Journal of University of Kerbala , Vol. 20, Issue 2, December 2023

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Research Article

Preparation, Characterization and Spectrophotometric determination of Chromium ion via Diazotization reaction and its application.

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Article Info

Article history:

Received 8-6-2023

Received in revised form
20-6-2023

Accepted 20-6-2023

Available online13-12 -2023

Keywords:
Spectrophotometric, Azo dye (EATDB), Chromium (III) niacin and chromium picolinate.

Abstract

The reagent of Azo compound Ethyl4-(5-acetyl-2,3,4-trihydroxyphenyl) diazenyl benzoate (EATDB), was prepared ,characterized, and examined by using UV-Vis., FT-IR, G.C/Mass spectrum, ^{1}HNMR spectrum and ^{13}C NMR. For a quick determination of Cr (III) ion employing (EATDB) as spectrophotometer reagent, which a sensitive and selective spectrophotometric approach is suggested. Chromium (III) and this reagent react instantly at (max=573nm) and pH= (8) to create prepull complexes with a mole ratio, Job's method and Mollard's method 1: 2 (Cr^{+3}: EATDB) for Cr (III), the absorbance is stable for more than 24 hours. With molar absorptivity (Ɛ) = (0.935x10^2 L/mol.cm and a limit of detection of 0.203 g/ml and a limit of quantification of 0.669 g/mL , Beer's law is observed in the range of (1-100) g/mL. The relative standard deviation was (0.742%). Chromium (III) in pharmaceuticals (drugs containing chromium and niacin) can be determined satisfactorily using this approach. The most interferences were brought on by Ni (II), Zn (II), Co (II), Fe (III), Pb (II), and Cd (II) and suitable masking agent were used.

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1. Introduction.

Several studies have been conducted recently on the detection of toxic compounds in sewage, industrial, and mining waste effluents. Their presence in streams and lakes has led to a variety of health problems in people, plants, and animals. One of these dangerous inorganic compounds is chromium ion.

Chromium is one of the most common elements in nature. Environmental chromium levels have gradually risen because of industrial activity, particularly that of mines, tanneries, and burning facilities. Hydrated chromium (III) species are the most prevalent chromium species in natural media. Trivalent chromium is present in biological tissues and supports the maintenance of healthy protein, carbohydrate, and lipid metabolism [1], include people, as well as having potential carcinogenic and mutagenic effects. Recent research on the analytical methods for chromium determination in liquid and solid matrices reflects the continued interest in monitoring hazardous elements. [2].

Chromium traces in saltwater have an impact on aquatic plant and animal life. The primary sources of metal discharge into the environment that causes chromium pollution include industries producing paint, pigment, dye, mordant, rubber, plastic, ceramic, textile, leather, tanneries, welding processes, smelting works, chrome plating facilities, steel, and its alloys. Cooling liquids used in industry are a substantial additional source of chromium contamination. The maximum allowable concentration of chromium in drinking water is typically 50 g/L, as stated in the Indian guidelines and US Public Health Department drinking water guidelines. [3].

There are various techniques for measuring chromium ions in the literature, but UV-Vis spectrophotometry is the one that is most usually employed. [4–8], HPLC Technique [9], Capillary Electrophoresis [10], Adsorptive Stripping Voltammetry [11–13], flame and FAAS [14–16], and mass spectrometry [17]. The spectrophotometric approach has a unique role in science because of its ease of use, sensitivity, accuracy, and rapidity. Due to the instrument's accessibility, this technique became crucial for modern analytical chemists. The basis for spectrophotometric processes used to identify compounds is the absorption of light. [18].

This study developed a new spectrophotometric method for the measurement of Cr (III) using a new ligand from the Azo compound (Ethyl4-(5-acetyl-2,3,4-trihydroxyphenyldiazenyl benzoate (EATDB) investigated). The stable-colored complex produced was measured at max = 573 nm under various conditions. Under ideal circumstances, the calibration curve was built. This technique was proven to be quick, accurate, straightforward, and repeatable.

2. Materials and Methods

2.1 Indicators and Solutions

The analytical reagents and solutions utilized in the preparation process are of high purity. This ensures that the substances used are free from impurities or contaminants that could potentially affect the accuracy and reliability of the analytical results. The use of high-purity reagents and solutions is crucial in maintaining the integrity of the experiments and obtaining precise measurements and reliable data.

2.2 Preparation of Standard Solutions.

Chromium (III) solution (1000µg/mL)

Prepared by dissolving 0.77 gm from Chromium (III) nitrate [Cr $(NO_3)_3.9H_2O$] in 100 mL distilled water.

Hydrochloric acid (HCl) solution (0.1M)

Prepared by diluting 0.83 mL concentrated hydrochloric acid (HCl) (37%, 1.19 g/cm^3) in 50 ml distilled water.

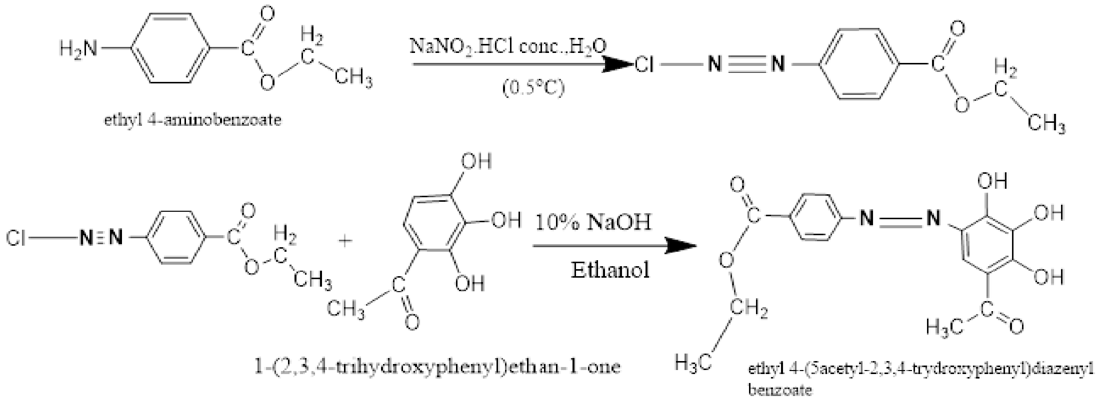
Sodium hydroxide (NaOH) solution (0.1M)

Prepared by addition of 100 mL D.W to 0.4g of NaOH solution.

