University of Kerbala
College of Science
Department of Chemistry

Spectrophotometric Determination of Micro Amount for Zn(II) and Cr(III) by Azo Imidazole Derivative, Study of Thermodynamic Functions and Their Analytical Application.

A Thesis

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for the Degree of Master of Science in Chemistry

By

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2022 AD 1444 AH

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Summary

This study contained the preparation and characterization of the new reagent sodium4-((4,5-diphenyl-imidazol-2-yl)diazenyl)-3-hydroxynaphthalene-1-sulfonate (SDPIHN), which is one of the Azo compounds using the classic nitrogenation process by duplicating the imidazole derivative with the diazonium salt of the 1-amino-2-napthol-4-sulfonic acid compound and conducting a preliminary study with 11 metal ion to determine the two ions zinc and chromium. The maximum absorption of the ligand that dissolved in ethanol (λ_{max}= 463 nm), and the formation of the zinc(II) and chromium(III) complexes created with the ligand in presence of non-ionic surfactant (Triton X-100) . Additionally, the optimal conditions for the reaction of these two ions with the reagent were investigated , like the acidity function, the concentration of Triton X-100, duration of time for the stability of the two complexes, concentration of the ligand, the temperature, the order of addition of the reaction components, the calibration curves for each of these two ions were shown with the ligand, which it was obyed the Beer's law in the range of the zinc(II) complex with the concentration ranges (1-11)µg/mL with the linearity coefficient (R^2 = 0.9996) and the absorbance value. The molar absorptivity (ε) was equal to (0.2229×10^4L.moL^{-1}.cm^{-1}) and Sandal's sensitivity was equal to (0.0293µg/cm^2), while chromium(III) was with range of concentrations (1-11)µg/mL and with a coefficient of linearity (R^2 = 0.9998). Value of the molar absorptivity (ε) = (0.244×10^4L.moL^{-1}.cm^{-1}) ,Sandal's sensitivity equal (0.0213µg/cm^2) . The equivalency of the two complexes was investigated by calculating the ratio of the metal ion to the ligand (M:L) using the Job's method and the mole ratio method for the zinc(II) and chromium(III) complexes. The stability constant (K_{sta}) for zinc (II) and chromium (III) complexes were

($K_{sta}=5.967\times10^{8}$) and ($K_{sta}=1.125\times10^{14}$) respectively . Moreover, the thermodynamic functions (ΔH , ΔG and ΔS) were calculated for both complexes, where the outcomes indicated that the reaction of forming the zinc(II) complex was endothermic and the chromium(III) complex was exothermic. The study demonstrated interference of the presence of a number of cations and anions ions as potential interactions when estimating the zinc(II) and chromium(III) ions, and the addition of appropriate masking agents was studied, as it was found that these ions interact to varying degrees depending on the nature and concentration of the interfering ion, and some of them did not show any effect. Remarkably, the charge of dissolving complexes was determined by measure the conductivity of two complexes, resulting in the zinc(II) complex being uncharged while the chromium(III) complex being charged. The accuracy and precision of the analytical method were determined using three various concentrations for each ion , the values of the relative standard deviation (RSD%) for the zinc(II) ion ranged between (0.700% - 1.772%) and the relative recovery ranged between (98.950% -103.930%), the values of the relative standard deviation (RSD%) for the chromium(III) ion values ranged between (0.552% - 1.250%) and the relative recovery ranging between (97.830% - 101.080%), through which the detection limit was found for the zinc(II) ion (3.475×10^{-6}M), the detection limit of the chromium(III) ion was equal to (2.194×10^{-6}M), which shows the sensitivity of the spectral technique using this ligand (SDPIHN). Determining physical properties such as melting point, solubility, and molar conductivity, the sedimentation of the reagent and the two complexes have also been investigated. The method was used to determine the amounts of zinc(II) and chromium(III) ions in the pharmaceutical sample. The method's sensitivity and accuracy were determined to be high.

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List of abbreviations and Symbols.

Symbol	Meaning
DMF	Dimethyl formamide
EDTA	Ethylene dianime tetra acetic acid
DMSO	Dimethyl sulfoxide
SDPIHN	4-((4,5-diphenyl-imidazol-2-yl)diazenyl)-3-hydroxynaphthalene-1-sulfonate
RSD%	Relative standard deviation
L.O.D	Detection Limit
L.O.Q	Limit of quantification
Rec%	Recovery%
S.D	Standard deviation
ε	molar absorptivity
x'	mean
λ_{max}	Maximum wavelength
Am	Maximum absorption
As	Slow absorption
Vm	volume of the metal
VL	volume of the reagent
E%	Relative error
Abs	Absorption
R^2	Linearity Coefficient
r	Correlation Coefficient
ΔH	Enthalpy
ΔG	Free energy
ΔS	Entopy
THF	Tetrahydrofuran
DMF	N,N-Dimethyl-form amid
S	Sandal sensitivity
a	Specific absorption cofficient
α	Degree of dissociation
K	Stability Constant
n	Number of mole
C	Molar cocentration
SD	Standard deviation
$\bar{x}$	Average

Chapter One

Introduction and Literature Review

Chapter One

Introduction And Literature Review

(1-1) Coordination Chemistry

Coordination chemistry is one of the most important scientific discoveries since the discovery of the compound ($CoCl_3.6NH_3$) and it has gained a wide area in chemistry due to its great development in the practical side in the discovery of a large number of organic compounds. Coordination compounds also play an important role in developing the fields of medicine, agriculture and industry, also are widely used in analytical chemistry[1,2]. Coordination chemistry has been used to prepare a large number of metal ion complexes, the purpose of preparing these complexes is to estimate the metal ions in the compounds by selective processes such as masking agents and changing the pH [3]. In analytical chemistry, a number of ways to measure the amount of an element in different ones. These include the electrical process, the thermal method, the spectral method, the method of ion chromatography, the method of extraction, the technique of flame ablation, and the method of spectroscopic [4]. Classical coordination chemistry is based on the idea that a central metal atom with one electron and a positive charge is bound to Lewis-base ligands with a certain number of coordination and a polyhedral shape. As coordination chemistry has grown and merged with other fields, it has been taken on the three dimensions of breadth, depth, and applications. Advanced coordination chemistry, as it is more broadly defined, only needs different species to form through binding interactions between metal functional groups. Also, the development of powerful spectroscopic analysis methods, such as X-ray absorption fine structure (XAFS) spectroscopy, makes the roles of coordination chemistry clearer [5]. In coordination chemistry, a metal–ligand system usually has a lot of different species in equilibrium, which is why spectra studies are so important. In pharmaceutical applications, for example, one of the species is the active agent, whereas others are neutral or even toxic. But the equilibrium speciation and the time it takes for the system to reach equilibrium are both very important. In pharmaceutical or environmental research, it is important to understand how metal complexes work because toxic metal ions in very dilute solutions lose their protective reagents over time, but this can take a very long time. [6].

(1-2) Azo dyes

Azo dyes represent the greatest amount of pigment preparation and synthesis. It is essential to the regulation of the dye and printing markets. These pigments are produced using a straightforward diazotization and coupling method. Various modifications and routes were utilized to achieve the desired color properties [7]. More than 60% of all dyes are azo dyes, making them the most widely used dyes [8, 9]. Approximately 70% of all dyes often used in the industry are azo dyes [10, 11].The functional group (-N=N-) unites two identical or non-azo alkyl or aryl radicals that are symmetrical and/or asymmetrical [12, 13]. The most important synthetic coloring agents are azo dyes [14]. Urgent calls have been made to treat effluents containing Azo dyes in order to eliminate them or convert them into useful and safe products [15].

(1-3) Kinds of Azo Dyes Investigate the Azo Grouping Number

According to the number of azo group linkages in the same pigment molecule, azo dyes are classified as monoazo, diazo, trisazo, and polyazo[16]. Figure (1-1) shows monoazo, diazo, and trisazo dyes.

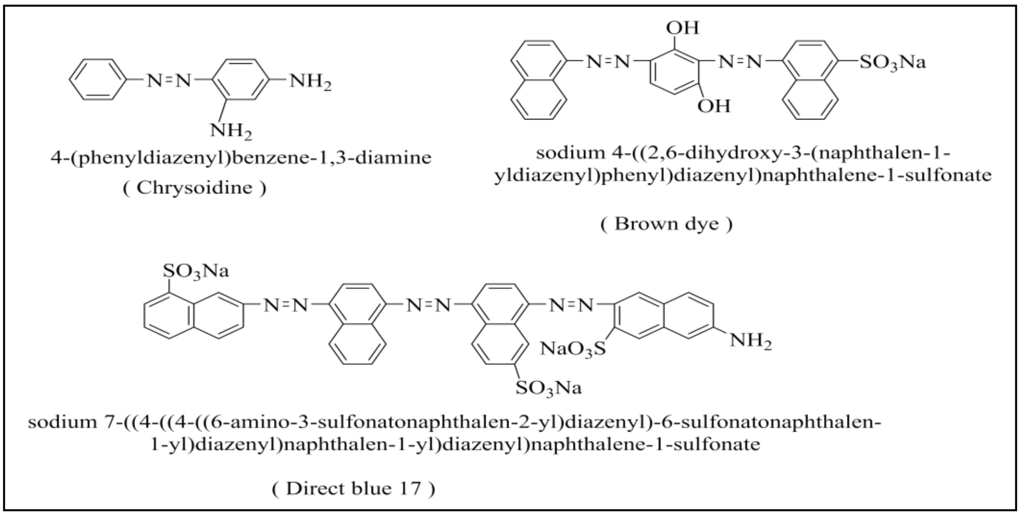
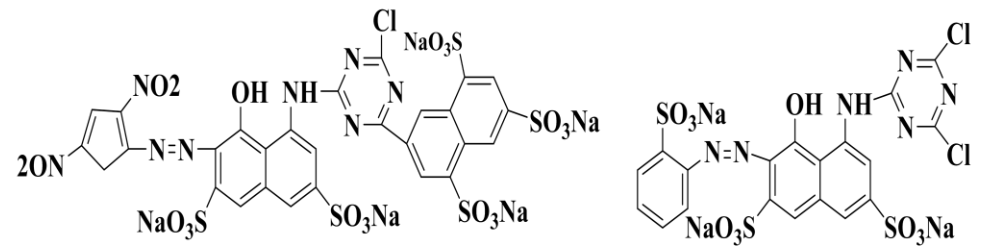


Figure (1-1) Monoazo, diazo, and trisazo dyes.

(1-4) Azo dyes are classified depending on their reactive functional groups

(1-4-1) Mono and dichlorotriazine

These dyes significantly affinity for cellulose between 20 and 30 degrees Celsius. Substituting a single chlorine ion with a hydroxyl or cellulose ion considerably lowers the reactivity of the second chlorine. Ionization of the hydroxyl group in an alkaline solution moves the negative charge of the triazine ring's atoms, while the chlorine atom becomes inactive and the carbon linked to the chlorine becomes less electrophilic [17, 18]. Figure (1-2) displays several dyes.



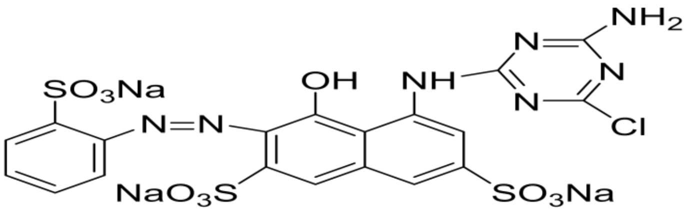
sodium 7-(4-chloro-6-((7-((2,4-dinitrocyclopenta-1,3-dien-1-yl)diazenyl)-8-hydroxy-3,6-disulfonatonaphthalen-1-yl)amino)-1,3,5-triazin-2-yl)naphthalene-1,3,5-trisulfonate

sodium (*Z*)-5-((4,6-dichloro-1,3,5-triazin-2-yl)amino)-4-hydroxy-3-((2-sulfonatophenyl)diazenyl)naphthalene-2,7-disulfonate

Figure (1-2) Mono and Dichlorotriazine Dyes

(1-4-2) Mono-amino-chlorotriazine

It possesses the same atoms groups which change its color as dichlorotriazine. In addition, it contains the NH_2 group and active chlorine, as seen in Fig (1-3). When it comes to dichlorotriazine, these groups are less active. The NH link between the chromophore and the reactive group which affects how the dye works and how well it dissolves [12, 13].

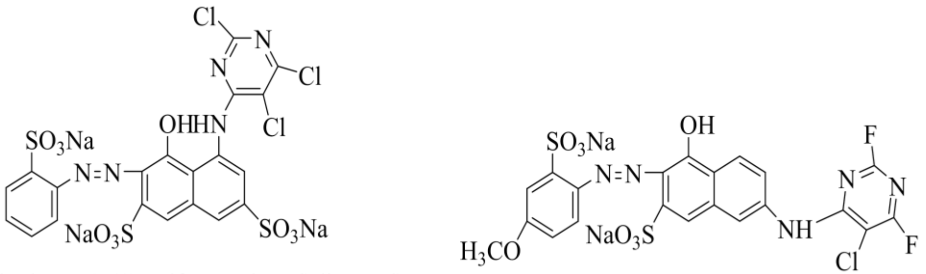


sodium (Z)-5-((4-amino-6-chloro-1,3,5-triazin-2-yl)amino)-4-hydroxy-3-((2-sulfonatophenyl)diazenyl)naphthalene-2,7-disulfonate

Figure (1-3) Mono-Amino-Chlorotriazine Dye

(1-4-3) Pyrimidines

Generally, they include the chlorfluoropyrimidine derivatives, fluoropyrimidine derivatives, and di- and tri-chor pyrimidine derivatives, as seen in Fig. (1-4) [12, 13].



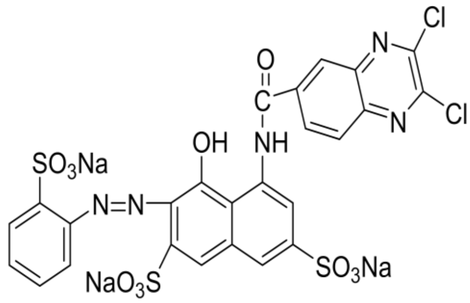
sodium 4-hydroxy-3-((2-sulfonatophenyl)diazenyl)-5-((2,5,6-trichloropyrimidin-4-yl)amino)naphthalene-2,7-disulfonate

sodium 7-((5-chloro-2,6-difluoropyrimidin-4-yl)amino)-4-hydroxy-3-((4-methoxy-2-sulfonatophenyl)diazenyl)naphthalene-2-sulfonate

Figure (1-4) Pyrimidines Dyes.

(1-4-4) Dichloroquinoxalin

This specie of dye reacts strongly with dichloropyrimidine dyes, dichlorotriazine dyes, and difluoropyrimidine dyes [12, 13]. One example is shown in Fig. (1-5).

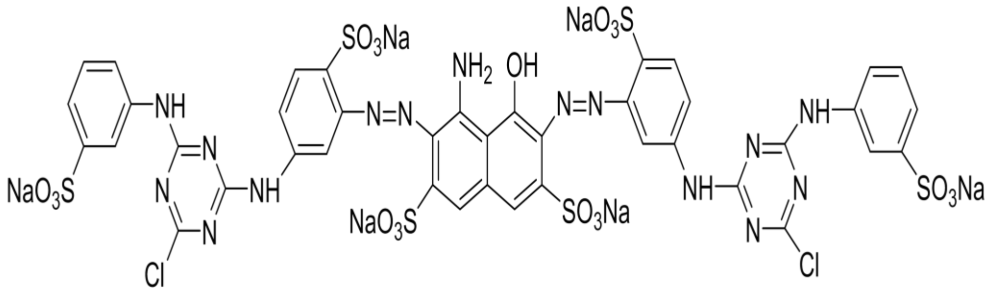


sodium 5-(2,3-dichloroquinoxaline-6-carboxamido)-4-hydroxy-3-((2-sulfonatophenyl)diazenyl)naphthalene-2,7-disulfonate

Figure (1-5) Dichloroquinoxaline Dye.

(1-4-5) Bis-mono chlorotriazine

Due to this dye having a higher affinity for depletion at 80 °C, it is employed on cellulosic fiber substrates. This leads to the fixation rate from 70% to 80% compared to their homo-functional counterparts [12, 13, 19]. In addition, the dimension of the molecules of this type of dye is double. one example is elucidated in Fig. (1-6).

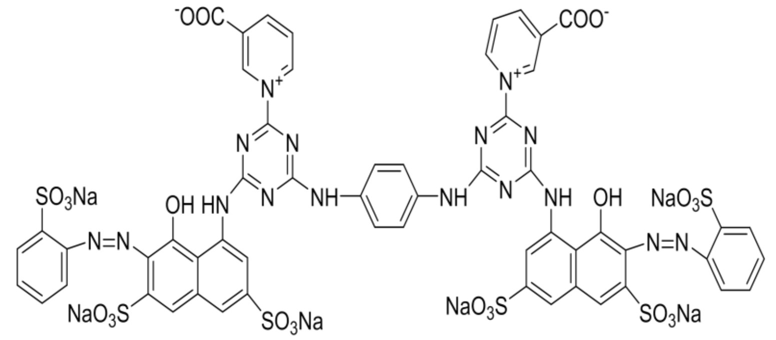


sodium 4-amino-3,6-bis((5-((4-chloro-6-((3-sulfonatophenyl)amino)-1,3,5-triazin-2-yl)amino)-2-sulfonatophenyl)diazenyl)-5-hydroxynaphthalene-2,7-disulfonate

Figure (1-6) Bis-Mono Chlorotriazine Dye.

(1-4-6) Bis-amino nicotinotriazine

As shown in Fig. (1-7), these dyes are generated by replacing the chlorine in the triazine ring with carboxy pyridine acid (1-7). The same happens to produce mono chlorotriazine, the application temperature at depletion being higher than the boiling point in a neutral media and may also be used at (80 °C) at pH = 11. [12, 13].

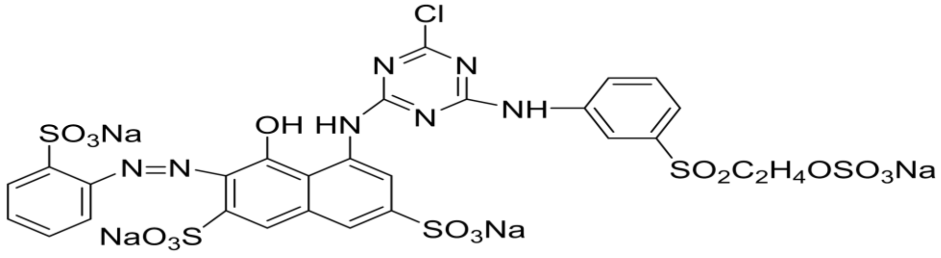


sodium 1-(4-((4-((4-(3-carboxylatopyridin-1-ium-1-yl)-6-((8-hydroxy-3,6-disulfonato-7-((*Z*)-(2-sulfonatophenyl)diazenyl)naphthalen-1-yl)amino)-1,3,5-triazin-2-yl)amino)phenyl)amino)-6-((8-hydroxy-3,6-disulfonato-7-((*Z*)-(2-sulfonatophenyl)diazenyl)naphthalen-1-yl)amino)-1,3,5-triazin-2-yl)pyridin-1-ium-3-carboxylate

Figure (1-7) Bis-amino nicotinotriazine dye.

(1-4-7) Monochlorotriazine–sulphatoethylsulphone

Monochlorotriazine-sulphatoethylsulfone can be produced when dichlorotriazine reacts with an aryl amine that included the sulphatoethylsulfone group [20] .



sodium -2-((3-((4-chloro-6-((8-hydroxy-3,6-disulfonato-7-((2-sulfonatophenyl)diazenyl)naphthalen-1-yl)amino)-1,3,5-triazin-2-yl)amino)phenyl)sulfonyl)ethyl sulfate

Figure(1-8): Monochlorotriazine–sulphatoethylsulphone dye

(1-5) Azo Dyes Properties

Azo compounds and their derivatives are one of the most commonly used reagents because of how stable they are, how quickly they react with metal ions, how sensitive they are, and how selective they are. The Azo bridge group (-N = N-) is what makes them so stable [21, 22]. Non-cyclic compounds are not as good as azo-cyclic compounds because of their color, stability, sublimity, and intensity of color. Also, the heterocyclic ring makes pigments that are good for the environment and very important because they absorb a lot of paint [23, 24] . Azo dyes have a variety of physical and optical properties that make them stable in a wide range of situations. Azo dyes have been used in optical treatments because they are bright and they absorb light and they work well in the infrared range [23, 25].

Azo dyes can absorb light in the ultraviolet range[26]. As a result, optical devices containing Azo compounds can be utilized for a broad variety of tasks, including data storage, pattern recognition, signal processing, optical modulation, holography, and nonlinear optics [27]. Azo compounds have been employed in a variety of electronic applications in recent years, including the manufacture of absorbable electronic chips and other sorts of electronic devices [28-30].

Azo compounds stop corrosion , and because they are cheap , they are used a lot [31]. Furthermore, the functional groups, structural impacts of the reagent , number of electrons on the donating atoms, and nature of the donated electrons' orbitals have all been discovered to have a role in the inhibitory impact of organic compounds.[32]. Since azo compounds can both give off and take in light, they are used in many industries, like making laser pigments. [22, 32].

(1-6) The Preparation of Azo Dyes[33]

There are two processes involved in the production of azo dyes: In the first step, the primary aromatic amine is diazotized with sodium nitrite in an acidic mineral media (HCl, H_2SO_4, etc.) at low temperatures (0-5) °C, utilizing an aqueous solution of sodium nitrite and acid to form diazonium salts that are readily soluble in water, as shown by the chemical equations below.

$$HCl + NaNO_2 \xrightarrow{(0\text{-}5)^oC} HONO$$

$$R\text{-}NH_2 + HCl + NaNO_2 \xrightarrow{(0\text{-}5)^oC} R\text{-}N_2^+Cl^- \longrightarrow N_2\uparrow + \text{Mixture}$$

$$Ar\text{-}NH_2 + HCl + NaNO_2 \xrightarrow{(0\text{-}5)^oC} Ar{-}N{\equiv}N^+Cl^- + NaCl + 2H_2O$$

$$Ar{-}NH_2 \xrightarrow[\text{diazatization}]{HNO_2} Ar{-}N_2^+ \xrightarrow[\text{coupling reaction}]{Ar^-{-}H} Ar{-}N{=}N{-}Ar$$

Scheme (1-1) Preparing Azo Dyes

The second step, referred to as the coupling step, involved the conjugation of the aromatic diazonium ion with active compounds under alkaline conditions, in which the diazonium salt transfers a halogen atom, such as chlorine, in exchange for an effective hydrogen atom in another aromatic compound (phenols and amines), as depicted in the preceding diagram.

(1-7) Surfactants

One definition of a surfactant is a surface-active substance that can bond with other substances and lead to the formation of micelles. For its obvious effect on surface properties, surfactant is one of the most ubiquitous materials and finds use in a wide variety of contexts[34, 35] . Surface active agents, or surfactants, are typically hydrophilic organic compounds. It is a long-chain hydrocarbon or aromatic ring with two hydrophobic groups (tails). Hydrophilic groups (heads) containing functional groups are often ionizable and have the opposite effect, decreasing solubility in water [36]. Normal electrolyte behavior is observed when surfactants are diluted in aqueous solutions, but a change in behavior is observed when the concentration of the surfactant is increased [37, 38]. The molecular architecture of a surfactant is shown in Fig. (1-9) [39] .

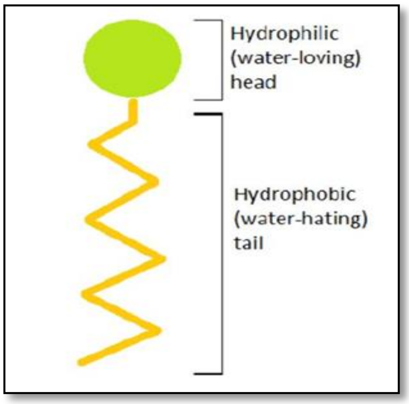


Figure (1-9) Structure of Surfactant Molecule

There are numerous applications in basic science and modern pharmaceutical biotechnology that make use of surfactants, which contribute significantly to their ability to form colloidal-sized clusters in solution[40]. Surfactants are able to dissolve hydrophobic compounds in water because of their amphiphilic nature. The shape and size of the molecules of surfactant in solutions, as well as the surfactant concentration and temperature, pH, and ionic strength, all affect the function of surfactants. Different configurations of these molecules are possible. Because of these properties, surfactants are able to dissolve in aqueous solutions when they are added to water. Figure (1-10) shows surfactant micelles in aqueous solution[41, 42] .

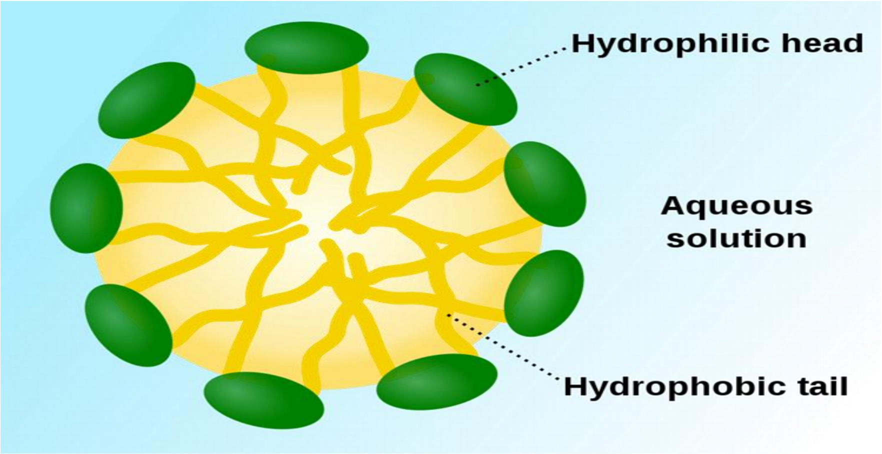


Figure (1-10) Surfactant-micelles structure in aqueous solution

The characteristic features of the typical properties of aqueous surfactant solutions are caused by a hydrophilic head group and a hydrophobic tail of the molecule. Generally, the polar or ionic head group substantially interacts with the aqueous environment [43]. In either situation, dipole-dipole or ion-dipole interactions lead to solving the issue. It reduces tension between surfaces resolved by the polar group system [44, 45]. Surfactants are divided into four types:

(1-7-1) Anionic Surfactants

Anionic surfactants often contain alkaline minerals such as K^+, Na^+, and quaternary ammonium [46]. In water, this kind of surfactant degraded into an amphiphilic anion and a cation. Examples include alkaline carboxylic salts (soap), alkyl-aromatic sulfonic salts, alkaline sulfonic salts (detergents), and sodium dodecyl sulfate (SDS) [47, 48].

(1-7-2) Cationic surfactants

It splits into an amphiphilic cation and an anion, most typically of the halogen type, in water [49]. For example, cetyl-trimethyl ammonium bromide (CTAB) comprises cationic functional groups like quaternary ammonium cations and amine salts [50]. Surfactants are skin-safe and non-irritating, although they can be used to clean wounds. Its water solutions can also be used to clean soiled utensils [51, 52].

(1-7-3) Zwitterion or Amphoteric

Amphoteric or zwitterion surfactants, such as carboxylate, sulfonate, sulfobetanie and long chain amino acid salts, are molecules with ionic and cationic centers[53, 54].

(1-7-4) Nonionic Surfactants

This type, like Triton X-100 and Triton X-114, does not ionize in aqueous solution because their hydrophilic groups are non-dissociable. This type of surfactant is divided into three major groups: esters ,alcohols and polyether. Figure (1-11) depicts the four major types of surfactants based on the main components of their heads and the structures of several surfactants [43, 55].

