

# Spectrophotometric Method for Determination of Chromium Ion in Aqueous Solution Using Ninhydrin

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## Abstract

A simple, precise, inexpensive and reproducible spectrophotometric method was investigated for the determination of chromium ion (III) in aqueous media, this method based on the formation of a complex between chromium ion (III) and ninhydrin, a deep greenish-violet colored product in the presence of potassium hydroxide was obtained. The absorption of this product was measured at  $\lambda_{\max} = 375$  nm. The reaction proceeds quantitatively at room temperature. The linear calibration curve was constructed over range of  $(4.8 \times 10^{-4} - 1.6 \times 10^{-2})$  mol/L of chromium ions with molar absorptivity of  $2.90 \times 10^2$  and correlation coefficient  $R^2 = 0.9989$ . The calculated Sandell's sensitivity value is  $0.179 \mu\text{g}/\text{cm}^2$ , the limits of detection (LOD) and the limit of quantification (LOQ) are found to be  $3.74 \times 10^{-5}$  and  $1.24 \times 10^{-4}$  mol/L, respectively. The method was successfully applied for determination of the chromium ion in aqueous solution. The stoichiometry of the reactions was determined molar combining ratio of 1:2 between chromium and ninhydrin.

## Keywords

Ninhydrin, Chromium Ions, Spectroscopy, Stoichiometry

## 1. Introduction

The identification of harmful chemicals in sewage, industrial, and mining waste effluents has been the subject of extensive research in recent years. Several different sorts of health issues in people, plants, and animals have been caused by their presence in streams and lakes. Chromium ions are one of these toxic inorganic substances.

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One of the most prevalent elements in nature is chromium. Chromium levels in the environment have gradually risen as a result of industrial activity, particularly that of tanneries, mines, and incinerators. The most common forms of chromium in natural media are hydrated chromium (III) species and chromium (VI) (chromate). Trivalent chromium is contained in biological tissues and aids in the maintenance of proper glucose, protein, and fat metabolism [1], whereas chrome (VI) (chromate) has unquestionably harmful effects on living things, including humans, and potentially carcinogenic and mutagenic qualities. Recent publications of in-depth studies of the analytical techniques used to determine chromium in liquid and solid matrices reflect the ongoing interest in dangerous element monitoring [2].

The aquatic animal and plant life are affected by chromium traces in seawater. Waste waters from industries including paint, pigment, dye, mordant, rubber, plastic, ceramic, textile, leather, tannery, welding process, smelting works, chrome plating facilities, steel and its alloys are the main sources of metal discharge into the environment that results in chromium pollution. Another significant source of chromium pollution comes from cooling fluids used in industry. According to the drinking water standards provided by the Indian Standards and the United States Public Health Department, the maximum permitted content of chromium is mostly  $50 \mu\text{g}\cdot\text{L}^{-1}$  [3].

There are several methods for chromium ion measurement in the literature; the most frequently used are ultraviolet-visible (UV-Vis) spectrophotometry [4], high-performance liquid chromatography [5], capillary electrophoresis [6], Adsorptive Stripping Voltammetry [7], flame and furnace atomic adsorption spectroscopy [8] [9], and mass spectrometry [10]. Because of its simplicity, sensitivity, accuracy, and speed, the spectrophotometric method holds a special place in science. This technique became essential to contemporary analytical chemists due to the instrument's accessibility. The absorption of light is the foundation for spectrophotometric procedures used to identify substances [11].

In this research, a new spectrophotometric method for the determination of Cr (III) using ninhydrin was investigated, Ninhydrin in this research acts as chromogenic agent [12]. The ability of ninhydrin (a bidentate ligand) to function as an analytical reagent was the subject of some interesting and practical data presented in this work [13] [14] [15]. The chromogenic reagent in this procedure was ninhydrin. The produced stable colored complex was measured at  $\lambda_{\text{max}} = 375 \text{ nm}$  under variable conditions. The calibration curve was constructed under optimum conditions. This method found to be rapid, sensitive, simple and reproducible one.

## 2. Experimental

### 2.1. Apparatus and Instruments

The instrument that used in this research are UV\Vis spectrometer (SPECORD S600), Analytical balance (METTLER TOLEDO, AL 104) and Digital pH meter

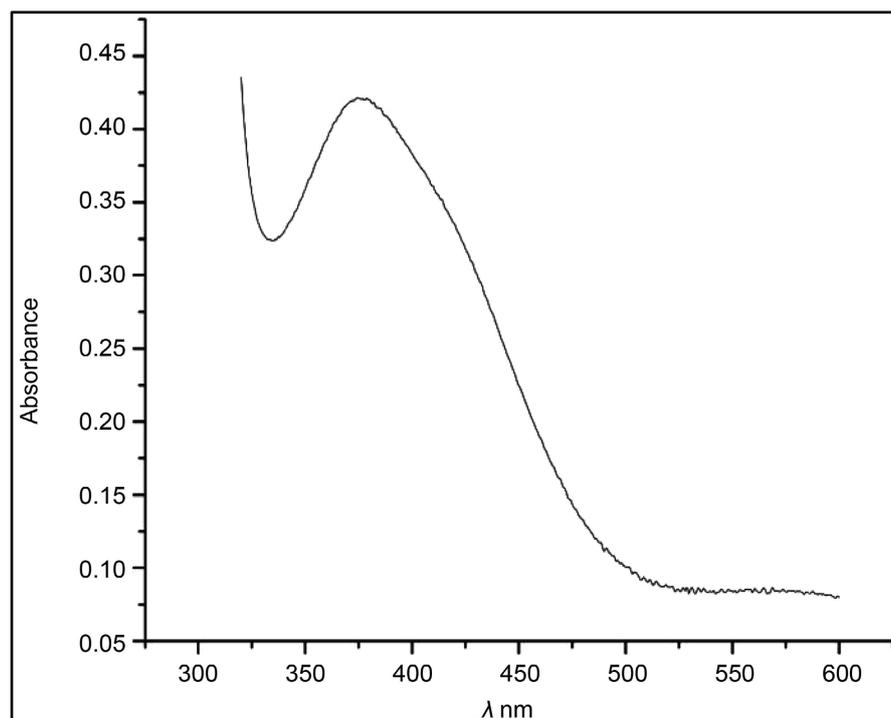
(METTLER TOLEDO, Seven Easy) shaker water bath (GFL 10983), Hot plate stirrer (HP-3000) and Heating Drying oven (Model DHG).