Reagent solution Ethyl4-(5-acetyl-2,3,4-trihydroxyphenal) diazenylbenzoate. (EATDB)(1000 µg/mL)

The solution was prepared by dissolving an appropriate amount (0.1g) of the substance in pure ethanol. The mixture was then carefully diluted by adding ethanol until the final volume reached 100 mL. This process ensured that the preparation of a homogeneous solution with the desired concentration, suitable for further analysis or experimental procedures.

2.3 Synthesis of Reagent Ethyl4-(5-acetyl-2,3,4-trihydroxyphenal)diazenyl)benzoate (EATDB).
The reagent was synthesis using a standard diazotization aromatic amine preparation method (ethyl4-aminobenzoate[19]. By combining (25 mL) of distilled water with (5 mL) of concentrated HCl to produce a solution, then adding (1.651 gm, 10 mmole) of benzocaine to the mixture. The novel imidazole liquor was produced using the diazonium salt pairs. Drop a solution of sodium nitrite (0.69 gm, 10 mmole), diluted in (10 mL) distilled water, into the mixture once it has cooled to 0–5°C. The nitrogenation process was completed by allowing the solution to settle for 15 minutes with consistent mixing at a temperature lower than 50 °C. After dissolving (1.681 gm) of the 2,3,4-Tri hydroxy aceto phenone in 10 mL of ethanol and 25 mL of NaOH (10%), the solution should be cooled to between (0-5) °C for 30 minutes. The salt solution was cooled to a temperature range of (0-5) °C while the solution of this imidazole derivative was slowly introduced. The solution obtained was a deep red, indicating the creation of a highly pigmented compound. Subsequently, the solution was left at a temperature range of 0 - 5 °C for one hour. The desired acidity range of pH 5–6 was subsequently achieved by gradually introducing diluted hydrochloric acid (5 mL, 1M) until a reddish-orange solid was formed. The resulting precipitate underwent filtration and was subsequently washed with distilled water to eliminate any sodium sulfate (Na_2SO_4) that might have formed during the reaction and neutralization processes, then subjected to drying and purification using ethanol to obtain its pure form, yielding 67%. The chemical equation for the synthesis can be shown in Scheme (1) [20]:-



Scheme (1): Preparation of (EATDB) Reagent

2.4 Preliminary Study:

In a test tube, a 1 mL solution containing Cr^{+3} ions at a concentration of 1000 µg/mL was carefully placed. Subsequently, drop by drop, 2 mL of a prepared solution containing the reagent (EATDB) at a concentration of 1000 µg/mL was added to the test tube while shaking, resulting in the formation of a colored precipitate.

To observe the effect of the acid function, a component of this mixture received drops of hydrochloric acid (0.1M), whereas a different fraction received drops of hydroxide of sodium (0.1M). Investigating how acid and base affected color creation was the goal.

It was observed that the color formed prominently under basic conditions, indicating a positive response. However, there was no change in color under acidic conditions, indicating a lack of reactivity or color formation. This observation suggests that the chromium (III) complex with the reagent (EATDB) exhibits a strong color response in basic environments, while acidic conditions do not elicit a visible color change.

2.5 Determination of Chromium (III) ion in drug:

Ten Tablets each of chromium (III) niacin (200 µg Cr^{+3}) and chromium picolinate (1000 µg Cr^{+3}) were taken separately, ground, and heated for 2 hours at approximately 300°C in a muffle furnace. The resulting liquid was transferred from the muffle furnace to a volumetric flask and then filled to the mark with 0.1 M HCl. The mixture was then filtered. Next, 10 mL of the chromium niacin solution and 5 mL of the chromium picolinate solution were separately filtered, and to each of them, 2.5 mL of 1 M KCl solution was added. After that, distilled water was used to dilute each solution to a final volume of 100 mL. Subsequently, 5 mL of each prepared drug solution (chromium niacin and chromium picolinate) was added to separate 10 mL volumetric flasks. To each flask, 2 ml of the ligand solution at ($2.032x10^{-3}$) M was added. The pH was then adjusted to 8, following the optimal conditions found in this study. Finally, the volume in each flask was filled to the appropriate mark with D.W. The same dilution technique was applied to prepare comparison solutions, but instead of using the medication solution, an equivalent volume of distilled water was used. This experimental procedure allowed for the preparation of solutions containing the drug samples and the ligand solution, under specific conditions, to investigate their complex formations. The comparison solutions prepared similarly, served as a control to evaluate the interactions and complex formations between the drugs and the ligand. [21]

3. Results and Discussion:

3.1 UV-visible spectroscopy:

The reagent solution (EATDB) with a concentration of (1000 µg/mL) was mixed with Cr^{+3} Ion solutions with a concentration of (100 µg/mL) to form the colored complex, then the spectra of both were taken against blank solution as illustrated in Figure (1).

