Republic of Iraq
Ministry of Higher Education
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University of Kerbala
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# *A Study on Liquid-Liquid Extraction of Cobalt (II) and Iron (III) Ions Using an (Azo) Derivative - Sequential Separation and Their Analytical Applications*

A Thesis Submitted to
The College of Science
University of Kerbala
In Partial Fulfillment of the Requirements
For the Master Degree of Science in
Chemistry

By

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2021 A.D. 1443 A.H.

In the name of Allah
The most compassionate and merciful praise be to Allah and pray on his prophet Muhammad and kinsfolk his home

*First of all; all thanks to Allah, the almighty, for uncountable help and guidance, who enabled me the power to achieve this study.*

*I wish to express my profound gratitude to my supervisor, Prof. Dr. Alaa Frak Hussain, whose encouragements, professional ideas, advice, and criticisms were unceasing from the first day this work was conceived. He has been responsible for my present scientific outlook.*

*Also, I wish to express my thanks to the dean of the college of science, the Head of the chemistry department, and to all chemistry staff members for all the assistance they offered. I am particularly grateful to my colleagues in the chemistry department.*

# Supervisors Certification

I certify this thesis conducted under my supervision at the department of chemistry, College of science, University of Kerbala, as a partial fulfillment of the requirements for the degree of M.Sc. in analytical chemistry.

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# Report of the Head of the Chemistry Department

According to the recommendation presented by the Chairman of the Postgraduate Studies Committee, I forward this thesis **“A Study on Liquid-Liquid Extraction of Cobalt (II) and Iron (III) Ions Using an (Azo) Derivative - Sequential Separation and Their Analytical Applications”** for examination.

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**Date: / /2021**

# Examination Committee Certification

We, the examining committee certify that we read this thesis **“A Study on Liquid-Liquid Extraction of Cobalt (II) and Iron (III) Ions Using an (Azo) Derivative - Sequential Separation and Their Analytical Applications”**
and have examined the student (**Hussein Mubarak Mohsin**) in its Contents and that our opinion, it’s adequate as a thesis for the degree of Master of Science in chemistry with ***Excellent***.

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# Abstract

This study includes synthesis a new azo derivative (7-((4-(dimethylamino) phenyl) diazenyl) quinoline-8-ol) (DPDQ) from 8-hydroxy quinoline by nitrogen method. The reagent was reddish orang powder, and characterized by spectroscopic methods such as UV-Vis., FT-IR, $^1$HNMR and $^{13}$CNMR. The new derivative has a molecular weight (292.1324g/mol).

The melting point was ( 164-166 °C) , it was soluble in many organic solvent such as carbon tetrachloride, Dimethylformamide, Dimethyl sulfoxide and chloroform , the reagent has maximum wavelength ($\lambda_{max}$=442.5nm) .

The process of extracting liquid-liquid for Cobalt (II) and Iron (III) ions, separately, by new azo reagent and Study the possibility of conducting the sequential separation of the extracted ions. A study has been done to show the influence of various factors on the distribution ratio (D) and the percentage of extraction (E %).

The optimum pH for the extraction of Cobalt (II) was (10) and (7) for Iron (III) , separately. The best period for equilibrium was (10) minute for Cobalt (II) and (15) minute for Iron (III), the results showed that Chloroform was the best solvent of extraction of both.

To evaluate the effect of the presence of cations and anions as common interfering on the extracting of Cobalt (II) and Iron (III) ions, individually. The results indicated that lead to differences in (D) and (E %) values with the existence of the variable concentration of cations and anions.

The effect of oxidizing and reducing agents also were studied. From the result for this study the (D) and (E %) decrease by using oxidizing agent and increase by using reducing agent.

The enrichment extraction technique leads to a decrease in (D) and (E %) values, the results indicate that a preferred (aqueous/organic) phase ratio in this study found to be (1:1). This is evident from the sharp increase in the separation efficiency as well as the distribution ratio of Co (II) and Fe (III) when phase ratio (A/O) changed from (25:5) to (5:5) for Co (II) and Fe (III), respectively.