## 2.2. Reagents and Chemicals

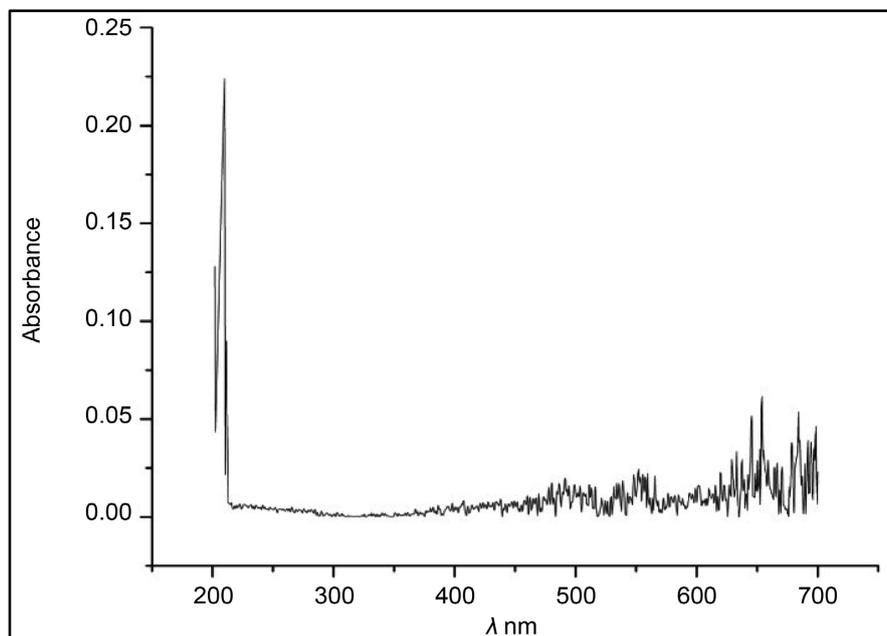
An analytical grade chemical reagents were used, as received without further treatment  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  98% Panreac, Ninhydrin 98.0% GCC Company, KOH 98.0% NTL (NEN TECH LTD), NaCl 99.0% GCC Company,  $\text{KNO}_3$  99.0% S.D Fine.chem. LTD,  $\text{CaCl}_2$  98.0% s S.D Fine-CHEM LTD INE,  $\text{CuSO}_4$  98.0% LOBA chemie and  $\text{ZnCl}_2$  98.0% GCC Company.

## 2.3. Selection of the Optimum Wavelength

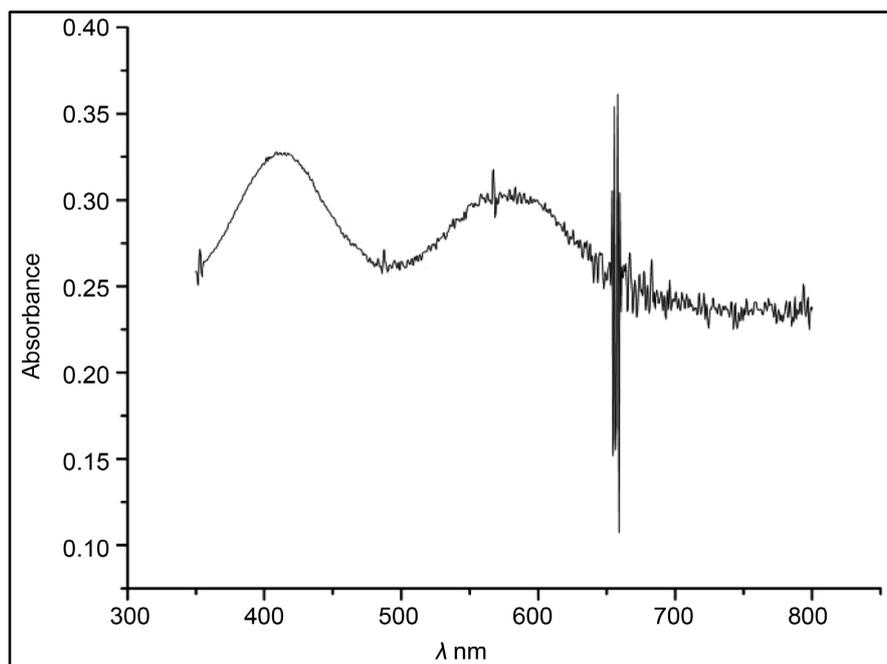
Many experiments were done to find the optimum wavelength which is the maximum one for the product of the reaction between  $\text{Cr}^{3+}$  ions with ninhydrin. All the experiments were done in alkaline media using 0.0089 M of KOH, at room temperature and with final volume of 50 mL. A stable greenish-violet colored complex ( $\text{Cr}^{3+}$  - ninhydrin) was obtained after many trials after 15 minutes, and its maximum value of absorption was found at 375 nm in the visible region using  $6.24 \times 10^{-3}$  M of  $\text{Cr}^{3+}$  ions with  $2.4 \times 10^{-3}$  M of ninhydrin. At each trial the absorbance was measured in the range of wave length (350 - 700) nm. The spectra of the each blank and  $6.24 \times 10^{-3}$  M of  $\text{Cr}^{3+}$  ions solutions were measured separately also in the range of wave length (350 - 700) nm as shown in **Figures 1-3**.



**Figure 1.** The absorption spectra Cr-Ninhydrin complex, condition:  $\text{Cr}^{3+} = 6.24 \times 10^{-3}$  M, Ninhydrin =  $2.4 \times 10^{-3}$  M, KOH =  $8.9 \times 10^{-3}$  M, total volume 50 ml and at room temperature.



**Figure 2.** The absorption spectra of blank, condition: Ninhydrin =  $2.4 \times 10^{-3}$  M, KOH =  $8.9 \times 10^{-3}$  M, total volume 50 ml and at room temperature.



**Figure 3.** The absorption spectra of Cr<sup>3+</sup>, condition: Cr<sup>3+</sup> =  $6.24 \times 10^{-3}$  M, KOH =  $8.9 \times 10^{-3}$  M, total volume 50 ml and at room temperature.