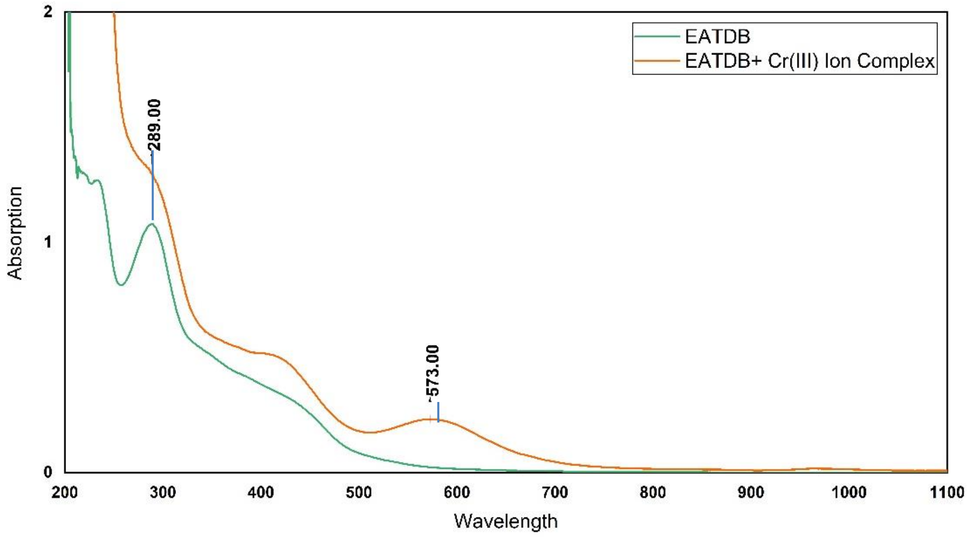
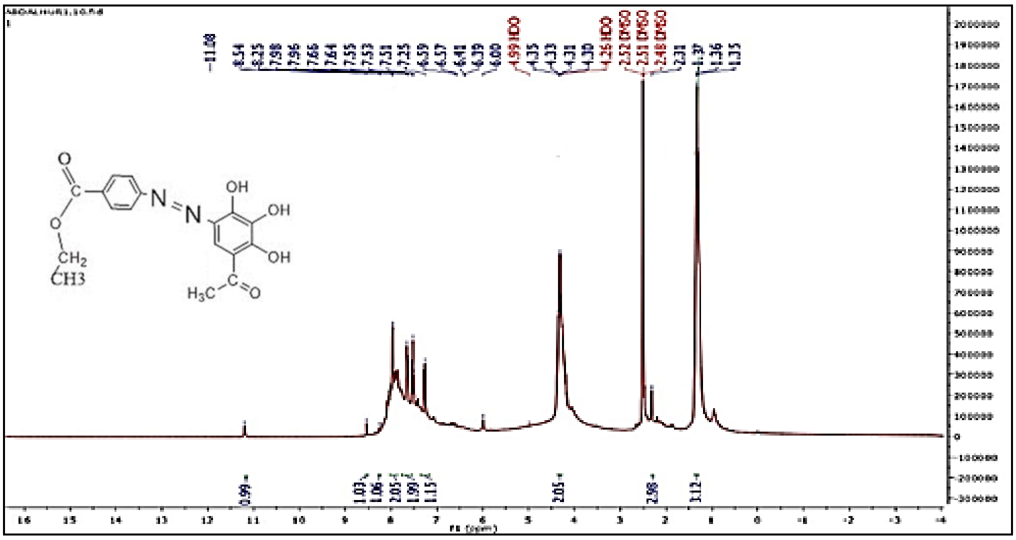


Figure (1): UV-visible of Reagent Cr (III) Complex.

The spectra in Fig (1) displayed a peak at 289 nm for the regent due to the (π-π*) electron transfer. Upon the complexation of the reagent with chromium (III) ion, a new peak appeared at 573 nm related to (n-π*) electron transfer. This change in electronic transition confirms the formation of the Cr-EATDB complex.

3.2 ^{1}HNMR Spectrums for the Reagent:

Utilizing DMSO-d6 as a solvent ^{1}H-NMR (Fig.2) and ^{13}CNMR (Fig.3) spectra corresponding to the reagent under study. Using DMSO-d6 as a solvent, both spectrums of ^{1}H-NMR and ^{13}CNMR that were associated to the reagent were determined. The 1HNMR spectrum of (EATDB) Figure 3.5 displayed three slight broadening signals for OH groups; the first signal was at 11.08 ppm corresponds to OH, the second signal at 8.54 ppm contributed OH, proton of the third signal at 8.25 ppm belongs to OH. The spectrum exhibits a triplet signal at 1.36ppm, representing the CH3 proton in CH3-CH2 which is adjacent to the CH2 group. Furthermore, there were also two signals displayed in the spectrum; the first signal was a quartet at 4.32 ppm corresponding to (CH2-CH3), and the second signal was a singlet at 3.65 ppm, corresponding to the methyl protons adjacent to the carbonyl group -CH3-C=O, also the spectrum showed the signals of five aromatic protons in the range of 7.79-7.25 ppm..



Figures (2): ^{1}HNMR spectroscopic spectrum of reagent (EATDB).

3.3 ^{13}CNMR

^{13}CNMR was used to verify the structure of the reagent which gives a distinct peak. The characteristic peak for carbonyl ester appeared at 166.4 ppm while for carbonyl ketone at 203.2 ppm. There were peaks between 61.1-14.2 ppm confirming the presence of CH_2- and CH_3- proton for the reagent. In addition to that, seven peaks appeared in the range of 152.4-108.5 ppm related to the aromatic carbons. The test showed that the molecular ion peaks match the exact molecular weight calculated from the ideal structure as shown in Fig. (3).