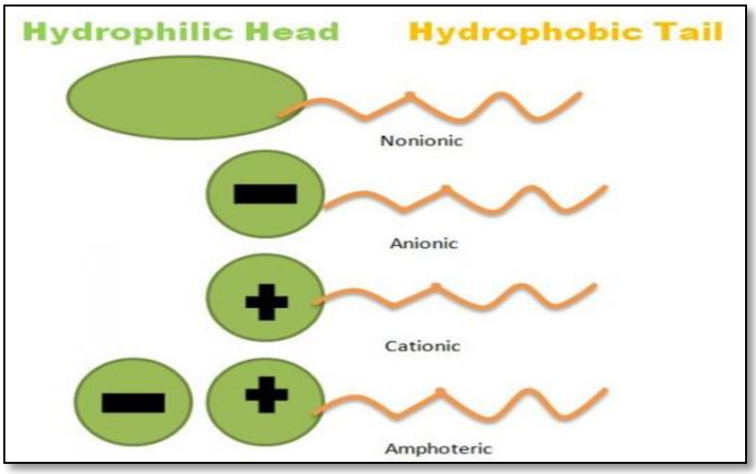


Figure (1-11) Surfactant classification according to the composition of their head

Some surfactant compounds are listed in Table (1-1)[56].

Table (1-1) Types of surfactants compounds

Surfactant	**Chemical formula**
Anionic surfactant	
Sodium stearate (soap)	$CH_3(CH_2)_{16}COO^- Na^+$
Sodium dodecyl sulfate (SDS)	$CH_3(CH_2)_{11}SO_4^- Na^+$
Sodium dodecyl benzene sulfonate	$CH_3(CH_2)_{11}C_6H_4SO_3^- Na^+$
Cationic surfactant	
Laurylamine hydrochloride	$CH_3(CH_2)_{11}NH_3^+ Cl^-$
Trimethyl dodecylammonium chloride	$C_{12}H_{25}N^+(CH_3)_3Cl^-$
Cetyl trimethylammonium bromide	$CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$
Nonionic surfactant	
Polyoxyethylene alcohol	$C_nH2_{n+1}(OCH_2CH_2)_m OH$
Alkylphenol ethoxylate	$C_9H_{19}-C_6H_4-(OCH_2CH_2)_n OH$

Octylphenoxypolyethethanol (Triton X-114), (Triton X-100)	$C_{14}H_{22}O(C_2H_4O)_n$ n = (7-8) , (9-10)
Zwitterionic surfactant	
Dodecyl betaine	$C_{12}H_{25}N +(CH_3)_2CH_2COO^-$
Lauramidopropyl betaine	$C_{11}H_{23}CONH(CH_2)_3N^+(CH_3)_2CH_2COO^-$
Cocoamido - 2-hydroxy-propyl sulfobetaine	$C_nH_{2n+1}CONH(CH_2)_3N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$

(1-8) Trace Elements and Chemical of Metals

Some heavy metals are helpful to health in low amounts, but increasing concentrations can be harmful [57, 58]. Anxiety is caused by antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc [59-61]. Heavy metals, as previously said, become hazardous as their concentration increases, diminishing energy levels and damaging the brain, lungs, kidneys, liver, and other organs in the short and long term [60]. These components have been linked to multiple sclerosis, Alzheimer's disease, muscular dystrophy, and even cancer [61]. Continuous and direct exposure to these elements might create buildup in the body. Mineral toxicity is affected by dose, type of exposure, and duration [62] [53]. Some trace elements, such as chromium, iodine, iron, manganese, cobalt, copper, molybdenum, selenium, and zinc, are present in the human body at low levels and varying rates [63]. Because of their impact, heavy element concentrations in environmental and biological samples should be assessed. Analytical chemistry can be used to estimate these elements [64]. Heavy metals found in wastewater include arsenic, cadmium, chromium, copper, lead, nickel, and zinc[60, 65]. Heavy metals enter the environment from a variety of sources, including natural weathering of the earth's crust, mining, soil erosion, industrial effluents, urban runoff, sewage discharge, and others [60, 66, 67]. Where environmental and occupational toxicology are used to uncover factors impacting element toxicity through biological monitoring and environmental investigations. Urine is typically associated with exposure. Significant element concentrations in urine suggest long-term exposure to arsenic, cadmium, nickel, chromium, and cobalt, or a delay in medical care following high occupational exposure [68-70]. Iron and copper account for 0.001% of all living organisms[71]. Although necessary for human survival, large quantities are harmful. Tables (1-2), (1-3) categorize trace elements based on their health advantages and effects [72-74].

Table (1-2): Classifications of trace elements according to the beneficial

Nutritionally essential metals	**Metals with possible beneficial effects**	**Metals with no known beneficial effects**
Co , Cr , Cu , Fe , Mn , Zn , Mo , Se	B , Ni , Si , V , I	Al , Ba , Cd , Sb , As , Be , Pb , Hg, Ag , Sr , Tl

Table (1-3) :Trace-elements-concentration-and-their-biological-effects-on-human-health.

Deficiency	Elements	Toxicity
Anemia	Iron	Haemochromatosis
Anemia (Say back)	Copper	Chronic poisoning-Wilson, Bedlington-disease
Dwarf growth, Retarded, Development of gonads Akrodermatitis entero-pathica	Zinc	Metallic fever Diarrhoea
Anemia (White liver disease)	Cobalt	Heart failure, Polycythaemia
Disturbance in the glucose metabolism	Chromium	Kidney damage (Nephritis)
Osteoarthritis Effects on male infertility	Selenium	Selenosis Nervous system abnormalities
→ Increasing concentration →		

(1-8-1) Trace Zinc Element

(1-8-1-1) Chemistry of Zinc

Zinc is a metallic element with the atomic number 30[75] and stable isotopes with masses of 66, 67, 68, and 70, with an average mass of 65.38 a.m.u[76]. Zinc is terrestrial chemistry is that of Zn (II) rather than Zn (I) (0). Because the Zn (II) ion has an electron configuration of $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$ it lacks unfilled d subshells in the well-known oxidation state, which is a requirement for transition metals. The ionic radius of zinc(II) is similar to that of magnesium(II), but it has the Lewis acidity of the smaller Cu(II) ion. Numerous zinc minerals have been described, including sulfides, sulfates, oxides, carbonates, phosphates, and silicates, with the majority containing tetrahedral or octahedral coordination polyhedral with either apical S or O[77]. Several minerals contain both tetrahedral and octahedral coordinated Zn(II), while others have polyhedral fivefold coordination alternating with octahedral coordinated Zn(II), indicating a full and spherical 3d subshell with no preference for one coordination over another[78]. For hydroxides, chlorides, carbonates, sulfates, sulfides, phosphates, simple organic acids, amino acids, and synthetic chelates, the stabilities of aqueous zinc complexes have been measured. Zn(II) is typically octahedral in aqueous complex, though fourfold and fivefold coordination are also known[79]. Because of their superior selectivity, sensitivity, and speed of analysis, sophisticated spectroscopic methods of analysis are now used to measure zinc concentrations in plants, soils, and water[80]. Colorimetric and wet chemical techniques for zinc determination are generally limited to laboratories without access to modern instrumentation[81].

(1-8-1-2) Biological effect of zinc

The appearance and biological significance of Zinc is a trace metal that is essential in humans, other animals, plants, and microorganisms[82]. It is a key ion in many enzymes, binds to albumin, stored and transferred in metal-lothionein [83], and functions as a structural ion in transcription factors. Zinc is the second most abundant transition metal in organisms and is the only metal that appears in all enzyme classes. The human body contains nearly 2-4 g of zinc, which is widely distributed in organs such as the brain, muscles, bones, kidneys, and liver[84]. Zinc concentrations are highest in the prostate and parts of the eye. It is required for microorganisms, plants, and animals to grow and develop. It is found in relatively high concentrations in all body tissues and fluids, accounting for 85 % body zinc in muscle and bone, 11% in skin and liver[85], and the remainder in all other tissues[86]. Zinc is essential for the normal development and function of the brain. However, excessive zinc accumulation in the brain causes symptoms such as lethargy, dizziness, and so on[87]. Many studies have shown that zinc acts as a neuromodulator[88].

(1-8-1-3) Zinc deficiency

Zinc deficiency causes a variety of issues[89]. Deficiency is usually caused by insufficient zinc levels in food or as a result of malabsorption caused by other problems such as acrodermatitis enteropathica, anemia, chronic liver or renal disease, sickle cell anemia, malignancy, and other chronic illnesses[90]. Mild zinc deficiency causes a variety of symptoms, including decreased growth, diarrhoea, eye and skin lesions, impaired appetite and altered cognition, impaired host defense properties, defects in carbohydrate utilization[91], and reproductive teratogenesis. Mild zinc deficiency is known to impair the body's immune function[92]. Excess zinc, on the other hand, reduces immune actions, emphasizing the importance of normal zinc levels for immune system stability[93]. The elderly and children, particularly in developing countries, are at risk of zinc deficiency [94].

(1-8-1-4) Zinc toxicity

Living things are essentially unaffected by zinc toxicity. It is the only element that is not teratogenic, carcinogenic, mutagenic, cytotoxic, or systematically toxic[95]. Because the body cannot store zinc, excessive intake reduces absorption and increases excretion. However, there are cases of both acute and chronic Zn poisoning that have been documented. Although acute toxicity in people is uncommon[96], storing food or beverages in galvanized containers has been linked to numerous cases of food poisoning. Even very large doses of zinc and all of its compounds administered or consumed do not have negative long-term effects[97]. Adverse systemic reactions in humans are only ever seen in extremely rare circumstances, such as when ingesting large amounts of the metal accidentally or inhaling Zn oxide fumes (metal fume fever)[98].

(1-8-1-5) Previous studies of zinc

Table (1-4) shows literature review of zinc by using spectrophotometric method with varies technique.

Table (1-4) The methods used to determination Zinc ion.

Method	Reagents	Results	Ref.
Spectrophoto metric	8-Hydroxyquinoline	Conc.(1-5 µg/ mL) , R^2=0.9960 , ε=(0.0157x10^3L.mol^{-1}.cm^{-1}) ,λ_{max}= 384 nm , L.O.D=(0.381µg/mL) , L.O.Q=(1.156µg/mL) , determine zinc(II) ion in Pharmaceutical Medication Samples	[99]
Flame atomic absorption method	8-Hydroxyquinoline	Conc.(0.1-1.5 µg/ mL) , R^2=0.9985 , ε=(0.0051x10^3L.mol^{-1}.cm^{-1}) ,λ_{max}= 213.9 nm , L.O.D=(0.216µg/mL) , L.O.Q=(0.655µg/mL) , determine zinc(II) ion in Pharmaceutical Medication Samples	[99]
Spectrophoto metric	(E)-3-(4-hydroxy-3-methoxyphenyl) acrylic acid (ferulic acid) (FA)	Conc.(2-70 µg/ mL) , ε=(1.3161x10^4L.mol^{-1}.cm^{-1}) ,λ_{max}= 430 nm , L.O.D=(2.2833µg/mL) ,	[100]

		L.O.Q=(6.9193µg/mL) , determine zinc(II) ion in industrial sample, biological sample, vegetables samples, water samples	
Spectrophotometric	Xylenol Orange and cetylpyridinium chloride	Conc.(0.5-1.5 µg/ mL) , R^2=0.9998 , pH=5.5, λ_{max}= 560 nm , Re=(98.29-100.55%), R.S.D%=(1.57% and 1.77%) , determine zinc(II) ion in Pharmaceutical sample	[101]
Spectrophotometric	pyridoxal thiosemicarbazone (PDT)	Conc.(0.26-2.62 µg/ mL) , R^2=0.99959 , ε=(1.8x10^{4}L.mol^{-1}.cm^{-1}) , λ_{max}= 360 nm ,R.S.D%=0.52 , L.O.D =(0.064 µg/ml) , determine zinc(II) ion in soil and vegetable samples	[102]
Spectrophotometric	2-acetyl pyridine thiosemicarbazone (2-APT)	Conc.(0.25-2.56 µg/ mL) , R^2=0.99983 , ε=(2.9x10^{4}L.mol^{-1}.cm^{-1}) , λ_{max}= 385 nm ,R.S.D%=1.2 , L.O.D =(0.084 µg/ml) , determine zinc(II) ion in soil and vegetable samples determine zinc(II) ion in soil and vegetable samples	[102]
Spectrophotometric	1-(2-pyridylazo)-2-naphthol	Conc.(0.16-3.27 mg/L), λ_{max}= 562 nm, pH=3.9 , L.O.D =(0.1 mg/L) , determine zinc(II) ion in pharmaceuticals.	[103]
Spectrophotometric	N,N′bis(salicylaldehyde)2,3-diaminonaphthalene (SDN)	Conc.(1.0×10^{-9}–2.0×10^{-3} mol L^{-1}), pH=7 , L.O.D=(0.0529659 µg.L^{-1}) , determine zinc(II) ion in in human hair samples,	[104]

		different brands of powdered milk and some pharmaceuticals.	
Spectrophotometric	2,6-diacetylpyridine-bis-4-phenyl-3-thiosemicarbazone (2,6-DAPBPTSC)	Conc.(1.06–13.6 µg/ mL) , , L.O.D =(0.0081 $\mu g.mL^{-1}$), (r = 0.985),pH=(4.5), λ_{max}=(490 nm), $\varepsilon=(0.471\times10^{4}L.mol^{-1}.cm^{-1})$, determine zinc(II) ion in food and environmental samples	[105]
Spectrophotometric	2-(5-bromo-2-pyridylazo)-5-diethylaminophenol	Conc.(2.2×10^{-2}-6.6×10^{-1}µg/ mL) ,D.L= 1.52 $\mu g.mL^{-1}$, (r = 0.9984), λ_{max}=554 nm, $\varepsilon=(1.19\times10^{5}L.mol^{-1}.cm^{-1})$,L.O.Q=5.05, RSD%=1.86 determine zinc(II) ion in environmental and biological samples	[106]
Micro Cloud Point Extraction (MCPE)	4-(2-pyridylazo) resorcinol	Conc.(0.15-0.60 µg/ mL), L.O.D=(51.7 $\mu g.\ L^{-1}$), (RSD%= 2.44), R^2 = 0.9666, pH=7.0, determine zinc(II) ion in water samples.	[107]
Spectrophotometric	7-(4-nitrophenylazo)-8-hydroxyquinoline-5-sulfonic acid (p-NIAZOXS)	Conc.(0.05-1.00 µg/ mL), L.O.D=(15 $\mu g.\ L^{-1}$), (RSD%= 0.02), , $\varepsilon=(3.75\times10^{4}L.mol^{-1}.cm^{-1})$, pH=7.0, determine zinc(II) ion in several pharmaceutical preparations and copper alloys	[108]
Spectrophotometric	1-(2-thiazolylazo)-2-naphthol	Conc.(0.03-1.55 µg/ mL), L.O.D=(9 ng/ mL), L.O.Q=(30 ng/ mL), (RSD%= 0.38) , $\varepsilon=(4.50\times10^{4}L.mol^{-1}.cm^{-1})$, pH=6.5, λ_{max}=582 nm determine zinc(II) ion in	[109]

		several copper-base alloys	
Spectrophoto metric	phenanthraquinone monophenyl thiosemicarbazone (PPT)	Conc.(0.05-1.0 mg L^{-1}), L.O.D=(10 ng/ mL), , ε=(1.83 $\times 10^5$L.mol^{-1}.cm^{-1}), pH=6, λ_{max}=526 nm determine zinc(II) ion in Human Bio fluids and Pharmaceutical Samples	[110]
Spectrophoto metric	Sodium 4-((4,5-diphenyl-imidazol-2-yl)diazenyl)-3-hydroxynaphthalene-1-sulfonate (SDPIHN)	Conc.(1-11 μg/mL), λ_{max}=599 nm, L.O.D=0.2271 μg/mL), L.O.Q =0.7496 μg/mL), determine zinc(II) ion in pharmicutcal samples .	In this study

(1-8-2) Trace Chromium Element

(1-8-2-1) Chemistry of Chromium

Chromium (Cr), also known as chrome, is the twenty-first most abundant element in the earth's crust but the seventh most abundant element because it is concentrated in the core and mantle. It has the atomic number 24 and is part of the periodic table's group (VI)B [111]. Chromium ranks fourth among metals and thirteenth among all mineral commodities in commercial production by tonnage. The ground state electronic configuration of chromium is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^5$, $4s^1$. Because of the increased stability of the half-filled 3d shell with one electron in each orbital, this distribution of the outermost electrons is preferred over $3d^4/4S^2$. The half-filled shell leads to the "S" state (L = 0), which is said to be especially stable due to the large amount of exchange energy[112]. The d orbitals project near the ion surfaces, allowing the electrons in them to interact with the chemical environment. Chromium, a common transition element, can be found in a variety of colored and paramagnetic compounds. Chromium has the following oxidation states: -2, -1, 0, +1, +2, +3, +4, +5, +6; the highest oxidation state, +6, corresponds to the sum of 3d and 4s electrons. The lowest oxidation states of chromium in compounds such as carbonyls, nitrosyls, and organometallic complexes are -2, -1, 0 and +1. Chromium (+3) is the element's most stable and important oxidation state[113].

Chromium is an element that occurs naturally in minerals, rocks, plants, soil, water, volcanic dust, and gases. Chromium is a gleaming, brittle, and hard metal[114]. It has a silver-gray color and can be highly polished. It gives birth to and forms green chromic oxide when heated, which does not tarnish in air. When chromium reacts with oxygen, a thin oxide layer forms that is impermeable to oxygen and protects the metal beneath. Chromium is primarily used in alloys such as stainless steel, chrome plating, and metal ceramics[115]. Once upon a time, chromium plating was widely used to give steel a polished silvery mirror coating. In metallurgy, chromium is used to impart corrosion resistance and a shiny finish, as well as in dyes and paints. Its salts give glass an emerald green color, and it is used to make synthetic rubies, as a catalyst in dyeing and tanning leather, and to make molds for brick firing[116, 117].

(1-8-2-2) Biological effect of chromium

Chromium (III) is a trace element that is required for human and animal vital activity. Chromium plays an important role in the breakdown of fats and carbohydrates[118]. It promotes the production of fatty acids and cholesterol. They are necessary for brain function as well as other bodily processes. Chromium also helps insulin work and glucose breakdown. Chromium is an essential element that the body does not produce[119]. It can only be obtained through diet. It enters the body through the digestive tract and is transported to the tissues, where it accumulates. The chromium-binding oligopeptide chromodulin may play a unique role in insulin signaling autoamplification. The authors describe efforts to create chromium-containing nutritional supplements and therapeutics[120]. Chromium (III) deficiency interferes with metabolic processes. The primary response of organisms to chromium (III) deficiency is decreased glucose tolerance, which results from changes in insulin affinity for its receptors on cells[121]. The significant amounts of chromium (III) found in nucleic acids. It has an impact on their metabolism, replication, and transcription. The ion reduces the amount of corticosteroids in plasma while increasing the functional activity of an organism's immune system[122].

(1-8-2-3) Chromium deficiency

Chromium deficiency is a common problem. Many people, including athletes, diabetics, pregnant women, and the elderly, are especially vulnerable to chromium deficiency, which can lead to impaired insulin function, inhibition of protein synthesis and energy production, and, eventually, type 2 diabetes and heart disease[123]. Numerous studies have found a strong link between chromium deficiency, high blood insulin levels, and elevated blood cholesterol levels. Chromium deficiency has been shown in rats to raise serum cholesterol levels and promote the formation of aortic plaques[124].

(1-8-2-4) chromium toxicity

Chromium toxicity is defined as any poisonous toxic effect in an organism or cell caused by exposure to specific forms of chromium, particularly hexavalent chromium[125]. When inhaled or ingested, hexavalent chromium and its compounds are toxic. Trivalent chromium is an essential trace mineral in human nutrition[126]. There is a theoretical risk of genotoxicity in humans if large amounts of trivalent chromium enter living cells, but normal metabolism and cell function prevent this from happening[127]. Side effects of Cr(VI) exposure include occupational asthma, eye irritation and damage, perforated eardrums, respiratory irritation, kidney damage, liver damage, pulmonary congestion and edema, upper abdominal pain, nose irritation and damage, respiratory cancer, skin irritation, and tooth erosion and discoloration[128].

(1-8-2-5) Previous studies of chromium

Table (1-5) shows literature review of chromium by using spectrophotometric method with varies technique.

Table (1-5) The methods used to determination Chromium ion.

Method	Reagents	Results	Ref.
cloud-point extraction (CPE)	2-[benzenethiazolylazo]-4-benzenenaphthol (BTABN)	Conc.(0.1-2.0 µg/mL), L.O.D=(0.017 µg/mL), L.O.Q=(0.0568 µg/mL), , ε=(4.47 $\times 10^{4}$L.mol^{-1}.cm^{-1}), λ_{max}=475 nm	[129]

		,r=(0.9999), determine chromium(III) ion in various environmental and botanical samples.	
Spectrophotometric	chromotropic acid (CA)	Conc.(30-1200 µg/mL), λ_{max}=370 nm , RSD%=(0.04), determine chromium(III) ion in water samples	[130]
Spectrophotometric	bis(salicylaldehyde) orthophenylenediamine (BSOPD)	Conc.(0.02 – 4.0 $mg.L^{-1}$), λ_{max}=478 nm , ε=($1.67\times10^4 L.mol^{-1}.cm^{-1}$), determine chromium(III) ion in several Standard Reference Materials (steels and alloys), environmental waters and solutions containing chromium (III)	[131]
Spectrophotometric	Bis(salicylaldehyde) orthophenylenediamine (BSOPD)	Conc.(0.01-12.0 $mg.L^{-1}$), λ_{max}=482 nm , ε=($3.5\times10^5 L.mol^{-1}.cm^{-1}$), r=(0.9987) determine chromium(III) ion in some environmental waters (potable and polluted), biological samples (blood and urine) and to determine chromium species	[132]
Spectrophotometric	variamine blue	Conc.(2-12 µg/mL), λ_{max}=556 nm , ε=($0.911\times10^4 L.mol^{-1}.cm^{-1}$), L.O.D=(0.02 µg/mL), L.O.Q=(0.07 µg/mL), determine chromium(III) ion in alloy steels, industrial effluents, natural water samples and soil samples.	[133]
Spectrophotometric	diphenylthiocarbazone (dithizone)	Conc.(0.05-10 mg/L), λ_{max}=520 nm , ε=($1.2\times10^5 L.mol^{-1}.cm^{-1}$), determine chromium(III) ion in	[134]

		environmental and water samples	
Ultrasound-assisted cloud point extraction (UACPE)	cetyltrimethylammonium bromide (CTAB)	Conc.(20–400 ng mL^{-1}), (R^{2} = 0.999),L.O.D=(12 ng mL^{-1}), RSD%= 2.2 ,determine chromium(III) ion in water samples	[135]
Spectrophotometric	Rhodamine 6G hydrochloride dye (RG+)	Conc.(0.0245–1.5 µg mL^{-1}) ,L.O.D=(0.0073 µg mL^{-1}), L.O.Q=(0.025 µg mL^{-1}) , λ_{max}=534, Enhancing sensitivity by surfactant in extractive spectrophotometric determination of chromium	[136]
A micro-volume spectrofluorimetric coupled ultrasound-assisted ion association dispersive liquid–liquid microextraction (USA-IA-DLLME)	rhodamine 6G hydrochloride dye (RG+)	Conc.(1.0–1000 µg L^{-1}), L.O.D=(0.57 µg L^{-1}), L.O.Q=(1.9 µg L^{-1}), determine chromium(III) ion in water samples	[137]
Spectrophotometric	Leuco Xylene cynaol FF	Conc.(0.05–0.45 µg mL^{-1}), λ_{max}=615 nm , ε=(8.23×10^{4} L.mol^{-1}.cm^{-1}), determine chromium(III) ion in steels, pharmaceutical samples, industrial effluents, natural water, and soil.	[138]
cloud point extraction (CPE)	4-(2-thiazolylazo)resorcinol (TAR)	Conc.(15.0–75.0 µg L^{-1}), L.O.D=(3.2 µg L^{-1}), L.O.Q=(10.5 µg L^{-1}), RSD%=3.7, determine chromium(III) ion in water	[139]

		samples	
Dispersive liquid-liquid microextraction (DLLME)	Rhodamine 6G hydrochloride dye (RG+)	Conc.(25–950 μg L^{-1}), L.O.D=(7.48 μg L^{-1}), RSD%= 2.16, determine chromium(III) ion in spiked water samples (tap and sea water)	[140]
Spectrophotometric	Sodium 4-((4,5-diphenyl-imidazol-2-yl)diazenyl)-3-hydroxynaphthalene-1-sulfonate (SDPIHN)	Conc.(1-11 μg/mL), λ_{max}=586 nm, L.O.D=0.1167 μg/mL), L.O.Q =0.3852 μg/mL), determine chromium(III) ion in pharmicutcal samples .	In this study

(1-9) The aims of the study

This study includes :

1. Preparation of a new reagent from an Azo derivative then characterization by UV.VISB. , FT.IR , Mass Spectrum , ^{1}H-NMR and ^{13}C-NMR methods, the prepared new reagent are used for the determination of trace amounts of the zinc(II) and chromium(III) ions.
2. Studying the optimization conditions for determination the zinc(II) and chromium(III) complexes such as the size of the reagent, pH, the effect of time, the succession of addition, temperature and the determination of the metal-Reagent(M-R) ratio……etc.
3. Studying the effect of surfactant doping and their types on the spectroscopy process.
4. The study of possible interferences and methods to address them.
5. Studying some of the physical and chemical properties of the reagent and its complexes, determining the charge of the complexes, preparing its solid complexes and proposing the structural formula of the complexes.
6. Study of thermodynamic functions (ΔH, ΔG and ΔS).
7. Study of applications of pharmicutcal samples .

Chapter Two

Experimental

Chapter Two

Experimental

(2-1) Apparatus

Table (2-1) Some of Instruments are used in this study

No.	Instrument name	Type
1	Spectrophotometer	[Double Beam UV-visible Spectrophotometer – 1800 , Shimadzu, (Japan)]. At the University of Kerbala.
2	Spectrophotometer	[Single Beam - visible Spectrophotometer - 721, FAITHFUL (China)]. At the University of Kerbala.
3	FTIR Spectrophotometer	FTIR – IRAffinity-1S Shimadzu (Japan). At the University of Kerbala.
4	Mass spectroscopy	Manufacturer Company: Agilent Technology (HP), MS Model: 5973 Network Mass Selective Detector In Iran
5	^{1}H-NMR and ^{13}C-NMR spectroscopy	INSTRUM AVANCE NEO 400,BRUKER At the University of Basra.
6	Sensitive balance	Electronic balance ,ABS 220-4,KERN (Germany). At the University of Kerbala.
7	Melting point measuring Instrument	Melting point Apparatus –SMP30,Stuart (England). At the University of Kerbala.
8	Water bath	BS-11 JEIO TECH (Korea). At the University of Kerbala
9	Conductivity meter	Digital conductivity Meter- WTW -720 – inoLab (Germany) At the University of Kerbala.
10	pH-meter	pH-meter-HI1271,HANNA (ROMANIA). At the University of Kerbala.
11	Electric heater	Hotplate Stirrer ,LMS-1003,tabTEch(Korea). At the University of Kerbala.

(2-2) Chemical Materials

Table (2-2) All chemicals and reagent that were used .