The results also showed that (D) and (E %) values augmented with the increase of the concentration of Co (II) and Fe (III) with (DPDQ).

To study the influence of temperature, it was found the values of (D) of Co (II) and Fe (III), decrease by increasing the temperature. The thermodynamic functions ($\Delta S$, $\Delta G$, $\Delta H$) were calculated, and the results showed that the reaction of [Co (III)-(DPDQ)] and [Fe (III) - (DPDQ)] were exothermic ($\Delta H$= -18.4, -57.258 $kJ.mol^{-1}$) respectively.

The 'salting out' effect using ammonium chloride, sodium chloride, sodium sulphate & sodium nitrate salts was study. The study showed that (D) and (E %) values for these ions were affected by this parameter. The batch extraction technique enhanced that this technique not effected.

The study of the stoichiometry of the extracted complexes by using three methods mole ratio method, Job's method (continues change), and substoichiometric extraction. The results showed that the ratio of Co (II) and Fe (III), with reagent was (1:2) & (1:3) respectively.

To use the new reagent (DPDQ) in applications, many samples were used (hair, Vitamin B12, and drugs samples containing Iron). The result showed that the reagent gave a good results, (Co (II) in hair, Vit.B12 is 10.875µg/g, 41.371µg/10mL respectively) and (Fe (III) is 191µg/5mL, 123µg/5mL respectively in drug samples used). The reagent was successful in the sequential separation of cobalt (II) and iron (III) ions.

# List of symbols and abbreviation

| Symbol | Meaning |
|---|---|
| DPDQ | 7-((4-(dimethylamino) phenyl) diazenyl) quinoline-8-ol) |
| aq. | The aqueous phase |
| Org. | The organic phase |
| D | Distribution ratio |
| E% | Percentage of extraction |
| [ ] | Molar concentration |
| $K_D$ | Distribution coefficient |
| A | Absorbance |
| RSD | Relative standard deviation |
| $\Delta G$ | Free energy |
| $\Delta H$ | Enthalpy |
| $\Delta S$ | Entropy |
| LLE | Liquid-liquid extraction |
| $\varepsilon$ | Dielectric constant |
| $\lambda_{\mathbf{max}}$ | Maximum wavelength |
| Cyanex 272 | Bis(2,4,4-trimethylpentyl )phosphinic acid |
| U.S. | United state |
| DMBA | Dimethyl Benzyl Amide |
| IS-RPB | laboratory scale Impinging Stream–Rotating Packed Bed |
| P507 | 2-ethylhexyl phosphoric acid-2-ethylhexyl ester |
| TBP/[TFSA] | tri-n-butyl phosphate/[Triethyl-pentyl-phosphonium bis(trifluoromethyl-sulfonyl)amide] |

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# Chapter One

# Introduction

## (1-1) Azo dyes

Azo dyes refer to the biggest preparation and syntheses volume of pigment chemistry. It plays a crucial role in the governance of the dye and printing market. These pigments synthesized from a simple approach of diazotization and coupling. Different routes and modifications were made to obtain the desired color properties[1]. Azo dyes are the most used dyes and account for more than 60 % of total dyes[2,3]. Approximately 70 % of all the dyes used in industry are azo dyes[4,5] .

The functional group (-N=N-) uniting two symmetrical and/or asymmetrical identical or non-azo alkyl or aryl radicals[6]. Characterize these compounds, Azo dyes are the most important synthetic colorants[7], as well as their harmful effects on humans and aquatic life, have aroused urgent calls for the treatment of effluents containing Azo dyes to eliminate them or convert them into useful and safe products[8,9].

## (1-2) Types of Azo Dyes Refer to Azo Grouping Number

Azo dyes are divide according to the number of azo group linkages, which is in the same molecule of the pigment such as monoazo, diazo, trisazo, polyazo[10].Figure (1-1) shows some monoazo, diazo and trisazo dyes.