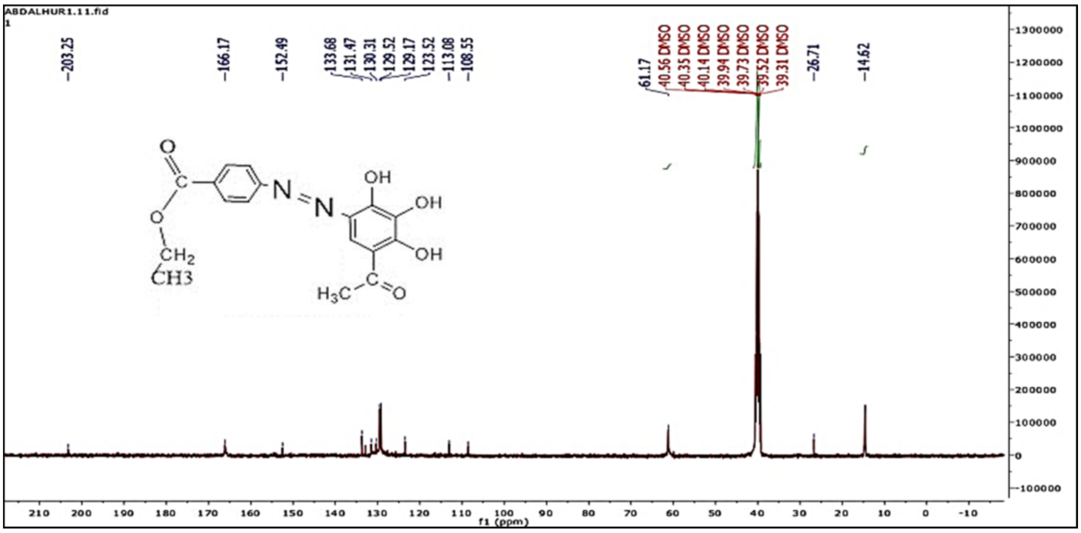


Figure 3. The ^{13}CNMR of the ligand (EATDB).

3.3 Gas Chromatography Mass spectroscopy test of the reagent.

Gas Chromatography / Mass Spectroscopy analysis (GC/MS) (Fig.4) for the reagent was clearly demonstrated that the calculated molecular weight (344 g/mL) aligns accurately with experimental results.

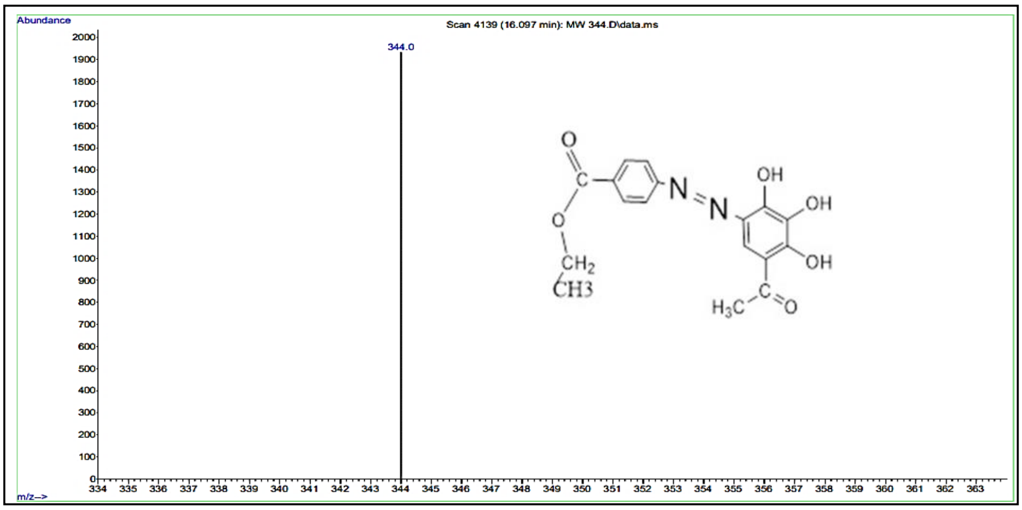


Figure (4): GC/ Mass of reagent (EATDB).

3.4 Optimization condition

3.4.1 Effect of pH

A sequences of chromium (III) ions solutions were prepared by mixing Cr (III) ion solution with reagent solution at a concentration of 500 µg/mL. The acidity of these prepared solutions was adjusted to various levels within the range of 2-10 using HCL (0.1M) and NaOH (0.1 M). The results explained in (Fig.5).

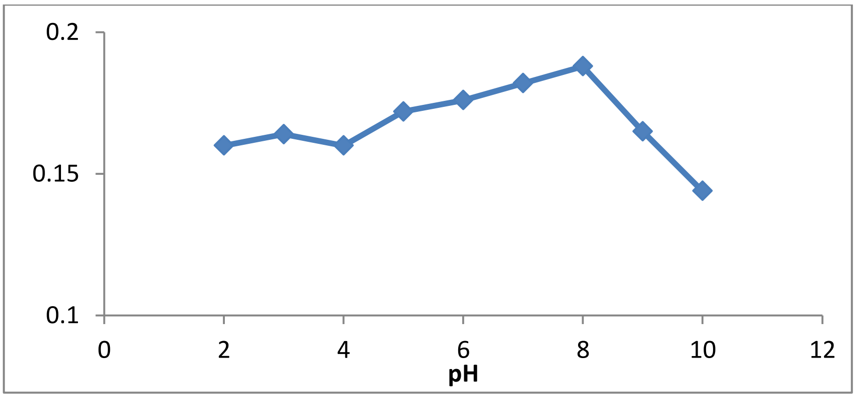


Figure (5): Effect of pH value.

A notable increase in the absorption was observed as shown in (Fig.5) up to pH = 8 after which the absorption decreased due to the formation of precipitate [22].

3.4.2 Sequence of Addition Influence.

The impact of various addition sequences was examined using the sequences provided in Table (1) under the optimum conditions to determine the influence of order addition on the formation of the complex and to identify the most advantageous sequence achieving desired result.

Table (1): Cr (III)-EATDB sequence influence

Seq.	Addition Seq.	Absorption of complex
1st	M+L+PH	0.189
2nd	M + PH + L	0.186
3rd	L + PH + M	0.180
4th	L+M+PH	0.185

Where; L=Reagent & M = Metal

Regarding the finding presented in Table (1), the first sequence was approved for further optimization due to the high absorbance achieved.