No	Subject name	Chemical formula	Company Name	Purity
1	Benzil	$C_{14}H_{10}O_2$	(B.D.H)	99.0%
2	Hexamethylenetetramine	$C_6H_{12}N_4$	(B.D.H)	99.8%
3	1-amino-2-naphthol-4-sulfonic acid	$C_{10}H_9NO_4S$	FUJIFILM	97.0%
4	Glacial acetic acid	CH_3COOH	GCC	99.6%
5	Ammonium acetate	NH_4CH_3COO	GRIFFFIM	99.0%
6	Sulfuric acid	H_2SO_4	GCC	99.0%
7	Sodium nitrite	$NaNO_2$	E.M.$_{\text{Darmstadt}}$	99.0%
8	Sodium hydroxide	NaOH	(B.D.H)	99.0%
9	Hydrochloric acid	HCl 36w/v%	HIMEDIA	Analar
10	Nitric acid	HNO_3 65w/v%	E.Merck,Darmstadt	Analar
11	Sodium nitrate	$NaNO_3$	Fluka	98.0%
12	Ethanol	C_2H_5OH	Fluka	99.0%
13	Cadmium(II) nitrate -4-hydrate	$Cd(NO_3)_2.4H_2O$	Fluka	99.0%
14	Nickel(II)nitrate -6-hydrate	$Ni(NO_3)_2.6H_2O$	(B.D.H)	98.0%
15	Cobalt(II)nitrate -6-hydrate	$Co(NO_3)_2.6H_2O$	(B.D.H)	99.0%
16	Iron(III)nitrate -9-hydrate	$Fe(NO_3)_3.9H_2O$	(B.D.H)	99.0%
17	Mercury(II)nitrate-1-hydrate	$Hg(NO_3)_2.H_2O$	MERCK	98.5%
18	Lead (II)nitrate	$Pb(NO_3)_2$	(B.D.H)	99.0%
19	Magnesium(II)nitrate -6-hydrate	$Mg(N0_3)_2.6H_2O$	(B.D.H)	99.5%
20	Silver nitrate	$AgNO_3$	(B.D.H)	99.0%
21	Copper (II)nitrate -3-hydrate	$Cu(NO_3)_2.3H_2O$	(B.D.H)	99.0%
22	Potassium Sulfate	K_2SO_4	MERCK	99.0%
23	Potassium bromide	KBr	NANIWA	99.0%
24	Potassium thiocyanate	KSCN	(B.D.H)	99.0%
25	Potassium Iodate	KIO_3	GCC	99.0%
26	Potassium dichromate	$K_2Cr_2O_7$	Riedel	99.0%
27	Potassium carbonate	K_2CO_3	(B.D.H)	99.0%

28	Potassium cyanate	KCN	(B.D.H)	99.0%
29	Thiourea	CH_4N_2S	AAG	99.0%
30	Ascorbic acid	$C_6H_8O_6$	(B.D.H)	99.0%
31	Ethylene diamine tetra acetic acid disodium salt	Na_2EDTA	Fluka	98.0%
32	Citric Acid	$C_6H_8O_7$	Scharlou	99.0%
34	Potassium chloride	KCl	GCC	98.0%
35	Dimethyl sulfoxide	DMSO	Fluka	98.0%
36	Triton X-100	$C_{18}H_{28}O_5$	Thermo	99.0%
37	Tween-80	$C_{24}H_{44}O_6$	Thermo	99.0%
38	(Triton X-114)	$C_{28}H_{50}O_8$	Thermo	99.0%
39	Sodium Dodecyl Sulfate(SDS)	$NaC_{12}H_{25}SO_4$	Thermo	99.0%
40	Zinc(II)nitrate .6-hydrate	$Zn(NO_3)_2.6H_2O$	HIAMEDIA	99.0%
41	Chromium(III)nitrate .9-hydrate	$Cr(NO_3)_3.9H_2O$	(B.D.H)	99.0%
42	Dimethyl ether	$C_4H_{10}O$	Scharlou	99.5%
43	N,N-Dimethyl-form amid(DMF)	C_3H_7NO	CHEMLIMIED	99.5%
44	Chloroform	$CHCl_3$	HIAMEDIA	99.4%
45	Ammonium chloride	NH_4Cl	Fluka	99.0%
46	Ammonia	NH_3	Fluka	99.0%
47	Magnesium chloride	$MgCl_2$	Fluka	99.0%
48	Diethanolamine	$C_4H_{11}NO_2$	Fluka	99.0%
49	Boric acid	BH_3O_3	Fluka	99.0%

(2-3) Preparation of the organic reagent

A-preparation of (4,5 Diphenyl imidazole)

(4.2g, 0.02mol) of benzil and (1.4g, 0.01mol) of hexamethylene tetraamine were mixed in a 250mL round flask with (12g, 0.155 mol) of ammonium acetate, after that comes (80mL) of glacial 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 sodium hydroxide precipitation of the imidazole derivative to clear the residue, followed by filtration and rinsing with distilled water ,and the result was dried and recrystallized with ethanol to produce yellowish-white crystals. The formed precipitate was dried and tested for melting point (229 - 230) ^{o}C and the yield ratio was (83 %) [141].

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

Dissolving (3.588 g, 0.02 mol) of 1-amino-2-naphthol-4-sulfonic acid in a solution made 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 (0-5)^{0}C, 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 below 5^{0}C, before allowing the solution to stay for 15 minutes to complete the nitrogenation process.

After cooling the solution to (0-5)^{0}C 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 (0-5)^{0}C. The solution was stained a dark red color, and it was then left at (0-5)^{0}C for 2 hours. The acidity function (PH=6) was then obtained by adding dilute sulfuric 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 was(57%).

(2-4) Preparation of the Standard Solution

(2-4-1) Prepare the zinc (II) standard solution (1 mg/mL)

The preparation of the zinc (II) ion standard solution began with the dissolution of (0.455 g) of zinc nitrate ($Zn(NO_3)_2$). $3H_2O$ dissolved in deionized water at a concentration of 1 mg/mL, which is equivalent to 1.529×10^{-2} M. (100 mL). This standard solution was used as a starting point for the preparation of further standard solutions by repeatedly diluting it with deionized water.

(2-4-2) Prepare the chromium (III) standard solution (1 mg/mL)

The chromium (III) ion standard solution was made at a concentration of 1 mg/mL, corresponding to (1.922×10^{-2} M) , by dissolving 0.769 g of chromium nitrate $[Cr(NO_3)_3].9H_2O$ in deionized water . This produced a concentration of the solution that was 1 mg/mL . (100 mL). This standard solution was used as a starting point for the preparation of other standard solutions, which involved step-by-step dilution with deionized water.

(2-4-3) Preparation of [SDPIHN] Reagent Solution (2.032×10^{-3} M)

In order to prepare a reagent, (0.1 g) of (SDPIHN), which has a molecular weight of (492.484 g/mole) , was dissolved in ethanol . The volumetric flask was then filled with 100% ethanol to the correct concentration (100 mL).

(2-4-4) Sodium hydroxide solution preparation (0.1M)

The sodium hydroxide solution with a concentration of 0.1 M was made by first dissolving 0.400 g into the volume of deionized water that was necessary, and then further diluting the solution with deionized water until it reached the desired volume (100 mL).

(2-4-5) Prepare a solution of hydrochloric acid (0.1M)

After adding (0.833 mL) of concentrated acid (37%) to a specific volume of deionized water, the resulting solution was diluted to (100 mL) using deionized water to produce hydrochloric acid with a concentration of (0.1 M).

(2-4-6) Cationic solution preparation

Dissolving the required amounts of elemental nitrate salts in an amount of deionized water equal to 100 mL, cationic ions solutions with a concentration of 1 mg/mL were produced. These standard solutions were used to prepare others, which were made by first diluting them with deionized water, then doing so in a number of steps. Installed using the procedure that is described further down.

Table (2-3): The weights which used prepare the cation solutions.

Seq.	Cations formula structure	Weight(g)
1	$Cd(NO_3)_2.4H_2O$	0.2731
2	$Ni(NO_3)_2.6H_2O$	0.4951
3	$Co(NO_3)_2.6H_2O$	0.4936
4	$Fe(NO_3)_3.9H_2O$	0.7234
5	$Hg(NO_3)_2.H_2O$	0.1701
6	$Pb(NO_3)_2$	0.1598
7	$Mg(N0_3)_2.6H_2O$	1.0551
8	$AgNO_3$	0.1570
9	$Cu(NO_3)_2.3H_2O$	0.3802

(2-4-7) Anions solution preparation

Anions solutions with a concentration of 1 mg/mL were generated from elemental potassium salts by dissolving the required weights in 25 mL of deionized water indicated. These standard solutions were used to prepare others, which were made by first diluting them with deionized water, then doing so in a number of steps. Installed using the approach outlined in the following paragraphs.

Table (2-4): The weights used to prepare the anions solutions

Seq.	Substance	Weight(g)
1	K_2SO_4	0.0453
2	KBr	0.0443
3	KSCN	0.0418
4	KIO_3	0.0301
5	$K_2Cr_2O_7$	0.0340
6	K_2CO_3	3.4550
7	KCN	0.0610

(2-4-8) Preparation of standard solutions at different concentrations to investigate the effect of ionic strength

A-Prepare a sodium sulfate solution of (0.5) M . (Na_2SO_4).

In order to prepare a sodium sulfate solution with a concentration of 0,5 M, first dissolve 1.780 g of sodium sulfate in 5 mL of deionized water, then transfer the solution to a volumetric flask with a capacity of 25 mL, and finally fill the flask to the top with deionized water 25 mL . Step-by-step dilution of the stock solution resulted in the preparation of the concentrations (5.00×10^{-2}, 5.00×10^{-3}, and 5.00×10^{-4} M).

B- Prepare a sodium nitrate solution of 0.5 M ($NaNO_3$) .

A sodium nitrate solution of 0.5 M was obtained by first dissolving 1.063 g of sodium nitrate ($NaNO_3$) in 5 mL of deionized water and then transferring the solution to the volumetric flask with a capacity of 25 mL, then filled it up with deionized water. The concentrations were $5.00\text{x}10^{-2}$, $5.00\text{x}10^{-3}$, and $5.00\text{x}10^{-4}$ M after the standard solution was diluted several times.

(2-4-9) Preparation of masking agent solutions

The preparation of masking agent solutions having a volume of 25 mL was fulfilled by first dissolving a specific weight of each constituent in a volume of 5 mL deionized water, then transferring the resulting solution to a volumetric flask having a capacity of 25 mL , and finally filling the volume to the mark with deionized water.

Table (2–5): The masking parameters utilized in this investigation

Seq.	Masking agent (0.1M)	Weight(g)
1	Thiourea	0.1900
2	Ascorbic acid	0.4400
3	Na_2EDTA	0.8900
4	Citric Acid	0.0200
5	KCl	0.1800
6	$Na_2HPO_4.12H_2O$	0.8900
7	Formaldehyde	0.0750

(2-4-10) Preparation of buffer solutions [142-144]

1. Ammonium chloride buffer solution (pH 10.5)

   Ammonium chloride, 8.750 g, dissolved in 25 mL of distilled water; concentrated ammonia, 41.250 mL; diluted to 125.0 mL using distilled water; final volume, 125.0 mL.

2. Borate buffer solution (pH 10.5)

   Dissolve 2.737 g of boric acid in 100 mL of distilled water . Adjust the pH using a 44.444 g/L solution of sodium hydroxide . Dilute to 100 mL with distilled water .

3. Ammonium chloride buffer solution (pH 10)

   After dissolving 5.4 g of ammonium chloride in 20 mL of distilled water, add 35.0 mL of ammonia , bring the total volume of the solution up to 100 mL .

4. Di ethanolamine buffer solution (pH 10)

   Diethanolamine, totaling 19.280 g, is dissolved in distilled water, and the resulting solution is diluted to a volume of 80 mL using the same solvent. After that, add (0.1 mL) of a solution that has 37,200 g/L of magnesium chloride, and then correct the pH using one million parts of hydrochloric acid. Dilute with distilled water to a total volume of 100mL.

(2-5)Procedure

(2-5-1) Preliminary experiments of the reagent's reactivity with varied metal ions

It was determined that a new color or precipitate was produced while adding the reagent solution. This was determined by shaking the test tubes by adding the reagent solution at a concentration of $2.032x10^{-3}$ M to 2 mL of solutions containing about eleven different metallic ions, each with a concentration of (100 µg/mL), added to each of them. Following this stage, the solution was separated into two sections, one of which had drops of a 0.1 M solution of hydrochloric acid added to it, and the other of which had drops of a 0.1 M solution of sodium hydroxide added to it to estimate the impact of acidic function.

(2-6) Study the reagent's (SDPIHN) absorption spectra, as well as the complexes generated with zinc (II) and chromium (III) ions

(2-6-1) Study the reagent's (SDPIHN) absorption spectra in the ultraviolet-visible range

Spectral scanning of the reagent SDPIHN at a concentration of ($2.032x10^{-3}$ M) was done in the limited region between (190-1100 nm) using ethanol as a similar solution (Blank) utilizing a dual-beam UV-visible spectrophotometer, and quartz cells with a light path of (1 cm) thickness. The maximum absorbance of the reagent was found at (λ_{max} =463 nm).

(2-6-2) Ultraviolet–visible absorption spectra of zinc (II) and chromium (III) complexes

In paragraphs (2-5-1), a clear definition was provided for the metal ions that interact with the reagent. It used two volumetric flasks, each one with a capacity of (10 mL). One of them was filled with (5 mL) of a solution containing zinc (II) ion at a concentration of (1.52×10^{-4} M), equal to (50 µg/5mL). The other volumetric flask was filled with (5 mL) of chromium (III) ion solution at a concentration of ($1.92x10^{-4}$ M) equivalent to (50 µg/5mL), then adding (1.0 mL) of the reagent solution to each volumetric flask at a concentration of ($2.032x10^{-3}$ M). Finally, deionized water was added to each volumetric flask till the mark. Each volumetric flask was labeled with the appropriate concentration of chromium (III) ion and zinc (II) ion. Except for adding zinc (II) and chromium (III) ions, the comparable solution referred to as Blank was made similarly.

The complex solutions generated in the previous paragraph were scanned using a spectrophotometric instrument across the wavelength range of 350-1100 nm, and the maximum absorbance values were determined. In this area, the complexes have the maximum absorption value when measured against the reagent solution, which is an analogous solution (Blank).

(2-7) Study of the absorption of both Zinc (II) and Chromium (III) complexes in presence of surfactant

The complexes of zinc(II) and chromium (III) were tested with the four different types of surfactants (Tween - 80, Triton X-100, Triton X-114, and SDS) in order to select the best one of the surfactants that gives highly absorption because the complexes may be more stable. For each type of surfactant, there are three concentrations of surfactant.

1-A collection of volumetric flasks (10 mL) were taken and, added to each of them (5mL) of Zinc(II) ion Solution at concentration of ($1.52x10^{-4}$M), equiv. to (50 µg /5 mL) , and then added to them (1.0 mL) of the reagent solution at a concentration of ($2.032x10^{-3}$ M) and then added to them (1.0 mL) of the surfactant in sequential various concentration (1%,2%,3%) of (Tween - 80, Triton X-100, Triton X-114, SDS) all alone , then the acidity function was modified at (pH = 10.5) followed by the volume completion to the mark with deionized water and the absorption record at the greatest wavelength of the zinc complex ,(λ_{max} = 599 nm) for each solution versus the reagent solution as it is a comparative solution with the exception of adding the ion to all the measured solutions.

2-A group of volumetric flasks (10 mL) were taken ,and added to each of them (5 mL) of chromium (III) ion Solution at concentration of ($1.92x10^{-4}$ M) , equiv. to (50 µg /5 mL) , and then added to them (1.0 mL) of the reagent solution at a concentration of ($2.032x10^{-3}$ M) and then added to them (1.0 mL) of the surfactant in sequential various concentration (1% ,2% ,3%) of (Tween – 80 , Triton X-100 , Triton X-114 , SDS) all alone , then the acidity function was modified at (pH = 10.0) followed by the volume completion to the mark with deionized water and the absorption record at the greatest wavelength of the chromium complex (λ_{max} = 586 nm) for each solution versus the reagent solution as it is a comparative solution with the exception of adding the ion to all the measured solutions.

(2-8) Determine the optimal conditions for the production of zinc (II) and chromium (III) complexes by using the (SDPIHN) reagent

After determining the maximum absorption (λ_{max}) for each of the complexes in pargraph (2-6-2), which was found to be 599 nm for zinc (II) and 586 nm for chromium (III), respective, the following tests were performed to determine the best possible conditions for the generation of the two complexes using the spectrophotometric method. This was done in order to achieve high selectivity and sensitivity in the ion estimate.

(2-8-1) Reagent optimal value limitation

1- A group of volumetric flasks (10 mL) were taken , and (5 mL) of zinc (II) ion solution were added to each of them that it were at a concentration of ($1.52x10^{-4}$M) , equivalent to (50 µg / 5 mL) , and then added to them in sequence various volumes of the reagent solution at a concentration of ($2.032x10^{-3}$ M) , where it ranged among (0.5-3.5 mL) , then the acidity function was adjusted at (pH =10.5) , accompanied by volume completing to the mark with deionized water and the absorption measurement at the maximum wavelength of the zinc complex (λ_{max} = 599 nm) for each solution versus the reagent solution as a comparison solution except for adding the ion to all of the tested solutions.

2- A group of volumetric flasks (10 mL) were taken , and (5 mL) of chromium (III) ion solution were added to each of them that it were at a concentration of ($1.92x10^{-4}$ M), equivalent to (50 µg / 5 mL), and then added to them in sequence various volumes of the reagent solution at a concentration of ($2.032x10^{-3}$ M) , where it ranged among (0.5-3.5 mL) , then the acidity function was adjusted at (pH =10.0) , accompanied by volume completing to the mark with deionized water and the absorption measurement at the maximum wavelength of the chromium complex (λ_{max} = 586 nm) for each solution versus the reagent solution as a comparison solution except for adding the ion to all of the measured solutions.

(2-8-2) Effect of surfactant volume

From (2-7) paragraph the Triton X-100 was choosen as the best surfactant that the zinc and chromium complexes record highly absorbance in presence of Triton X-100.

1- A group of volumetric flasks (10 mL) was taken and added to each of them (5 mL) of zinc (II) ion solution at a concentration of ($1.52x10^{-4}$M) , equiv. to (50 µg / 5 mL) ,followed by (3 mL) of the reagent solution at a concentration of ($2.032x10^{-3}$ M) and then added to them in sequential different volumes of a Triton X-100 solution at a concentration of (3 v/v%) , where it ranged between (0.25-2mL) , then the acidity function was modified at (pH =10.5) followed by the volume completion to the mark with deionized water and the absorption record at the greatest wavelength of the zinc complex (λ_{max} = 599 nm) for each solution versus the reagent solution as it is a comparative solution with the exception of adding the ion to all the measured solutions.

2- A group of volumetric flasks (10 mL) was taken and added to each of them (5 mL) of chromium (III) ion solution at a concentration of ($1.92x10^{-4}$ M) , equiv. to (50 µg / 5 mL),) , with (3 mL) of the reagent solution at a concentration of ($2.032x10^{-3}$ M) and then added to them in sequential various volumes of a Triton X-100 solution at a concentration of (3 v/v%) , where it ranged between (0.25-2mL) , then the acidity function was modified at (pH =10.0) followed by the volume completion to the mark with deionized water and the absorption record at the greatest wavelength of the chromium complex (λ_{max} = 586 nm) for each solution versus the reagent solution as it is a comparative solution with the exception of adding the ion to all the measured solutions.

(2-8-3)The effect of pH value

1-study the effect of zinc(II) complex's acidic function.

A series of zinc (II) ion solutions were prepared at a concentration of ($1.52x10^{-4}$M) equal to (50 µg / 5 mL) by combining (5 mL) zinc ion (II) with (3 mL) of the reagent solution at a concentration of ($2.032x10^{-3}$M) , and then adding (0.5 mL) of a Triton X-100 at a concentration of

(3%) and modify the compound's acidity function with various values with the range (2.0-11.5) using HCl (0.1M)/ NaOH (0.1M) , and the final pH of each solution was calculated with a pH-meter , then moving the mixture to volumetric flasks (10 mL) ,and fill to the mark with deionized water . The comparison solution used in the spectroscopic measurements of the above group was prepared by adding (5 mL) from deionized water , then placing (3 mL) of reagent solution at a concentration of ($2.032x10^{-3}$M) and then transferring to them (0.5 mL) of Triton X-100 at a concentration of (3%) with the modification of the acidic function and moved to a volumetric flask (10 mL) and finish the volume to the mark with deionized water , and the absorbance was measured at the zinc compound's maximum wavelength (λ_{max} =599 nm)

2-study the effect of chromium (III) complex's acidic function.

A series of chromium (III) ion solutions were prepared at a concentration of ($1.92x10^{-4}$ M) equal to (50 µg / 5 mL) by combining (5 mL) chromium(III) ion with (3 mL) of the reagent solution at a concentration of ($2.032x10^{-3}$ M), and then adding (0.5 mL) of a Triton X-100 at a concentration of (3%) and modify the compound's acidity function with various values within the range (2.0-11.5) using HCL(0.1M)/ NaOH (0.1M), and the final pH of each solution was calculated with a pH-meter , then moving the mixture to volumetric flasks (10 mL) and fill to the mark with deionized water . The comparison solution used in the spectroscopic measurements of the above group was prepared by adding (5 mL) from deionized water , then placing (3 mL) of reagent solution at a concentration of ($2.032x10^{-3}$M) and then transferring to them (0.5 mL) of Triton X-100 at a concentration of (3%) with the modification of the acidic function and moved to a volumetric flask (10 mL) and finish the volume to the mark with deionized water , and the absorbance was measured at the zinc compound's maximum wavelength (λ_{max} = 586 nm).

(2-8-4) The influence of time on the stability of a complex

The diagrams show how the time factor influences the stability of zinc (II) and chromium (III) complexes . For the two produced complexes , the absorption measurement was followed up on at different time intervals at the prescribed wavelength (λ_{max}) for the two complexes.

1- Investigate the influence of time on the absorption of zinc (II) complexes.

The zinc (II) complex was prepared by combining (5 mL) of zinc (II) ion solution at a concentration of ($1.52x10^{-4}$M) equal to (50 µg / 5mL) with (3 mL) of reagent solution at a concentration of ($2.032\ x10^{-3}$ M) , and then adding (0.5 mL) of Triton- X100 at a concentration of (3%) with the value of the optimum acidic function set at (pH =10.5) .

The volume is then reduced to (10 mL) using deionized water . The absorbance of the produced complex was then measured at (λ_{max}=599 nm) for the complex versus the comparator solution (Blank) for time periods ranging from the start of the reaction to the end of the experiment (24hr) .

2- Investigate the influence of time on the absorption of chromium (III) complexes.

The chromium (III) complex was prepared by combining (5 mL) of chromium (III) ion solution at a concentration of ($1.92x10^{-4}$ M) equal to (50 µg / 5mL) with (3 mL) of reagent solution at a concentration of ($2.032\ x10^{-3}$ M) , and then adding (0.5 mL) of Triton- X100 at a concentration of (3%) with the value of the optimum acidic function set at (pH =10) .

The volume is then reduced to (10 mL) using deionized water . The absorbance of the produced complex was then measured at (λ_{max}=586 nm) for the complex versus the comparator solution (Blank) for time periods ranging from the start of the reaction to the end of the experiment (24hr) .

(2-8-5) The effect of sequential addition

As indicated below , this study includes varying the order of additions and work in terms of addition of ion , reagent, Triton X-100 , and pH measure.

(2-8-5-1) Zinc (II) ion complex

1. Addition sequential includes an addition (5 mL) of zinc (II) ion solution at a concentration of ($1.52x10^{-4}$M) equivalent to (50 µg / 5mL) with (3 mL) of the reagent solution at a concentration of

$(2.032 \times 10^{-3}$ M) ,and then added to them (0.5 mL) of Triton X-100 at concentration (3%) with adjusting the value of the optimum acidic function at (pH =10.5) .Then the volume is completed to (10 mL) with deionized water . As for the comparative solution , it was prepared by mixing the solutions with the same previous steps, with the size of the zinc (II) ion replaced by deionize water . Then the absorption of the prepared complex was measured at (λ_{max}=599 nm).

2. Addition sequential includes an addition (5 mL) of zinc (II) ion solution at a concentration of (1.52×10^{-4}M) equivalent to (50 µg / 5mL) with (0.5 mL) of Triton X-100 at concentration (3%) ,and then added to them (3 mL) of the reagent solution at a concentration of (2.032×10^{-3} M) with adjusting the value of the optimum acidic function at (pH =10.5) .Then the volume is completed to (10 mL) with deionized water . As for the comparative solution , it was prepared by mixing the solutions with the same previous steps , with the size of the zinc (II) ion replaced by deionize water . Then the absorption of the prepared complex was measured at (λ_{max}=599 nm).
3. Addition sequential includes an addition (0.5 mL) of Triton X-100 at concentration (3%) with (5 mL) of zinc (II) ion solution at a concentration of (1.52×10^{-4}M) equivalent to (50 µg / 5mL) and then added to them (3 mL) of the reagent solution at a concentration of (2.032×10^{-3} M) , with adjusting the value of the optimum acidic function at (pH =10.5) .Then the volume is completed to (10 mL) with deionized water. As for the comparative solution , it was prepared by mixing the solutions with the same previous steps , with the size of the zinc (II) ion replaced by deionize water . Then the absorption of the prepared complex was measured at (λ_{max}=599 nm).
4. Addition sequential includes an addition (3 mL) of the reagent solution at a concentration of (2.032×10^{-3} M) with (5 mL) of zinc (II) ion solution at a concentration of (1.52×10^{-4}M) equivalent to (50 µg / 5mL) and then added to them (0.5 mL) of Triton X-100 at concentration (3%) , with adjusting the value of the optimum acidic function at (pH =10.5) . Then the volume is completed to (10 mL) with deionized water. As for the comparative solution , it

was prepared by mixing the solutions with the same previous steps , with the size of the zinc (II) ion replaced by deionize water . Then the absorption of the prepared complex was measured at(λ_{max}=599 nm).

5. Addition sequential includes an addition (5 mL) of zinc (II) ion solution at a concentration of ($1.52x10^{-4}$M) equivalent to (50 µg / 5mL) with adjusting the value of the optimum acidic function at (pH =10.5) with (3 mL) of the reagent solution at a concentration of ($2.032\ x10^{-3}$ M) ,and then added to them (0.5 mL) of Triton X-100 at concentration (3%) . Then the volume is completed to (10 mL) with deionized water. As for the comparative solution , it was prepared by mixing the solutions with the same previous steps , with the size of the zinc (II) ion replaced by deionize water . Then the absorption of the prepared complex was measured at (λ_{max}=599 nm).
6. Addition sequential includes an addition (5 mL) of zinc (II) ion solution at a concentration of ($1.52x10^{-4}$M) equivalent to (50 µg / 5mL) with (3 mL) of the reagent solution at a concentration of ($2.032\ x10^{-3}$ M) with adjusting the value of the optimum acidic function at (pH =10.5) ,and then added to them (0.5 mL) of Triton X-100 at concentration (3%) . Then the volume is completed to (10 mL) with deionized water. As for the comparative solution , it was prepared by mixing the solutions with the same previous steps , with the size of the zinc (II) ion replaced by deionize water . Then the absorption of the prepared complex was measured at (λ_{max}=599 nm).

(2-8-5-2)chromium (III)ion complex.

1. Addition sequential includes an addition (5 mL) of chromium (III) ion solution at a concentration of ($1.92x10^{-4}$ M) equivalent to (50 µg / 5mL) with (3 mL) of the reagent solution at a concentration of ($2.032\ x10^{-3}$ M) , and then added to them (0.5 mL) of Triton X-100 at concentration (3%) with adjusting the value of the optimum acidic function at (pH =10.0) . Then the volume is completed to (10 mL) with deionized water . As for the comparative solution , it was prepared by mixing the solutions with the same previous steps

, with the size of the chromium (III) ion replaced by deionize water . Then the absorption of the prepared complex was measured at (λ_{max}=586 nm).

2. Addition sequential includes an addition (5 mL) of chromium (III) ion solution at a concentration of ($1.92x10^{-4}$ M) equivalent to (50 µg / 5mL) with (0.5 mL) of Triton X-100 at concentration (3%) ,and then added to them (3 mL) of the reagent solution at a concentration of ($2.032 x10^{-3}$ M) with adjusting the value of the optimum acidic function at (pH =10.0) . Then the volume is completed to (10 mL) with deionized water. As for the comparative solution , it was prepared by mixing the solutions with the same previous steps , with the size of the chromium (III) ion replaced by deionize water . Then the absorption of the prepared complex was measured at (λ_{max}=586 nm).
3. Addition sequential includes an addition (0.5 mL) of Triton X-100 at concentration (3%) with (5 mL) of chromium (III) ion solution at a concentration of ($1.92x10^{-4}$ M) equivalent to (50 µg / 5mL) and then added to them (3 mL) of the reagent solution at a concentration of ($2.032 x10^{-3}$ M) , with adjusting the value of the optimum acidic function at (pH =10.0) . Then the volume is completed to (10 mL) with deionized water. As for the comparative solution , it was prepared by mixing the solutions with the same previous steps , with the size of the chromium (III) ion replaced by deionize water . Then the absorption of the prepared complex was measured at (λ_{max}=586 nm).
4. Addition sequential includes an addition (3 mL) of the reagent solution at a concentration of ($2.032 x10^{-3}$ M) with (5 mL) of chromium (III) ion solution at a concentration of ($1.92x10^{-4}$ M) equivalent to (50 µg / 5mL) and then added to them (0.5 mL) of Triton X-100 at concentration (3%) , with adjusting the value of the optimum acidic function at (pH =10.0) . Then the volume is completed to (10 mL) with deionized water. As for the comparative solution , it was prepared by mixing the solutions with the same previous steps , with the size of the chromium (III) ion replaced by deionize water . Then the absorption of the prepared complex was measured at (λ_{max}=586 nm).