#### 2.4. Variables Studies

Different parameters were used to get the best circumstances for the reaction between chromium ions and ninhydrin. The following variables were examined to develop this analytical method: contact time, temperature, initial ninhydrin concentration, initial chromium ion concentration, initial concentra-

tion of KOH. The thermodynamic and kinetic studies were done at the found optimum conditions.

### 2.5. Effect of Reaction Time

Three prepared solutions which of  $\text{Cr}^{3+}$ , ninhydrin and KOH which have the following concentration respectively  $6.24 \times 10^{-3}$  M,  $2.4 \times 10^{-3}$  M and of  $8.9 \times 10^{-3}$  M are mixed with together at room temperature with final volume of 50 mL to investigate the effect of time of reaction on the absorbance of the colored product. The intervals time were 5, 10, 15, ... until 155 minutes. The absorbance of the product was measured every 5.0 minutes over the 155 minutes. All of the experiments were repeated and the average result was taken.

### 2.6. Initial Chromium Ions Concentration

Different initial concentrations of  $\text{Cr}^{3+}$  ions were prepared in the range of ( $2.00 \times 10^{-4}$  -  $1.86 \times 10^{-2}$ ) M, each single solution was mixed separately with constant amount of each KOH with final concentrations of 0.0089 M and ninhydrin with final concentration of 0.0024 M. The solution was left for 15 min to complete the reaction and developing the deep greenish-violet colored complex with constant intensity the solution was diluted to 50 mL using distilled water. The absorbance was measured at 375 nm. All of the experiments were repeated and the average result was taken.

### 2.7. Effect of Initial Concentration of Ninhydrin

By measuring the absorbance of solutions containing fixed concentrations of both  $\text{Cr}^{3+}$  ( $6.24 \times 10^{-3}$  M) and KOH ( $8.9 \times 10^{-3}$  M) together with varying concentrations of ninhydrin ( $4.8 \times 10^{-4}$  -  $9.6 \times 10^{-3}$  M) in a final volume of 50 mL, it was possible to determine the impact of ninhydrin concentration on the intensity of the colored complex at the chosen wavelength which is at 375 nm, the absorbance of each solution was determined. The average outcome was determined after repeating each experiment.

### 2.8. Effect of Initial Concentration of KOH

The effects of the initial potassium hydroxide concentration on the outcomes of this combination were investigated through a number of experiments while keeping the other conditions constant, the concentrations of both  $\text{Cr}^{3+}$  of  $6.24 \times 10^{-3}$  M and ninhydrin of  $2.4 \times 10^{-3}$  M also kept constant, different volumes of 0.0089 M of KOH were transfers into a series of 50 ml volumetric flask 0, 1, 3, 5, 7, 9, 11, 13, 15, 17, 19 mL these solutions were completed to final volume. At 375 nm, the absorbance of each solution was determined. The average outcome was determined after repeating each experiment.

### 2.9. Effect of Solution Temperature

The following temperatures were chosen: R.T (room temperature),  $15^\circ\text{C}$ ,  $20^\circ\text{C}$ ,

25°C, 30°C, 35°C, 40°C, 45°C, 50°C, 55°C, and 60°C. Several tests were conducted to examine the impact of temperature on the stability of the complex (Cr-Ninhydrin). The concentration of  $\text{Cr}^{3+}$  is  $6.24 \times 10^{-3}$  M, ninhydrin is  $2.4 \times 10^{-3}$  M, and KOH is  $8.9 \times 10^{-3}$  M, with other conditions being held constant. At 375 nm, the absorbance of each solution was determined. After conducting each experiment a second time, the average result was established.

### 2.10. Effect of Interfering Ions

The experiment was conducted using 50 mL volumetric flasks containing  $3.12 \times 10^{-3}$  M of  $\text{Cr}^{3+}$ ,  $8.9 \times 10^{-3}$  M of KOH, and  $2.4 \times 10^{-3}$  M of ninhydrin under the optimum conditions. Separate amounts of the ionic salts NaCl,  $\text{NaNO}_3$ ,  $\text{ZnSO}_4$  and  $\text{CaCl}_2$  were added separately to each flask before filling it to the mark. The absorbance of each individual solution was then measured at 375 nm. The average outcome was determined after repeating each experiment.

### 2.11. Construction of the Calibration Curve

The calibration curve was created using the spectrophotometric method under the ideal conditions: the concentration of Ninhydrin is  $2.4 \times 10^{-3}$  M and  $8.9 \times 10^{-3}$  M KOH kept constant while different initial concentration of  $\text{Cr}^{3+}$  ions were used. The final volume of each solution is 50 mL using volumetric flask, After 15 minutes, and the reaction of each solution results in a greenish-violet color. The solution is then diluted to the appropriate concentration with The absorbance in the visible range was measured in comparison to a reagent blank made in the same way but without  $\text{Cr}^{3+}$  and kept at room temperature.

### 2.12. Validation Parameters

#### Accuracy and Precision

The method's precision was calculated using intermediate precision (intra-day and inter-day). On the same day (with intra-day precision) and four days in a row, three replicates of three distinct standard  $\text{Cr}^{3+}$  concentrations were examined (inter-day precision). The similarity of the reference value and the obtained value is what determines how accurate an analytical procedure is.

### 2.13. Studying the Kinetic

#### 2.13.1. Initial Rate Method

Under the ideal conditions; five experiments with various concentration of  $\text{Cr}^{3+}$  were prepared in the range of (0.0011 - 0.016) M in 50 mL volumetric flasks. After 15 minutes, successive additions of distilled water brought the volume up to the desired level. After thoroughly mixing the contents of each flask, the absorbance was measured at 375 nm as a function of time. The slope of the tangent to the absorbance-time plot was used to calculate the initial rate constant of the reaction ( $k$ ) at various concentrations. Plotting the initial reaction rate constant ( $k$ ) against the molar concentration of the  $\text{Cr}^{3+}$  ions resulted in the calibration graphs.