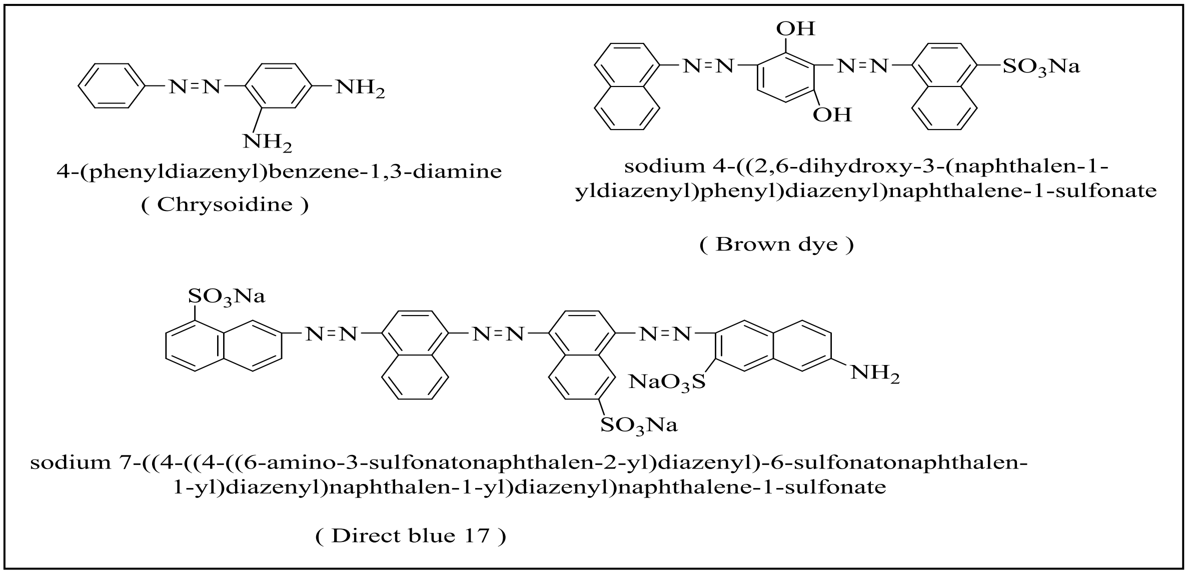
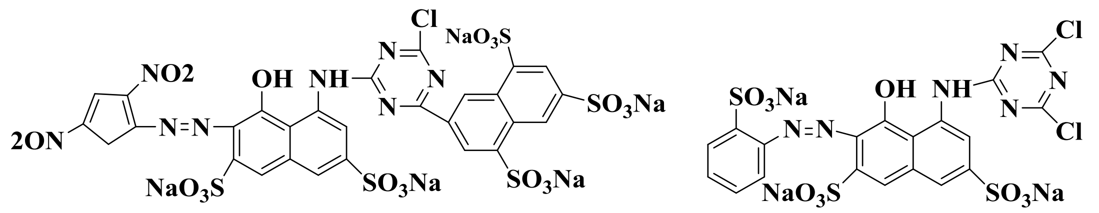


Figure (1-1) shows some monoazo, disazo and trisazo dyes.

## (1-3) Divided of azo dyes according to reactive functional groupings

### (1-3-1) Mono and Dichlorotriazine: -

These dyes have a good affinity for cellulose at a temperature of (20–30 °C). The replacement of a single chlorine by the hydroxyl ion or the cellulosic ion leads to a remarkable decrease in the reactivity of the second chlorine. In an alkaline medium, the ionization of the hydroxyl group results in a relocation of the negative charge of the atoms of the triazine ring, while the chlorine atom is inactivated and the carbon which bonds to the chlorine becomes less electrophilic[11,12] . Figure (1-2) shows some dyes.