5. Addition sequential includes an addition (5 mL) of chromium (III) ion solution at a concentration of ($1.92x10^{-4}$ M) equivalent to (50 µg / 5mL) with adjusting the value of the optimum acidic function at (pH =10.0) with (3 mL) of the reagent solution at a concentration of ($2.032\ x10^{-3}$ M) , and then added to them (0.5 mL) of Triton X-100 at concentration (3%) . Then the volume is completed to (10 mL) with deionized water. As for the comparative solution , it was prepared by mixing the solutions with the same previous steps , with the size of the chromium (III)ion replaced by deionize water . Then the absorption of the prepared complex was measured at (λ_{max}=586 nm).
6. Addition sequential includes an addition (5 mL) of chromium (III) ion solution at a concentration of ($1.92x10^{-4}$ M) equivalent to (50 µg / 5mL) with (3 mL) of the reagent solution at a concentration of ($2.032\ x10^{-3}$ M) with adjusting the value of the optimum acidic function at (pH =10.0) ,and then added to them (0.5 mL) of Triton X-100 at concentration (3%) . Then the volume is completed to (10 mL) with deionized water. As for the comparative solution , it was prepared by mixing the solutions with the same previous steps, with the size of the chromium (III) ion replaced by deionize water. Then the absorption of the prepared complex was measured at(λ_{max}= 586nm).

(2-8-6)Temperature effect

1- Study the influence of temperature on the zinc (II) complex.

The impact of temperature of the zinc complex was investigated by filling a group of volumetric flasks (10 mL) with (5 mL) of zinc (II) ions at a concentration of ($1.52x10^{-4}$M) equivalent to (50 µg/5 mL) , then adding (3 mL) from the reagent at a concentration of ($2.032\ x10^{-3}$ M) ,and then adding to them (0.5 mL) of Triton X-100 at a concentration of (3%) . Then , after modifying the optimal acidic function to (pH = 10.5), transporting to a volumetric flask (10 mL) and filling to the mark with deionized water , putting these flasks in a water bath with a temperature range of (10 – 60) ^{0}C , and measuring the absorption at the complex's maximum absorption wavelength against a comparator solution prepared in the same way but without zinc ion.

2- Study the influence of temperature on the chromium(III) complex.

The impact of temperature of the chromium(III) complex was investigated by filling a group of volumetric flasks (10 mL) with (5 mL) of chromium(III) ions at a concentration of ($1.92x10^{-4}$ M) equivalent to (50 µ g/5 mL) , then adding (3 mL) from the reagent at a concentration of ($2.032\ x10^{-3}$ M) ,and then adding to them (0.5 mL) of Triton X-100 at a concentration of (3%) . Then, after modifying the optimal acidic function to (pH = 10.0) , transporting to a volumetric flask (10 mL) and filling to the mark with deionized water , putting these flasks in a water bath with a temperature range of (10 – 60) ^{0}C , and measuring the absorption at the complex's maximum absorption wavelength against a comparator solution prepared in the same way but without chromium(III) ion.

(2-9) Ionic strength's effect

The degree of solubility of the reactants , the speed of their reaction, and the sensitivity of the estimation are all affected by the ions of varying ionic forces . As a result, it is critical to investigate this affecting element . The following steps were used to demonstrate this.

1- A set of volumetric flasks (10 mL) were used to add (5 mL) of a zinc(II) ion solution at a concentration of ($1.52x10^{-4}$M) , equivalent to (50 µg/5 mL) , and then (0.5 mL) of sodium nitrate and sodium sulfate solutions were added , each one separately at various concentration. Their concentrations ranged from ($0.5\text{-}5.0x10^{-4}$ M) individually , then (3 mL) of reagent solution at a concentration of ($2.032\ x10^{-3}$ M) was added to each of them , along with (0.5 mL) of Triton X-100 at a concentration of (3%) , and the volumetric flasks were filled to the mark with deionized water after the optimal acidic function was adjusted at (pH=10.5) to form the zinc(II) complex . The absorbance at the complex's maximum wavelength (λ_{max} =599 nm) was measured vs a reagent solution produced in the same way as a comparable solution (Blank) but for the addition of the ion and for all the measured solutions.

2- A set of volumetric flasks (10 mL) were used to add (5 mL) of a chromium (III) ion solution at a concentration of ($1.92x10^{-4}$ M) , equivalent to (50 µg/5 mL) , and then (0.5 mL) of sodium nitrate and sodium sulfate solutions were added , each one separately at various concentration . Their concentrations ranged from ($0.5-5.0x10^{-4}$ M) individually , then (3 mL) of reagent solution at a concentration of ($2.032 x10^{-3}$ M) was added to each of them , along with (0.5 mL) of Triton X-100 at a concentration of (3 %) , and the volumetric flasks were filled to the mark with deionized water after the optimal acidic function was adjusted at (pH=10.0) to form the chromium (III) complex . The absorbance at the complex's maximum wavelength (λ_{max} =586 nm) was measured versus a reagent solution produced in the same way as a comparable solution (Blank) but for the addition of the ion and for all the measured solutions.

(2-10) The influence of the buffer solution on each complex's optimal acidic function

1-To each of two volumetric flasks (10 mL) , add (5 mL) of zinc (II) ion solution at a concentration of ($1.52x10^{-4}$M) equivalent to (50 µg/5 mL) and then (3 mL) of reagent solution at a concentration of ($2.032 x 10^{-3}$M) with (0.5 mL) of Triton X-100 at concentration (3 %) , and the zinc(II) complex's optimal acidic function was adjusted at (pH=10.5) using the buffer solutions prepared in 1,2 of paragraph (2-4) , after which the volume was filled to the mark with deionized water and the absorption register was taken at the complex's maximum wavelength (λ_{max}=599 nm) against solution , with the exception of adding the ion and for all the measured solutions , prepare the reagent in the same way as a comparable solution (Blank).

2- To each of two volumetric flasks (10 mL) , add (5 mL) of chromium (III) ion solution at a concentration of ($1.92x10^{-4}$M) equivalent to (50 µg/5 mL) and then (3 mL) of reagent solution at a concentration of ($2.032 x 10^{-3}$M) with (0.5 mL) of Triton X-100 at concentration (3 %) , and the chromium (III) complex's optimal acidic function was adjusted at (pH=10.0) using the buffer solutions prepared in 3,4 of paragraph (2-4), after which the volume was filled to the mark with deionized water and the absorption register was taken at the complex's maximum wavelength (λ_{max}=586 nm) against solution, with the exception of adding the ion and for all the measured solutions, prepare the reagent in the same way as a comparable solution (Blank).

(2-11) Calibration curves

(2-11-1) Calibration curve for the zinc(II) complex

A set of volumetric flasks (10 mL) were taken and added varied concentrations of zinc(II) ion solution (5 mL) to them , ranging from (1.52×10^{-5}-1.68×10^{-4}M) , corresponding to (1 µg/mL - 11 µg/mL) . Then (3 mL) of the reagent solution at a concentration of (2.032 x10^{-3} M), with (0.5 mL) of Triton X-100 at a concentration of (3 %) , and the pH was adjusted (pH = 10.5) with following the other optimum conditions reached in this study , and the volume was completed with deionized water to the mark , prepared using the same complex process , but substituting an equivalent volume of deionized water for the volume of a zinc(II) ion solution . The relationship between absorption and concentration was determined by measuring the absorption of all solutions at (λ_{max}= 599 nm) of the complex.

(2-11-2) Calibration curve for the chromium(III) complex

A set of volumetric flasks (10 mL) were taken and added varied concentrations of chromium(III) ion solution (5 mL) to them, ranging from (1.92×10^{-5}-2.11×10^{-4}M), corresponding to (1 µg/mL - 11 µg/mL). Then (3 mL) of the reagent solution at a concentration of (2.032 x10^{-3} M), with (0.5 mL) of Triton X-100 at a concentration of (3 %), and the pH was adjusted (pH = 10.0) with following the other optimum conditions reached in this study, and the volume was completed with deionized water to the mark , prepared using the same complex process, but substituting an equivalent volume of deionized water for the volume of a chromium(III) ion solution. The relationship between absorption and concentration was determined by measuring the absorption of all solutions at (λ_{max}= 586 nm) of the complex.

(2-12) The complexes' stoichiometry

The metal to ligand ratio (M: L) is investigated under optimal conditions using both the mole ratio approach and the Job method (continuous variations).

(2-12-1) Job's (continuous variation) method [145]

1- Zinc(II) ion complex.

This method entails preparing two solutions with the same concentration of metal ion and reagent for zinc(II) complex at concentration (1.0 x 10^{-4} M) , then reacting these solutions with various volumetric ratios with Triton X-100 (0.5 mL) and modifying the acidity function at (pH =10.5) with equal final volume every time , and finally drawing a curve between the absorbance and the volumetric ratio at the appropriate maximum wavelength (λ_{max} =586 nm) for zinc complex . The mole ratio of the complex produced is represented by the ratio (VL/VM) , where VM is the volume of the metal ion (Zn) solution and VL is the volume of the reagent solution.

2- Chromium(III) ion complex.

This method entails preparing two solutions with the same concentration of metal ion and reagent for chromium(III) complex at concentration (0.795 x 10^{-4} M) , then reacting these solutions with various volumetric ratios with Triton X-100 (0.5 mL) and modifying the acidity function at (pH =10.0) with equal final volume every time, and finally drawing a curve between the absorbance and the volumetric ratio at the appropriate maximum wavelength (λ_{max} =586 nm) for chromium (III) complex . The mole ratio of the complex produced is represented by the ratio (VL/VM) , where VM is the volume of the metal ion (Cr) solution and VL is the volume of the reagent solution.

(2-12-2) Mole Ratio Method [146]

1- Zinc(II) ion complex.

In this method , a set of volumetric flasks (10 mL) were taken and each one was filled with a fixed and known concentration of the zinc(II) ion (6.127×10^{-4}M) (5mL) with increasing and proportional concentrations of the reagent (1.53×10^{-4}- 1.838×10^{-3} M) (3 mL) with (0.5 mL) of Triton

X-100 at concentration (3%) and the acidity function was adjusted at (pH =10.5) . The comparative solutions were prepared in the same approach as the complex preparation , except that the volume of zinc (II) ion solution was substituted with an equivalent volume of deionized water . The compound absorbs all solutions at (λ_{max}=599 nm).

2- Chromium(III) ion complex.

In this method , a set of volumetric flasks (10 mL) were taken and each one was filled with a fixed and known concentration of the chromium (III) ion ($7.692x10^{-4}$ M) (5mL) with increasing and proportional concentrations of the reagent ($1.923x10^{-4}$-$3.461x10^{-3}$ M) (3 mL) with (0.5 mL) of Triton X-100 at concentration (3%) and the acidity function was adjusted at (pH =10.0) . The comparative solutions were prepared in the same approach as the complex preparation , except that the volume of chromium (III) ion solution was substituted with an equivalent volume of deionized water . The compound absorbs all solutions at (λ_{max}=586 nm).

(2-13) Calculate the degree of dissociation , stability constant , and thermodynamic functions of the two produced complexes [147, 148]

1-Complex of zinc(II).

Two volumetric flasks were taken (10 mL) and placed in the first volumetric flask (5mL) of zinc (II) ion at concentration of ($6.127x10^{-4}$M) with (3 mL) from the reagent at a concentration of ($1.225x10^{-3}$ M) , and then added to them (0.5 mL) of triton x100 at concentration (3 %) then modifying the optimal acidic function at (pH = 10.5) , then fill the volumetric flask (10 mL) with deionized water to the mark , then adding to the second volumetric flask (5 mL) of zinc (II) ion at a concentration of ($6.127x10^{-4}$M) , then adding to it (3 mL) from the reagent at a concentration of ($1.838x10^{-3}$ M) , and adding to them (0.5 mL) of Triton X-100 at concentration (3%) . Then modifying the optimal acidic function at (pH = 10.5) , then transferring to a volumetric flask (10 mL) and filling it with deionize water to the mark . The two volumetric flasks were put in a water bath at a temperature of (10 – 30) ^{0}C, and the absorption of the solutions was measured at the wavelength of maximal absorption of the solutions at each temperature against the comparator solution . The dissociation constant was calculated using the absorption values for the first volumetric flask (As) and the second volumetric flask (Am).

2- Chromium(III) ion complex.

Two volumetric flasks were taken (10 mL) and placed in the first volumetric flask (5mL) of chromium (III) ion at concentration of (7.692×10^{-4} M) with (3 mL) from the reagent at a concentration of (2.307×10^{-3} M) , and then added to them (0.5 mL) of Triton X-100 at concentration (3 %) then modifying the optimal acidic function at (pH = 10.0) , then fill the volumetric flask (10 mL) with deionized water to the mark , then adding to the second volumetric flask (5 mL) of chromium (III) ion at a concentration of (7.692×10^{-4} M) , then adding to it (3 mL) from the reagent at a concentration of (4.615×10^{-3} M) , and adding to them (0.5 mL) of Triton X-100 at concentration (3%) . Then modifying the optimal acidic function at (pH = 10.0) , then transferring to a volumetric flask (10 mL) and filling it with deionize water to the mark . The two volumetric flasks were put in a water bath at a temperature of (10 – 30) ^{0}C , and the absorption of the solutions was measured at the wavelength of maximal absorption of the solutions at each temperature against the comparator solution . The dissociation constant was calculated using the absorption values for the first volumetric flask (As) and the second volumetric flask (Am).

(2-14) Effect of masking agents, cations and anions interference [149]

(2-14-1) Interaction of cations interference

1-Determination zinc (II) ions with certain interference cations ions.

The zinc(II) ion was identified in this study by adding solutions of metal ions that could interfere with the zinc (II) ion under study , taking a group of volumetric flasks (10 mL) . (5 mL) of a zinc(II) ion solution at a concentration of (50 μg/5 mL) was added and followed by the addition of (1 mL) of metallic ion solutions (50 µg/mL) (Hg^{2+}, Ni^{2+},Mg^{2+}, Ag^{2+}, Pb^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}, Cd^{2+}) which can be interfered with the zinc(II) ion separately and then added to it (3mL) of reagent solution at a concentration of ($2.032x10^{-3}$ M) with (0.5 mL) of Triton X-100 at concentration (3%) . After the acidic function was adjusted at (pH = 10.5) to generate a Zn (II) complex , the volume was finished to the mark with deionized water and the absorbance was scored at (λ_{max} = 599 nm) vs the comparison solution (Blank).

2- Determenation chromium(III) ions with some interference cations ions.

The chromium (III) ion was identified in this study by adding solutions of metal ions that could interfere with the chromium (III) ion under study , taking a group of volumetric flasks (10 mL) . (5 mL) of a chromium(III) ion solution at a concentration of (50 µg/5 mL) was added and followed by the addition of (1 mL) of metallic ion solutions (50 µg/ mL) (Hg^{2+}, Ni^{2+},Mg^{2+}, Ag^{2+}, Pb^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}, Cd^{2+}) which can be interfered with the zinc(II) ion separately and then added to it (3mL) of reagent solution at a concentration of ($2.032x10^{-3}$ M) with (0.5 mL) of Triton X-100 at concentration (3%). After the acidic function was adjusted at (pH = 10.0) to generate a chromium (III) complex , the volume was finished to the mark with deionized water and the absorbance was scored at (λ_{max} = 586 nm) vs the comparison solution (Blank).

(2-14-2) Interaction of anions interference

1-Determination zinc (II) ion with certain interference anions ions.

The zinc(II) ion was identified in this study by adding solutions of anions that could interfere with the zinc (II) ion under study , taking a group of volumetric flasks (10 mL) . (5 mL) of a zinc (II) ion solution at a concentration of (50 µg/5 mL) was added and followed by the addition of (1 mL) of anion solutions (50 µg/mL , 100 µg/mL) (SO_4^{2-}, Br^{1-}, SCN^{1-}, IO_3^{1-}, CrO_7^{2-}, CO_3^{2-}, CN^{1-}) ,which can be interfered with the zinc(II) ion separately and then added to it (3mL) of reagent solution at a concentration of ($2.032x10^{-3}$ M) with (0.5 mL) of Triton X-100 at concentration (3%) . After the acidic function was adjusted at (pH = 10.5) to generate a Zn (II) complex , the volume was finished to the mark with deionized water and the absorbance was scored at (λ_{max} = 599 nm) vs the comparison solution (Blank).

2-Determenation chromium(III) ion with some interference anions ions.

The chromium(III) ion was identified in this study by adding solutions of anions that could interfere with the chromium (III) ion under study , taking a group of volumetric flasks (10 mL) . (5 mL) of a chromium (III) ion solution at a concentration of (50 µg/5 mL) was added and followed by the addition of (1 mL) of anion ion solutions (50 µg/ mL , 100 µg/mL), (SO_4^{2-}, Br^{1-}, SCN^{1-}, IO_3^{1-}, CrO_7^{2-}, CO_3^{2-}, CN^{1-}) which can be interfered with the zinc(II) ion separately and then added to it (3mL) of reagent solution at a concentration of ($2.032x10^{-3}$ M), with (0.5 mL) of Triton X-100 at concentration (3%). After the acidic function was adjusted at (pH = 10.0) to generate a chromium (III) complex , the volume was finished to the mark with deionized water and the absorbance was scored at (λ_{max} = 586 nm) vs the comparison solution (Blank).

(2-14-3) Optimum masking agents

1- Zinc(II) ion complex.

The influence of the masking agents prepared in paragraph (2-4) on the absorption of the compound under study was investigated by filling a group of volumetric flasks (10 mL) with (5 mL) of zinc (II) ion solution at a concentration of (50 µg/5 mL) , then separately adding (1 mL) of the various masking agent solutions , then adding the best volume (3 mL) of the reagent solution at a concentration of ($2.032x10^{-3}$ M) with (0.5 mL) of Triton X-100 at concentration (3%) . After the acidic function was adjusted at (pH = 10.5) for the production of the Zn (II) complex , the volume was completed to the mark with deionized water, and the absorption was recorded at (λ_{max} = 599 nm). in comparison to the comparator solution (Blank) , following the discovery that the masking agents had no effect on the absorption of the zinc (II) complex, a study was carried out to establish the best masking agent and its size for each of the ions interfering with the zinc (II) ion.

2- Chromium(III) ion complex

The influence of the masking agents prepared in paragraph (2-4) on the absorption of the compound under study was investigated by filling a group of volumetric flasks (10 mL) with (5 mL) of chromium (III) ion solution at a concentration of (50 µg/5 mL), then separately adding (1 mL) of the various masking agent solutions, then adding the best volume (3 mL) of the reagent solution at a concentration of ($2.032x10^{-3}$ M) with (0.5 mL) of Triton X-100 at concentration (3%). After the acidic function was adjusted at (pH = 10.0) for the production of the chromium(III) complex , the volume was completed to the mark with deionized water , and the absorption was recorded at (λ_{max} = 586 nm) . In comparison to the comparator solution (Blank), following the discovery that the masking agents had no effect on the absorption of the chromium(III) complex , a study was carried out to establish the best masking agent and its size for each of the ions interfering with the chromium (III) ion.

(2-14-4) Use of a better masking agent to determine the zinc (II) ion and chromium(III) ion in the presence of cations interferers

1- Zinc (II) ion complex

Take a set volumetric flasks (10 mL) and fill it with (5mL) zinc (II) ion at a concentration of (50 µg/5 mL), then add (1 mL) cations ion at a concentration of (50 µg/mL) with (1 mL) masking agent (0.1 M) then add (3 mL) of the reagent at a concentration ($2.032x10^{-3}$ M) solution with (0.5 mL) of Triton X-100 at a concentration (3%). Finally , the acidity function was adjusted at (pH = 10.5) to fill the volume to the point of the mark with deionized water. In comparison to the comparator solution , absorption was measured at (λ_{max} = 599 nm).

2- Chromium(III) ion complex

Take a set volumetric flasks (10 mL) and fill it with (5 mL) chromium(III) ion at a concentration of (50 µg/5 mL) , then add (1 mL) cations ion at a concentration of (50 µg/mL) with (1 mL) masking agent (0.1 M) then add (3 mL) of the reagent at a concentration ($2.032x10^{-3}$ M) solution with (0.5 mL) of Triton X-100 at a concentration (3%). Finally, the acidity function was adjusted at (pH = 10.0) to fill the volume to the point of the mark with deionized water. In comparison to the comparator solution , absorption was measured at (λ_{max} = 586 nm

(2-15) Statistical treatment of the results

(2-15-1) Precision [150]

Specify the precision of the analytical methods by calculating the standard deviation (S.D.) , and percentage relative standard deviation (RSD %), for four reading and three various concentrations of each metal ion, after which the absorption was measured at maximum wave length for each complex against a comparator solution prepared under the same conditions.

$$S.D = \sqrt{\frac{\sum(x_i - \bar{x})}{n-1}} \ldots\ldots\ldots\ldots\ldots (2\text{-}1)$$

$$RSD\% = \frac{S.D}{\grave{x}} \times 100 \ldots\ldots\ldots\ldots (2\text{-}2)$$

S.D =Standard deviation

RSD% =Relative standard deviation

x_i =The value in the data absorption

$\bar{x}$ =The sample mean

n =Total number of the values

(2-15-2) Accuracy [151]

The synthesized reagent was used to identify the control of the method which was using to estimate these metal ions by implementing the best conditions for the calibration curves obtained from prior studies . The relationship was used to compute the percentage error (Ere %).

$$E_{re}\% = \frac{E}{X_t} \times 100 \quad \ldots\ldots\ldots (2\text{-}3)$$

$$E = X_i - X_t \ldots\ldots (2\text{-}5)$$

$$Re\% = 100 \pm E_{re}\% \quad \ldots\ldots (2\text{-}5)$$

E= The difference between analytical reading and truth.

X_t= The real value.

(2-16) Preparation of the solid complex of zinc(II) and chromium (III) ions

1-The solid zinc(II) complex

The solid zinc (II) complex was created by mixing (0.250mmole) (0.117g) of the reagent (SDPIHN) in (10 mL) ethanol with (0.125mmole) (0.037g) of zinc(II) ion dissolved in (10 mL) deionized water in a (1:2) ratio. The zinc (II) ion solution is put in a circular flask with continual instrument stirring , then the reagent solution is progressively added so that stirring continual for two hours with the acidic function set to (pH = 10.5). After the ethanol solvent dried for 24 hours at room temperature , a dark brown precipitate was noticed , which was then filtered and washed with deionized water before recrystallization with ethanol and drying in the air.

2-The solid chromium(III) complex

The solid chromium(III) complex was created by mixing (0.375mmole) (0.176g) of the reagent (SDPIHN) in (10 mL) ethanol with (0.125mmole) (0.050g) of chromium(III) ion dissolved in (10 mL) deionized water in a 1:3 ratio. The chromium(III) ion solution is put in a circular flask with continual instrument stirring, then the reagent solution is progressively added so that stirring continual for two hours with the acidic function set to (pH = 10.0). After the ethanol solvent dried for 24 hours at room temperature , a dark green precipitate was noticed , which was then filtered and washed with deionized water before recrystallization with ethanol and drying in the air.

(2-17) Determine the melting point of the reagent, zinc(II) complex, and chromium(III) complex [152]

The melting points of the two complexes zinc (II) and chromium (III) ion prepared in paragraph (2-16) have been determined for the purpose of comparing the melting points of the reagent and the melting points of the two complexes . The purpose of determining the melting points is to ensure the formation of the two complexes through a difference between the melting points of the reagent and the zinc (II) and chromium (III) complexes.

(2-18) Measurement of molar conductivity of the, zinc(II) complex and chromium(III) complex [153]

The preparation of a zinc(II) complex solution at a concentration of ($1x10^{-3}$ M) by dissolving (0.009 g) of the complex precipitate in (10 mL) of deionized water, followed by the measurement of molar conductivity at room temperature , the same previous work method was replicated for the chromium (III) complex at a concentration of ($1x10^{-3}$ M) by dissolving (0.132 g) of chromium (III) complex precipitate in (10 mL) of deionized water and molar conductivity was measured at room temperature .

(2-19) Estimation spectroscopy

1-UV-Vis Spectrophotometer

The UV-visible spectrum of the reagent and its dissolved complexes were measured by using a device Double Beam UV-visible Spectrophotometer, and Single Beam UV- visible Spectrophotometer .

2-Study of the infrared spectra (FTIR)

The infrared spectra were recorded for the reagent (SDPIHN) , zinc (II) complex, and chromium (III) complex.

3-Nuclear Magnetic Resonance Spectroscopy (1H.NMR , 13C.NMR)

A NMR spectra using the solvent was used to determine the number of carbon and hydrogen atoms (DMSO) .

4-Mass spectrum

Based on the ablation procedure, use diamond spectrometry to measure the molecular weight of the reagent.

(2-20) Application

The spectroscopic method used to determine the zinc(II) complex and chromium(III) ions were applied in pharmaceutical prepared samples.

(2-20-1) Determination of zinc(II) ion in drug [154, 155]

A sample drug tablet- contains the zinc(II) ion . Zinc Sulphate Monohydrate (50 mg Zn^{2+}/tablet) , Zinc Sulfate (20 mg Zn^{2+}/tablet) and Zinc Picolinate (10 mg Zn^{2+}/tablet) ,ten tablets of each Pills were taken separately and grinded then heated for 2 hours in a muffle furnace at around 300°C then dissolved it in(3 mL) of (1 M) HCl and transferred to (50 mL) volumetric flask, which was completed with (0.1 M) HCl to the mark ,and filtered . (2.5 mL) of (1M) KCl was added to the filtrate (0.0625 mL) of Zinc Sulphate Monohydrate, (0.25 mL) of Zinc Sulfate and (0.25 mL) of Zinc Picolinate , separately. Then it was diluted to (100 mL) with deionized water.

(5 mL) of each drug solution was taken and putting in (10 mL) volumetric flask and added to it (3 mL) of the reagent solution at a concentration of (2.032×10^{-3} M), with (0.5 mL) of Triton X-100 at a concentration of (3 %), and the pH was adjusted (pH = 10.5) with following the other optimum conditions reached in this study, and the volume was completed with deionized water to the mark, prepared using the same complex process, but substituting an equivalent volume of deionized water for the volume of a drug solution.

(2-20-2) Determination of chromium(III) ion in drug [156]

A sample drug tablet- contains the chromium(III) ion . Chromium Niacin (200 µg (Cr^{3+}) / tablet) , Chromium Picolinate (500 µg (Cr^{3+}) / tablet) and Chromium Picolinate (1000 µg (Cr^{3+}) / tablet), ten tablets of each Pills were taken separately and grinded then heated for 2 hours in a muffle furnace at around 300°C then dissolved in(3 mL) of (1 M) HCl and transferred to (50 mL) volumetric flask, which was completed with (0.1 M) HCl to the mark ,and filtered . (2.5 mL) of (1M) KCl was added to the filtrate (10 mL) of Chromium Niacin , (8 mL) of Chromium Picolinate and (5 mL) of Chromium Picolinate , separately. Then it was diluted to (100 mL) with deionized water.

(5 mL) of each drug solution was taken and putting in (10 mL) volumetric flask and added to it (3 mL) of the reagent solution at a concentration of (2.032 x10^{-3} M), with (0.5 mL) of Triton X-100 at a concentration of (3 %), and the pH was adjusted (pH = 10) with following the other optimum conditions reached in this study, and the volume was completed with deionized water to the mark. Prepared using the same complex process, but substituting an equivalent volume of deionized water for the volume of a drug solution.