### 2.13.2. Fixed Time Method

The absorbance of each sample of  $\text{Cr}^{3+}$  solution was measured at 375 nm in accordance with a reagent blank made similarly but without the  $\text{Cr}^{3+}$  solution, also at the most favorable experimental conditions previously mentioned. At regular intervals of 2 minutes, the absorbance of each solution was measured as a function of time. Between the times  $t_1$  (2 min) and  $t_2$  (4, 6, 8, 20 min), the change in absorbance ( $\Delta A$ ) was estimated. Plotting the absorbance against the initial concentration of  $\text{Cr}^{3+}$  ions and this process was repeated for each concentration of  $\text{Cr}^{3+}$  ions produced the calibration curve.

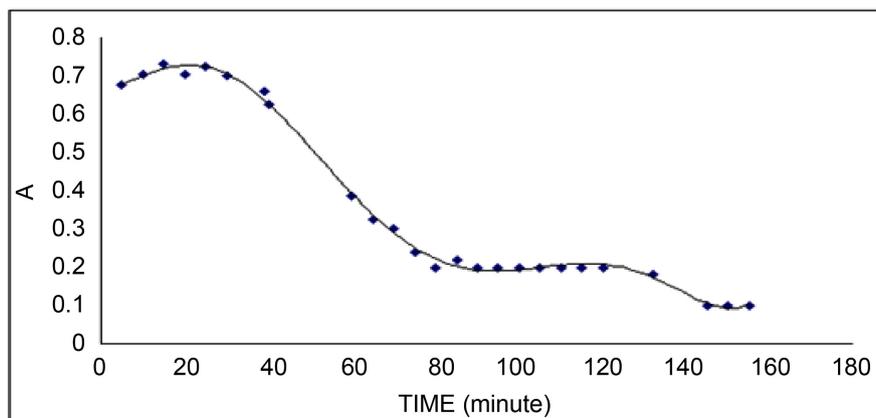
## 3. Results and Discussion

### 3.1. Effect of Contact Time

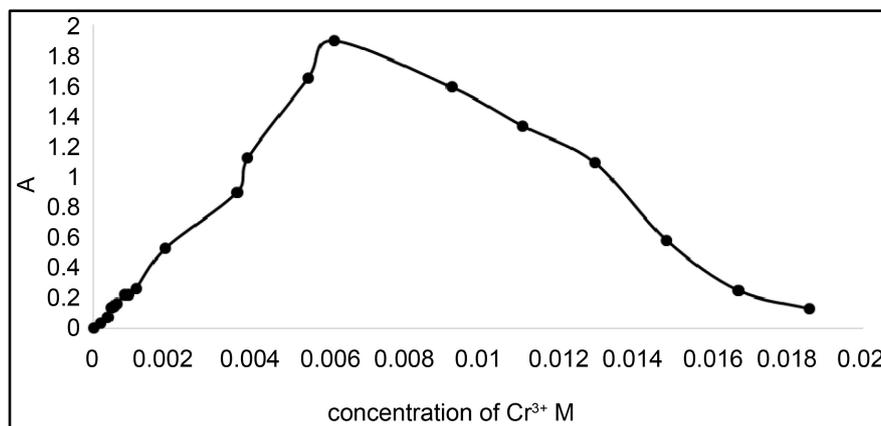
The optimum contact time of the reaction between the chromium ions and ninhydrin was reached by following the development of the maximum absorbance at specific time at room temperature, several experiments were done to investigate the influence of time on the absorbance of the  $\text{Cr}^{3+}$ -ninhydrin reaction, whilst the other conditions remained constant, The following time intervals were recorded: 5, 10, 15, 30, ..., and 155 minutes. Every 5 minutes, the product's absorbance was measured over the 155 minutes, after 5 minutes of reaction the initial absorbance was 0.67 then it is increasing until reaching 0.73 after 15 minutes, which is the time for the full developed color of the product, at 20 minutes and after the signal of absorbance decreasing to reach 0.1 at 155 minutes as shown in **Figure 4**. Dissociation of this complex may begin to occur after about 20 minutes. The optimum time for measurement of this complex is after about 15 minutes.

### 3.2. Effect of Initial Concentration of $\text{Cr}^{3+}$ Ion

The effect of initial concentration  $\text{Cr}^{3+}$  was investigated while keeping the other variables constant. As was observed from **Figure 5**, the absorbance of the



**Figure 4.** Absorbance – time curve for the reaction of  $\text{Cr}^{3+}$  with Ninhydrin. Conditions:  $\text{Cr}^{3+} = 6.24 \times 10^{-3}$  M, Ninhydrin =  $2.4 \times 10^{-3}$  M, KOH =  $8.9 \times 10^{-3}$  M, total volume 50 ml at room temperature and  $\lambda = 375$ .



**Figure 5.** Effect of initial concentration of Cr<sup>3+</sup>. Conditions: M, Ninhydrin =  $2.4 \times 10^{-3}$  M, KOH =  $8.9 \times 10^{-3}$  M, total volume 50 ml, at room temperature,  $\lambda = 375$  and contact time = 15 minutes.

complex increased by increasing the concentration of Cr<sup>3+</sup> ions in the range (0.0008 - 0.02) M while the concentration of ninhydrin kept constant, then sharp decreasing in the absorbance was observed by raising the concentration of Cr<sup>3+</sup> ions in the range of (0.024 - 0.04) M, this decreasing may be due to the dissociation of the complex as the concentration of metal ions increased, the equilibrium of reaction will shift to left.

### 3.3. Effect of Ninhydrin Initial Concentration

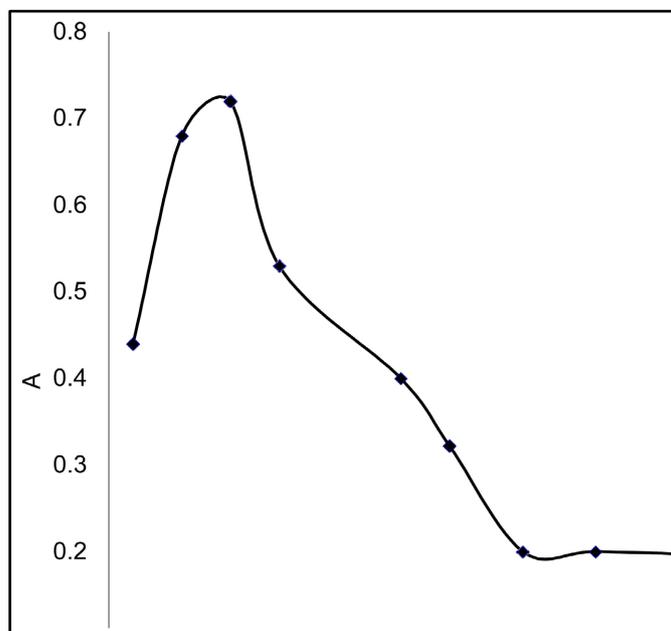
Various ninhydrin concentrations between ( $4.8 \times 10^{-4}$  -  $2.1 \times 10^{-2}$ ) M were added to constant concentration of Cr<sup>3+</sup> ions, the other variables kept constant, According to the standard procedure, the absorbance was measured. **Figure 6** shows how the concentration of ninhydrin affects the intensity of the produced complex. The findings show that the absorbance decreases as ninhydrin solution concentrations increase.

