | 7 | 6 | 10 | 10 | 9 | 13 | 13 | 12 |
| 2 |  | 1 | 1 | 8 | 9 | 10 | 5 | 6 | 7 | 5 | 6 | 7 |
|  |  | 4 | 3 | 11 | 12 | 13 | 11 | 12 | 13 | 8 | 9 | 10 |
| 3 |  |  | 1 | 9 | 10 | 8 | 7 | 5 | 6 | 6 | 7 | 5 |
|  |  |  | 2 | 13 | 11 | 12 | 12 | 13 | 11 | 10 | 8 | 9 |
| 4 |  |  |  | 10 | 8 | 9 | 6 | 7 | 5 | 7 | 5 | 6 |
|  |  |  |  | 12 | 13 | 11 | 13 | 11 | 12 | 9 | 10 | 8 |
| 5 |  |  |  |  | 1 | 1 | 2 | 3 | 4 | 2 | 4 | 3 |
|  |  |  |  |  | 7 | 6 | 11 | 13 | 12 | 8 | 10 | 9 |
| 6 |  |  |  |  |  | 1 | 4 | 2 | 3 | 3 | 2 | 4 |
|  |  |  |  |  |  | 5 | 13 | 12 | 11 | 10 | 9 | 8 |
| 7 |  |  |  |  |  |  |  |  |  |  | 3 |  |
|  |  |  |  |  |  |  | 12 | 11 | 13 | 9 | 8 | 10 |
| 8 |  |  |  |  |  |  |  | 1 | 1 | 2 | 3 | 4 |
|  |  |  |  |  |  |  |  | 10 | 9 | 5 | 7 | 6 |
| 9 |  |  |  |  |  |  |  |  | , | 4 | 2 | 3 |
|  |  |  |  |  |  |  |  |  | 8 | 7 | 6 | 5 |
| 10 |  |  |  |  |  |  |  |  |  | 3 | 4 | 2 |
|  |  |  |  |  |  |  |  |  |  | 6 | 5 | 7 |
| 11 |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |  | 13 | 12 |
| 12 |  |  |  |  |  |  |  |  |  |  |  | 1 |
|  |  |  |  |  |  |  |  |  |  |  |  | 11 |

## Assignment of experiments

In an OAD matrix each column may be used as an independent parameter to assign a factor or twovariable interaction. The triangular table can be employed to assign two-variable interaction in OAD matrix.
As an example, the use of Table 2 is illustrated as follows. Suppose that variables A and B are assigned to column 3 and 6 respectively, from Table 2 it can be seen that the interaction between column 3 and 6 is numbers 10 and 11, and thus the interaction between A and B must be assigned to column 10 and 11. Further, if another variable C is to be considered, it can be randomly assigned to one of these columns except column 3, 6, 10 and 11. Suppose that variable C is assign to column 5, then according to Table 2, the interaction between A and C must be assigned to column 9 and 13, the interaction between $B$ and $C$ to columns 1 and 7 , and so forth.

## Optimization Strategy

To estimate the factors' effects after implementing the three-level OAD, the analysis of variance (ANOVA) technique was employed where both $S S^{\prime}$ (purified sum of the squares) and PC (\%)
(Percentage contribution) value for each factor can be computed. $S S^{\prime}$ is defined as the sum of squares minus the variance due to error, while PC (\%) is the relative contribution of $S S^{\prime}$ for each factor, or the error to the total variance. The importance of a variable and/or interaction can be estimated from the PC (\%) values due to each significant factor. Furthermore, the PC (\%) value due to the error provides an estimate of the adequacy of the experiment. The ANOVA equations including percentage contribution for a three-level orthogonal array design are shown in Table 3.