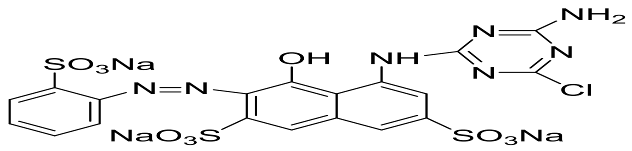
**sodium 7-(4-chloro-6-((7-((2,4-dinitrocyclopenta-1,3-dien-1-yl)diazenyl)-8-hydroxy-3,6-disulfonatonaphthalen-1-yl)amino)-1,3,5-triazin-2-yl)naphthalene-1,3,5-trisulfonate**

**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) Some Mono and Dichlorotriazine Dyes.

### (1-3-2)Mono-amino-chlorotriazine:-

It has the same chromophoric groups of dichlorotriazine. It carries an active chlorine and the group $NH_2$, figure (1-3). These groups are less active with respect to dichlorotriazine. The link -NH- linking the chromophore and the reactive group have an influence on the dyeing properties and the solubility of the dye[6].

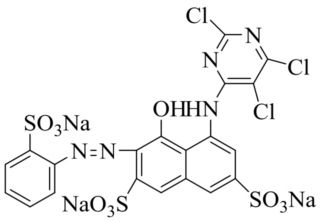


sodium (Z)-5-((4-amino-6-chloro-1,3,5-triazin-2-yl)amino)-4-hydroxy-3-((2-sulfonatophenyl)diazenyl)naphthalene-2,7-disulfonate

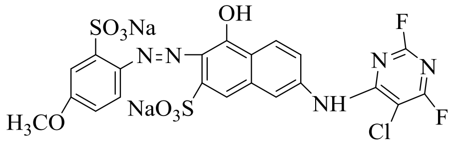
**Figure** (1-3) Shows Mono-Amino-Chlorotriazine Dye Example.

## (1-3-3)Pyrimidines:-

In general, include the di and tri-chorpyrimidine derivatives, chlorfluoropyrimimidine and fluoropyrimidine derivatives figure (1-4)[6].



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

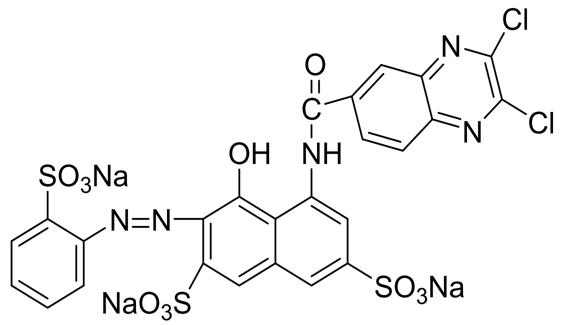


sodium 7-((5-chloro-2,6-difluoropyrimidin-4-yl)amino)-4-hydroxy-3-((4-methoxy-2-sulfonatophenyl)diazenyl)naphthalene-2-sulfonate

**Figure** (1-4) Shows Pyrimidines Dyes Example.

## (1-3-4)Dichloroquinoxaline: -

This type of dye characterized by high reactivity to dichloropyrimidine dyes, dichlorotriazine dyes, and difluoropyrimidine dyes [6]. Figure (1-5) show example.

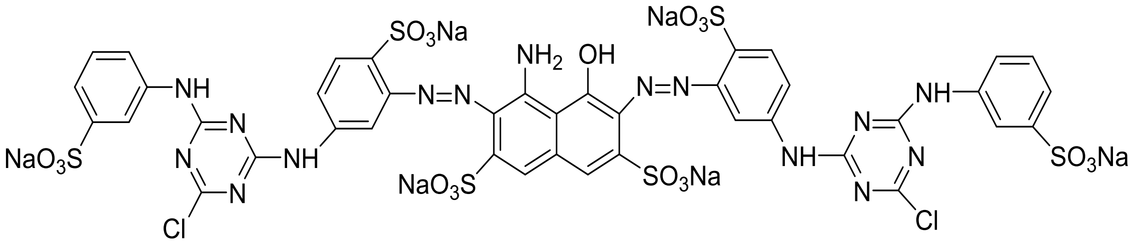


sodium 5-(2,3-dichloroquinoxaline-6-carboxamido)-4-hydroxy-3-((2-sulfonatophenyl)diazenyl)naphthalene-2,7-disulfonate

**Figure** (1-5) Dichloroquinoxaline Dye Example.

## (1-3-5)Bis-mono chlorotriazine: -

This type of dye applied to the cellulosic fiber substrates because of its better affinity for depletion at a temperature of 80°C, which makes it possible to obtain a fixation rate between 70 and 80 %. The molecules of this kind of dye have been characterized by a twifold dimension to its homo-functional counterpart [6,13] .Figure (1-6) shows example.