Chapter Three

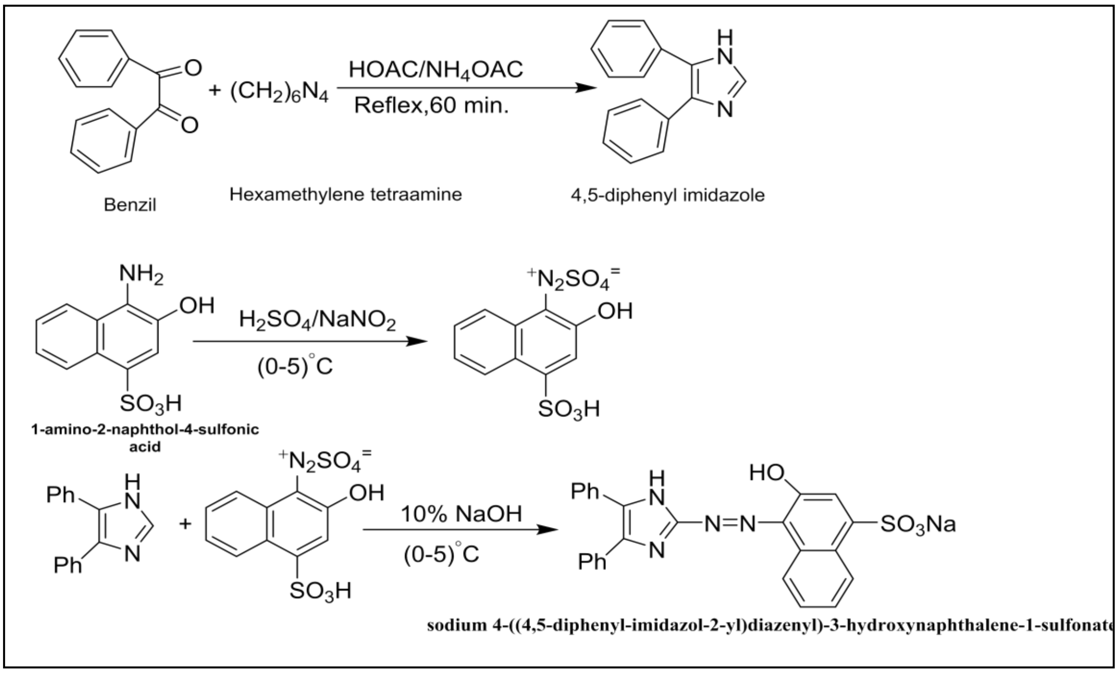
Results and Discussion

Chapter Three

Results and Discussion

(3-1) Preparation of the Reagent

The reagent (SDPIHN)is prepared from diazonium salt pairs of (1-amino-2-naphthol-4-sulfonic acid) and (4,5-Diphenyl imidazole) in an alcoholic medium by dissolving 1-amino-2-naphthol-4-sulfonic acid in a solution that had prepared by mixing concentrated sulfuric acid with distilled water, sodium nitrite dissolved in distilled water. While stirring, the temperature was maintained at less than 5 °C and left the solution in the container so the zonation process was completed, and a diazonium salt was produced. This salt solution was progressively added to it with continuous stirring of a solution of 4,5 Diphenyl imidazole that had been dissolved in a combination of ethanol and sodium hydroxide. This was done to produce the reagent (SDPIHN) with a hue that was reddish orange. The following is a list of the chemical steps that needed to be taken to get the reagent (SDPIHN) that has the color reddish orang:



Scheme (3- 1): Preparation of (SDPIHN) ligand

(3-2) The solubility of reagent (SDPIHN)

Table (3-1) presents the findings of an experiment that investigated how soluble the reagent was in several different solvents (3-1).

Table (3-1): The solubility of the reagent in various solvents

Solvent	Result	Solvent	Result
H_2O	†	Ether	†
$CHCl_3$	†	THF	+
Ethanol	+	DMSO	+
Methanol	+	DMF	+
1-Propanol	+	Acetone	†
Acetonitrile	-		

(+):soluble , (†) :partial solubility ,(-) : insoluble

(3-3) The physical properties of (SDPIHN)

Table (3-2) is described the physical properties of (SDPIHN).

Table (3-2) : The physical properties of (SDPIHN)

Compound	Formula	Molecular weight (g/mole)	Melting pointe (^oC)	Color
SDPIHN	$C_{25}H_{17}N_4NaO_4S$	492.4848	219-223	reddish-orange

(3-4) Spectroscopic studies of reagent (SDPIHN)

(3-4-1) (UV-Vis.) spectrum of the reagent

The absorption spectra of the reagent shown in fig.(3-1) . The reagent solution spectra has an absorption maximum of (λ max=463 nm) which assigned to ($n \rightarrow \pi^*$) transition , and it has an absorption peak at (336.0 nm) which assigned to ($\pi \rightarrow \pi^*$) transition [157] .

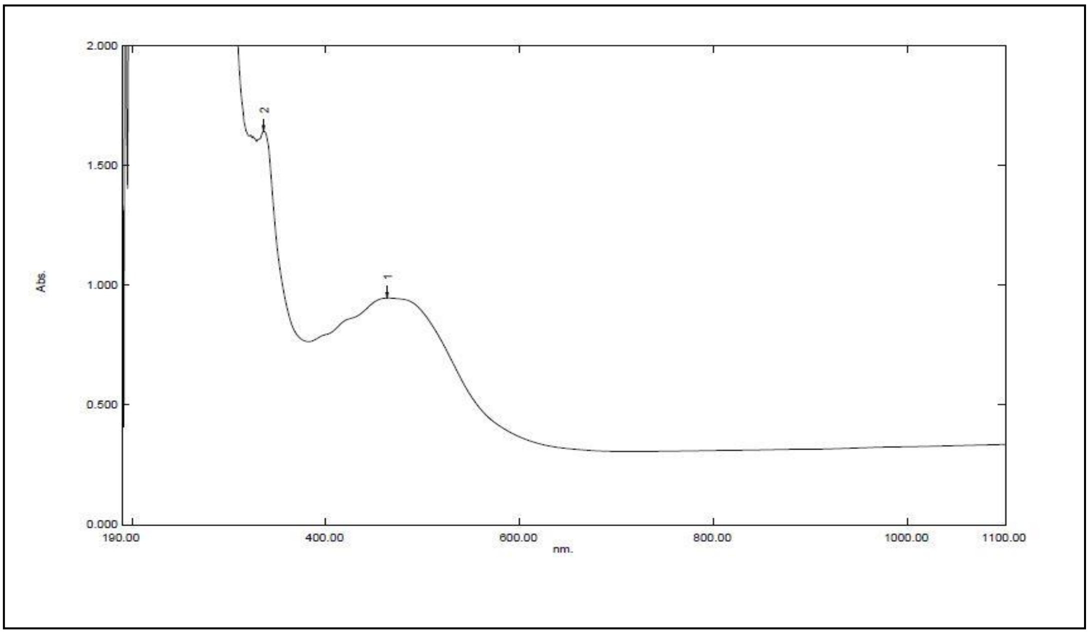


Figure (3-1) : The electronic spectrum data of reagent [SDPIHN]

(3-4-2) FTIR Spectra for the reagent and its raw materials

1-FTIR spectrum of 4,5 Diphenyl imidazole .

The spectrum of 4,5-diphenylimidazole was identified by FTIR spectroscopy as shown in Figures (3-2).

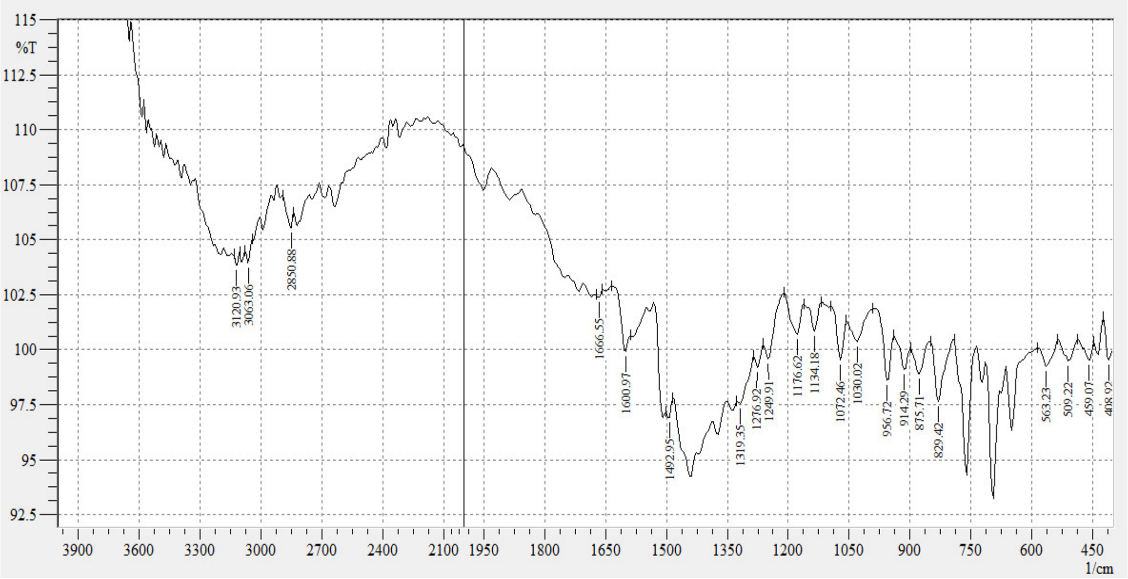


Figure (3-2): FTIR spectrum of 4,5 Diphenyl imidazole

2-FTIR spectrum of 1-amino-2-napthol-4-sulfonic acid

Figure (3-3) shows the spectrum of 1-amino-2-napthol-4-sulfonic acid by FTIR spectroscopy .

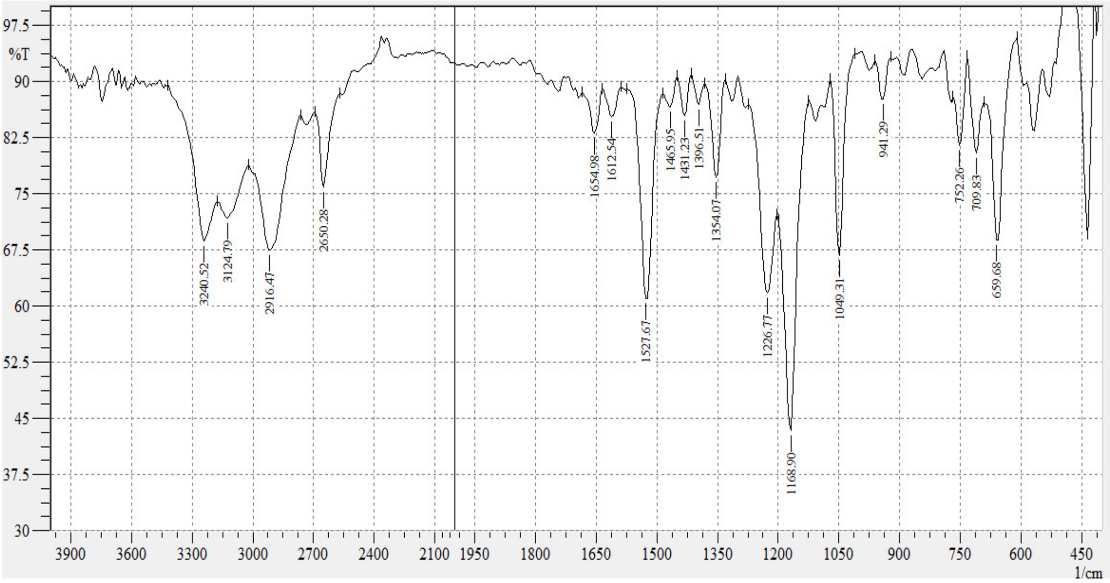


Figure (3-3) FTIR spectrum of 1-amino-2-napthol-4-sulfonic acid

3- FTIR spectrum of reagent (SDPIHN)

Figure (3-4) shows the spectrum of reagent (SDPIHN) by FTIR spectroscopy .

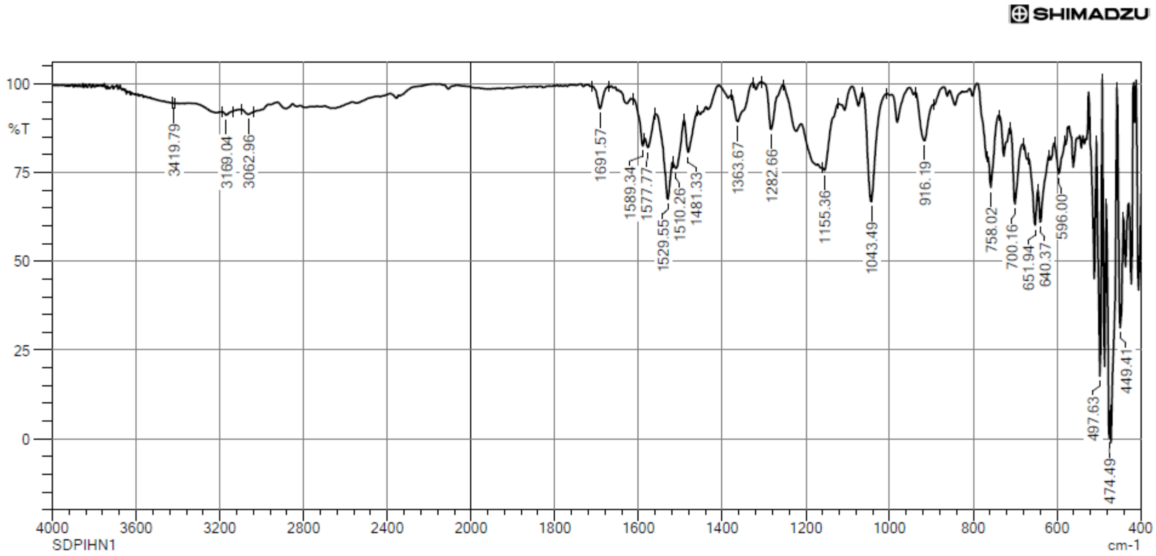


Figure (3-4): FTIR spectrum of reagent (SDPIHN)

Table (3-3): The major data of FTIR spectrums of the reagent and its raw materials [158-160]

Bond	4,5 Diphenyl imidazole	1-amino-2-napthol-4-sulfonic acid	(SDPIHN) reagent
St.(N-H)	3200	3240 , 3124	3169
St.(C-H) Aromatic	3063	3090	3062
St.(C=N)	1600	--------	1691
St.(C=C) Aromatic	1510, 1492, 1435	1527, 1465, 1431	1577, 1529, 1510
St.(N=N)	----------	----------	1481
St.(S=O)	----------	1354, 1168	1363, 1155
St.(C-N)	1319	1290	1282

(3-4-3) NMR spectrums for the reagent

Figures (3-5),(3-6) show the ^{1}HNMR and ^{13}CNMR spectroscopic spectrum of the reagent (SDPIHN).

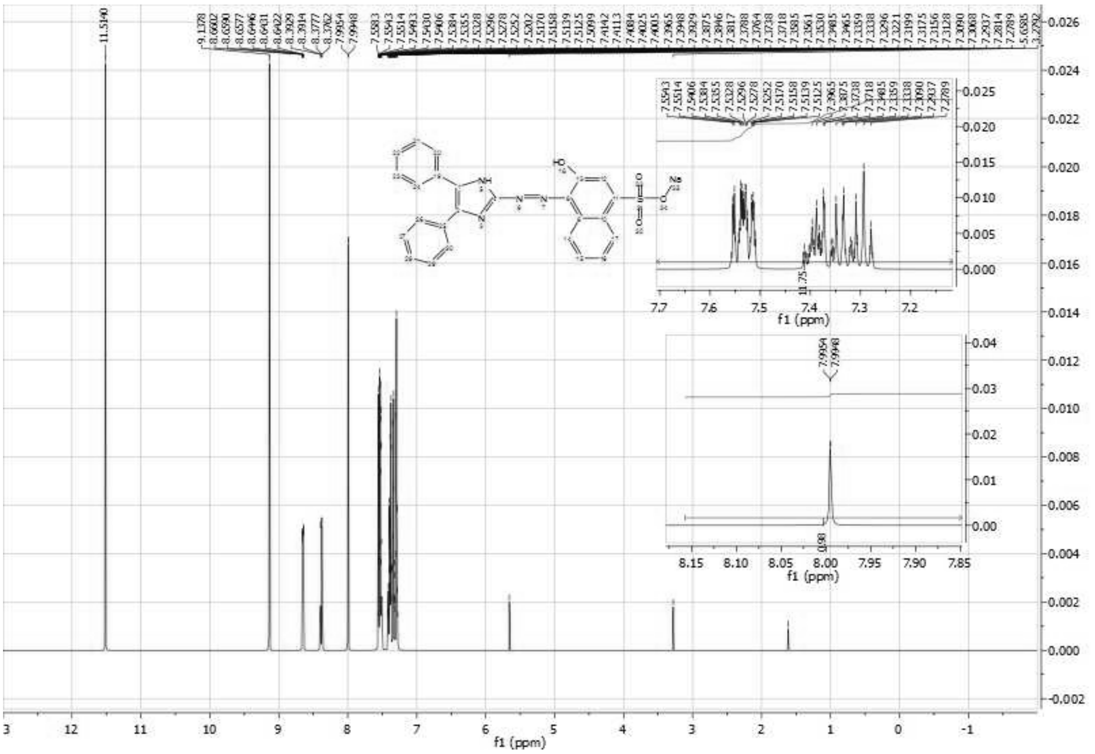


Figure (3-5) ^{1}HNMR spectrum of reagent (SDPIHN)

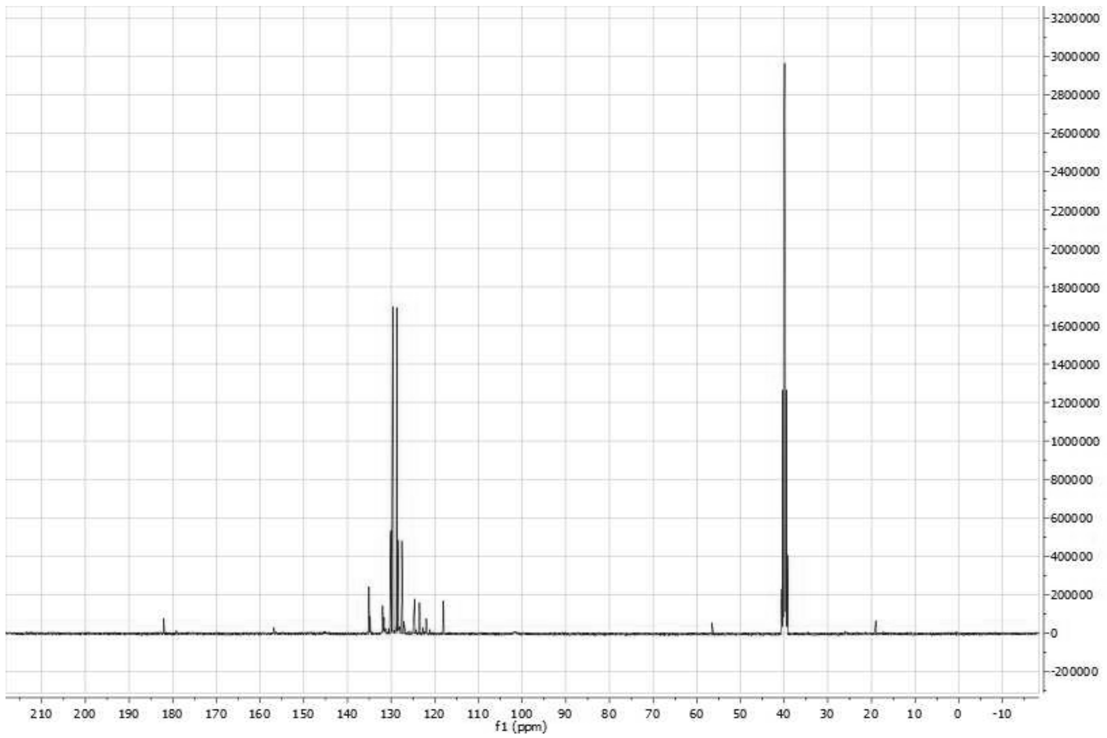
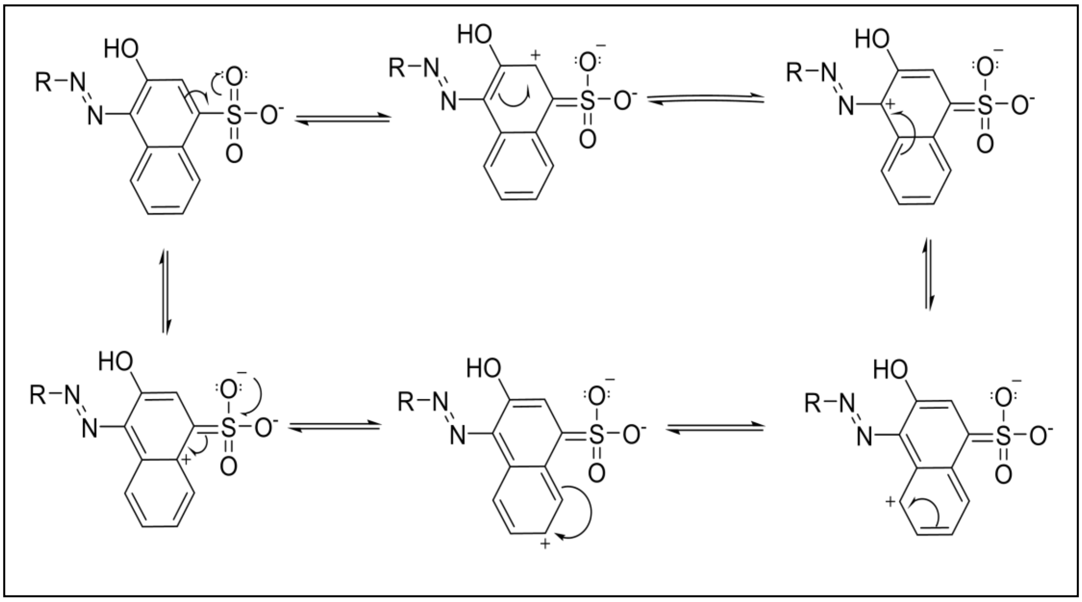


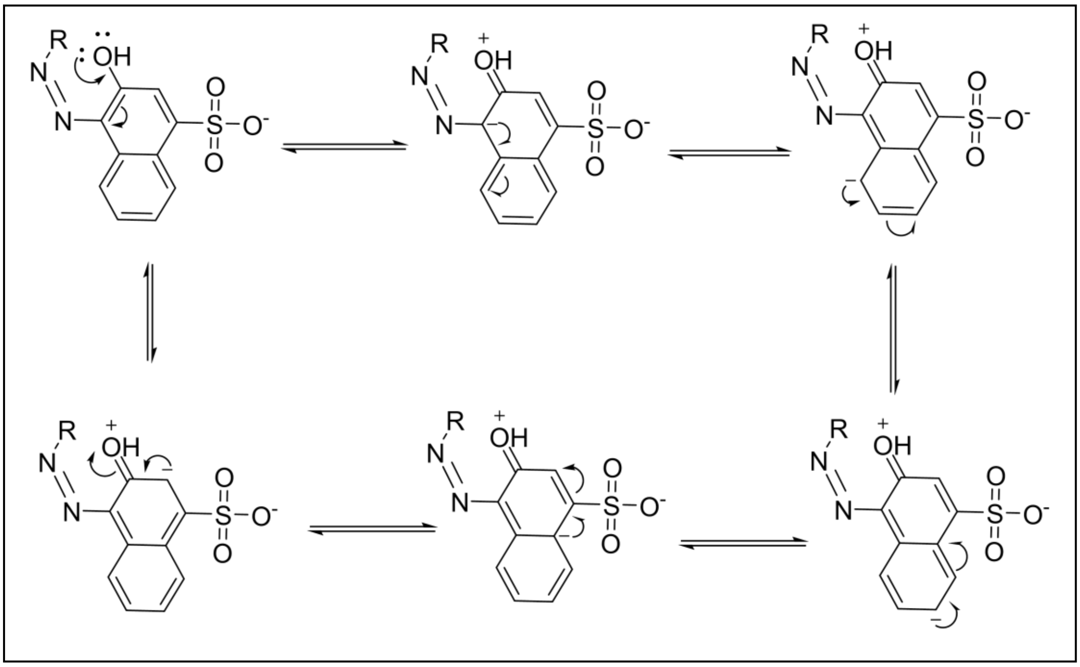
Figure (3-6) ^{13}CNMR spectrum of reagent (SDPIHN)

Proton nuclear magnetic resonance spectrometry is one of the most effective methods to identify the chemical structure of organic compounds. The structure of the reagent (SDPIHN) was further confirmed by 1D NMR spectroscopy. The 1H-NMR and 13C-NMR spectra of the ligand (L) were tested using DMSO-d^6 as a solvent. The 1H NMR spectrum of reagent (SDPIHN) is presented in Figures (3-5) which show fifteen peaks that indicate signals originating from fifteen types of protons. A singlet at 11.51ppm with the integration of one proton was assigned to proton 18 (s, 1H, N-H). While a singlet at 9.14 ppm with the integration of one proton was assigned to proton 5 (s, 1H, Ar-O-H), which indicates the absence of proton with its adjacent C1 and C4, it was seen in higher downfield due to N-H located in imidazole ring. The multiple signals at δ 7.34-7.54 ppm were attributed to ten aromatic protons of two rings bonded to imidazole (m, 10H, Ar-H). Due to these two rings being symmetric, all protons bonded to these two rings are equivalent and have the same environments. The reason that H19, H20, H25, and H26 were seen more down-field compared to other protons of these two rings is experienced the diamagnetic anisotropy effect of the vinyl group, which is considered a deshielding group. The singlet at 8.00

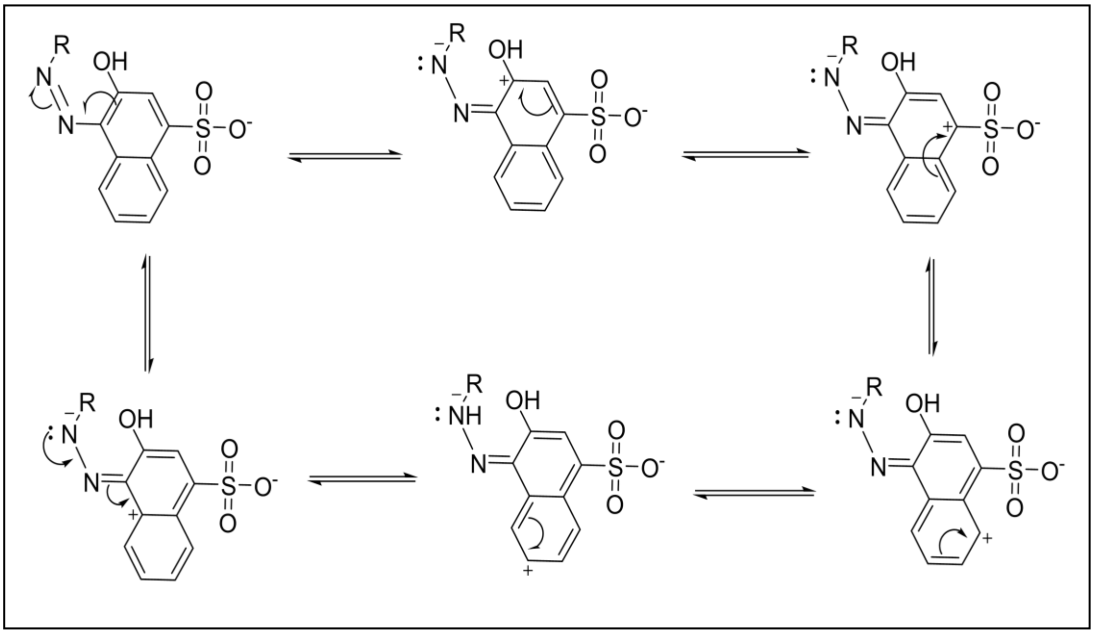
ppm was assigned to H12 with the integration of one proton based on the absence of proton with its adjacent C11 and C13, due to H12 was experienced the electron inductive withdrawing effect of the sulfonate group, as is described in Scheme (3-2), and also experienced the resonance of the electron-donating effect from the hydroxy group as is given in Scheme (3-3) because the effect of electron inductive withdrawing was dominant appeared higher down-field. A doublet at 8.65 was corresponded to H17 with the integration of one proton based on the coupling with adjacent protons H16. However, due to the resonance withdrawing effect of the Azo electronegativity group as is described in Scheme (3-4), it was deshielded; hence, it has appeared down-field. The doublet at 8.34 ppm was assigned to H14 with the integration of one proton based on the coupling with its adjacent proton 15. H14 was shown in a down-field shift due to the same effect that H12 subjected. H16 was seen at 7.37 ppm due to H16 experiencing an electron-donating resonance effect from the hydroxy group as given in Scheme (3-3), which let to appear in the upper-field shift value. Finally, H15 was seen as triplets at 7.53 ppm.