Note that when no replicate experiments are carried out, the computational formula for the variance of error given in Table 3 is not suitable because no degrees of freedom resulting from replicate experiments are available $(I(J-1)=0)$. Hence, in this event the variance of error and its degrees of freedom need to compute by pooling the variances of the dummy columns (in which no main variables and significant interactions are assigned) and their degrees of freedom. Alternatively, the total variance and total degrees of freedom can be computed by using the equations given in Table 3, and then the error variance and its degrees of freedom can be calculated by the following equations:

$$
\begin{align*}
& S S_{\text {error }}=S S_{\text {total }}-\sum S S_{x}  \tag{13}\\
& d f_{\text {error }}=d f_{\text {total }}-\sum d f_{x} \tag{14}
\end{align*}
$$

On the basis of the results obtained from ANOVA, according to eqn. (7), a quadratic regression equation representing a response surface can be expressed as follows:

$$
\begin{equation*}
y=\beta_{0}+\sum_{x_{s}} \beta_{x_{s}} \Phi_{x_{s}}+\sum_{x_{s}} \beta_{x_{s} s_{s}} \Phi_{x_{s}}^{2}+\varepsilon \tag{15}
\end{equation*}
$$

In which if $\mathrm{x}_{\mathrm{s}}$ represents a two-variable interaction, e.g., $\mathrm{A} \times \mathrm{B}$, the following formula must be employed:

$$
\begin{equation*}
\Phi_{(A \times B)_{1}}=\Phi_{(A \times B)_{2}}=\Phi_{A} \Phi_{B} \tag{16}
\end{equation*}
$$

According to the derivative algorithm, the optimum $\Phi_{x}$ value for each variable considered can be calculated, and then if each optimum $\Phi_{x}$ value obtained is substituted into eqn. (2), the optimum input value ( $\mathrm{Z}_{\mathrm{x}}$ ) for each variable considered can be achieved.

## Result and Discussion

Many methods have been developed for determination of V (IV). They include titrimetic [17], X-ray fluorescence [18], liquid-liquid extraction [19], liquid chromatography [20], Capilary zone
electrophoretic [21], and Flow injection [22], chemiluminescent [23]. In this study, three level OAD was used as a chemometric approach for determination of V (IV). Four variables are considered in this work: (A) IC Concentration (M); B $\mathrm{KBrO}_{3}$ Concentration (M); (C) pH ; (D) Temperature. In the OAD matrix all of the possible two-variable interactions are considered. The assignment of the main variables and two-variable interactions, and their levels are given in Table 4. After conducting all the experiments, the results obtained are given in Table 1. The average of the accuracy for each factor at level 1,2 , and 3 (r1, r2, r3) are also calculated and given in Table 1 so as to facilitate ANOVA and establish a quadratic regression model. The computed results of sums of squares (shown in Table 5) indicate that the four two-variable interactions assigned to columns $3,4,12$, and 13 . Therefore columns $3,4,12,13$ must be treated as dummies and the error variance must be pooled from the sums of the squares for the total of four columns ( $3,4,12,13$ ). Then by using eqns. (13) and (14), the variance of error and its degrees of freedom can be obtained (shown in Table 6). From Table 6, it can be seen that the variance of error pooled from dummies is in good agreement with that computed by eqn. (13).

Table (3) ANOVA equations including percentage contribution for a three-level orthogonal array design: SS, sum of square ; df, degrees of freedom; MS, mean square; SS', purified sum of square; and PC, percentage contribution.

| Source of <br> variance | $\boldsymbol{S S}$ | $d \boldsymbol{f}$ | $\boldsymbol{M S}$ | $\boldsymbol{F}-$ <br> value | $S S^{\prime}$ | $\boldsymbol{P C}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| X | $L J \sum_{k=1}^{3}\left(r_{x k}-u\right)^{2}$ | 2 | $S S_{x} / 2$ | $\frac{M S_{x}}{M S_{\text {error }}}$ | $S S_{x}-2 M S_{\text {error }}$ | $\frac{S S_{x}^{\prime}}{S S_{\text {total }}} \times 100 \%$ |
| Error | $\sum_{i=1}^{I} \sum_{j=1}^{J}\left(y_{i g}-\bar{y}_{i}\right)^{2}$ | $I(J-1)$ | $\frac{S S_{\text {eror }}}{I(J-1)}$ |  | $S S_{\text {total }}-\sum S S_{x}^{\prime}$ |  |
| Total | $\sum_{i=1}^{I} \sum_{j=1}^{J}\left(y_{i g}-\bar{y}_{i}\right)^{2}$ | $I J-1$ |  |  |  |  |