The findings show that the absorbance of the complex decreases as ninhydrin solution concentrations increase because the intensity of the colored complex increased, the absorbance reached the maximum value when  $2.4 \times 10^{-3}$  M of ninhydrin is used, the decreasing in absorbance was noticed when higher concentration of ninhydrin is used, dissociation of the complex may occurred by increasing ninhydrin concentration.

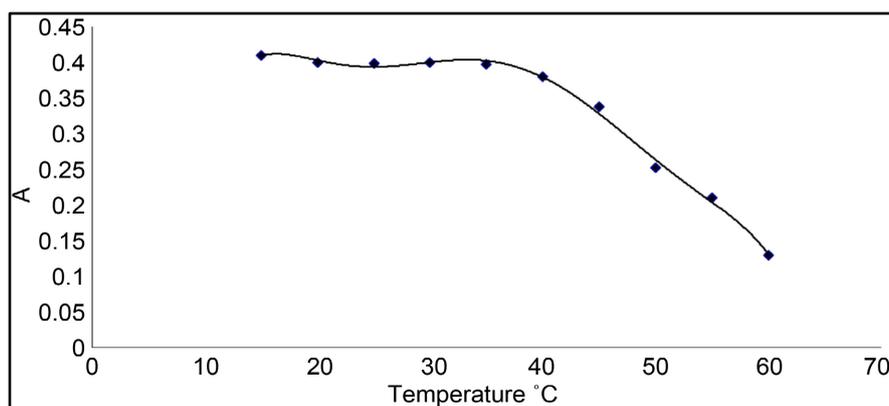
According to the accepted practice, the absorbance was measured. Figure shows how the concentration of ninhydrin affects the complex (6). The findings show that the absorbance decreases as ninhydrin solution concentrations increase.

### 3.4. Effect of Temperature

The influence of temperature was investigated at various temperature intervals were chosen in the range of 15°C until reaching 60°C as shown in **Figure 7**, the temperature values from 15°C to 40°C showed that the stability of the formed



**Figure 6.** Effect of initial concentration of Ninhydrin. Conditions:  $\text{Cr}^{3+} = 6.24 \times 10^{-3} \text{ M}$ ,  $\text{KOH} = 8.9 \times 10^{-3} \text{ M}$ , total volume 50 ml at room temperature,  $\lambda = 375$  and the contact time = 15 minutes.

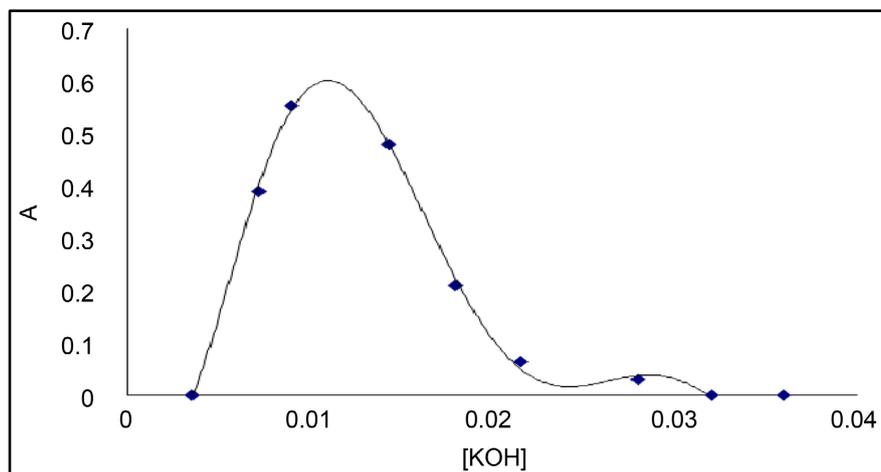


**Figure 7.** Effect of temperature on the absorbance of the complex. Conditions:  $\text{Cr}^{3+} = 6.24 \times 10^{-3} \text{ M}$ , Ninhydrin =  $2.4 \times 10^{-3} \text{ M}$ ,  $\text{KOH} = 8.9 \times 10^{-3} \text{ M}$ , total volume 50 ml at room temperature,  $\lambda = 375$  and the contact time = 15 minutes.

colored complex has not been impacted, while in the range of  $45^{\circ}\text{C}$  to  $60^{\circ}\text{C}$  the stability decreased gradually and the color of the complex became less dense, and decreasing in absorbance readings was observed. This means that the reaction is stable at low and moderately high temperature range, while at higher temperature instability of the complex is observed which means an exothermic reaction may be occurs.

### 3.5. Effect Concentration KOH

Investigations were also done into the effect of KOH concentration on the reaction product's absorbance. From **Figure 8**, it was observed that the absorbance



**Figure 8.** Effect of KOH concentration on the absorbance of the colored product. Conditions:  $\text{Cr}^{3+} = 6.24 \times 10^{-3}$  M, Ninhydrin =  $2.4 \times 10^{-3}$  M, total volume 50 ml at room temperature,  $\lambda = 375$  and the contact time = 15 minutes.

of this colored complex decreased when the KOH concentration was raised until it was zero. A competition between ninhydrin and  $\text{OH}^-$  to interact with the  $\text{Cr}^{3+}$  ions may occurred and another complex was formed.