Scheme (3-2): The resonance of the electron inductive withdrawing effect of the sulfonate group



Scheme (3-3): the resonance of the electron-donating effect from the hydroxy group



scheme (3-4): The resonance of the electron inductive withdrawing effect of the Azo group

(3-4-4) Mass spectrum for the reagent

The mass spectroscopy spectrum of the reagent (SDPIHN) is shown in Figures (3-7); it was evident from the figure that the theoretically estimated molecular weight (492.48 g / mole) and the practical result are precisely the same.

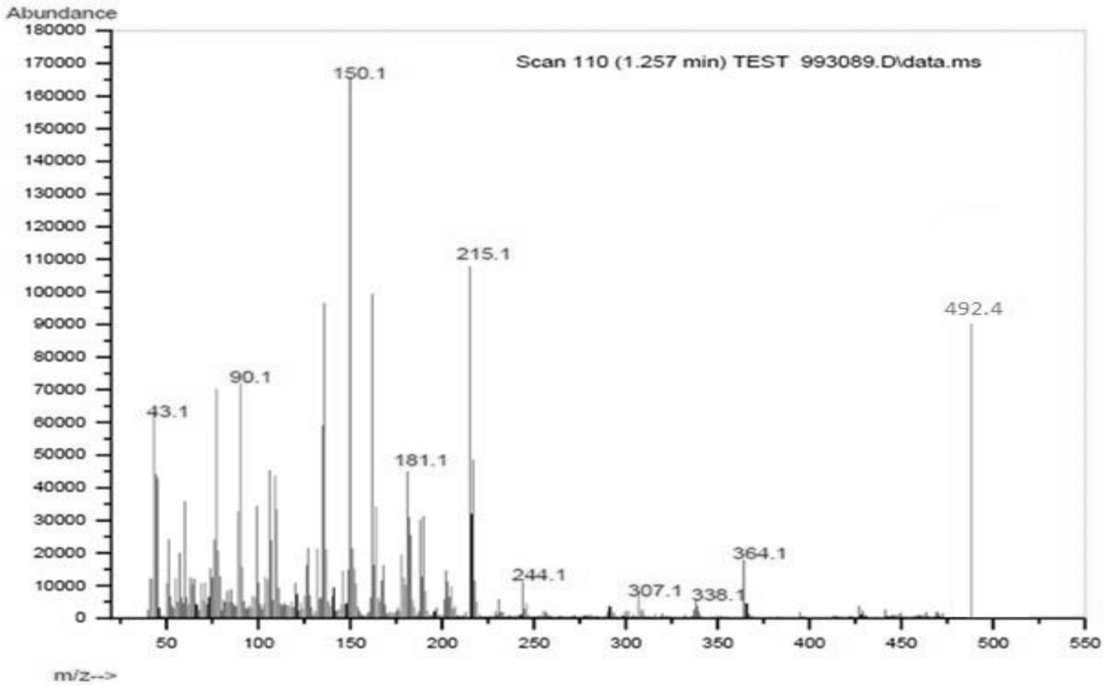


Figure (3-7) Mass spectrum of reagent (SDPIHN)

(3-5) Preliminary testing to see how the reagent (SDPIHN) reacts with various metal ions and to find out which metal ions interact best with the reagent

Several experiments were carried out to study the possibilities of the reagent interacting with (11) metal ions. These experiments were identified the color change due to mixing the reagent solution with solutions containing metal ions. It was discovered that the reagent interacts with these ions (Hg^{2+}, Ni^{2+},Mg^{2+}, Ag^{2+}, Pb^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+} and Cr^{3+}), and colored solutions indicated that a reaction between the reagent and these ions occured were used to demonstrate this interaction. The findings of the initial examinations of the reaction reagent with zinc (II) and chromium (III) ions are shown in Table (3-4).

These ions were selected among the others for the study and spectrophotometric evaluation.

Table (3-4): The results of the preliminary test for the reaction of the reagent with the zinc (II) and chromium (III) ions

Ion	Complex color	color base medium	color acid medium
Zn(II)	Light orang	Brown	Light orang
Cr(III)	Purple	Light green	Purple

(3-6) Study of UV-visible spectra of complexes [161]

(3-6-1) Study of UV-visible spectrum of Zn(II) complex with [SDPIHN] reagent

Figure (3-8) shows the absorption spectra of zinc (II) complex with the reagent , it’s absorption spectrum was recorded in a range of (350-1100 nm) wavelengths . The zinc (II) complex has an absorption maximum of (λ max= 599nm) , indicating that the complex formation is accompanied by a significant increase in absorbance and a bathochromic shift of approximately (136 nm).

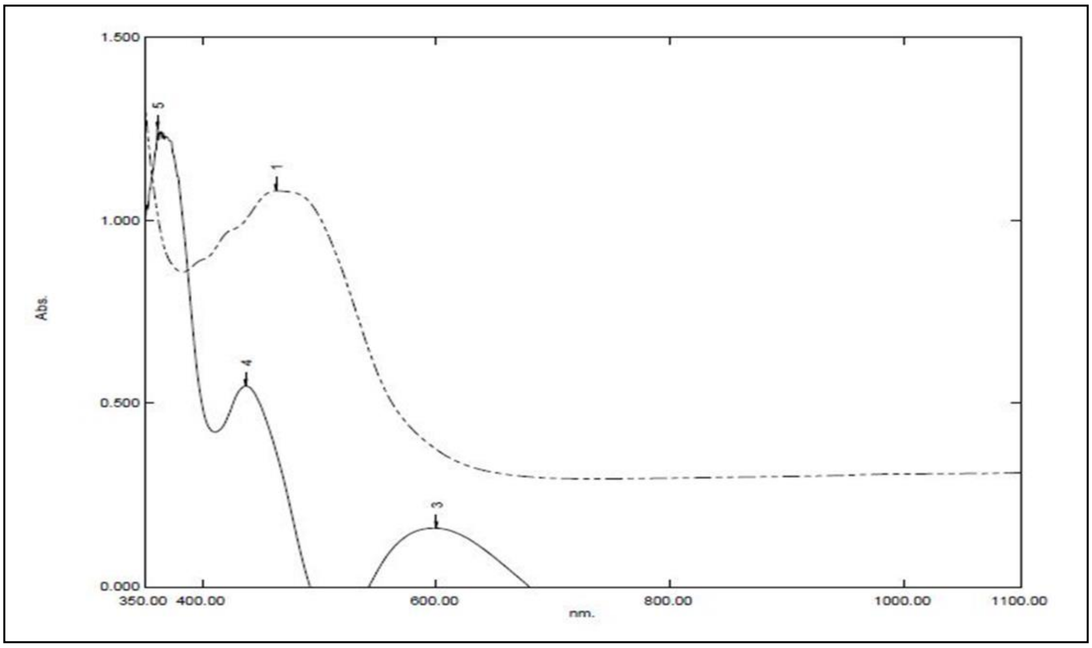


Figure (3-8): UV-visible spectrum of Zn(II) complex with [SDPIHN] reagent

The dashed line represents the spectrum of the reagent and the solid line represent the spectrum of Zn(II) complex.

(3-6-2) Study of UV-visible spectrum of Cr (III) complex with [SDPIHN] reagent

Figure (3-9) shows the absorption spectra of chromium (III) complex with the reagent , it's absorption spectrum was recorded in a range of (350-1100 nm) wavelengths . The chromium (III) complex has an absorption maximum of (λ max= 586nm) , indicating that the complex formation is accompanied by a significant increase in absorbance and a bathochromic shift of approximately (123 nm) .

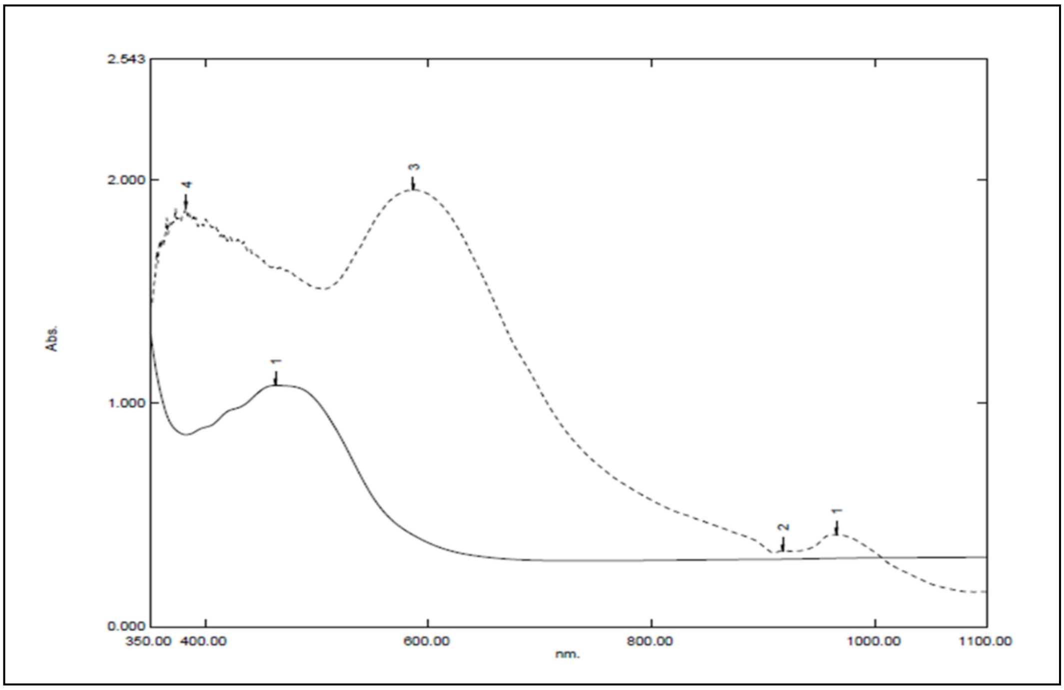


Figure (3-9): UV-visible spectrum of Cr (III) complex with [SDPIHN] reagent

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

(3-7) Study of the absorption of both zinc (II) and chromium (III) complexes in presence of surfactants

Surfactants have a major impact on spectrophotometry and chromatography , particularly in the development of new ions 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) , (Triton X-114) , (Tween-80) , and (Sodium Dodecyl Sulfate) was investigated in the absorbance of zinc (II) and chromium (III) complexes , as shown in Tables (3-5) , (3-6).

Table (3-5) : Effect of adding the surfactants on the absorption of Zn(II) complex

Concentration of surfactant (v/v %)	Absorption values of Zn complex in (Tween-80)	Absorption values of Zn complex in (Triton X-114)	Absorption values of Zn complex in (Triton X-100)	Absorption values of Zn complex in (Sodium Dodecyl Sulfate)
1%	0.116	0.115	0.117	0.111
2%	0.118	0.117	0.122	0.085
3%	0.120	0.119	0.126	0.061
Absorption of Zn complex without addition =0.114				

Table (3-6) : Effect of adding the surfactants on the absorption of Cr(III) 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				

The data in the Tables above demonstrated that adding Triton X-100 at a concentration of (3%) leads to achieving the best absorption. The Triton X-100 is classified as a nonionic surfactant. As a result of the inability of its hydrophilic groups to dissociate when placed in an aqueous solution, this type of surfactant is considered not ionized, resulting in the best absorption.

(3-8) Optimization of Reaction Conditions

(3-8-1)Effect volume of reagent

The researchers examined how significant an impact the volume of the reagent solution had on the synthesis of zinc (II) and chromium (III) complexes. According to the findings shown in Tables (3-7) and (3-8), when the reagent solution is added to zinc (II) and chromium (III), the absorbance values of the two complexes rise until they reach their maximum value. This is because the complex is synthesized by interacting the metal ion with the reagent in the direction of the synthesized complex, which provides better color intensity. However, as the volume of the reagent increase, the absorption values begin to decrease. This might be because the completeness or sufficiency of the coordination failed of the ion in the reagent, or it might be because the reagent is insoluble in the solvent.

Table (3-7) : Effect of reagent volume on Zn (II) complex

Volume of reagent(mL)	0.5	1	1.5	2	2.5	3	3.5
Abs.	0.055	0.116	0.168	0.246	0.304	0.322	0.311

Table (3-8) : Effect of reagent volume Cr (III) complex

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

(3-8-2) Effect of surfactant (Triton X-100) volume

As revealed in the experiment , the influence of surfactant (Triton X-100) volume on zinc (II) and chromium (III) complexes absorbance is displayed in Tables (3-9) , (3-10).

Table(3-9) : The effect of (Triton X-100) volume on Zn (II) complex

Volume of (Tx-100) (mL)	0.25	0.5	1	1.5	2
Abs.	0.336	0.337	0.331	0.328	0.326

Table (3-10) : The effect of (Triton X-100) volume on Cr (III) complex

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

According to the findings presented in the Tables above, the absorbance values of the zinc (II) and chromium (III) complexes increase after the solution containing Triton X-100 is added to them. This increase continues until the complexes reach their maximum value. As the volume of the surfactant increases, the absorption values start to decrease.

(3-8-3) Effect of pH value

Figures 3-10 and 3-11 show the effect of the acidic function on the absorption of solutions of zinc (II) and chromium (III) complexes, respectively. It was observed that the color intensity of the two complex solutions gradually increased to reach their maximum absorbance at the acidic functions (10.5,10), respectively. These figures illustrate this phenomenon. The higher absorbance of the zinc (II) and chromium (III) complexes under these conditions could be attributed to an increase in the reagent's sensitivity at this pH value. On the other hand, the absorbance value of the two complexes decreases when the acidic function increases, which can be attributed to either the precipitation of the two ions or the formation of unstable complex ions.

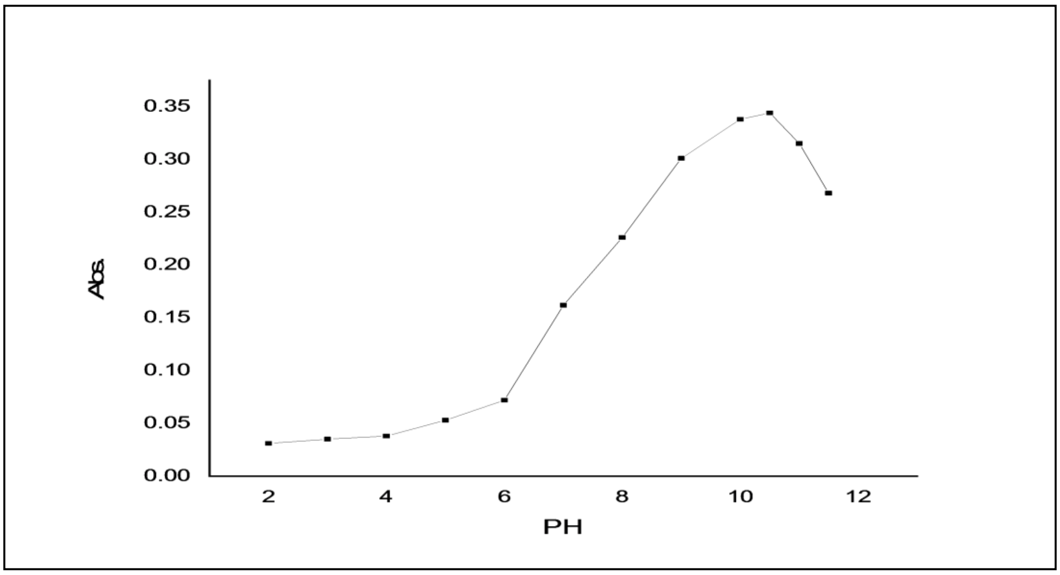


Figure (3-10) :Effect of pH on absorption of Zn(II) complex

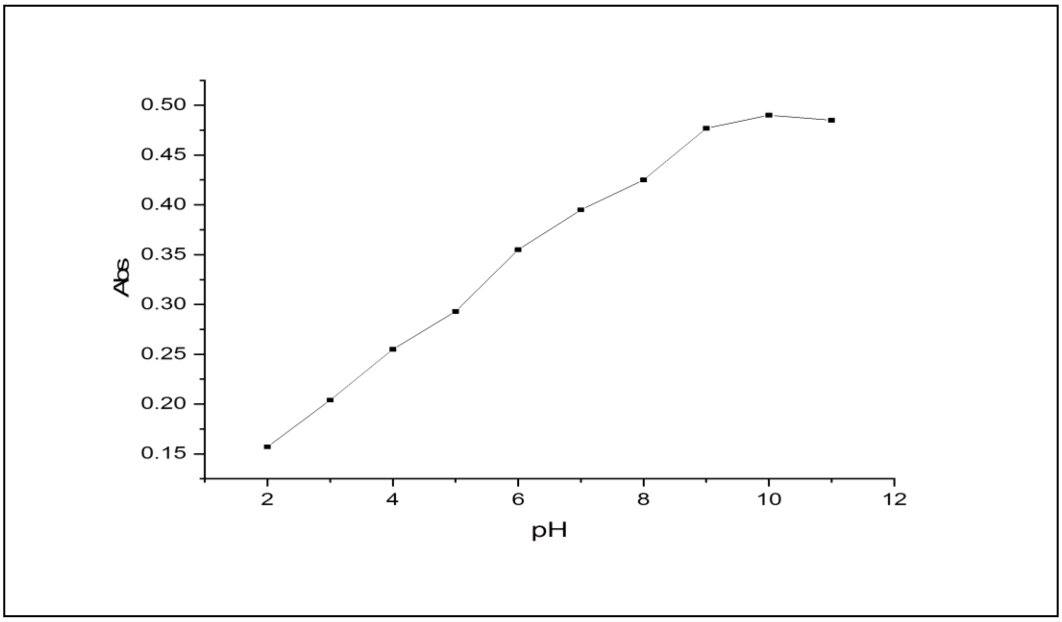


Figure (3-11) :Effect of pH on absorption of Cr(III)complex

(3-8-4) The Influence of Time on Complexes Stability

The influence on the stability of the prepared complexes was investigated as an important factor in order to determine the best time period during which the complex can sustain its stability, where the absorption values of the zinc (II) and chromium (III) complexes are investigated with the reagent (SDPIHN) under the best conditions achieved , and the results are shown in Tables (3-11) , (3-12) . The results of this investigation show that the zinc (II) and chromium (III) complexes are very stable (in terms of absorption values) for 24 hours after formation with the zinc (II) complex and stable for 24 hours after creation with the chromium (III) complex . The findings of this study improve the reagent's usability as one of the significant reagents used to determine the quantity of ionic zinc (II) and chromium (III) ions.

Table (3-11): Effect of time on Zn (II)-(SDPIHN)

Time (min.)	1	10	20	30	60	120	180	240	1440
Abs.	0.342	0.343	0.343	0.343	0.343	0.342	0.341	0.338	0.331

Table (3-12): Effect of time on Cr (III)-(SDPIHN)

Time (min.)	1	10	20	30	60	120	180	240	1440
Abs.	0.485	0.488	0.488	0.488	0.486	0.483	0.479	0.475	0.464

(3-8-5) Effect of Temperature

Studies have determined how temperature influences the amount of zinc (II) and chromium (III) complexes absorbed by solutions. The findings are shown in Tables (3-13) and (3-14), where it was seen that the absorption values of the zinc (II) complex and the chromium (III) complex reach their highest point and provide the best outcomes. Whereas chromium (III) complex gives the best color intensity at temperatures ranging from (10-20) ^{o}C, zinc (II) complex gives the best color intensity at temperatures ranging from (10-30) ^{o}C. Then the absorption values decrease with rising temperature, which could be attributed to a decrease in its stability or dissolution at high temperatures.

Table (3-13) : Effect of Temperature on Zn(II)-(SDPIHN)

Temperature^{o}C	10	20	30	40	50	60
Abs.	0.324	0.342	0.361	0.280	0.244	0.201

Table (3-14) : Effect of Temperature on Cr(III)-(SDPIHN)

Temperature^{o}C	10	15	20	30	40	50	60
Abs.	0.477	0.491	0.487	0.445	0.380	0.274	0.211

(3-8-6) Effect of Sequence

Six different addition arrangements were examined to investigate the sequence of the reaction content in a complex absorbance. According to the data shown in Tables (3-15) , (3-16) below, both zinc (II) and chromium(III) complexes had an impact on the rate of absorption.

Table (3-15): Effect of Sequence on Zn(II)-(SDPIHN)

Sequence of number	Sequence of addition	Abs. of Zn complex
1	M+L+Tx-100+pH	0.341
2	M+ Tx-100+L+pH	0.332
3	Tx-100+M+L+pH	0.301
4	L+M+Tx-100+pH	0.340
5	M+pH+L+Tx-100	0.326
6	M+L+pH+Tx-100	0.205

Tx-100 = Triton X-100 , pH = hydrogen ion functions, M = metal, L = ligand.

Table (3-16) : Effect of Sequence on Cr(III)-(SDPIHN)

Sequence of 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	0.485
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 = metal, L = ligand.

The results in Tables (3-15) , (3-16) demonstrate that the first sequence is the best , but the other sequence results in a drop in complexes absorbance , which might be due to the impact of acid , base inions with metal , therefore the first sequence was used to determine the zinc(II) and chromium (III) complexes in this approach .

(3-8-7) Effect of Ionic Strength

The influence of ionic strength on the absorption of zinc (II) and chromium (III) complexes was demonstrated after adding (1 mL) from solutions of sodium nitrate and sodium sulfate salts that had been prepared at different concentrations ranging from (0.0005-0.5 M) for each salt. Tables (3-17) , (3-18) elucidate the influence of ionic strength on the absorption of zinc (II) and chromium (III) complexes.

Table (3- 17): Effect of Ionic Strength on Zn(II)-(SDPIHN)

Adding salt	Conc.(M) of add salt	Abs.	Added salt	Conc.(M)of add salt	Added salt
Na_2SO_4	0.5	0.330	$NaNO_3$	0.5	0.336
	0.05	0.335		0.05	0.338
	0.005	0.338		0.005	0.340
	0.0005	0.340		0.0005	0.339
Abs. of Zn(II)-(SDPIHN) without adding = 0.341					

Table (3-18): Effect of Ionic Strength on Cr(III)-(SDPIHN)

Adding salt	Conc.(M) of add salt	Abs.	Added salt	Conc.(M)of add salt	Added salt
Na_2SO_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)-(SDPIHN) without adding = 0.487					

The results provided in Tables (3-17) , (3-18) demonstrate that all of the concentrations specified in the tables have no significant effect on the absorption value , and we infer that the ions have no effect on the solubility , and sensitivity of the zinc (II) ion determination . When concentrating 0.5M , however , sodium sulfate has an effect . The chromium (III) estimate table yields conflicting findings , indicating that the chromium (III) complex is unstable with additional salts .

(3-9) Calibration curve of zinc(II) and chromium(III) complexes

The calibration curves for zinc(II) and chromium(III) ions were created using the optimum the best condition was identified and obtained. For the zinc(II) ion and the chromium(III) ion , respectively , the study's findings are shown in Figs. (3-12) , (3-13).

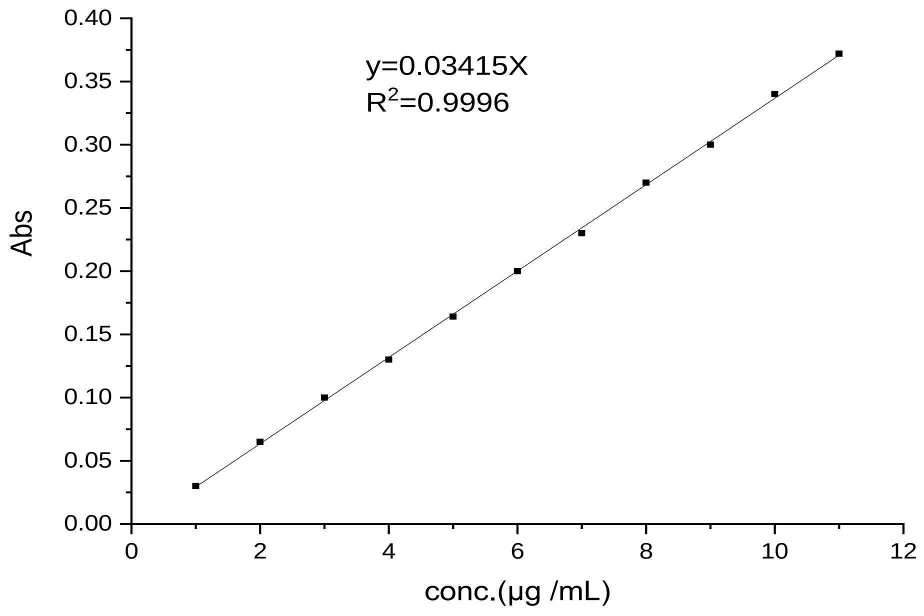


Figure (3-12): Calibration curve for spectrophotometric determination of zinc (II) complex.

Figure (3-12) shows that the zinc (II) ion obeys Lambert-Beer law in the concentration range (1 µg/mL –11 µg/mL) . The molar absorptivity is (0.222×10^4 L mol^{-1} cm^{-1}) and the absorbance of zinc complex was found to be linear based on the metal concentration.

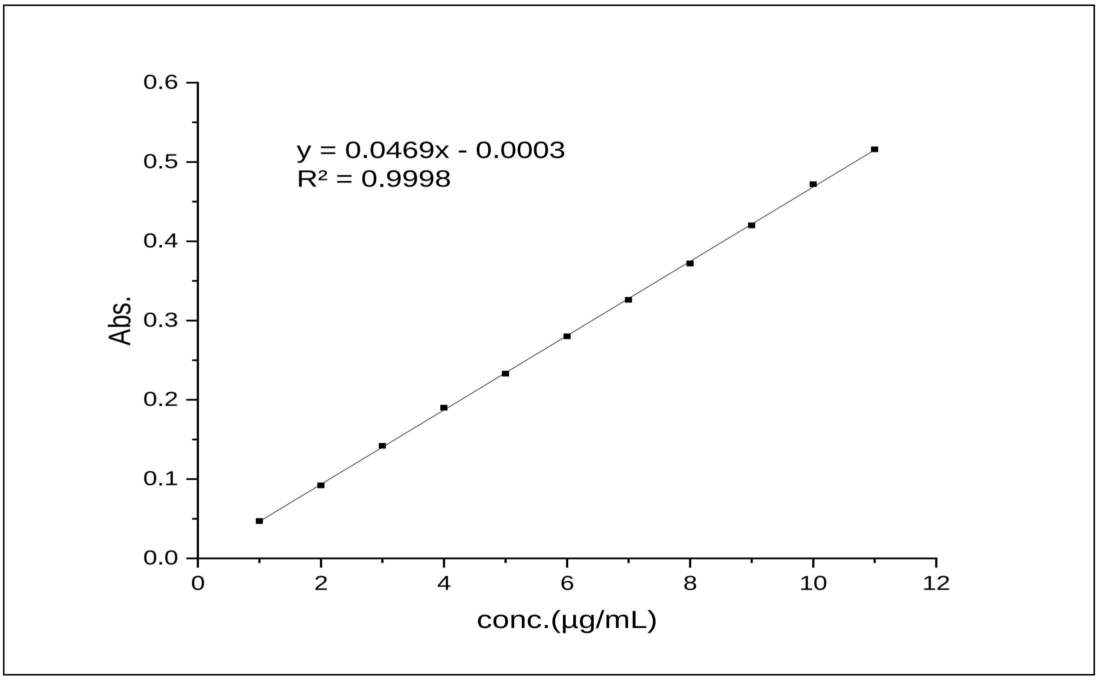


Figure (3-13): Calibration curve for spectrophotometric determination of chromium(III) complex.