Table (4) The assignment of factors levels of experiment using an $\mathrm{OA}_{27}\left(\mathbf{3}^{13}\right)$ matrix

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | (AXB)1 | (AXB)2 | C | (AXC) 1 | (AXC)2 | (BXC)1 | D | (AXD)1 | (BXC)2 | (BXD)1 | (CXD)1 |
| A | B | (CXD)2 |  |  | (BXD)2 |  | (AXD)2 |  |  |  |  |  |
| $5 \times 10^{-5}$ | $0.6 \times 10^{-3}$ |  |  | 1 |  |  |  | 20 |  |  |  |  |
| $8 \times 10^{-5}$ | $1.8 \times 10^{-3}$ |  |  | 3 |  |  |  | 25 |  |  |  |  |
| $11 \times 10^{-5}$ | $3.0 \times 10^{-3}$ |  |  | 5 |  |  |  | 30 |  |  |  |  |

$\mathrm{A}=\mathrm{IC}$ Concentration $(\mathrm{M}) ; \mathrm{B}=\mathrm{KBrO}_{3}$ Concentration $(\mathrm{M}) ; \mathrm{C}=\mathrm{pH} ; \mathrm{D}=$ Temperature $\left({ }^{\circ} \mathrm{C}\right)$

ANOVA including percentage contribution is calculated and shown in Table 6. Table 6 indicates that the main variable $A, C$ the interactions $A \times C$ are statistically significant at $\mathrm{p}<0.001$ and the main variable $B$ and $D$ at $p<0.01$, whereas no statistical differences are observed for any other main variable $B$ and any other main interactions at $\mathrm{p}>0.1$. Moreover, from the percentage contribution calculated (shown in Table 6, it can be seen that the most significant effect contributing to the output response is A (37.81\%), C (31.34\%), $\mathrm{A} \times \mathrm{C}(17.75 \%), \mathrm{B}(6.032 \%)$ and D ( $3.02 \%$ ). The percentage contribution due to errors (unknown and uncontrolled factors) is low ( $0.528 \%$ ). This means that no important variables and/or interactions have been omitted in this work. Therefore, it is reasonable to neglect the italicized two-variable interactions mentioned earlier.
By using equn (9) and (10), we can calculate $\beta_{\mathrm{x}}$ and $\beta_{\mathrm{xx}}$ for each factor that has a significant influence. Then, according to the eqns. (15), (16), the following quadratic regression equation can be obtained:

$$
y=\beta_{0}+0.0133 \phi_{A}+0.0835 \phi_{A}^{2}+0.0038 \phi_{B}+0.035 \phi_{B}^{2}-0.00739 \phi_{C}+0.078 \phi_{C}^{2}-
$$

$$
\begin{equation*}
0.00287 \phi_{D}+0.0254 \phi_{D}^{2}-0.0372 \phi_{A} \phi_{C}+0.0308 \phi_{A}^{2} \phi_{C}^{2}+\varepsilon \tag{17}
\end{equation*}
$$

As $-1<\Phi_{\mathrm{A}}<1$ or $-1<\Phi_{\mathrm{C}}<1$, the second- order effect of the interaction $\left(0.03 \Phi_{A}^{2} \Phi_{C}^{2}\right)$ can be incorporated into the $\varepsilon$ item. In addition, for each
experimental trial, by substituting the $\Phi_{\mathrm{xk}}$ values [given in eqn. (5)], in which the level setting (k) for each factor is varied with the level number of the intersection in Table 1, into eqn. (17), the polynomial value excluding the $\beta_{0}$ item (Y) can be computed and the figures are given in Table 1. Combined with eqn. (12), it is clear that the mean of the difference between y and $\mathrm{Y}(\overline{y-Y}, \mathrm{i}=27$; shown in Table 1) can be considered as the $\beta_{0}$ item. Thus, eqn. (17) can be rewritten as:

$$
y=0.116+0.0133 \phi_{A}+0.0835 \phi_{A}^{2}+0.0038 \phi_{B}+0.035 \phi_{B}^{2}-0.00739 \phi_{C}+0.078 \phi_{C}^{2}-
$$

$$
\begin{equation*}
0.00287 \phi_{D}+0.0254 \phi_{D}^{2}-0.0372 \phi_{A} \phi_{C}+0.0308 \phi_{A}^{2} \phi_{C}^{2}+\varepsilon \tag{18}
\end{equation*}
$$

