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Spectrophotometric Determination of Micro Amount of Chromium (III) Using Sodium 4-((4,5-diphenyl-imidazol-2-yl)diazenyl)-3-hydroxynaphthalene-1-sulfonate in the Presence of Surfactant, Study of Thermodynamic Functions and Their Analytical Applications

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Abstract:

Using sodium 4-((4,5-diphenyl-imidazol-2-yl)diazenyl)-3-hydroxynaphthalene-1-sulfonate (SDPIHN) as a chromogenic reagent in presence of non-ionic surfactant (Triton x-100) to estimate the chromium(III) ion if the wavelength of this reagent 463 nm to form a dark greenish-brown complex in wavelength 586 nm at pH=10, the complex was stable for longer than 24 hours. Beer's law, molar absorptivity $0.244 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, and Sandal's sensitivity $0.021 \mu\text{g}/\text{cm}^2$ are all observed in the concentration range 1-11 $\mu\text{g}/\text{mL}$. The limits of detection (LOD) and limit of quantification (LOQ), respectively, were 0.117 $\mu\text{g}/\text{mL}$ and 0.385 $\mu\text{g}/\text{mL}$. (mole ratio technique, job's method) were employed to investigate the stoichiometry of complexes, and both methods revealed that the metal to reagent ratio is equal 1:3. The absorption impact value of the reagent concentration, surfactant concentration, pH, reaction duration, temperature, addition sequences, ionic strength, masking agent, and the influence of many parameters such as affect cations and anions, among others. The influence of temperature on the reaction, which was referred to as an exothermic reaction, was also taken into account while calculating thermodynamic functions. Researchers investigated some of the complex solid's physical properties, such as solubility, molar conductivity, and melting point, as part of its development. UV-visible rays were used to investigate the chromium complex, while Relative Standard Deviation (RSD%) and Relative Error (E %) were used to assess the precision and accuracy of the novel method.

Keywords: Azo dye(SDPIHN), Chromium (III), Spectrophotometry, Triton x-100, Drug tablet.

Introduction:

Azo dyes are one of the most important chemicals because they repel metal ions from the periodic table very effectively¹. $\text{R}-\text{N}=\text{N}-\text{R}'$ is the Azo chemical formula, where $(-\text{N}=\text{N}-)$ is the Azo group and R or R' could be aryl or alkyl compounds. Azo compounds with the formula $(\text{R}-\text{N}=\text{N}-\text{R})$ are known as Azo fibrous groups and are not widely used in various fields because they are unstable due to their rapid decomposition into nitrogen, whereas Azo compounds with the formula $(\text{Ar}-\text{N}=\text{N}-\text{Ar})$ are known as aromatic Azo compounds and are more stable due to their active donor $(\text{N}=\text{N})^{2-5}$. When heterocyclic Azo compounds combine with metal ions, they form chelates coordination complexes that are useful in analytical

and biological chemistry⁶⁻⁹. Azo compounds have potent pharmacological activity, and when administered as a metal complex, the drug becomes exceedingly potent¹⁰.

Chromium is an essential nutrient that is required for optimal sugar and fat metabolism. It acts primarily by increasing the effectiveness of insulin. It is found throughout the body, with the largest quantities in the liver, kidneys, spleen, and bone. Chromium exists in the environment in two oxidation states: chromium(III) and chromium(VI). Chromium(III) is a necessary nutrient for appropriate physiological function¹¹. It is a transition element in the periodic table's group VI-B

with the ground-state electrical structure $Ar(3d^5 4s^1)^{12}$.

Surfactants are chemicals that lower the surface tension between two liquids or between a liquid and a solid. Surface tension is a characteristic of liquids. It is the amount of effort or energy required to increase a liquid's surface area due to intermolecular forces¹³. The concentration of molecules at the surface of a liquid determines the proportion of molecules at the surface to those in the liquid's bulk. Surfactants stay on the liquid's surface in low quantities. As additional surfactant is added, the surface tension of water drops. More molecules produce micelles as the surface becomes clogged with surfactants. This is referred to as the critical micelle concentration (CMC)¹⁴.

The aim of this research includes the preparation and characterization of one of the (AZO) derivatives, using the approved spectroscopic methods. A spectrophotometric method for the determination the small amounts of the chromium(III) ion by studying the best conditions for determining the ion with the reagent was developed in a Surfactant medium, the research also includes the study of thermodynamic functions. Finally, this method is applied to some pharmaceutical samples.

Material and Methods:

Preparation of (SDPIHN) ligand¹⁵⁻¹⁷.