Figure (3-13) shows that the chromium (III) ion obeys Lambert-Beer law in the concentration range (1 µg/mL –11 µg/mL) .The molar absorptivity is (0.244×10^4 L mol^{-1} cm^{-1}) and the absorbance of chromium complex was found to be linear based on the metal concentration.

$$A = \varepsilon\, b\, C \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3-1)$$

$$slope\ = \frac{\varepsilon}{At.Wtx1000} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3-2)$$

$$S = \frac{10^{-3}}{a} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3-3)$$

ε = molar absorptivity

S = Sandal sensitivity

a= Specific absorption coefficient

Table (3-19) supplied analytical data for quantifying zinc ion using reagents (SDPIHN) .

Table (3-19): Data collected for zinc (II) analysis

Analytical Data	**Value**
Molar Absorptivity (L.mol^{-1}·cm^{-1})	0.2229×10^{4}
Slope	0.0341
Linear equation	Y=0.03415X
Linear range(µg/mL)	(1-11)
Sandal sensitivity(µg/cm^{2})	0.0293
Detection limit (µg/mL)	0.2271
Limit of quantification (µg/mL)	0.7496
Linearity coefficient (R^{2})	0.9996
Correlation coefficient (r)	0.9998
λ_{max}	599nm
Color of product	Dark brown

Table (3-20) supplied analytical data for quantifying chromium ion using reagents (SDPIHN).

Table (3-20): Data collected for chromium(III) analysis

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

As seen in Tables (3-19) and (3-20), the reagent (SDPIHN) is complexed with the particles of zinc (II) and chromium (III) ions. Due to its absorption in the visual area, it is increased to estimate the low amounts of zinc (II) and chromium (III) ions present in a sample using this method. The negative deviation at high concentrations may be caused by a combination of factors, including the complex molecules interacting with the solvent or their aggregation with other molecules.

(3-10) Stoichiometry of the complexes

To investigate the composition of zinc (II) and chromium (III) complexes produced, the mole ratio method and Job's method (continuous variations) were studied under optimum condition.

(3-10-1) Job's Method [162]

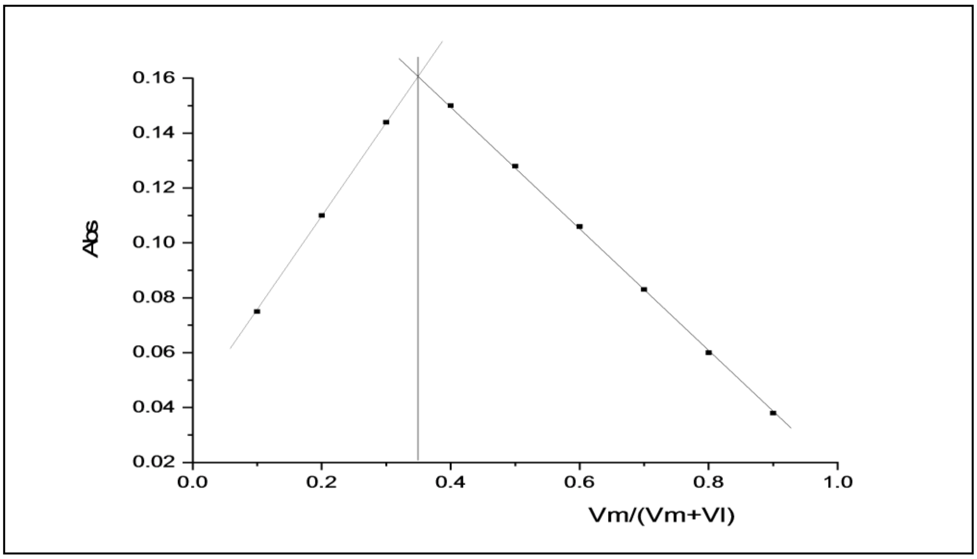


Figure (3-14) : Job`s method of zinc (II) complex

Figure (3-14) shows that the bonding in the zinc (II) complex was in the ratio (M:L) (1:2) where the complex consists of two moles of the reagent to one mole of the ion .

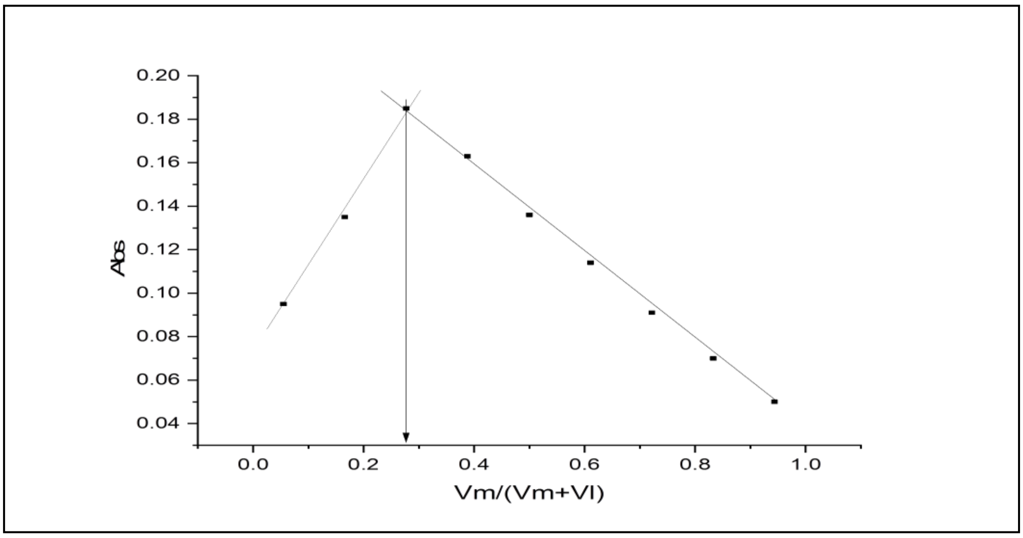


Figure (3-15) : Job`s method of chromium (III) complex

Figure (3-15) shows that the bonding in the chromium (III) complex was in the ratio (M:L) (1:3) where the complex consists of three moles of the reagent to one mole of the ion .

(3-10-2) Mole Ratio Method [163]

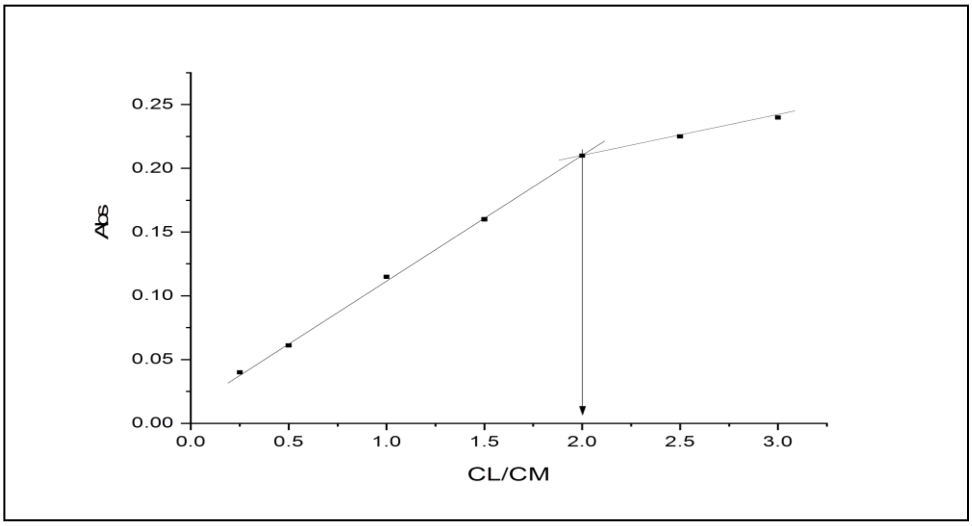


Figure (3-16): Method of Mole Ratio zinc (II) complex

Figure (3-16) shows that the bonding in the zinc (II) complex was in the ratio (M:L) (1 : 2) where the complex consists of two moles of the reagent to one mole of the ion.

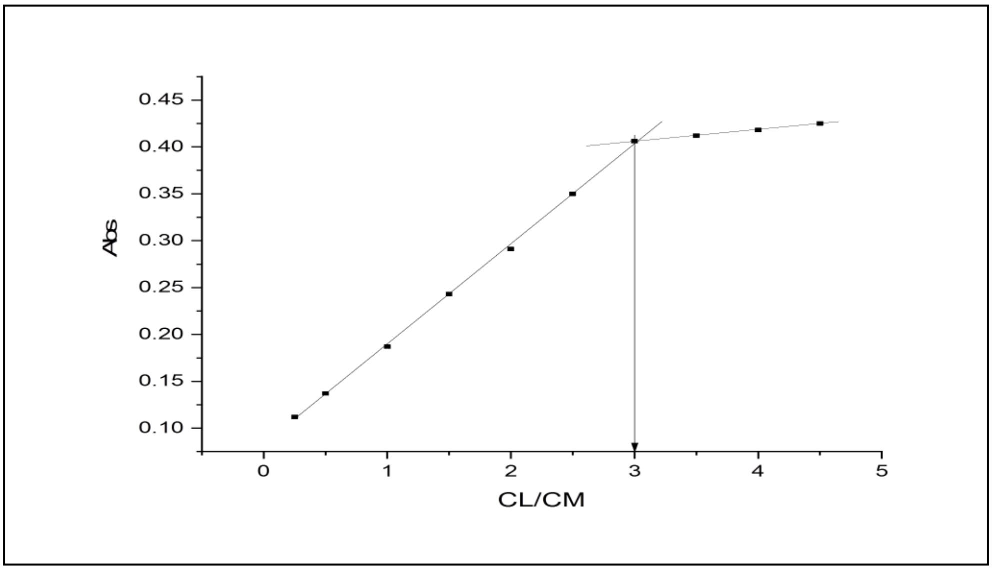


Figure (3-17): Method of Mole Ratio chromium (III) complex

Figure (3-17) shows that the bonding in the chromium (III) complex was in the ratio (M:L) (1:3) where the complex consists of three moles of the reagent to one mole of the ion.

(3-11) Calculation the stability constant of complexes

Using the absorption values collected from the molar ratios of the two complexes, which were debated in paragraphs (3-10-2), we were able to calculate the stability constants of the zinc (II) complex and the chromium (III) complex. Spectral methods can be used to calculate the stability constants of the colored complexes by using concentrations of zinc (II) and chromium (III) ions in their solutions, especially if they are mixed. The following equations were used to arrive at the results you see for the constants mentioned above.

$$\boldsymbol{M^{+n}} + \mathbf{nL} \leftrightarrow \mathbf{MLn} \qquad \ldots\ldots\ldots\ldots\ldots\mathbf{(3\text{-}4)}$$

$$\boldsymbol{\alpha} + \mathbf{nc}\boldsymbol{\alpha} \leftrightarrow \mathbf{(1\text{-}}\boldsymbol{\alpha}\mathbf{)c}$$

$$\mathbf{K}=\frac{[\boldsymbol{MLn}]}{[\boldsymbol{M^{+n}}][\boldsymbol{L}]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\mathbf{(3\text{-}5)}$$

$$\mathbf{K}=\frac{(\mathbf{1}-\boldsymbol{\alpha})\boldsymbol{c}}{\boldsymbol{\alpha c}(\boldsymbol{n\alpha c})^{\boldsymbol{n}}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\mathbf{(3\text{-}6)}$$

$$\mathbf{K}=\frac{\mathbf{1}-\boldsymbol{\alpha}}{\boldsymbol{n^{n}\alpha^{n+1}c^{n}}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\mathbf{(3\text{-}7)}$$

$$\boldsymbol{\alpha}=\frac{\boldsymbol{Am}-\boldsymbol{As}}{\boldsymbol{Am}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\mathbf{(3\text{-}8)}$$

Where (As) is the absorption of the complex at the equivalence point, (Am) is maximum absorption.

(α): degree of dissociation

(K): Stability Constant

M^{n+}: ion

L : ligand

C : molar concentration

n : no. of mole

The calculated results are displayed in the table below (3-21).

Table (3-21): The value of stability constants for zinc (II) and chromium (III) complexes

Complex	(Am) Value	(As) Value	(α)	(K)
[Zn (SDPIHN)$_2$]	0.240	0.210	0.125	5.967×10^{8}
[Cr (SDPIHN)$_3$]	0.406	0.425	0.045	1.125×10^{14}

Table (3-21) shows the high stability of the formed complexes, which increases the process of this complexes , allowing the ligand (SDPIHN) to be used in the estimation of zinc (II) and chromium (III) ions' spectrum.

(3-12) Calculation of the degree of dissociation , stability Constant , and thermodynamic functions of the two complexes

(3-12-1) The impact of temperature on the degree of dissociation and the stability constant for the two complexes

The influence that temperature has on the degree of dissociation and the stability constant of complexes containing zinc (II) and chromium (III) has been studied, and the findings of this study are shown in the two tables (3-22) that follow (3-23).

Table (3-22) The impact of temperature difference on the values of the degree of stability and stability constant of the Zn (II) complex

T (^{0}C)	T (K)	α	K×10^8
10	283.15	0.208	1.172
15	288.15	0.227	0.880
20	293.15	0.250	0.639
25	298.15	0.276	0.458
30	303.15	0.290	0.387

Table (3-23): The impact of temperature difference on the values of the degree of stability and stability constant of the Cr (III)complex.

T (^{0}C)	T (K)	α	K×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 Tables (3-22) , (3-23) showed that temperature had only a minor impact on the stability of the complexes . The remarkable stability of the zinc (II) and chromium (III) complexes increases the potential for using the reagent (SDPIHN) in spectrophotometric analysis [164].

(3-12-2) Calculation of the thermodynamic functions of the two complexes

Using the findings from the previous paragraph, a calculation was made to determine the effect that temperature had on the thermodynamic functions of the zinc (II) and chromium (III) complexes in this research. After deciding the thermodynamic functions ΔG, ΔH, and ΔS, the results are shown in Table (3-24) with Figure (3-18) for the zinc (II) complex and in Table (3-25) with Figure (3-19) for the chromium (III) complex.

Table (3-24): The impact of temperature on thermodynamic function for zinc (II) complex

T(K)	$1/T\times10^{-3}(K^{-1})$	log K	ΔH	ΔG (K.J/mole)	ΔS (K.J/mole .K)
283.15	3.532	7.931	40.764	-42.942	0.2956
288.15	3.470	8.055		-44.383	0.2954
293.15	3.411	8.194		-45.932	0.2957
298.15	3.354	8.338		-47.537	0.2961
303.15	3.298	8.411		-48.757	0.2953

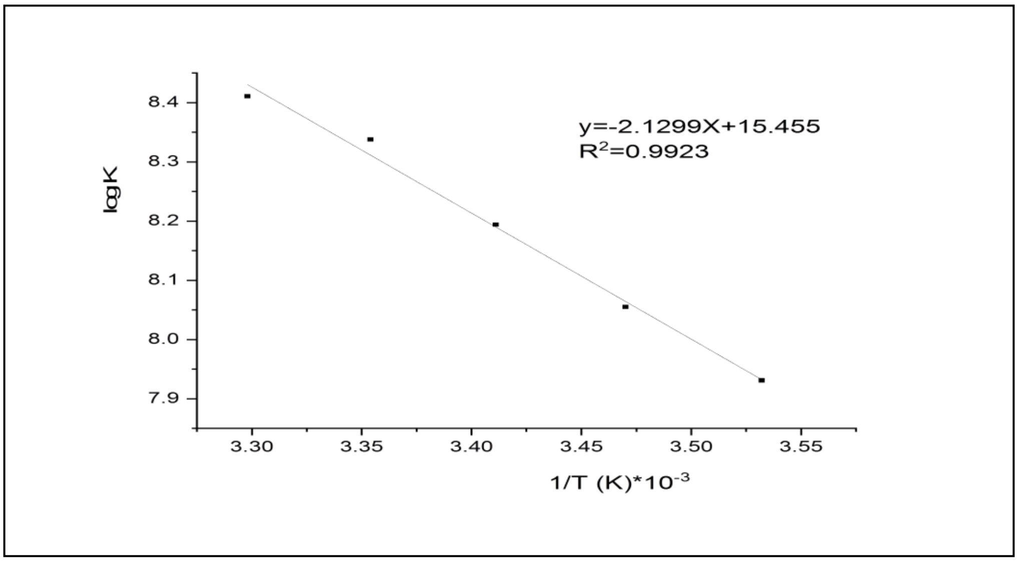
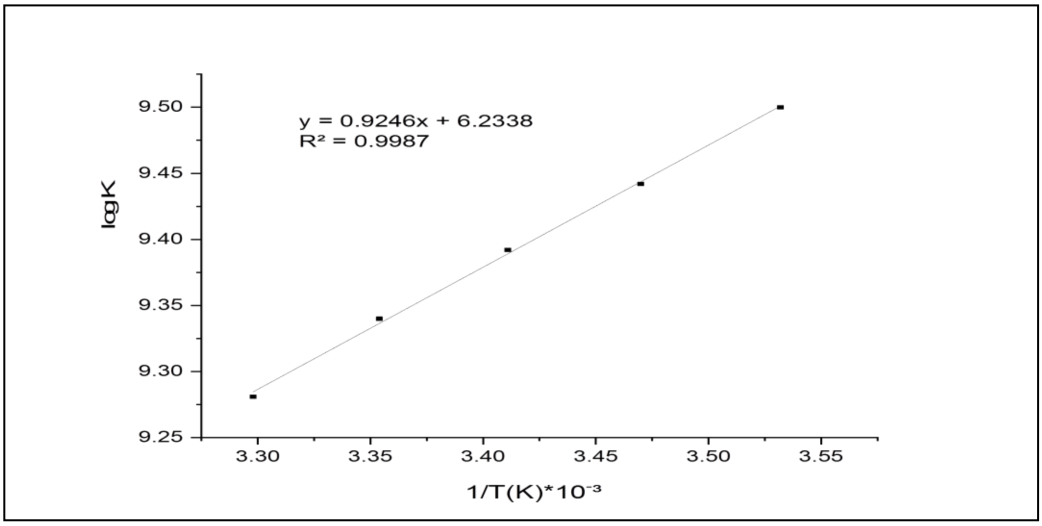


Figure (3-18): Relationship between Log K and 1/T values of zinc(II) complex

Table (3-25): The impact of temperature on thermodynamic function for chromium (III) complex

T(K)	$1/T\times10^{-3}(K^{-1})$	log K	ΔH	ΔG (K.J/mole)	ΔS (K.J/mole .K)
283.15	3.532	9.500	-18.3744	-51.437	0.11916
288.15	3.470	9.442		-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



Figure(3-19): Relationship between Log K and 1/T values of chromium (III) complex

As it was observed in Table (3-24) and Fig. (3-18), the values of ΔH for the zinc (II) complex are positive, which indicate that the reaction is endothermic. This is because of the positive temperature effect on the hydrolysis shells surrounding the zinc ion. In addition, the zinc ion has a concentrated charge, which prevents it from dissolving readily. However, removing the hydrolysis shell from the zinc ion is simple. The values of ΔH for the chromium (III) complex are negative in Table (3-25) and Fig. (3-19) , which shows that the process is exothermic, and this means that the more closely the reagent interacts with the Lewis acid , the more heat is released during the reaction , increasing the stability of the complex results . The fact that the values of ΔG are negative shows that the reaction of both ions was spontaneously and that more automatic reactions consume more energy , leading to more stable complexes. The positive interaction of both complexes is indicated by a slight rise in the ΔS values with rising temperature [165-167].

(3-13) The effect of anions and cations ions interference on zinc (II) and chromium (III) complexes

(3-13-1) Determination zinc (II) ion with some interference anions and cations ions

When calculating the zinc (II) ion , the influence of anions and cation ion interference was investigated . A variety of ions were chosen to investigate the effect of their interaction on the absorbance of the zinc (II) complex. Tables (3-26) , (3-27) show the findings of this investigation .

Table (3-26) Effect of cations interference with zinc (II) complex.

Foreign /ions	**Cations formula structure**	**(50µg/mL)** **Abs. after addition of Cations**	**Error%**
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	0.209	38.88
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	0.321	6.14
Co^{2+}	$Co(NO_3)_2.6H_2O$	0.402	-17.54
Fe^{3+}	$Fe(NO_3)_3.9H_2O$	0.167	51.16
Hg^{2+}	$Hg(NO_3)_2$	0.088	74.26
Pb^{2+}	$Pb(NO_3)_2$	0.190	44.44
Mg^{2+}	$Mg(N0_3)_2.4H_2O$	0.294	14.03
Ag^{+}	$AgNO_3$	0.392	-14.61
Cu^{2+}	$Cu(NO_3)_2.3H_2O$	0.266	22.22
Absorbance without interferences = 0.342			

Table (3-27): Effect of anions interference with zinc (II) complex.

Foreign ions	Formula structure of Anions	(50µg/mL) Absorption after addition of Anions	E%	(100µg/mL) Absorption after addition of Anions	E%
SO_4^{2-}	K_2SO_4	0.250	26.87	0.290	15.20
Br^{1-}	KBr	0.440	-28.64	0.470	-37.42
SCN^{1-}	KSCN	0.206	39.76	0.280	18.12
$IO3^{1-}$	KIO_3	0.111	67.54	0.201	41.22
CrO_7^{2-}	K_2CrO_7	0.314	8.18	0.320	6.43
CO_3^{2-}	K_2CO_3	0.390	-14.03	0.340	0.58
CN^{1-}	KCN	0.190	44.44	0.137	59.94
Absorbance without interferences = 0.342					

According to the tables above, most ions impact the zinc (II) ion complex absorption values when combined with the reagent. This depends on the nature and concentration of the added ions. Due to interference, the cation ions either reduce or increase the amount of zinc absorption. The presence of both of these ions with the reagent results in the formation of a complex, which reduces the amount of competition present and raises the method sensitivity of the zinc (II) ion. Because anions function as concealing agents, there is a lower absorption rate when present. This may be explained by the fact that anions are present [168, 169].

(3-13-2) Determination chromium (III) ion with some interference anions and cations ions

When calculating the chromium (III) ion, the influence of anions and cation ion interference was investigated. A variety of ions were chosen to investigate the effect of their interaction on the absorbance of the chromium (III) complex. Tables (3-28) , (3-29) show the findings of this investigation .

Table (3-28) : Effect of cations interference with chromium (III) complex

Foreign/ ions	**Cations formula structure**	**(50µg/mL) Abs. after addition of Cations**	**Error%**
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	0.162	65.96
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	0.398	16.38
Co^{2+}	$Co(NO_3)_2.6H_2O$	0.215	54.83
Fe^{3+}	$Fe(NO_3)_3.9H_2O$	0.277	41.80
Hg^{2+}	$Hg(NO_3)_2.H_2O$	0.332	30.25
Pb^{2+}	$Pb(NO_3)_2$	0.109	77.10
Mg^{2+}	$Mg(N0_3)_2.6\ H_2O$	0.409	14.07
Ag^{+}	$AgNO_3$	0.358	24.78
Cu^{2+}	$Cu(NO_3)_2.3H_2O$	0.244	48.73
Absorbance without interferences = 0.481			

Table (3-29): Effect of anions interference with chromium (III) complex

Foreign ions	**Formula structure of Anions**	**(50µg/mL) Absorption after addition of Anions**	**E%**	**(100µg/mL) Absorption after addition of Anions**	**E%**
SO_4^{2-}	K_2SO_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
$IO3^{1-}$	KIO_3	0.235	50.63	0.311	34.66
CrO_7^{2-}	K_2CrO_7	0.105	77.94	0.161	66.17
CO_3^{2-}	K_2CO_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 in the above tables demonstrate that the majority of the ions affect the chromium (III) ion complex absorption values with the reagent . This relies on the nature and concentration of the added ions , and generally , the cations ions either decrease or increase the absorption of chromium (III) complex due to interference . The combination of these ions forms a complex with the reagent , which decreases competition and increases the method's sensitivity to the chromium (III) ion. The decrease in absorption observed in the presence of anions is related to their action as masking agents [169].

(3-14) Effect of Masking agents

(3-14-1) Limitation the optimal masking agent for the determination of the zinc (II) and chromium (III) complexes

Since most cations overlap with the zinc (II) and chromium (III) complexes formed, a strategy must be proposed to eliminate this influence. Therefore, masking agents were selected (7) to observe the effect of the contest process between these agents and the reagent as it interacts with the interfering ions. This issue was not seen in this research because it was eliminated by adding (1mL) of each masking agent, as shown in Tables (3-30), (3-31).

Table (3-30) :The effect of masking agent on zinc(II) complex absorption

Masking agent (0.1M)	Abs of Zn(II)complex
Without Masking agent	0.342
Thiourea	0.503
Ascorbic acid	0.195
Na_2EDTA	0.165
Citric Acid	0.366
KCl	0.243
$Na_2HPO_4.12H_2O$	0.092
Formal dehyde	0.280

According to what is shown in Table 3-30, Citric acid has little minimal impact on the absorption of the generated complex. This suggests that it could be utilized as a masking agent. However, due to the other rest dissociation with zinc (II) ion, they can̓t be used as a masking agent.

Table (3-31):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
Na2EDTA	0.220
Citric Acid	0.395
KCl	0.343
Na2HPO4.12H_2O	0.244
Formal dehyde	0.304

Table (3-31) reveals that (Thiourea) has minimal effect on synthesized complex absorption, suggesting that it might be utilized as a masking agent. Because of the other remained dissociation with chromium (III) ion, they can’t be employed as a masking agent.

(3-14-2) Use of a better masking agent to determine the zinc (II) and chromium (III) ions in the presence of cations interference

1- zinc (II) complex.

To obtain the best estimate of the zinc (II) complex in the presence of interfering cationic ions, the best masking agent (Citric acid) given in Table (3-30) was utilized.

Table (3-32): The effect of masking agent in the presence of cations on zinc(II) complex absorption.

Foreign ions	Absorption after addition cation (50µg/mL) and addition masking agent(0.1M)	Relative Error (E%)
Cd^{2+}	0.344	-0.580
Ni^{2+}	0.340	0.584
Co^{2+}	0.348	-1.750
Fe^{3+}	0.339	0.870
Hg^{2+}	0.341	0.290
Pb^{2+}	0.345	-0.870
Mg^{2+}	0.349	-2.040
Ag^{+}	0.338	1.160
Cu^{2+}	0.346	-1.160

Table (3-32) shows the absorption values of the zinc (II) complex in the presence of interfering cations when a better masking agent is added, as well as absorbance values close to those before the interference (3-32).

2- chromium(III) complex

To obtain the best estimate of the chromium(III) complex in the presence of interfering cationic ions, the best masking agent (Thiourea) given in Table(3-31) was applied.

Table (3-33): The effect of masking agent in the presence of cations on chromium (III) complex absorption

Foreign ions	Absorption after addition cation (50μg/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

Table (3-33) shows the absorption values of the chromium (III) complex in the presence of interfering cations when a better masking agent is added, and absorbance values close to those before the interference.

(3-15) Precision and accuracy of the proposed method

The accuracy of the method is represented by the relative standard deviation (RSD%), and the accuracy of the way is characterized by the relative recovery of the zinc (II) and chromium (III) complexes under research studied by studying the absorption of various concentrations at a rate of four readings for each concentration [151]. Tables (3-34) ,(3-35) show the results for the zinc (II) complex and chromium (III) complex , respectively.

Table (3-34): The Precision and accuracy of the Zn(II) complex

Conc. of Zn^{+2} present[M]	Conc. of Zn^{+2} found[M]	RSD%	Recovery%	Error%
4.588×10^{-5}	4.550×10^{-5}	1.772	99.17	0.83
7.640×10^{-5}	7.560×10^{-5}	1.579	98.95	1.05
1.830×10^{-4}	1.902×10^{-4}	0.700	103.93	-3.93

Table (3-35): The Precision and accuracy of the Cr(III) complex

Conc. of Cr^{+3} present[M]	Conc. of Cr^{+3} found[M]	RSD%	Recovery%	Error%
5.769×10^{-5}	5.693×10^{-5}	1.250	98.68	1.32
1.154×10^{-4}	1.129×10^{-4}	0.939	97.83	2.16
2.307×10^{-4}	2.332×10^{-4}	0.552	101.08	-1.08

The findings above indicate that the analytical technique employed for measuring the reagent (SDPIHN) has high precision and accuracy.