Hence, according to eqn. (18), the expected value ( $\hat{y}$ ) (polynomial value including the $\beta_{0}$ term) and the random error item $(\varepsilon=y-\hat{y})$ for each experimental trial in the $\mathrm{OA}_{27}\left(3^{13}\right)$ matrix are calculated and given in Table (1). The results obtained show that the expected value for each experimental trial is in good agreement with the corresponding experimental value. The mean of the random error item $(\overline{y-\hat{y}}, \mathrm{i}=16)$ equals zero (see Table (1)), which is in accordance with the assumption given in eqn. (12). Therefore, the quadratic regression equation given in eqn. (18) can adequately and accurately represent the described response surface.

Table (5) ANOVA including percentage contribution for output responses in the $\mathbf{O A}_{27}\left(\mathbf{3}^{13}\right)$ matrix

| Source | $\boldsymbol{S S}$ | $\boldsymbol{V}$ | $\boldsymbol{M S}$ | $\boldsymbol{F}^{*}$ | $\boldsymbol{S S}^{\boldsymbol{*}}$ | $\boldsymbol{P C}(\%)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\boldsymbol{I C}(\boldsymbol{A})$ | 0.045 | 2 | 0.0225 | $99.39^{* * *}$ | 0.045 | 37.81 |
| $\boldsymbol{K B r O 3}(\boldsymbol{B})$ | 0.008 | 2 | 0.004 | $16.7^{* *}$ | 0.0071 | 6.032 |
| $\boldsymbol{p H}(\boldsymbol{C})$ | 0.037 | 2 | 0.0165 | $82.58^{* * *}$ | 0.037 | 31.34 |
| $T(D)$ | 0.004 | 2 | 0.002 | $8.87^{* *}$ | 0.0035 | 3.02 |
| $A \times C$ | 0.022 | 4 | 0.0055 | $24.9^{* * *}$ | 0.021 | 17.75 |
| $B \times C$ | 0.0051 | 4 | 0.00127 | 5.6 | 0.0042 | 3.52 |
| $A \times D$ | 0.003 | 4 | 0.00075 | 3.32 | 0.0021 | - |
| Errors $^{*}$ | 0.0018 | 8 | 0.00023 | - | 0.0045 | 0.528 |
| Errors $^{*}$ | 0.00191 | 8 |  |  |  |  |

[^0]According to the derivative algorithms, the optimum $\Phi$ value for each factor that has a significant influence is $\Phi_{\mathrm{A}}=-0.0088 ; \Phi_{\mathrm{B}}=-0.0542 ; \Phi_{\mathrm{C}}=-0.045$ and; $\Phi_{\mathrm{D}}=0.056$. Therefore, by means of eqn. (2), the following optimum conditions (i) $7.9 \times 10^{-5} \mathrm{M}$ of IC (ii) $1.73 \times 10^{-3} \mathrm{M} \quad$ (iii) $\mathrm{pH}=2.91$ (iv) $25.3{ }^{\circ} \mathrm{C}$ temperature can be obtained.

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## Conclusion

Application of an orthogonal design for determination of V (IV), based on the catalytic effected on the oxidation reaction of Indigo Carmin by bromate was considered. This method provides precise results and the reaction was monitored spectrophotometrically by measuring the decrease in absorbance of Indigo Carmin at 612 nm . Three-level orthogonal array design (OAD) was used as a chemometric approach to optimize the reaction and study the effect of various factors on recovery of extraction.

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[^0]:    *Critical F value is $18.5(* * * \mathrm{p}<0.001)$, and $8.6(* * \mathrm{p}<0.01)$
    $\dagger$ Resulted from pooling dummy variances.
    $\ddagger$ Computed by eqn. (13).