3.4.3 Effect of Time.

The impact of the degree of stability of the newly produced compounds was looked into as a key component in Figuring out how long the molecule could remain stable. The stability of the complex is crucial for its storage and practical usage.

Table 2 Time influence on Cr (lll)-(EATDB).

Time (min.)	1	10	20	30	60	120	240	1440
Absorbance.	0.188	0.188	0.186	0.190	0.192	0.189	0.184	0.185

The finding explained in Table (2) demonstrated that the chromium (III) complex has impressive notable stability for a period of 24 hr. regarded to the constant absorption values. These findings improve the importance and usefulness of the reagent to determine the chromium (III) ion.

3.4.4 Effect of Temperature

The impact of temperature on the absorption of Cr (lll) complex was investigated and the results were reported in Table (3).

Table (3): Temperature influence on Cr (III)-(EATDB)

Temp. °C	10	20	30	40	50	60
Absorption	0.190	0.189	0.188	0.189	0.154	0.139

It was noticed that chromium (III) complex exhibited high absorption within the temperature range from 10-40 °C. This temperature range enables the most prominent and preferred color development, indicating the highest stability and reactivity of the complex with this temperature range.

Taking into account the effect of temperature on the stability of complex, the impact of temperature was examined within the range of 10-60 °C under optimized conditions. This analysis offers valuable understanding of the behavior and stability of the complex. As a result, from the data illustrated in Table (3) it was found that increased temperature affects the stability of the complex leading to dissociation.

3.4.5 Effect of ionic strength

Through the addition of 1 mL of prepared solutions of sodium nitrate and sodium sulfate at various concentrations ranging from 0.0005-0.5 M for each salt, the effect of ionic strength on the absorption of chromium (III) complex was assessed. Observed outcomes were sorted in Table (4).

Table (4): ionic strength influence on Chromium (lll) - (EATDB).

Salt added	Conc.(M)	Absorbance	Salt added	Conc.(M)	Absorbance
Na_2SO_4	0.0005	0.189	$\mathbf{NaNO_3}$	0.0005	0.188
	0.005	0.182		0.005	0.186
	0.05	0.186		0.05	0.181
	0.5	0.180		0.5	0.183
Abs0rbance of chromium (lll)-(EATDB) without adding =0.189					

The findings presented in Table (4) indicate that the varying concentrations of salts had no significant impact on the absorption values. Based on this observation, we can conclude that the presence of these ions does not affect the solubility and sensitivity of chromium (III) ion detection.

3.4.6 Effect of different concentration of reagent

The absorption of chromium (II) ion solution at pH 8.0 was examined against the concentration of the reagent within the range from (10-600 µg. mL^{-1}) to demonstrate the impact of excessive concentration on the absorption of the complex. It was found that the absorbance rise as the amount of reagent increased, finally, concentration of (500 µg. ml^{-1}) was selected.

Table (5): Effect of different concentration of reagent on absorbance measured.

Conc. (µg/mL)	10	20	30	50	70	100	200	300	400	500	600
Abs.	0.038	0.044	0.055	0.065	0.073	0.098	0.155	0.225	0.312	0.361	0.438

3.4.7 Calibration Curve.

A series of different concentrations of Cr (III) ion ranging from (1-200 µg/mL) were prepared and mixed with the reagent at the concentration of 500 µg/mL to conduct the calibration curve under optimized conditions. The calibration curve was generated by plotting the absorbance of each solution against its corresponding concentration as shown in Fig.6.

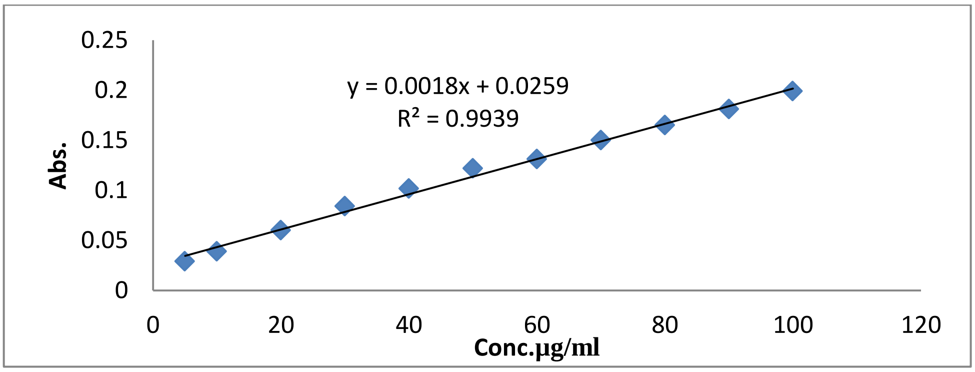


Figure.6 calibration curve of chromium (lll)

Calibration curve, explained in (Fig.6), obeys the Lambert-Beer rule within the range of (1-100 µg/mL). All analytical parameter of calibration curve was sorted in Table (6).

Table (6): Analytical parameter for Chromium (III) analysis.

Analytical Data	Value
Limit of Detection (L.O.D) (µg/mL)	0.203
Limit of Quantification (L.O.Q)(µg/mL)	0.669
Linear equation	Y=0.0018X+0.02
Linear range(µg/mL)	(1-100)
Linearity coefficient (R2)	0.9939
Molar Absorptivity (L/mol cm)	0.935x10^{2}
Sandal sensitivity(µg/cm^{2})	0.556
Slope	0.0018
λ max	573nm

3.4.8 Accuracy and Precision.

The accuracy and precision for the method were a proved due to the values of percentage recovery and relative standard deviation (RSD %), respectively. Table (7) displays the results of percentage recovery and RSD%.