(3-16) Sensitivity of spectrometric method in determination the zinc (II) and chromium (III) ions

It was pointed out in this method that the sensitivity of the technique used to determine the zinc (II) and chromium (III) ions by the expression limit of detection. Furthermore, the results showed that this spectroscopic method could estimate the lowest concentration of zinc ion to be (3.475×10^{-6} M), while the lowest concentration of chromium (III) (2.194×10^{-6} M), indicates that the method is successful in determining zinc (II) ion and has high sensitivity, as shown in the following equation for calculating sensitivity (D.L).

$$D.L = \frac{3x\ conc\ x\ S.D}{\bar{x}} \ldots\ldots\ldots\ldots\ldots\ldots(3-9)$$

SD = standard deviation

$\bar{x}$ = Average

(3-17) Preparation of solid complexes

The reagent was used to prepare the two ion complexes under the optimal circumstances found in this study of reagent volume, temperature, molar ratios, acidity function, etc. This was accomplished by mixing the reagent (SDPIHN) dissolved in ethanol separately with the metal ionic (Zn^{2+}, Cr^{3+}) in an aqueous solution. It was discovered that a precipitate developed during the mixing of the solutions and after they had been cooled. The physical properties of the two solid complexes were examined after allowing the solutions to precipitate fully, filter, and recrystallize.

(3-18) Study of FTIR Spectra of the zinc (II) and chromium (III) complexes

Infrared spectroscopy is an essential tool for identifying absorption beams induced by active groups that are likely to coordinate with metal ions. The difference in the intensity, shape, and placement of absorption beams in the spectrum of complexes spectrum towards lower or higher frequencies compared to their locations in the spectrum of reagent alone illustrates how the link between the metal ion and the donor atoms in the reagent is produced.

FTIR spectra were recorded for the complexes , and the results can be seen in Figs. (3-20) , (3-21), respectively. The table below contains the FTIR spectra data .

Table (3-36) Typical FTIR absorption frequencies of the reagent and complexes (cm^{-1}) [170-172].

Bond	**Reagent**	**Zinc(II) complex**	**Chromium (III) complex**
St.(N-H)	3169	3116	3116
St.(C-H) Aromatic	3062	3061	3061
St.(C=N)	1691	1666	1666
St.(N=N)	1481	1440	1442
St.(M-N)	-------	457	457
St.(M-O)	-------	501	528

Can explain the results as blow:

1. The stretching vibration of the (N-H) amino group of the imidazole ring has shifted from (3169 cm^{-1}) in the reagent to (3116 cm^{-1}) in Zinc (II) complex and to (3116 cm^{-1}) in Chromium (III) complex.
2. The absorption in (3062 cm^{-1} - 3061 cm^{-1}) is due to stretching vibration of (C-H) aromatic in the ligand and complexes.
3. The stretching vibration of the (C=N) group has shifted in (1691 cm^{-1}) of the reagent and (1666 cm^{-1}) in both Zinc (II) complex and Chromium (III) complex , which suggests that the electron pairs on N group is not involved in bonding .
4. The stretching vibration of the (N=N) group has shifted from (1481 cm^{-1}) in the reagent to (1440 cm^{-1}) in Zinc(II) complex and (1442 cm^{-1}) in Chromium (III) complex .

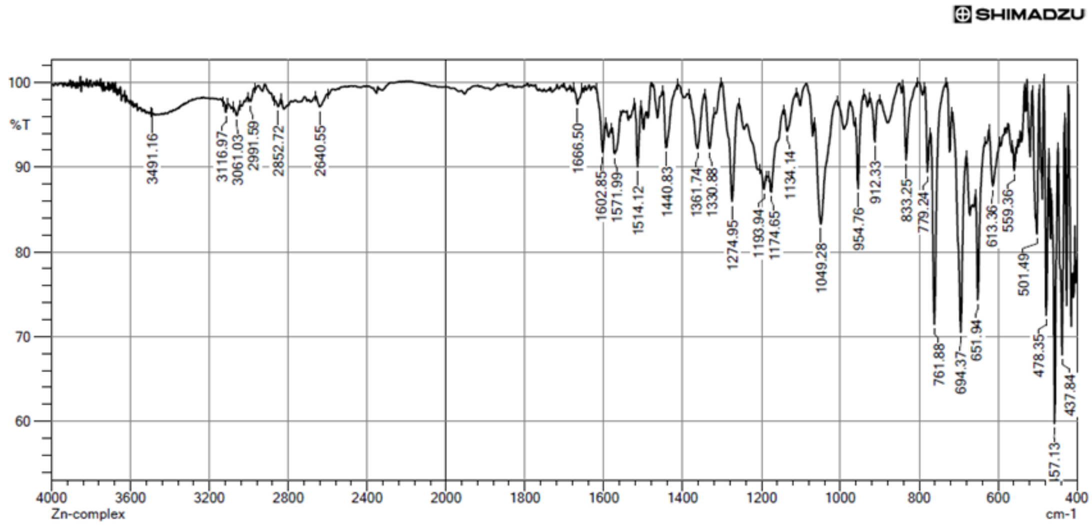


Figure (3-20) FTIR spectrum of Zinc(II) complex

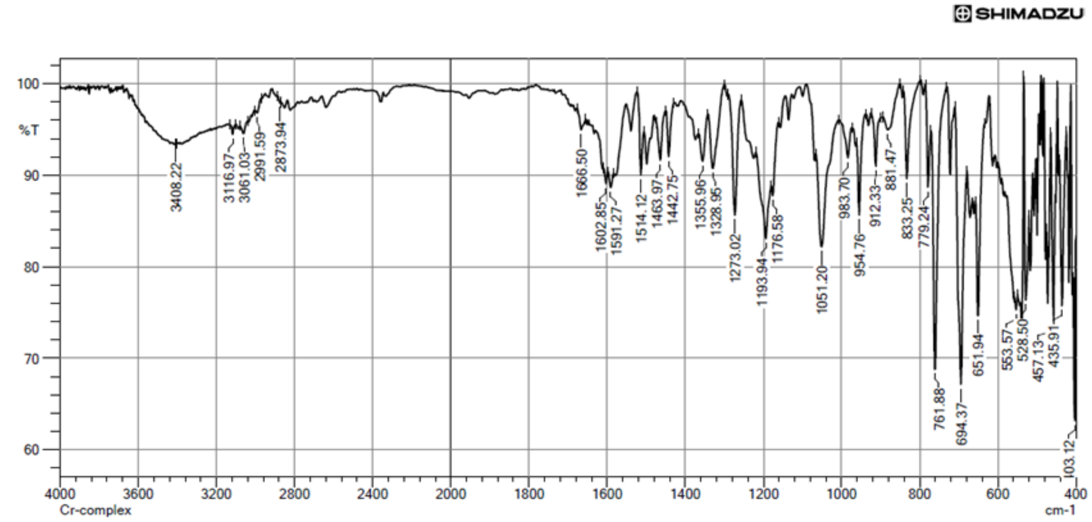


Figure (3-21) FTIR spectrum of Chromium (III) complex .

(3-19) Determination of the melting point of the complexes

When the melting points of the zinc (II) and chromium (III) complexes were determined , it was observed that the zinc (II) complex melts at a temperature between (261-263)°C and the chromium (III) complex melts at a temperature between (231-234)°C , while the reagent's melting point values range between (219-223)°C. This difference in melting point values between the reagent and two complexes indication of new complex formation .

(3-20) Measurement of molar Conductivity of the zinc (II) and chromium (III) complexes

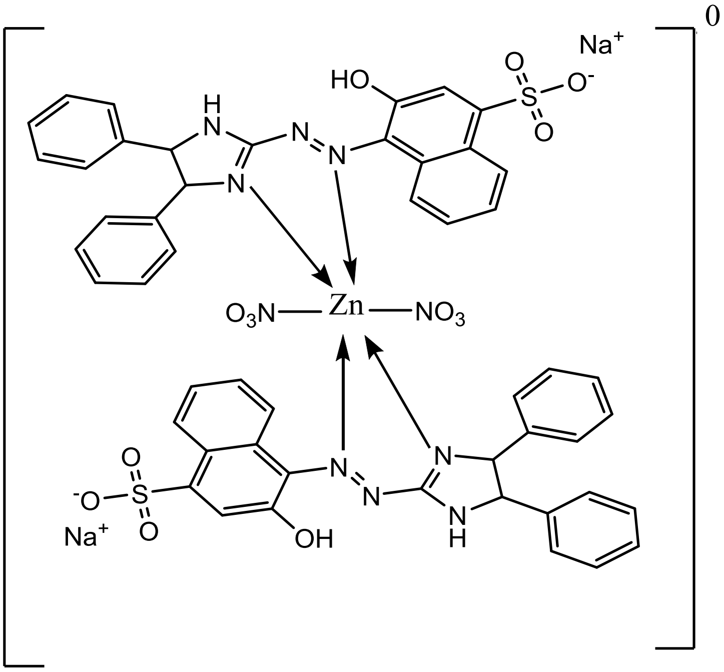
The quantity of charged ions in a solution capable of carrying an electric current is directly proportional to the degree of electrical conductivity. When no ionic characteristic is present in the complex solution, it can be taken on low values close to zero. Consequently, the molar conductivity of the metal ion complexes was measured at room temperature. The results for the molar conductivity of the zinc (II) and chromium (III) complexes with the reagent are shown in Table (3-37). According to the findings, the zinc (II) complex has not an ionic character, while the chromium(III) complex has ionic character [173].

Table (3-37) The molar conductivity values of the two solutions of the zinc (II) and chromium (III) complexes

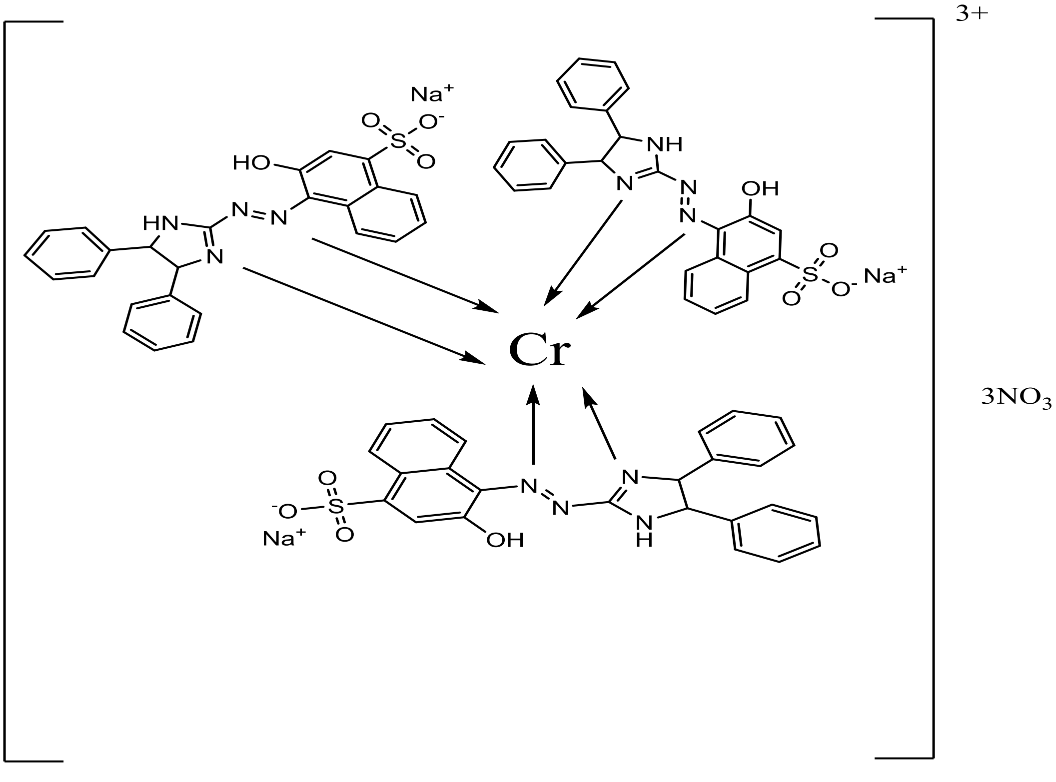
No	Complex	Λ_m(μS/cm)
1	[Zn(SDPIHN)$_2$]	15.5
2	[Cr(SDPIHN)$_3$]	360

(3-21) The suggested structure of the zinc (II) and chromium (III) complexes

According to the results of this study , the stoichiometry of complexes (M:L) for the zinc (II) and chromium (III) is (1:2) and (1:3) respectively [174]. Complexes' proposed structures are displayed in the Figs. (3-22) ,(3-23).



Figure(3-22) The suggested structure of the zinc (II) complex.



Figure(3-23) The suggested structure of the chromium (III) complex.

(3-22) Application

The suggested method was used to determine the levels of zinc (II) and chromium (III) ions in samples of drugs. It was based on the proportion of the zinc (II) and chromium (III) ions stated in the medicine, and the practical findings were quite near to what was mentioned in the drugs. Therefore, the results of the experiment are summarized in tables (3-38) and (3-39), respectively, for the determination of chromium (III) and zinc (II) ions.

Table (3-38): Results of application for zinc(II) determination.

Pills	The company	Conc. present (µg/mL)	Abs.	Conc. found (µg/mL)	Recovery %	E%
Zinc Sulphate Monohydrate	D PYXUS	6.25	0.225	6.08	97.28	2.72
Zinc Sulfate	Jink	10.00	0.338	9.88	98.8	1.20
Zinc Picolinate	THORNE	5.00	0.177	5.14	102.8	-2.80

Table (3-39): Results of application for chromium (III) determination.

Pills	The company	Conc. present (µg/mL)	Abs.	Conc. found (µg/mL)	Recovery %	E%
Chromium Niacin	MADAMAR	4.00	0.211	4.16	104	-4.00
Chromium Picolinate	THORNE	8.00	0.373	7.95	99.37	0.63
Chromium Picolinate	SPRING VALLEY	10.00	0.475	9.75	97.5	2.50

Analytical results that obtained by spectrophotometric method were statistically compared with real sample were in good agreement . The method can be applied for quality control of pharmaceutical dosage forms that containing zinc(II) and chromium(III) ions.

(3-23) Conclusions

1. There is an ability to prepare the new reagent (SDPHIN) via conventional nitrogenation of the compound diazonium salt (1-amino-2-napthol-4-sulfonic acid).
2. The SDPHIN spectrophotometric , which has colored complexes , can be used to measure very small amounts of Zn (II) and Cr (III) ions . These complexes have points where they absorb the most.
3. The Triton x-100 at concentration 3% was chosen to interact with zinc (II) and chromium (III) complexes.
4. The method for determining zinc (II) and chromium (III) ions with the prepared reagent is quick and simple, as compliance with the Lambert-Beer law gives a wide range of concentrations. After determining the optimum conditions of the acidic function, the volume of the reagent, the sequence of addition, and the temperature, the method is straightforward.
5. The results of determining the equivalence of the two complexes by molar ratios , or the Job's method , show that the reagent-to-ion ratio is (1:2) for the zinc (II) complex and (1:3) for the chromium (III) complex.
6. During the coordination process with the ions of zinc and chromium (III), the reagent acts in a way that is bidentate.
7. The masking agent effect results show that (Citric acid) has no effect on the process of estimating zinc (II) , so it can be used as a masking agent . The results showed that (Thiourea) has no effect on the chromium (III) ion estimation process and can be used as a chromium (III) ion masking agent.
8. The thermodynamic function results show that the positive values of ∆H and ∆S for the zinc (II) complex with the reagent indicate that the reaction is spontaneous at high temperatures and that it is an endothermic reaction . The negative values of ∆G and ∆H for the chromium (III) complex with the reagent indicate that the reaction occurs spontaneously at low temperatures and is exothermic.
9. According to the findings of the stability constant value comparison between the zinc (II) and chromium (III) complexes, the chromium (III) complex with the reagent (SDPHIM) is more stable than the zinc (II) complex with the reagent.

10. Studying the effect of the interference cations and anions ions on the spectroscopic estimation process for the zinc (II) and chromium (III) ions that were under study led to the discovery that there is a differential effect of these cations and anions ions on the estimation process.
11. Determining the charge of the zinc (II) and chromium (III) complexes , as well as studying their molar conductivity , revealed that the zinc complex was not charged while, the chromium complex was charged .
12. The results of the calculation of the relative standard deviation and the relative error of percent showed that the spectral method being investigated has a high sensitivity, is straightforward, quick, accurate, and precise, and does not call for any prior preparations or complications such as separation, ion exchange, etc.
13. The possibility of using the prepared reagent (SDPHIN) to estimate the trace amounts of zinc (II) and chromium (III) complexes present in drug sample.

(3-24) Recommendations

1. Conduct research into the viability of using the reagent (SDPIHN) to estimate the concentrations of other ions in various media.
2. The production of novel derivatives of the reagent to improve its selectivity and features, as well as the ability to use the reagent to estimate other components.
3. Because the produced reagent can be consistent with many of these ions, it may be used in the research to extract some of the transition elements.
4. Due to azo compounds which represent an important part of restricting biological activity; it should monitor the influence of the produced reagent on biological activity.

Appendices

Appendices

1- Statistical treatment.

-Calculation of the Relative standard deviation.

1- Statistical treatment and calculation of %RSD values for zinc (II) ion.

Table (1) Calculation of the %RSD of the zinc (II) ion at concentration 4.588x10^{-5}M

Abs (Xi)	**Mean ($\bar{x}$)**	**(xi-$\bar{x}$)**	**Σ(xi-$\bar{x}$)^2**	$\mathbf{S.D} = \sqrt{\frac{\Sigma(\mathrm{xi}-\bar{x})^2}{\mathrm{N}-1}}$	$\%RSD = \frac{SD}{\bar{x}} \times 100$
0.101	0.103	-0.002	1×10^{-5}	1.825×10^{-3}	1.772 %
0.102		-0.001			
0.104		-0.001			
0.105		-0.002			

Table (2) Calculation of the %RSD of the zinc (II) ion at concentration 7.640x10^{-5}M

Abs (Xi)	**Mean ($\bar{x}$)**	**(xi-$\bar{x}$)**	**Σ(xi-$\bar{x}$)^2**	$\mathbf{S.D} = \sqrt{\frac{\Sigma(\mathrm{xi}-\bar{x})^2}{\mathrm{N}-1}}$	$\%RSD = \frac{SD}{\bar{x}} \times 100$
0.165	0.1675	-0.0025	2.1×10^{-5}	2.6457×10^{-3}	1.579 %
0.168		0.0005			
0.171		0.0035			
0.166		-0.0015			

Table (3) Calculation of the %RSD of the zinc (II) ion at concentration 1.830x10^{-4}M

Abs (Xi)	Mean ($\bar{x}$)	(xi-$\bar{x}$)	Σ(xi-$\bar{x}$)^2	$\mathrm{S.D} = \sqrt{\frac{\Sigma(\mathrm{xi}-\bar{x})^2}{\mathrm{N}-1}}$	$\%RSD = \frac{SD}{\bar{x}} \times 100$
0.375	0.3775	-0.0025	2.1×10^{-5}	2.645×10^{-3}	0.700 %
0.381		0.0035			
0.378		0.0005			
0.376		-0.0015			

2- Statistical treatment and calculation of %RSD values for chromium (III) ion.

Table (4) Calculation of the %RSD of the chromium (III) ion at concentration 5.769x10^{-5}M

Abs (Xi)	Mean ($\bar{x}$)	(xi-$\bar{x}$)	Σ(xi-$\bar{x}$)^2	$\mathrm{S.D} = \sqrt{\frac{\Sigma(\mathrm{xi}-\bar{x})^2}{\mathrm{N}-1}}$	$\%RSD = \frac{SD}{\bar{x}} \times 100$
0.145	0.146	-0.001	1×10^{-5}	1.825×10^{-3}	1.250 %
0.144		-0.002			
0.148		0.002			
0.147		0.001			

Table (5) Calculation of the %RSD of the chromium (III) ion at concentration 1.154x10^{-4}M

Abs (Xi)	Mean ($\bar{x}$)	(xi-$\bar{x}$)	Σ(xi-$\bar{x}$)^2	$\mathrm{S.D} = \sqrt{\frac{\Sigma(\mathrm{xi}-\bar{x})^2}{\mathrm{N}-1}}$	$\%RSD = \frac{SD}{\bar{x}} \times 100$
0.272	0.275	-0.003	2×10^{-5}	2.51082×10^{-3}	0.939 %
0.274		-0.001			
0.278		0.003			
0.276		0.001			

Table (6) Calculation of the %RSD of the chromium (III) ion at concentration $2.307x10^{-4}$M

Abs (Xi)	Mean ($\bar{x}$)	(xi-$\bar{x}$)	Σ(xi-$\bar{x}$)^2	$S.D = \sqrt{\frac{\Sigma(xi-\bar{x})^2}{N-1}}$	$\%RSD = \frac{SD}{\bar{x}} \times 100$
0.522	0.523	-0.001	2.5×10^{-5}	2.886×10^{-3}	0.552 %
0.525		0.002			
0.527		0.004			
0.521		-0.002			

- Calculation of Detection limit .

1- Statistical treatment and calculation of D.L values for zinc (II) ion.

Table (7) Calculation of the D.L of the zinc (II) ion at concentration $1.530x10^{-4}$M.

Abs (Xi)	Mean ($\bar{x}$)	(xi-$\bar{x}$)	Σ(xi-$\bar{x}$)^2	$S.D = \sqrt{\frac{\Sigma(xi-\bar{x})^2}{N-1}}$	$D.L = \frac{3 \times conc \times S.D}{\bar{x}}$
0.340	0.341	-0.001	2×10^{-5}	2.582×10^{-3}	3.475×10^{-6}
0.338		-0.003			
0.344		0.003			
0.300		0.001			

2- Statistical treatment and calculation of D.L values for chromium (III) ion.

Table (8) Calculation of the D.L of the chromium (III) ion at concentration $1.923x10^{-4}$M.

Abs (Xi)	Mean ($\bar{x}$)	(xi-$\bar{x}$)	Σ(xi-$\bar{x}$)^2	$S.D = \sqrt{\frac{\Sigma(xi-\bar{x})^2}{N-1}}$	$D.L = \frac{3 \times conc \times S.D}{\bar{x}}$
0.479	0.480	-0.001	1×10^{-5}	1.825×10^{-3}	2.194×10^{-6}
0.478		-0.002			
0.481		0.001			
0.482		0.002			

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بِسْمِ اللَّـهِ الرَّحْمَـٰنِ الرَّحِيمِ

{ يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ
وَاللَّهُ بِمَا تَعْمَلُونَ خَبِيرٌ}

صدق الله العلي العظيم

(سورة المجادلة آية ١١)

الخلاصة :

اشتملت الدراسة على تحضير وتشخيص ليكاند ازو الجديد

Sodium4-((4,5-diphenyl-imidazol-2-yl)diazenyl)-3-hydroxynaphthalene-1-sulfonate (SDPIHN)

وهوأحد مركبات Azo المحضر باستخدام طريقة الازوتة التقليدية عن طريق تفاعل الديازونيوم بواسطة تفاعل ملح مركب 1-amino-2-napthol-4-sulfonic acid مع مشتق الأميدازول وإجراء دراسة أولية باستخدام (11) ايون من الأيونات الفلزية و دراسة التحليل الطيفي لها وقد تم اختيار ايوني الزنك والكروم لتقديرهما باستخدام الكاشف المذاب في الإيثانول حيث اعطا محلول الكاشف اعلى امتصاص باستخدام تقنية UV-vis $(\lambda_{max} = 463\ nm)$. تم دراسة معقدات الزنك (II) والكروم (III) المتكونة مع الكاشف بوجود الماده المنشطه للسطوح Triton x-100 بالإضافة إلى ذلك ، تمت دراسة الضروف الفضلى لتفاعل هذه الأيونات مع الكاشف ، مثل الدالة الحامضية ، وحجم وتركيز الكاشف وحجم وتركيزTriton X-100 ، وزمن الاستقرار للمعقدات ، درجة الحرارة . تم دراسة منحني المعايرة لكل من هذه الأيونات مع الكاشف ، بحيث يكون معقد الزنك (II) ضمن مدى من التركيز (1µg/mL-11µg/mL) و معامل الخطية $(R^2=0.9996)$ وقيمة الامتصاصية المولارية (ε) تساوي $(0.2229\times10^4 L.moL^{-1}.cm^{-1})$ وحساسية Sandal تساوي $(0.0293\mu g/cm^2)$ ، بينما كان ايون والكروم (III) يقع في مدى من التركيز (1µg/mL-11µg/mL) ومعامل الخطية $(R^2= 0.9998)$. قيمة الامتصاصية المولارية$(0.244\times10^4 L.moL^{-1}.cm^{-1})$, تساوي حساسية ساندل $(0.0213\mu g/cm^2)$، وتمت دراسة تكافؤ ية المعقدات المحظرة من خلال إيجاد نسبة أيون الفلز إلى الكاشف (M:L) باستخدام طريقة التغييرات المستمرة والنسبة المولية لمعقدات الزنك (II) والكروم (III) . كما حسبت ثابت الاستقرار (K_{sta}) للمعقدين وكانت قيمته لمعقد الزنك $(K_{sta} = 5.967\times10^8)$ ولمعقد الكروم $(K_{sta} = 1.125\times10^{14})$. بالإضافة إلى ذلك ، تم حساب الدوال الثرموديناميكية للمعقدات المحضرة (ΔH، ΔG، ΔS) ، حيث أشارت النتائج إلى أن التفاعل الناتج من تكوين معقد الزنك (II) ماص للحرارة ومركب الكروم (III) باعث للحرارة. تم دراسة تأثير وجود الايونات السالبة والموجبة على المعقدات المحضرة ، كما تمت دراسة إضافة عوامل الحجب لتقليل تاثير تداخل الايونات المتداخلة في المحلول ، حيث وجد أن هذه الأيونات تتفاعل بدرجات متفاوتة حسب طبيعة وتركيز الأيونات المتداخلة . ، تم تحديد

شحنة المعقدات الصلبة المحضرة الذائبة في الايثانول عن طريق قياس توصلية المعقدات ، حيث اظهرت النتائج ان معقد الزنك(II) غير مشحون لكن معقد الكروم (III) يكون مشحون. تم تحديد دقة وتوافقية الطريقة التحليلية المستخدمة باستخدام ثلاثة تراكيز مختلفة لكل أيون ، فتراوحت قيم النسبة المئوية للانحراف المعياري النسبي لأيون الزنك (II) بين (1.772% - 0.700%) وتراوح نسبة التوافقية بين (103.930% - 98.950%) أما بالنسبة للكروم (III) فقد تراوحت الانحراف المعياري النسبي بين (1.250% - 0.552%) ونسبة التوافقية تتراوح بين (101.080% - 97.830%) . تم حساب حد الكشف لأيون الزنك وكان (3.475×10^{-6}M) اما حد الكشف لأيون الكروم فيساوي (2.194×10^{-6}M)، مما يدل على ان الطريقة الطيفية ذات حساسية عالية باستخدام الكاشف(SDPIHN). تم دراسة بعض الخصائص الفيزيائية مثل درجة الانصهار والتوصلية المولارية لكل من معقد الزنك والكروم . تم تطبيق الطريقة على عينات صيدلانيه ووجد ان الطريقة المتبعة في التقدير ذات حساسية ودقة عالية.

جامعة كربلاء

كلية العلوم

قسم الكيمياء

التقدير الطيفي لكميات ضئيلة لايوني الزنك الثنائي والكروم الثلاثي باستخدام مشتقات صبغة الايمدازول , دراسة الدوال الثرموديناميكية وتطبيقاتها التحليلية

رسالة

مقدمة الى مجلس كلية العلوم – جامعة كربلاء كجزء من متطلبات نيل درجة الماجستيرفي علوم الكيمياء

من قبل

حوراء عبدالهادي عبدالامير

بأشراف

الاستاذ الدكتور

علاء فراك حسين

1444 هـ 2022م