A-preparation of (4,5 Diphenyl imidazole)

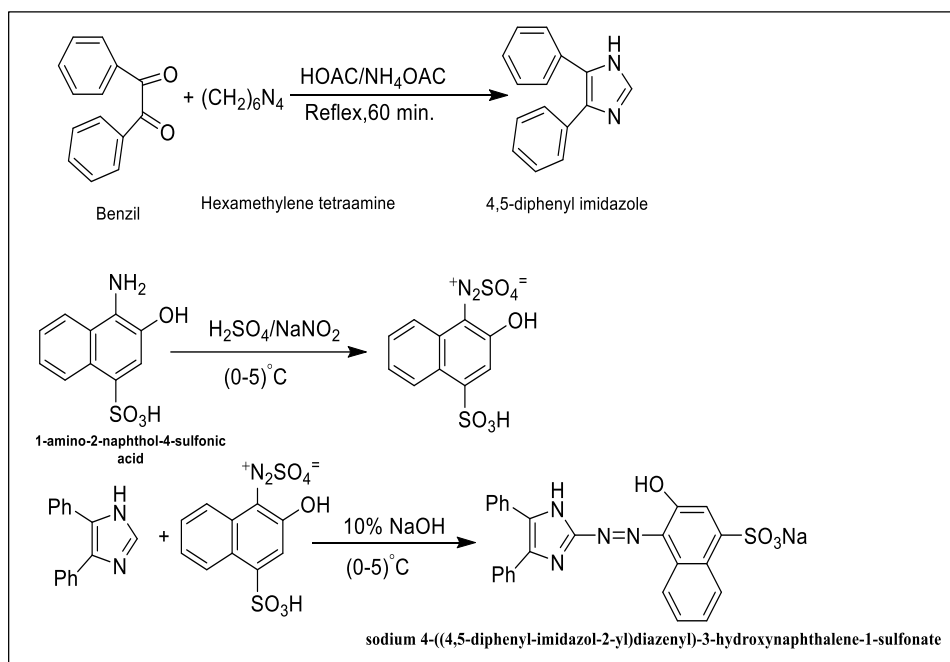
4.2g, 0.02mol of benzil and 1.4g, 0.0099 mole of hexamethylenetetraamine were mixed in a 250mL round flask with 12g,0.155 mole of ammonium acetate, after that comes 80mL of ice acetic acid, and the sublimation of the solution with continued stirring for an hour, then transfer the solution after cooling it to a Baker s capacity 1 L and dilute by adding 400 mL of distilling water, followed by

ammonium hydroxide precipitation of the imidazole derivative to clear the residue, followed by filtration and rinsing with distilled water. The excess base was air-dried and recrystallized from ethanol to form a white precipitate, which was dried and tested for melting point 229⁰C - 230 ⁰C and the yield ratio was 83 %.

B-Synthesis of Ligand Sodium 4-((4,5-diphenyl-imidazol-2-yl)diazenyl)-3-hydroxynaphthalene-1-sulfonate (SDPIHN).

By dissolving 3.588 g, 0.02 mole of 1-amino-2-naphthol-4-sulfonic acid in a solution prepared by combining 4 mL of concentrated sulfuric acid with 50 mL distilled water. The diazonium salt pairs were used to make the new imidazole liquor. Cool the mixture to 0⁰C, then drop in a solution of sodium nitrite 1.38 g, 0.02 mole dissolved in 10 mL distilled water, stirring constantly and keeping the temperature beneath 5⁰C, before allowing the solution to stay for 15 minutes to complete the nitrogenation process.

After cooling the solution to 0⁰C and leaving it for half an hour after dissolving 3.3 g of the imidazole derivative in 50 mL ethanol with 50 mL NaOH 10%. This imidazole derivative solution was gradually added to the salt solution while it was being cooled to 0⁰C as shown in scheme 1. The solution was stained a dark crimson color, and it was then left at 0⁰C for 2 hours. The acidity function pH=6 was then obtained by adding dilute hydrochloric acid 50mL,1M to it drop by drop to generate a reddish-orange precipitate. The precipitate was filtered and rinsed with pure water to remove the sodium sulfate formed during the pairs and neutralization procedures, then dried and recrystallized with ethanol to produce its pure form and the yield ratio was 57%.



Preparation of Standard Solutions:

1. Chromium (III) solution 1 mg/mL: prepared by dissolving 0.769 g of $[\text{Cr}(\text{NO}_3)_3] \cdot 9\text{H}_2\text{O}$ in 100 mL distilled water.
2. Sodium hydroxide solution 0.1M: 100 mL of distilled water was added to 0.4 g sodium hydroxide to prepare this solution.
3. Hydrochloric acid solution 0.1M: 0.40 mL concentrated hydrochloric acid 38 %, 1.19 g/mL was diluted in 50 mL of distilled water to prepare this solution.
4. Reagent solution (SDPIHN) 2.032×10^{-3} M : was prepared by dissolving 0.1g of the reagent in absolute ethanol then completing the volume to 100 mL volumetric flask with ethanol, the purity of this reagent is 99.5 %.

Interferences:

Cations solution of (Cd^{2+} , Ni^{2+} , Fe^{3+} , Cu^{2+} , Pb^{2+} , Co^{2+} , Mg^{2+} , Hg^{2+} and Ag^+) ions 0.1mg/mL were prepared by dissolving 0.219g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$,

0.495g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.723g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.380g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 0.159g of $\text{Pb}(\text{NO}_3)_2$, 0.493g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1.055g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.170g of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 0.157g of AgNO_3 respectively in 100 mL of distilled water for each.

Results and Discussion:

The absorption spectra of the reagent and chromium (III) complex are shown in Figs.1,2. The reagent solution spectra has an absorption maximum of $\lambda_{\text{max}} = 463$ nm, while the chromium (III) complex formed at pH=10 has an absorption maximum of $\lambda_{\text{max}} = 586$ nm, indicating that the complex formation is accompanied by a significant increase in absorbance and a bathochromic shift (red shift) of approximately 123 nm. This indicates a complex composition.