Table (7): The accuracy and precision for Chromium (III) ion determination

The Concentration of the present Ion [M]	S.D	The Concentration of the Ion found [M]	Relative standard deviation RSD%	Recovery Percentage %	Error Percentage %
1.738×10^{-4}	1.732×10^{-3}	1.740×10^{-3}	0.479 %	100.115	-0.115
3.400×10^{-4}	3.674×10^{-3}	3.46×10^{-3}	0.874 %	101.764	-1.764
5.100×10^{-4}	1.870×10^{-3}	5.02×10^{-3}	0.437 %	98.430	1.57

The accuracy and precision of the established method is a proved by the finding illustrated in Table (7), where the RSD% was found to be less than 0.9% and the percentage recovery between 98.530-101.764 %.

3.4.9 Stoichiometry and Formation Constant.

The composition of the complex formed was examined using Mole ratio, Job`s and Mollared methods.

3.4.9.1 Mole Ratio Method [23].

In this method, different quantities of reagent solutions with the same concentration (3×10^{-4} M) of both Cr (III) ion and reagent were mixed and absorption measurement were taken. The result were represented in (Fig.7). **λ_{max}=573nm.**

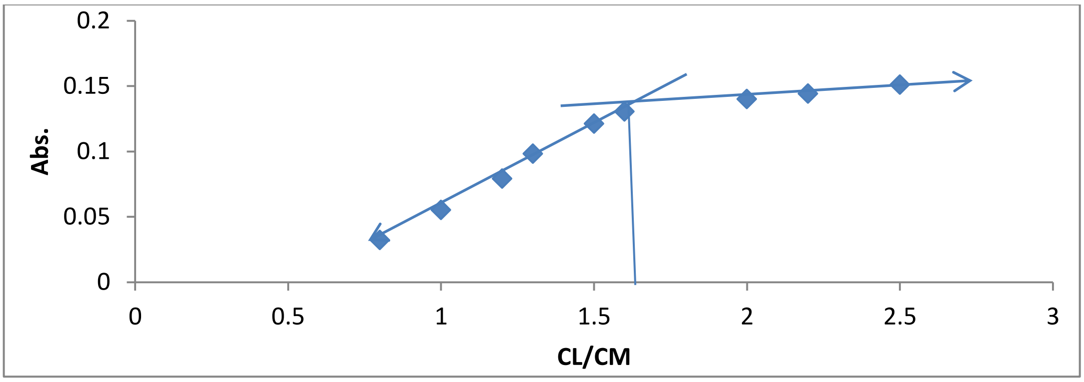


Figure (8): Mole ratio of Chromium (III) complex.

3.4.9.2 Job' s Method [24]

The method involved mixing different volumes of Cr (lll) ion solutions at equal concentration (3.43×10^{-4} M) with the reagent at concentration of (1.45×10^{-3} M). The total volume of the mixture was adjusted to 10 mL. The measurements were performed at optimized conditions at maximum wavelength (λ_{max}) of 573 nm.

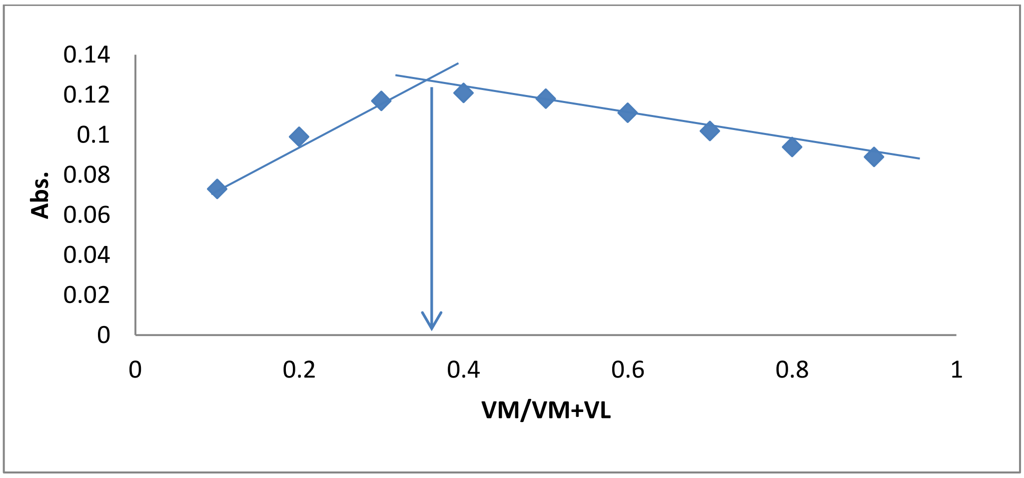


Figure (8): Job`s method of continuous variation

3.4.9.3 Mollerd Method [25]**.**

Mollerd method was applied, firstly, mixing a solution of Chromium(II) ion (1.00×10^{-4} M) with reagent solution (3.00×10^{-4} M), adjusting the pH to 9, and measuring the absorbance at λ_{max}= 573 nm under optimized conditions. The absorbance obtained for this solution was 0.119 which represents (As).

The second step involved mixing of dilute solution of reagent (1.00×10^{-4} M) with a concentrated solution 3×10^{-4}Mof Cr (III) ion under the same conditions applied in the first step and measuring the absorbance which represented (Am)

$$\frac{m}{s} = \frac{Am}{As} = \frac{0.119}{0.062} = 1.91$$

Where As=absorbance at stoichiometry, Am=absorbance at max, A=absorbance

3.4.10 Foreign Ions Influence.

A specific amount of cations and anions were examined as foreign ions to investigate their possible interference with Cr (III) ion, the results were sorted in Tables (8) and (9).

Table (8) Cations interference influence on Cr (III) complex.