### 3.6. Effect of Interfering Ions on Complex Stability

The impact of foreign species frequently discovered with  $\text{Cr}^{3+}$  were examined under optimal conditions to evaluate the efficiency of the suggested technique by adding known concentrations of diverse ions of standard  $\text{Cr}^{3+}$ , the influence of three different cations on the determination of  $\text{Cr}^{3+}$  was investigated and results are shown in **Table 1**. The results indicate that almost all salts had no effect on absorbance reading and hence have no influence on complex stability.

### 3.7. Linearity, Detection and Quantification Limits

Based on Beer's Lambert law, the linear correlation coefficient between absorbance and  $\text{Cr}^{3+}$  ion concentration was determined, from the regression analysis the data used to estimate the intercept (a), slope (b), and the correlation coefficient ( $R^2$ ) as can we see in **Table 2** and illustrated in **Figure 9**, the limit of detection and the limit of quantification also contained in **Table 2**.

### 3.8. Precision

With three different  $\text{Cr}^{3+}$  solution concentrations, the precision and accuracy were studied. The precision was confirmed [16] [17] in terms of intra-day intermediate precision, and these solutions were created and merged with ninhydrin under the optimal conditions. For intra-day precision, the products were examined three times on the same day. For each concentration of  $\text{Cr}^{3+}$  ions, the standard deviation (SD) and relative standard deviation (%RSD) were estimated, and the range of (%RSD) for the three different concentrations was 0.90% - 3.18% as shown in **Table 3**. The repeatability in three days (inter-day) for each

**Table 1.** Effect of foreign ions from different salts on the determination  $\text{Cr}^{3+} = 6.24 \times 10^{-3}$  M and  $2.4 \times 10^{-3}$  M of Ninhydrin at room temperature.

| Cr <sup>3+</sup> solution number | Absorbance (Without interfering salts) | Interfering salts | Absorbance (with interfering salts) | % Interference |
|----------------------------------|--|-------------------|-------------------------------------|----------------|
| 1                                | 0.81                                   | NaCl              | 0.80                                | 1.23           |
| 2                                | 0.83                                   | NaNO <sub>3</sub> | 0.81                                | 2.4            |
| 3                                | 0.82                                   | CaCl <sub>2</sub> | 0.83                                | 1.22           |
| 4                                | 0.85                                   | ZnSO <sub>4</sub> | 0.80                                | 5.88           |

**Table 2.** Analytical parameters for the developed spectrophotometric method of the determination of Cr<sup>3+</sup> using ninhydrin.

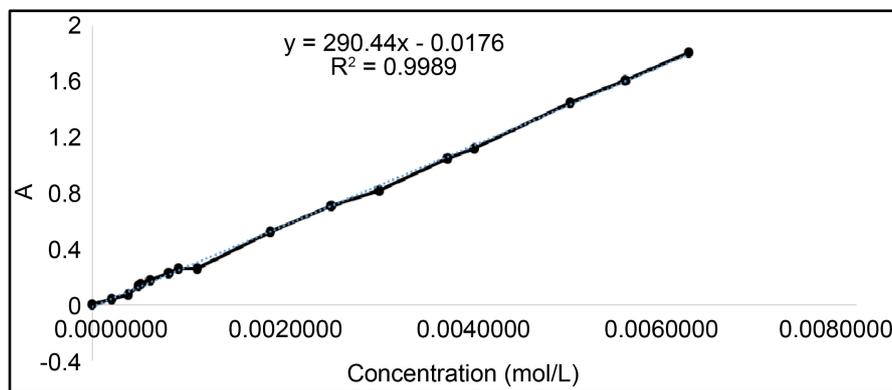
| Parameter                                 | Value                                       |
|---|---|
| Color                                     | Deep greenish-violet                        |
| $\lambda_{\text{max}}$ (nm)               | 375   |
| Linearity range (mol/l)                   | $(4.8 \times 10^{-4} - 1.6 \times 10^{-2})$ |
| $\epsilon$ (L/mol/cm)                     | $2.90 \times 10^2$                          |
| Range time for Color stability            | 15  |
| pH  | 10  |
| Sandell's sensitivity                     | $0.179 \mu\text{g}/\text{cm}^2$             |
| Temperature °C                            | Room temperature                            |
| Correlation coefficient (R <sup>2</sup> ) | 0.9989                                      |
| LOD ( $\mu\text{g}\cdot\text{mL}^{-1}$ )  | $9.12 \times 10^{-6}$                       |
| LOQ ( $\mu\text{g}\cdot\text{mL}^{-1}$ )  | $3.04 \times 10^{-5}$                       |
| LOL                                       | $6.24 \times 10^{-3}$                       |

The absorbance measured in a glass cuvette of-section are 1 cm<sup>2</sup>.

**Table 3.** Evaluation of intra-day and inter-day accuracy and precision.

| Method                           | [Cr <sup>3+</sup> ] taken mol/L | [Cr <sup>3+</sup> ] found mol/L | Absolute error | % RSD |
|----------------------------------|---------------------------------|---------------------------------|----------------|-------|
| Intra-day Accuracy and precision | 0.00110                         | 0.00130                         | 0.00020        | 0.90  |
|                                  | 0.00400                         | 0.00380                         | -0.00020       | 5.40  |
|                                  | 0.00080                         | 0.00084                         | 0.00040        | 3.18  |
| Inter-day Accuracy and precision | 0.00110                         | 0.00132                         | 0.00022        | 1.24  |
|                                  | 0.00400                         | 0.00494                         | 0.00094        | 1.78  |
|                                  | 0.00080                         | 0.00087                         | 0.00007        | 3.71  |

concentration of Cr<sup>3+</sup> ions in terms of %RSD were acquired in the range 1.24% - 3.71%. The precision was also determined in terms of intermediate precision inter-day. The products were examined in three repeats over three consecutive



**Figure 9.** Calibration curve.

days (inter-day precision) by selecting three different concentrations of  $\text{Cr}^{3+}$  ions that mixed with ninhydrin under the optimal parameters.

### 3.9. Accuracy

Investigation of the analytical method's accuracy resulted in the calculation of the absolute error for each analysis (both intra- and inter-day accuracy), as indicated in **Table 3**. The taken amount and the found amount are likely close to one another based on the minimal absolute error values [16] [17]. The F-test was used in the statistical analysis for the intraday and interlay, and the results demonstrated that there is no bias between the taken values and the observed ones at  $\alpha = 0.05$ , disproving the null hypothesis.