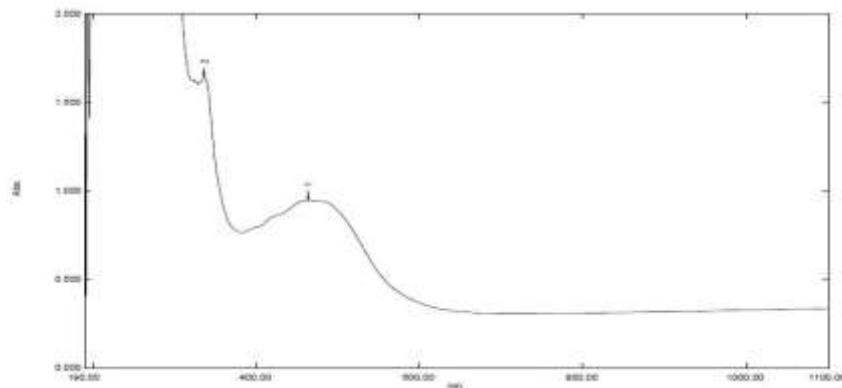


Figure 1. The electronic spectrum data of reagent [SDPIHN]

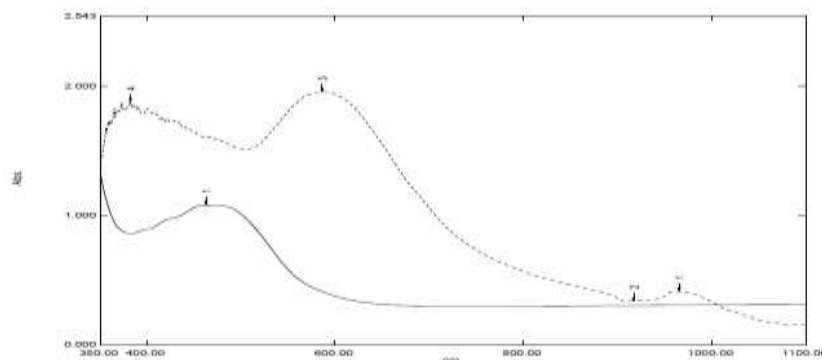


Figure 2. UV-visible spectrum of Cr (III) complex with [SDPIHN] reagent

The dashed line represents the spectrum of Cr (III) complex and the solid line represent the spectrum of the reagent.

The Effect of Adding Surfactants:

Surfactants have a major impact on spectrophotometry and chromatography, particularly in the development of new ion estimation methods. Numerous studies have emphasized the importance of the development of (metal-ligand) complexes in systems including the

(Micelle) system, for reasons such as the creation of the complex may be more stable in these systems, therefore the effect of adding (Triton X-100) was investigated and (Triton X-114), (Tween-80), and (Sodium Dodecyl Sulfate) was investigated in the absorbance of chromium (III). The anionic, cationic and neutral surfactants were used to show the effect of these species on the formation of the complex, as shown in Table 1.

Table 1. Absorption values of chromium complex

Concentration of surfactant (v/v %)	Absorption values of Cr complex in (Tween-80)	Absorption values of Cr complex in (Triton x-114)	Absorption values of Cr complex in (Triton x-100)	Absorption values of Cr complex in (Sodium Dodecyl Sulfate)
1%	0.143	0.141	0.155	0.114
2%	0.145	0.144	0.160	0.109
3%	0.164	0.153	0.172	0.099

Absorption of Cr complex without addition =0.138

Optimization of Reaction Conditions:

1- Effect of optimum value of reagent.

The influence of the reagent solution volume on the production of the chromium (III) complex was investigated. The results in Table 2 show that when the reagent solution is added to chromium (III) complex, the absorbance values of the complex increase until it reaches its peak. The reason is that when the metal ion interacts with the reagent in the direction of creating the complex and giving better color intensity. The absorption values begin to decrease as the volume of the reagent increases, and this could be due to the fullness or adequacy of the coordination failure of the ion in the reagent or the insolubility of the reagent with the solvent.

Table 2. Effect of reagent volume on Cr(III)-SDPIHN

Volume of reagent (mL)	Abs.
0.5	0.074
1	0.141
1.5	0.201
2	0.325
2.5	0.379
3	0.440
3.5	0.382

2-Effect of surfactant (Tx-100) volume

As revealed in the experiment, the influence of surfactant (Tx-100) volume on chromium complex absorbance is displayed in Table 3.

Table 3. The effect of (Tx-100) volume

Volume of (Tx-100) (mL)	Abs.
0.25	0.450
0.5	0.483
1	0.478
1.5	0.401
2	0.384

The results in the tables above show that when the (Tx-100) solution is added to the chromium (III) complex, the absorbance values of the complex increase until it reaches its peak. The absorption values begin to decrease as the volume of the surfactant increases.

3-The effect of pH value:

The absorbance was measured at 586nm at 20°C using a standard amount of chromium(III) and reagent (SDPIHN) buffered at several pH-ranges from 2 to 11 using HCl 0.1M/ NaOH 0.1M as shown in Fig.3, and the final pH of each solution was calculated with a pH-meter.