Foreign ions	Chemical Structure	Absorbance after addition of Cations (100 µg/mL)	Error%
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	0.202	-3.6
Mn^{2+}	$Mn(NO_3)_2.6H_2O$	0.177	7.8
Fe^{3+}	$Fe(NO_3)_3.9H_2O$	0.207	-7.8
Zn^{2+}	$Zn(NO_3)_2$	0.211	-9.89
Pb^{2+}	$Pb(NO_3)_2$	0.189	1.50
Ag^{+}	$AgNO_3$	0.198	-3.78
Cu^{2+}	$Cu(NO_3)_2.3H_2O$	0.178	7.29
Absorbance without interferences = 0.190			

Table (9): Anions interference influence on Cr (III) complex.

Foreign ions	Chemical Structure	Abs. after addition of Anions	E%	Abs. after addition of	E%
SO_4^{-2}	K_2SO_4	0.178	6.7	0.193	-1.30
$Br-^{1}$	KBr	0.180	6.2	0.168	12.50
$SCN-^{1}$	KSCN	0.181	5.7	0.192	0.00
IO_3^{-1}	KIO_3	0.185	3.6	0.195	-1.40
CrO_7^{-2}	K_2CrO_7	0.194	-1.4	0.210	-9.30
CO_3^{-2}	K_2CO_3	0.176	6.7	0.183	3.60
$CN-^{1}$	KCN	0.177	6.9	0.179	6.70
Absorbance without interferences = 0.190					

The finding obtained in Table (8) and (9) explained that specific ions resulted in increasing the absorbance m on the other hand, others led to decreasing the absorbance. This impact can be attributed to the competition between these ions and Cr (III) ion for complex formation with the reagent.

3.4.11 Effect of Masking agent

Seven masking agents were examined to overcome the interferences caused by positive ions. Masking agents can compete with the interfering ions when interacting with the reagent.

The method involved adding 1 ml of each masking agent (0.1 M) to chromium (III) complex solution aiming to minimize the effect of the interfering caused by some of the positive cations on the detection of Cr (III) ion leading to enhance accuracy and reliability of the method.

Table (10): Masking agent influence on Cr (III) complex absorption

Masking agent (0.1M)	Absorption of complex
Ascorbic acid	0.179
Citric Acid	0.149
Formaldehyde	0.149
KCl	0.160
Na_2EDTA	0.155
$Na_2HPO_4.12H2O$	0.154
Thiourea	0.166
Without Masking agent	0.190

The finding presented in Table (10) shows that the effect of ascorbic acid on the absorbance of the complex is negligibly significant. This implies that ascorbic acid can be used successfully as masking agent to overcome the problem of interference as approved in data illustrated in Table (11). 0.1M

Table (11): Effect of masking agent in the presence of cations on Cr (III) ion absorption.

Foreign ions	Abs. after masking agent addition , (0.1M)	Relative Error percentage (E %)
Cd^{+2}	0.170	10.526
Fe^{3+}	0.160	15.780
Zn^{+2}	0.166	12.631
Pb^{+2}	0.186	2.121
Mn^{+2}	0.175	7.894
Ag^{+}	0.191	-0.526
Cu^{+2}	0.184	3.157

3.4.12 Complex Stability Study.

The equilibrium reaction of the complex was used to determine the stability constant of the complex depeleft-rightft-right met left in the calcuations, depending on Mole ratio method. The calculated results, outlined in Table (12), demonstrated that this value is constant [26]. The following equations were employed in the calculations:

$$M^{+n} + nl \leftrightarrow Mln$$

$$a + nca \leftrightarrow (1-a)c$$

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

$$K = \frac{(1-a)c}{ac(nac)^n}$$

$$K = \frac{1_a}{n^n a^{n^{+1}} c^n}$$

As = the absorption of the complex at the equivalence point.
Am = the greatest absorption with a complex.
α = is calculated through the following equations.
n= no. of mole, C=molar concentration, L=reagent M=ion

$$a = \frac{Am\_As}{Am}$$

Table (12): Stability constant values of the complex.

Complex	Am	As	α	K(stability)
$Cr[(EATDB)_2$	0.191	0.122	0.361	$1.125x10^{8}$

According to the high stability of the complex ($1.125x10^{8}$), the reagent (EATDB) can be successfully adopted in the spectroscopic analysis of Cr (III). This stability constant was examined at temperature ranging from 10-30 °C, the corresponding results are presented in Table (13)

Table (13): The stability constant and degree of stability of the complex after temperature effect.

T	T (K)	α	K×10^8
10	283.15	0.333	7.233
15	288.15	0.347	6.250
20	293.15	0.362	5.433
25	298.15	0.367	5.122
30	303.15	0.372	4.879

Results obtained in Table (13) explained that there is a limited effect of temperatures on the stability of complex.

Table (14): Thermodynamic function for Cr (III) complex.

T(K)	1/T×10^{-3}	log K	ΔH	ΔG (K.J. mole$^-$	ΔS (K.J.mole^{-1} .K$^{-1)}$
283.15	3.532	8.579	-18.15	-46.655	0.109
288.15	3.470	8.485		-46.710	0.110
293.15	3.411	8.480		-47.515	0.108
298.15	3.354	8.376		-47.730	0.109
303.15	3.298	8.334		-48.371	0.109

The negative values of enthalpy (ΔH**)** in Table (14) demonstrated that the reaction is exothermic lowering the temperature of the reaction and leading to an increase in the probability of complex formation. On the other hand, negative values of free energy (ΔG) refereed that the reaction is spontaneous without any external impact. The stability of the complex is approved by its approaching zero entropy (ΔS) implementing to the randomness and higher stability during the formation of the complex.

3.5 FT-IR Test for the Reagent and Complex.

IR spectrum of the prepared reagent produced peaks at 3371 cm^{-1}, 2961.5 cm^{-1}, 2834-2932 cm^{-1}, 1450 cm^{-1}, 1712 cm^{-1}, 1604-1512 cm^{-1}, and 1276 cm^{-1} representing NH, C-H aromatic, C-H aliphatic, N = N, C = O, C= C and C-O, respectively as explained in Figures (9) and (10).