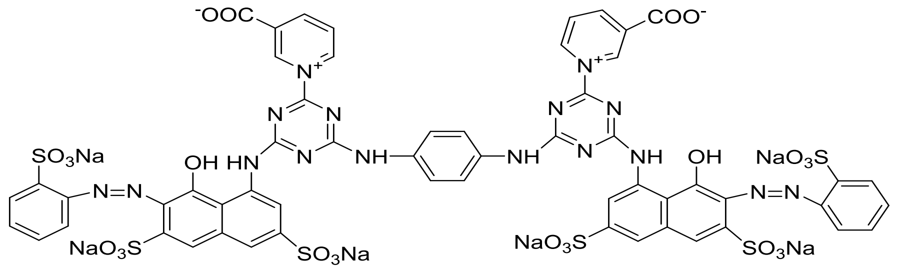


sodium 4-amino-3,6-bis((5-((4-chloro-6-((3-sulfonatophenyl)amino)-1,3,5-triazin-2-yl)amino)-2-sulfonatophenyl)diazenyl)-5-hydroxynaphthalene-2,7-disulfonate

**Figure** (1-6) Bis-Mono Chlorotriazine Dye Example

## (1-3-6) Bis-amino nicotinotriazine: -

These dyes obtained by a substitution reaction of the chlorine in the triazine ring by a carboxy pyridine acid, figure (1-7). The application temperature at depletion is higher than boiling in a neutral medium and can also be applied at 80 ˚C at pH = 11 as in the case of mono chlorotriazine[6].

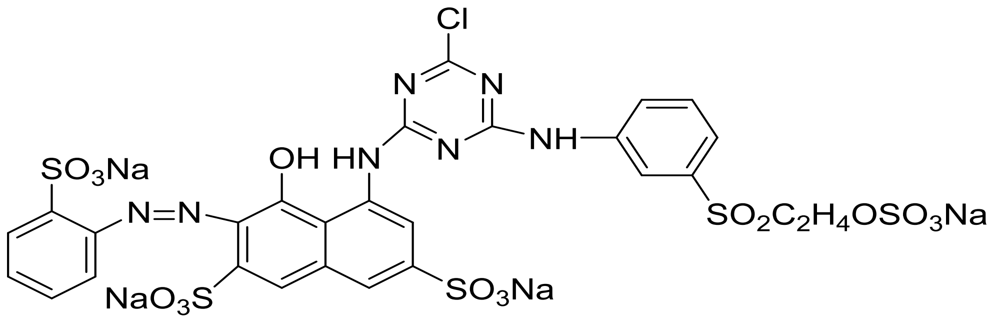


sodium 1-(4-((4-((4-(3-carboxylatopyridin-1-ium-1-yl)-6-((8-hydroxy-3,6-disulfonato-7-((*Z*)-(2-sulfonatophenyl)diazenyl)naphthalen-1-yl)amino)-1,3,5-triazin-2-yl)amino)phenyl)amino)-6-((8-hydroxy-3,6-disulfonato-7-((*Z*)-(2-sulfonatophenyl)diazenyl)naphthalen-1-yl)amino)-1,3,5-triazin-2-yl)pyridin-1-ium-3-carboxylate

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

## (1-3-7)Monochlorotriazine –sulphatoethylsulphone:-

The Monochlorotriazine-sulphatoethylsulfone can be synthesized by the reaction of dichlorotriazine with the aryl amine containing the sulphatoethylsulfone group[14].



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 example.