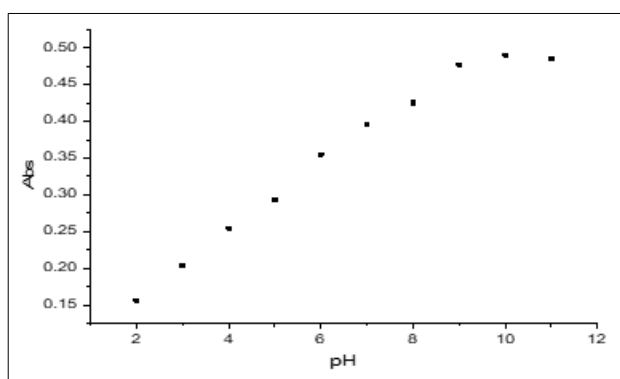


Figure 3. Effect of pH on absorption of Cr(III) complex with reagent.

The absorbance of the chromium complex solution grew steadily as the pH increased from 2 to 10, but rapidly declined above pH 10. The higher absorbance of the chromium complex solution under these circumstances could be attributed to an increase in the reagent's sensitivity at pH 10 .

4-The effect of Time:

Table 4 shows the reagent's follow-up interaction with the ion under optimal conditions. These findings reflect the composition of the chromium(III) complex, which is stable (in terms of absorption values) 24 hours after the experiment started.

Table 4. The effect of Time on Cr(III) complex

Time(min.)	Absorbance
1	0.485
10	0.488
20	0.488
30	0.488
60	0.486
120	0.483
180	0.479
240	0.475

1440 0.464

5-Effect of Temperature:

The influence of temperature variation on the development of complexes was investigated. Table 5 illustrates the findings of this study, which reveal that at the temperature of 30 °C. The complex's absorption values reach their peak and produce the best color intensity; however, the absorption values thereafter diminish, possibly due to a decrease in the complex's stability.

Table 5. Temperature effect on Cr(III) complex

Temperature °C	Abs.
10	0.477
15	0.491
20	0.487
30	0.445
40	0.380
50	0.274
60	0.211

6-Effect of Sequence:

The six addition arrangements were used to investigate the sequence of the reaction content in a complex absorbance. The findings are summarized in Table 6.

Table 6. Sequence effect on Cr(III) complex

Sequence number	Sequence of addition	Abs. of Cr complex
1	M+L+Tx-100+pH	0.489
2	M+ Tx-100+L+pH	0.416
3	Tx-100+M+L+pH	0.430
4	L+M+Tx-100+pH	0.425
5	M+pH+L+Tx-100	0.401
6	M+L+pH+Tx-100	0.411

Tx-100 = triton x-100, pH = hydrogen ion functions
M = chromium ion, L = ligand

The results in table 6 demonstrate that the first sequence is the best, but the other sequence results in a drop in complex absorbance, which might be due to the impact of acid, base inions with metal, therefore the first sequence was used to determine the chromium ion complex in this approach.

7- Ionic Strength Effect:

The sodium nitrate and sodium sulfate salts were prepared at different concentrations ranging from 0.0005 M -0.5 M for each salt in order to demonstrate the influence of ionic strength on the absorption of chromium(III) complex after adding 1mL from solutions of these salts to complex chromium(III) as shown in Table 7.

Table 7. Effect of ionic strength on Cr(III) complex.

Adding salt	Conc.(M) of add salt	Abs.	Added salt	Conc.(M)of add salt	Abs.
Na ₂ SO ₄	0.5	0.385	NaNO ₃	0.5	0.388
	0.05	0.372		0.05	0.391
	0.005	0.401		0.005	0.415
	0.0005	0.473		0.0005	0.452

Abs. of Cr (III) complex without adding =0.489

According to the data provided in Table 7, all of the concentrations listed in the table have little effect on the absorption value.

Calibration Curve:

In the concentration range 1 µg/mL –11 µg/mL, Beer's law is obeyed. The molar absorptivity is $0.244 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and the absorbance of the chromium ion complex was found to be linear based on the metal concentration. Figure 4 depicted the ion chromium calibration curve, while Table 8 supplied analytical data for quantifying chromium ions using reagents (SDPIHN).

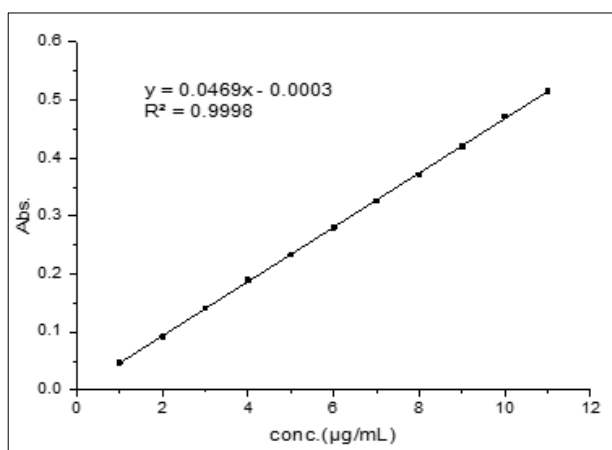


Figure 4. Calibration curve for spectrophotometric determination of chromium (III)