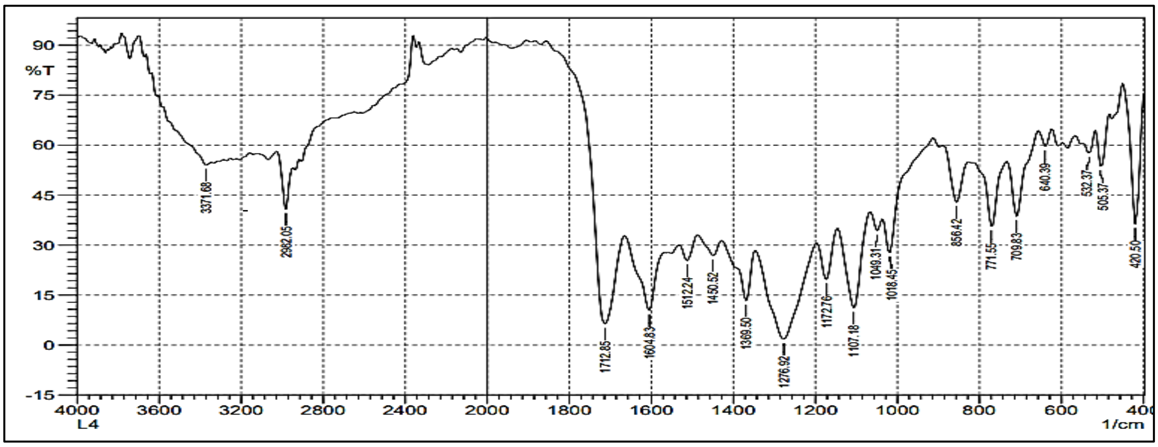


Figure (9): FT-IR spectrum of reagent.

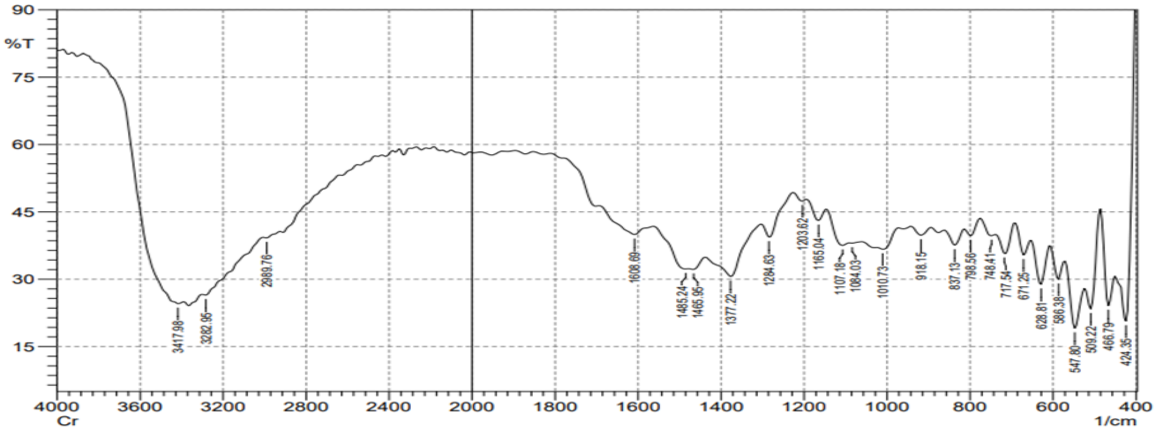


Figure (10). FT-IR of Cr (lll) – (EATDB) complex.

3.6 The Suggested Chemical Structure for the Complex.

FT-IR spectra and stoichiometric analysis (Mole ratio, Job and Mollerd methods) were utilized to determine the complex structure. FT-IR spectrum offered valuable information about the functional group involved in the complex formula. Due to the data obtained a proposed structure for the complex was suggested, as shown in Fig. (11)

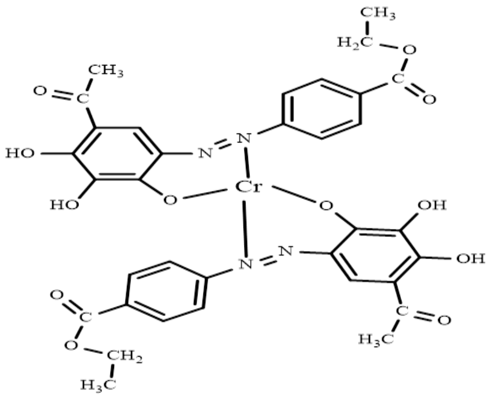


Figure (11): The suggested structure for the complex.

3.7 Physical properties of the complex

The molar conductivity and melting point were examined as physical property of the complex formed. The test results revealed a molar conductivity value of 14.8 Λ m (µS/cm), this value suggested that the complex dose not utilize significant conductivity lacking an ionic character. Regarding the melting point, it was found that the reagent melted in the range between 218-228 °C, while the complex formed melt at a temperature above 390 °C.

4. Applications:

In this analysis, we explore the concentration and recovery of Chromium Niacin in pills produced by a company. The measured concentration of 3.95 µg/mL showcases a recovery rate of 98.75% as expressed in Table (15).

Table (15): Results of application for Chromium (III) determination.

Pills	Manufacturer	Present Concentration (µg/mL)	Absorbance	Found Concentration (µg/mL)	Recovery %	E%
Chromium Niacin	MADAMAR	4.00	0.033	3.95	98.75	1.25

5. Conclusion: -

In this research, Chromium (III) was analyzed using a fast, easy, and cost-effective technique. The suggested procedure has been tested, verified, and proven suitable for quantifying the amount of Chromium (III) ion. Based on the findings, the reagent employed in this method is selective for Chromium (III) ion in pharmaceutical samples. Additionally, various analytical parameters, such as selectivity, detection limit, precision, and recovery percentage, demonstrate the effectiveness of this method for Chromium (III) determination

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