## (1-4) Azo Dyes Properties:-

Azo compounds and their derivatives are among the most widely used reagents, as these compounds are characterized by high stability, speed of reaction with metal ions, the severity of sensitivity, and very high selectivity, and the reason for this high stability is the presence of the Azo bridge group (-N = N-).

Azo-cyclic compounds are preferred over non-cyclic compounds due to their remarkable color, stability, sublimity, and strong coloration. In addition, the heterocyclic ring gives pigments that are of great importance due to their high absorption during coating and is considered environmentally friendly [15, 16].

Azo dyes possess a group of optical properties and physical properties where they can remain stable in many different conditions. Azo dyes have been used in optical treatments due to the luminosity property due to light absorption and also these dyes can be effective in the infrared region which is excellent in the pharmaceutical industry [17, 18].

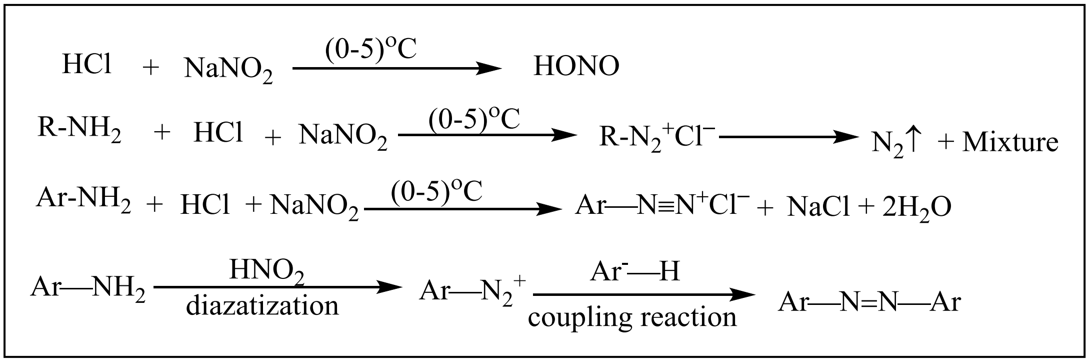
Azo dyes have the ability to absorb in the ultraviolet region where Azo compounds can be used in a wide variety of optical applications such as optical storage, optical recognition, signal processing, optical modulators, holographic and nonlinear optical devices as well as in various types of multi-use optical devices [19–21]. In recent years, Azo compounds have entered many electronic applications including the manufacture of electronic absorbable chips and other electronic manufacturing [22].

Azo compounds act as corrosion inhibitors, which are used frequently due to their low costs. It has also been found that the inhibition effect is influenced by some of the physical and chemical properties of the organic inhibitor related to their functional groups, the structural effects of the reagent, the electron density on the donor of atoms and the orbital nature of the donated electrons[23].

Azo compounds have both emission and absorption properties; therefore, they have entered many industries, including the manufacture of laser pigments [24–26].

## (1-5) Preparation of Azo Dyes[27]:-

The azo dyes are prepared in two steps: The first step is called a diazotization of the basic aromatic amine with sodium nitrite in an acidic mineral medium (HCl, $H_2SO_4$, etc.), using an aqueous solution of sodium nitrite and acid at low temperatures (0 – 5 °C)to give easily soluble salts in water called diazonium salts. , as shown in the following chemical equations.



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

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

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

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

**Scheme** (1- 1) Preparing Azo Dyes

The second step: the coupling step (synthesis of azo dyes),which included the conjugation of the aromatic diazonium ion with active aromatic compounds in alkaline conditions, where the diaziume salt loses a halogen atom, such as chlorine, with an active hydrogen atom in another aromatic compound (phenols and amines) in the form of hydrochloric acid, as shown in the previous diagram.