Table 8. Data collected for chromium (III) analysis

Analytical Data	Value
Molar Absorptivity ($\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)	0.244×10^4
Slope	0.0469
Linear equation	$Y=0.0469X$
Linear range ($\mu\text{g/mL}$)	(1-11)
Sandall sensitivity ($\mu\text{g/cm}^2$)	0.0213
Detection limit ($\mu\text{g/mL}$)	0.1167
Limit of quantification ($\mu\text{g/mL}$)	0.3852
Linearity coefficient (R^2)	0.9998
Correlation coefficient (r)	0.99989
λ_{max}	586 nm
Color of product	Dark greenish brown

Stoichiometry and Formation Constant Estimation¹⁸:

To investigate the composition of the complex produced, the mole ratio method was combined with Job's method of continuous variations. At pH=10, both approaches revealed that the metal ion to reagent ratio (M:L) was 1:3.

1-Job's Method¹⁹

In this procedure, a mixture of various identical concentrations of the ion (Cr^{3+}) and the ligand were generated in different amounts of solution $1 \times 10^{-4} \text{ M}$ as shown in Fig.5.

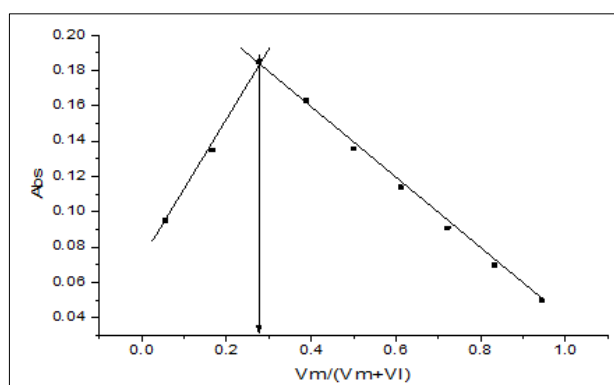


Figure 5. Job's method

2-Mole Ratio Method²⁰

The approach indicates that chromium ion forms a 1:3 complex (M-L) with reagent by utilizing a known and constant concentration of chromium (III) ion $6.127 \times 10^{-4} \text{ M}$ with increasing concentration of reagent (SDPIHN) $1.53 \times 10^{-4} \text{ M}$ – $27.508 \times 10^{-4} \text{ M}$ as shown in Fig.6.

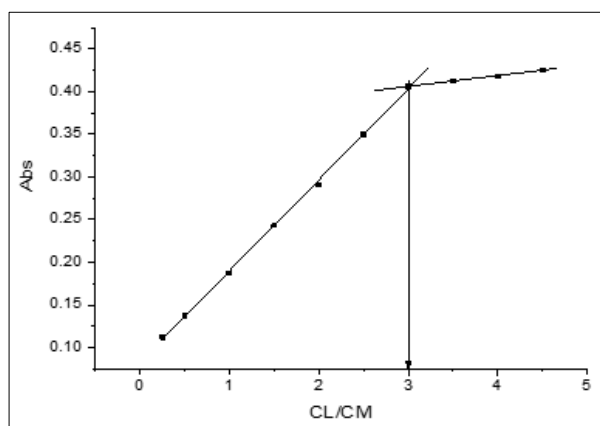
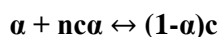


Figure 6. Method of Mole Ratio



$$K = \frac{[ML_n]}{[M^{+n}][L]^n}$$

$$K = \frac{(1-\alpha)c}{\alpha c(n\alpha c)^n}$$

$$K = \frac{1-\alpha}{n^n \alpha^{n+1} c^n}$$

$$\alpha = \frac{Am - As}{Am}$$

Where (As) is absorption at the stoichiometric concentration and (Am) is maximum absorption.

The stability constant was calculated using the mole ratio technique from the equilibrium reaction of the colored complex. The calculated findings are displayed in Table 9.

Table 9. The value of the complex stability constant

Complex	(Am) Value	(As) Value	degree of dissociation (α)	Stability Constant (K)
[Cr (SDPIHN) ₃]	0.406	0.425	0.045	1.125×10^{14}

Results in Table 9 show that the complex is stable, and allowing the ligand (SDPIHN) to be used in the estimation of chromium ions' spectrum.

The impact of temperature on the stability constant of the [Cr(SDPIHN)₃] complex:

At temperatures ranging from 10⁰C-30⁰C, the values of the Cr(III) stability constant with the reagent (SDPIHN) were investigated. Table 10 displays the results

Table 10. The impact of temperatures on the stability constant of Cr (III) complex.

T (°C)	T (K)	α	$K \times 10^{10}$
10	283.15	0.320	3.133
15	288.15	0.311	3.609
20	293.15	0.302	4.053
25	298.15	0.294	4.565
30	303.15	0.285	5.235

The data in Table 10 showed that temperature had only a minor impact on the stability of the complex.

Complex's Thermodynamic Function:

Thermodynamic functions ΔG , ΔH and ΔS were determined, and the results are shown in Fig. 7 and Table 11.