### 3.10. Stoichiometry of the Reaction

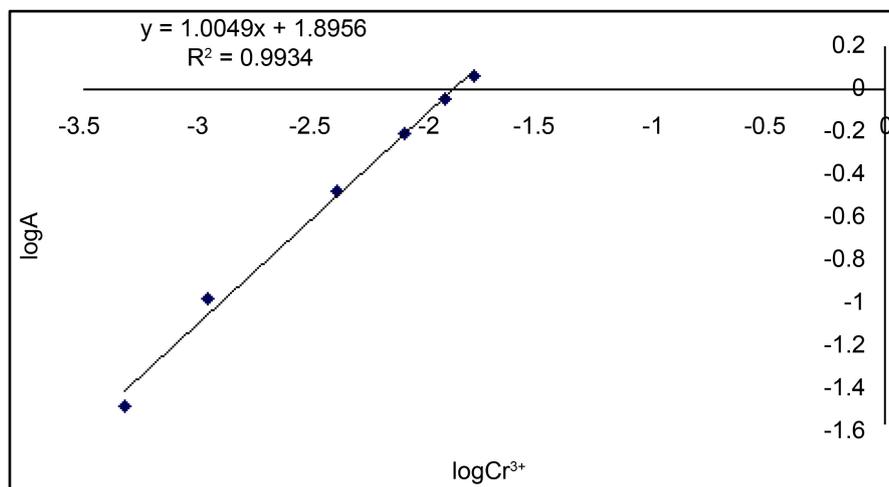
By using the limiting logarithmic technique under ideal conditions, the stoichiometric ratio between the  $\text{Cr}^{3+}$  ion and the ninhydrin was assessed [18]. Two sets of tests were made using this method: the first set varied the concentration of  $\text{Cr}^{3+}$  while maintaining a constant concentration of ninhydrin, and the second set varied the concentration of  $\text{Cr}^{3+}$  while maintaining a constant concentration of ninhydrin. To identify the order of reaction of the  $\text{Cr}^{3+}$  with respect to ninhydrin or vice versa, log absorbance versus log  $[\text{Cr}^{3+}]$  and log ninhydrin were plotted to evaluate the slope of the corresponding line, as shown in **Figure 10**. It was observed that the slope was 1.0049 for various concentrations of  $\text{Cr}^{3+}$ . The slope of **Figure 11** is at varying ninhydrin concentrations. At different ninhydrin concentrations, the slope from **Figure 11** was equal to about 2. This validated the 1:2 molar ratio of coupling between  $\text{Cr}^{3+}$  and ninhydrin.

Depending on the data that obtained from **Figure 10** and **Figure 11**, the proposed chemical equation of the reaction between  $\text{Cr}^{3+}$  and ninhydrin is shown at **Scheme 1**.

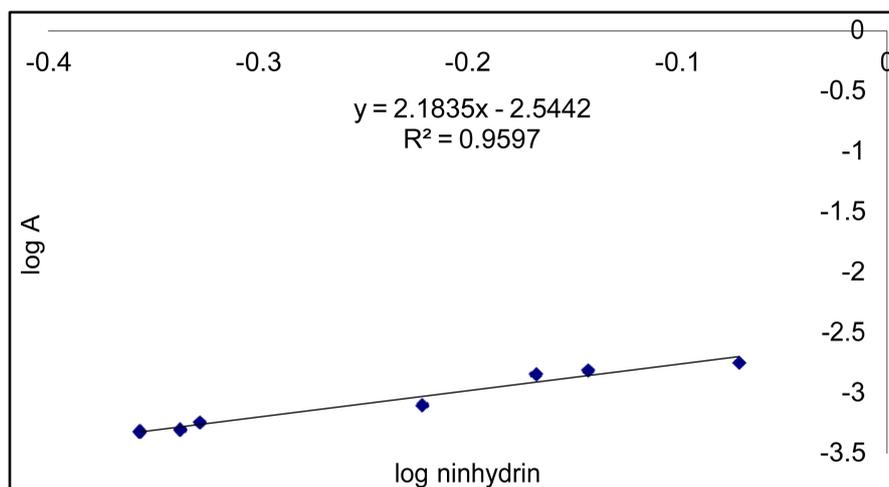
### 3.11. Kinetic Studies

#### 3.11.1. Initial Rate of Reaction

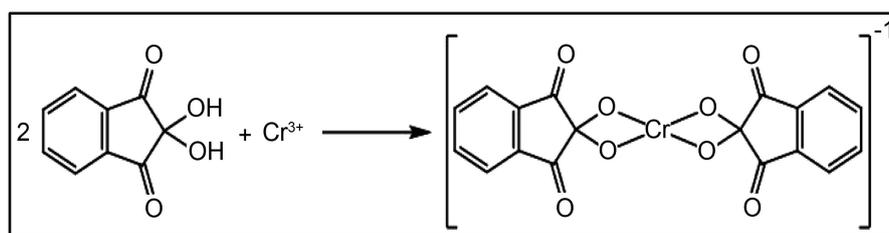
By measuring the slopes of the initial tangent to the absorbance-time curves and



**Figure 10.** Limiting logarithmic plot for  $\text{Cr}^{3+}$  reaction.



**Figure 11.** Limiting logarithmic plot for ninhydrin reaction.



**Scheme 1.** Proposed reaction of complex formation (Cr-Ninhydrin)

getting the linear range from each curve to determine the slope, the initial rate constant ( $K$ ) of the reaction was identified from the absorbance-time plot under the most favorable conditions. In four experiments with various concentration of  $\text{Cr}^{3+}$  prepared in 50 mL volumetric flasks between ( $1.1 \times 10^{-3}$  -  $1.6 \times 10^{-2}$ ) M, the measured absorbance at 373 nm increased as a function of time, and the limiting logarithm absorbance versus the time plots were constructed under the the best possible conditions.