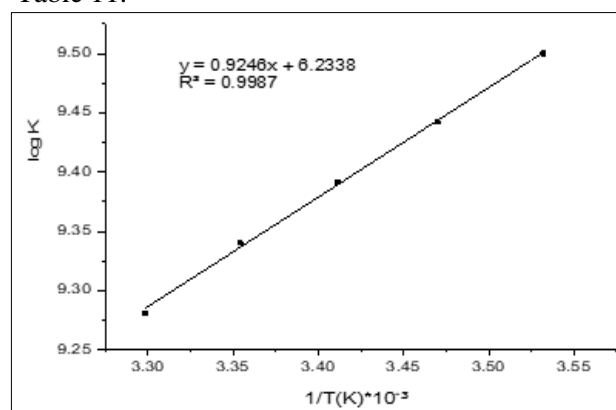


Figure 7. Relationship between Log K and 1/T values of chromium (III) complex

Table 11. The impact of temperature on thermodynamic function for chromium (III) complex.

T(K)	$1/T \times 10^{-3} (K^{-1})$	log K	ΔH	ΔG (K.J/mole)	ΔS (K.J/mole .K)
283.15	3.532	9.500		-51.437	0.11916
288.15	3.470	9.442	-18.3744	-52.026	0.11913
293.15	3.411	9.392		-52.648	0.11922
298.15	3.354	9.340		-53.249	0.11924
303.15	3.298	9.281		-53.801	0.11909

When the enthalpy value is negative, the reaction is exothermic, which may be seen by decreasing the temperature. Because of the negative sign of free energy, the complex formation will be decreased, and the reaction will be spontaneous.

Effect of Foreign Ions:

To explore the interference effect, a specific concentration of different cation and anion solutions as shown in Tables 12, 13, which were utilized as foreign ions, were mixed with chromium solution.

A- The cations effect

B- The inions effect

Table 12. The Cations effect

Foreign/ ions	Cations formula structure	(10µg/mL) Abs. after addition of Cations	Error%
Cd ²⁺	Cd(NO ₃) ₂ .4H ₂ O	0.162	65.96
Ni ²⁺	Ni(NO ₃) ₂ .6H ₂ O	0.398	16.38
Co ²⁺	Co(NO ₃) ₂ .6H ₂ O	0.215	54.83
Fe ³⁺	Fe(NO ₃) ₃ .9H ₂ O	0.277	41.80
Hg ²⁺	Hg(NO ₃) ₂ .H ₂ O	0.332	30.25
Pb ²⁺	Pb(NO ₃) ₂	0.109	77.10
Mg ²⁺	Mg(NO ₃) ₂ .6 H ₂ O	0.409	14.07
Ag ⁺	AgNO ₃	0.358	24.78
Cu ²⁺	Cu(NO ₃) ₂ .3H ₂ O	0.244	48.73

Absorbance without interferences = 0.481

Table 13. The inions effect

Foreign ions	Formula structure of Anions	(906µg/0.5mL) Absorption after addition of Anions	E%	(0.453µg/0.25mL) Absorption after addition of Anions	E%
SO ₄ ²⁻	K ₂ SO ₄	0.420	11.76	0.365	23.31
Br ¹⁻	KBr	0.514	-7.98	0.262	44.95
SCN ¹⁻	KSCN	0.331	30.46	0.107	77.52
IO ₃ ¹⁻	KIO ₃	0.235	50.63	0.311	34.66
CrO ₇ ²⁻	K ₂ CrO ₇	0.105	77.94	0.161	66.17
CO ₃ ²⁻	K ₂ CO ₃	0.382	19.74	0.465	2.31
CN ¹⁻	KCN	0.269	43.48	0.176	63.02

Absorbance without interferences = 0.480

The results obtained in the tables 12 and 13 show that most of the ions have an effect on the absorption values of the chromium(III) complex; depending on the nature of the added ions, some of these ions increased absorbance while others decreased absorbance; this was due to competition of these ions with Cr(III) to form the complex with the ligand, which decreased competition and increased the sensitivity of this method towards Cr(III) ion. The reaction for Cr(III) was both selective and sensitive. By using appropriate agents of omission and substitution, the ability to be discerning in response can be validated.

Effect of Masking agents:

For the determination of the chromium(III) complex, the optimal masking agent is limited. This investigation was done by adding 1mL from each masking agent, as stated in Table14, to see the effect of the competitive process between them and the reagent in interacting with the interfering ions and withholding them.

Table 14. The effect of masking agent on chromium(III) complex absorption

Masking agent (0.1M)	Abs of Cr(III)complex
Without Masking agent	0.487
Thiourea	0.493
Ascorbic acid	0.164
Na ₂ EDTA	0.220
Citric Acid	0.395
KCl	0.343
Na ₂ HPO ₄ .12H ₂ O	0.244
Formaldehyde	0.304

Table 14 shows that (Thiourea) has no influence on the absorption of the produced complex, indicating that it could be utilized as a masking agent.

Use of a best masking agent to determine the chromium (III) complex in the presence of cat ions interference:

The best masking agent (Thiourea) described in table 15 was used to obtain the best estimate of the chromium(III) complex in the presence of interfering cationic ions.

Table 15. The effect of masking agent in the presence of cat ions on chromium (III) complex absorption.

Foreign ions	Absorption after addition cat ion (10µg/mL) and addition masking agent(0.1M)	Relative Error (E%)
Cd ²⁺	0.470	1.26
Ni ²⁺	0.477	-0.21
Co ²⁺	0.440	7.56
Fe ³⁺	0.473	0.63
Hg ²⁺	0.480	-0.840
Pb ²⁺	0.475	0.210
Mg ²⁺	0.462	2.940
Ag ⁺	0.491	-3.150
Cu ²⁺	0.453	4.830

The absorption values of the chromium(III) complex in the presence of interfering cations when adding a better masking agent, absorbance values

near to the absorbance values before adding the interference, can be shown in table 15.

Statistical treatment of the results:

By making three series of chromium ion solution with varying concentrations, reading the absorption three times for each concentration, and then treating the results to determine the value of (RSD %), as shown in Table16, the relative standard deviation was accepted as a measure of precision.

Table 16. Calculation the value of Relative Standard Deviation

chromium added [M]	Abs. of Cr(III) complex	RSD%
5.769×10^{-5}	0.145, 0.144, 0.148, 0.147	1.250
1.154×10^{-4}	0.272, 0.274, 0.278, 0.276	0.939
2.307×10^{-4}	0.522, 0.525, 0.527, 0.521	0.552

Sensitivity of spectrometric method in determination chromium (III) ion

The sensitivity of the method employed to determine chromium in this way was indicated by the expression limit of detection. The results showed that this spectroscopic method can estimate the lowest concentration of chromium ion to be 2.194×10^{-6} M, indicating that the method is successful in determining chromium (III) ion.

Determination of the melting point of the complex:

The melting point of the chromium complex ranged from 231°C - 234°C , while the reagent's melting point was 219°C - 223°C . The discrepancies in melting point values at different degrees of disintegration confirm the complex's complexity and reveal the partial weight gain of the complex relative to the detector's partial weight.

Measurement of Conductivity:

The complex's molecular conductivity was measured at room temperature and under ideal conditions, and it was found to be $360 \mu\text{S}/\text{cm}$. Because conductivity is a measure of an electrolyte solution's ability to charge electricity through the migration of ions under the influence of an electric field, the complex is clearly ionic.

ATR-FTIR spectra for the reagent & Chromium (III) Complex:

ATR-FTIR spectroscopy is one of the common methods of diagnosing and studying the composition of reagents and their complexes. The prepared heterogeneous azo reagent and its complex had studied with infrared spectroscopy. ATR-FTIR spectra was recorded for the reagent and chromium (III) complex explains as shown in Figs.8, 9.

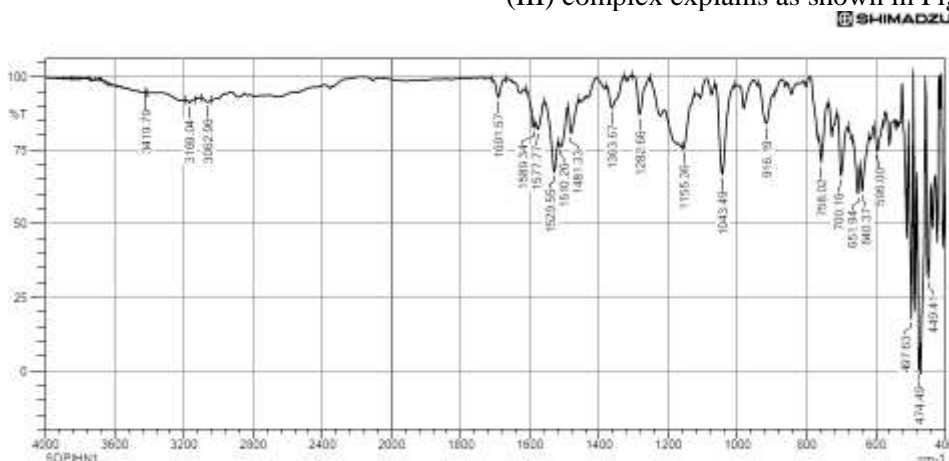


Figure 8. ATR-FTIR Spectrum of the Reagent (SDPIHN)

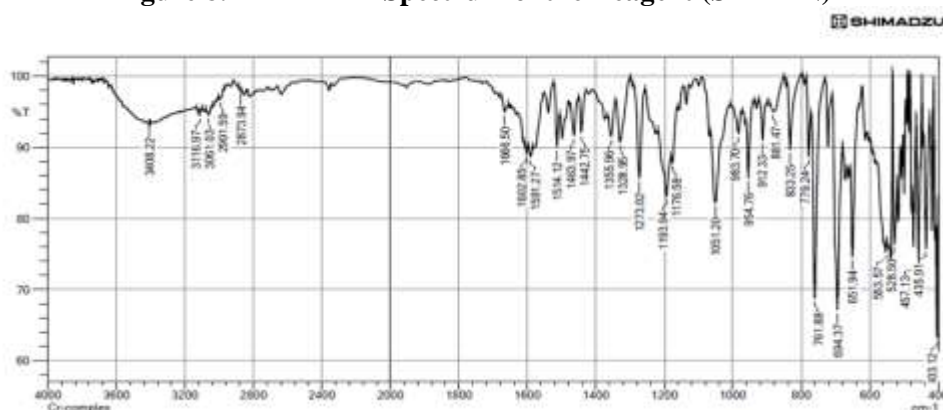


Figure 9. ATR-FTIR Spectrum of Cr(III) complex

The data of ATIR-FTIR Spectra listed in Table 17.