For each curve, the slope, which corresponds to the reaction's initial rate constant ( $k$ ), was calculated at various concentrations, as shown in **Table 4**. The following equation was used to estimate the reaction's order:

$$\text{Log}K = \log k' + n \log C$$

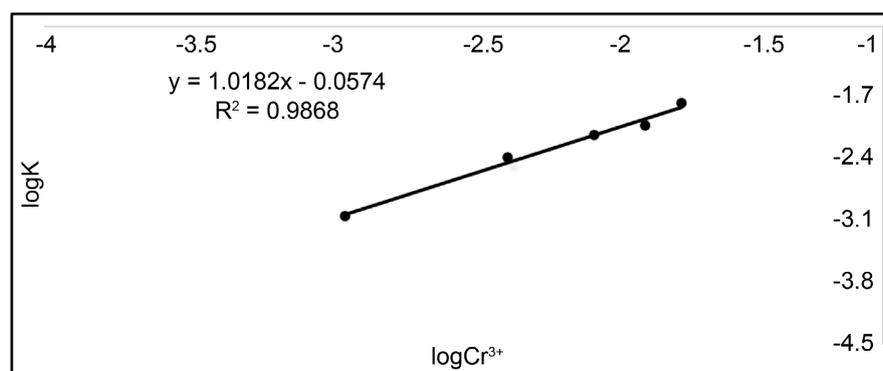
where  $K$  is the initial rate of the reaction,  $C$  is the molar concentration of  $\text{Cr}^{3+}$ ,  $n$  is the order of the reaction, and  $k'$  is the apparent rate constant. The linear regression equation is:  $\text{Log}K = 1.0182x - 0.0574$  with  $R^2 = 0.9868$ , the slope value which is  $n$  is 1.0182 ( $\approx 1$ ) therefore confirming that the order of the reaction is the first one. The experimental  $K$  values were utilized to plot the linear curve;  $\log K$  vs  $\log C$  as shown in **Figure 12**. The data analysis was carried out with a 95% level of confidence; the standard errors of the slope and intercept are 0.0648 and 0.1535, respectively [19] [20].

### 3.11.2. The Fixed-Time Method

At various  $\text{Cr}^{3+}$  concentrations, the reaction's rate was calculated by measuring the absorbance at a predetermined fixed time that was precisely calculated [20]. As shown in **Table 5**, calibration curves of absorbance ( $\Delta A$ ) vs initial  $\text{Cr}^{3+}$

**Table 4.** Initial rate of reaction at different concentrations of  $\text{Cr}^{3+}$  Ninhydrin = 0.0024 M and 0.0089 M KOH at room temperature.

| $[\text{Cr}^{3+}]$<br>mol/L | Regression equation                       | Initial rate<br>reaction ( $k$ ) | $\log \text{Cr}^{3+}$ | $\text{Log}k$ |
|-----------------------------|---|----------------------------------|-----------------------|---------------|
| 0.0011                      | $y = -0.0008x + 0.1023$<br>$R^2 = 0.9552$ | $8 \times 10^{-3}$               | -2.96                 | -3.09         |
| 0.004                       | $y = -0.0075x + 0.3375$<br>$R^2 = 0.9549$ | $7.5 \times 10^{-3}$             | -2.40                 | -2.12         |
| 0.008                       | $y = -0.0078x + 0.6436$<br>$R^2 = 0.9295$ | $7.8 \times 10^{-3}$             | -2.10                 | -2.10         |
| 0.012                       | $y = -0.0087x + 0.9542$<br>$R^2 = 0.892$  | $8.7 \times 10^{-3}$             | -1.92                 | -2.06         |
| 0.016                       | $y = -0.0142x + 1.1707$<br>$R^2 = 0.9886$ | $1.42 \times 10^{-2}$            | -1.80                 | -1.84         |



**Figure 12.** Linear plot for  $\log C$  vs.  $\log k$  for the kinetic reaction of  $\text{Cr}^{3+}$ .

**Table 5.** Regression equations for Cr<sup>3+</sup> ions over range ( $1.1 \times 10^{-3}$  -  $1.6 \times 10^{-2}$ ) M at room temperature.

| $\Delta A$ | Time interval (min) | Regression equation    | Correlation coefficient ( $R^2$ ) |
|------------|---------------------|------------------------|-----------------------------------|
| A4 - A2    | 2 - 4               | $y = 3.5089x - 0.0034$ | 0.794                             |
| A6 - A2    | 2 - 6               | $y = 4.6634x - 0.0041$ | 0.7724                            |
| A8 - A2    | 2 - 8               | $y = 7.4594x - 0.0067$ | 0.8962                            |
| A10 - A2   | 2 - 10              | $y = 6.8909x + 0.002$  | 0.8255                            |
| A12 - A2   | 1 - 12              | $y = 7.9068x + 0.0242$ | 0.7553                            |
| A14 - A2   | 2 - 14              | $y = 10.104x + 0.0043$ | 0.9131                            |
| A16 - A2   | 2 - 16              | $y = 11.495x + 0.0173$ | 0.8976                            |
| A18 - A2   | 2 - 18              | $y = 12.687x + 0.0277$ | 0.8465                            |
| A20 - A2   | 2 - 20              | $y = 23.097x - 0.0325$ | 0.8131                            |

concentration were created at specified intervals of 2, 4, 6, 8, 10, 12, 14, 16, and 20 min (5).

From this table it can be conclude that the best time for measurement is at the time A14-A2 because at this interval the  $R^2$  is 0.913 which is the highest, also we can consider the slope which represent the molar absorptivity, the time interval A20-A2 is also can be applied because it has the higher molar absorptivity.

#### 4. Conclusion

In this research, a new spectrophotometric method for the determination of Cr (III) using ninhydrin was investigated. Ninhydrin in this research acts as chromogenic agent. The ability of ninhydrin (a bidentate ligand) to function as an analytical reagent was the subject of some interesting and practical data presented in this work. The chromogenic reagent in this procedure was ninhydrin. This technique does not require strict requirements to generate stable colored complex which measured at  $\lambda_{\max} = 375$  nm under variable conditions. Also the experimental results showed that this method is reliable, simple, sensitive, and reproducible for the determination of chromium ions in low concentrations utilizing the inexpensively available ninhydrin. The calibration curve was constructed under optimum conditions. This method has large calibration sensitivity with low values of LOD and LOL and wide working range. Kinetic studies are investigated and the validity is applied. The inter-day and intra-day experiments under the optimum conditions were studied also and the validity was tested.

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## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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