Table 17. Typical ATIR-FTIR absorption frequencies for reagent and chromium (III) complex in (cm⁻¹).

Bond	Reagent	Cr (III) complex
St.(N-H)	3419.79	3408.22
St.(O-H)	3169.04	3116.97
St.(C-H)Aromatic	3062.96	3061.03
St.(C=N)	1691.56	1666.50
St.(C=C)Aromatic	1589.34	1591.27
St.(N=N)	1481.33	1463.97
St.(S=O)	1363.67	1355.69
St.(C-N)	1282.65	1273.02
St.(M-N)	-----	457.13

Table 18. Result of application for chromium (III) in a drug

Abs. of a drug	Conc. Cr(III) present (µg/mL)	Conc. Cr(III) found (µg/mL)	Recovery%	Error%
0.365	8	7.7	96.25	3.75

MADAMAR: the name of company that made (Chromium Niacin).

Conclusion:

A simple, low-cost, rapid, and accurate analytical method for measuring chromium (III) in various samples has been developed. According to the findings, the reagent can detect chromium (III) in a variety of materials. Analytical measures like identification, detection limit, and precision suggest that this technique can determine Cr (III). Because it forms a dark greenish-brown chromium complex, the method is ideal for spectrophotometric examination.

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Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Kerbala.

Authors' contributions statement:

H. A. H. A. A. wrote the manuscript, collected the samples and interpretation the data. A. F. H. analyzed all Results and read the manuscript carefully and approved the final version of MS.

Application:

The proposed method was utilized to determine the amount of chromium(III) in the pharmaceutical sample (Chromium Niacin) that contained chromium as an active component. The sample was prepared using acid digestion (HCl)²¹ procedure before being introduced to a reagent (SDPIHN) to evaluate the chromium concentration in the sample²², the results are shown in table 18.

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التقدير الطيفي لكميات ضئيلة من الكروم الثلاثي باستخدام الكاشف Sodium 4-((4,5-diphenyl-imidazol-2-yl) diazenyl)-3-hydroxynaphthalene-1-sulfonate بوجود المواد المنشطة للسطوح، دراسة الدوال الترموديناميكية وتطبيقاته

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الخلاصة:

تضمنت الدراسة تحضير وتشخيص الكاشف sodium 4-((4,5-diphenyl-imidazol-2-yl) diazenyl)-3-hydroxynaphthalene-1-sulfonate (SDPIHN) وذلك عن طريق الازوتة التقليدية و اجراء دراسة اولية مع ايونات فلزية وتم اختيار ايون الكروم لتقديره طيفيا باستخدام الكاشف المذاب بالايثانول بوجود المادة المنشطة للسطوح (Tx-100) اذ كان الطول الموجي الاعظم للكاشف هو 463nm اما المعقد الكروم المتكون مع الكاشف فكان 586 nm الى جانب ذلك تم دراسة الظروف المثلى لتفاعل هذا الايون مع الكاشف كدالة الحامضية وحجم وتركيز الكاشف وحجم وتركيز المادة المنشطة للسطوح والمدة الزمنية لاستقرارية المعقد المتكون 24 hours ودرجة الحرارة وترتيب الاضافة لمكونات التفاعل وتأثير القوة الايونية كما تم اعداد منحني المعايرة لهذا الايون مع الكاشف فكان الكروم يقع ضمن مدى التراكيز 1-11 $\mu\text{g/mL}$ وقيمة الامتصاص المولارية تساوي $0.244 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$ وحساسية ساندل تساوي 0.021 $\mu\text{g/cm}^2$ وكانت قيمة حد الكشف تساوي 0.117 $\mu\text{g/mL}$ وقيمة الحد الكمي تساوي 0.385 $\mu\text{g/mL}$. كذلك تم دراسة طبيعة المعقد المتكون بين ايون الكروم والكاشف من خلال ايجاد نسبة الأيون الفلزي الى الكاشف (M:L) باستعمال طريقة التغيرات المستمرة والنسبة المولية فكانت تساوي 1:3 كما اوضحت الدراسة تأثير وجود عدد من الايونات الموجبة والسالبة كمتمدخالات محتملة عند تقدير ايون الكروم، وتم دراسة اضافة عوامل حجب مناسبة وايضا تأثير درجة الحرارة على التفاعل والذي تمت الاشارة اليه على انه تفاعل باعث للحرارة حيث تم اخذه بالاعتبار ايضا اثناء حساب الدوال الترموديناميكية الحرارية كما تم دراسة الخصائص الفيزيائية للمعقد الصلب مثل الذوبان ودرجة الانصهار والتوصيلية المولارية وتم تحديد ضبط ودقة الطريقة التحليلية المتبعة من خلال دراسة الانحراف القياسي النسبي (RSD%) والخطأ النسبي (E %).

الكلمات المفتاحية: صبغة الازو، الكروم الثلاثي، المطيافيه، منشط السطح، اقراص دوائيه.