## (1-6)Cobalt and Iron founded and uses:

### (1-6-1) Cobalt:-

Pure Cobalt is a steel-gray, shiny, hard metal and has a molecular weight of 58.933 g/mol. Cobalt metal that is commonly used in various metal alloys is in the ground state (zero valence state), and it's compounds occur in two predominant oxidation states ($2^+$ and $3^+$). While Co (II) and Co (III) are the common oxidation states, Co (II) is far more stable in normal aqueous conditions; Co (III) may be stabilized by changing the reagent environment , Cobalt is present in its $2^+$ valence state in most commercially available Cobalt compounds and in the environment. Currently available data indicate that implant derived from Cobalt -containing metal prosthesis exists primarily in the $Co^{2+}$ oxidation state. While $Co^{3+}$ is thermodynamically unstable under typical redox and pH conditions, the interconversion between $Co^{2+}$& $Co^{3+}$ is important in the biological reactions of vitamin $B_{12}$ [28].

Cobalt is a hard ferromagnetic, silver-white, hard, lustrous, brittle element. It is a member of group VIII of the periodic table. Like Iron, it can be magnetized. It is similar to Iron and nickel in its physical properties. The element is active chemically, forming many compounds. Cobalt is stable in air and unaffected by water, but is slowly attacked by dilute acids[29].

Cobalt is found in the minerals cobaltite, smaltite, and erythrite, and is predominately linked with nickel, silver, lead, copper, and Iron ores, from which it is most repeatedly acquired as an after-effect. It is also ready in meteorites. Essential ore deposits are, establish in Zaire, Morocco, and Canada. The U.S. Geological Survey has declared that the undermost of the north-central Pacific environment may have cobalt-rich deposits at comparatively surface depths in the water close to the Hawaiian Islands and other U.S. Pacific territories [29] .

Cobalt is an essential element for living organisms as a component of vitamin $B_{12}$, which plays an important role for the production of red blood cells and the prevention of pernicious anemia[28]. Insufficient levels of cobalt causes several diseases such as anemia, metabolic disorders, retarded growth and degeneration of nerve cells[30,31]. On the other hand, when it is taken in excessive amounts, this element has been reported as toxic causing goiter, vomiting, diarrhea, increased blood pressure, slowed respiration, giddiness, tinnitus, deafness due to nerve damage and cardiomyopathy[30].

It is mixed with Iron, nickel, and other metals to produce Alnico, an alloy of, the uncommon magnetic force with much substantial use. Satellite alloys included cobalt, chromium, and tungsten, utilized for high-speed, strong, high-temperature, harvesting material. Cobalt is also hired in other magnetic steels & stainless steels and in alloys used in jet turbines and gas Cobalt turbine dynamo. The mineral is used in electroplating because of its aspect, solidity, and, impedance to oxidation. The salts were used for centuries to make bright and regular blue colors in porcelain, glass, pottery, tiles. It is the master component in Sevre's and the nard’s blue. A solution of the chloride used as a sympathetic ink. Cobalt accurately used in the form of chloride, sulfate, acetate, or nitrate has been established active in mend a confirmed, metal insufficiency disease in animals[29].

### (1-6-2) Iron:-

Iron is a chemical element with Fe as its symbol. It belongs to group 8, periodic number 4 of the periodic table. Its atomic number is 26. Iron metal is greyish in appearance, and is very ductile and malleable. It begins to rust in damp air and at elevated temperatures, but not in dry air. It dissolves readily in dilute acids, and is chemically active .

Iron is a comparatively considerable element in the world. It is found in the sun and many kinds of stars in large amounts. Its nuclei are very, constant. Iron is a major component of a meteorite portion known as siderites and is a secondary constituent of the other two meteorite portions. The core of the earth – 2150 miles in radius thought to be in general collected of Iron together about 10% hydrogen. Metal is the fourth most abundant element, by weight, which industrializes the crust of the earth. The most collective ore is hematite, which is frequently seen as black sands along beaches and banks of streams[29].

Iron is a vital constituent of plant and animal life and appears in hemoglobin. Taconite is becoming increasingly important as a commercial ore. The pure metal is not often. Iron encountered in commerce, but usually alloyed with carbon or other metals. Iron is a lustrous, ductile, malleable, silver-gray metal (group VIII of the periodic table). It known to exist in four distinct crystalline forms. Iron rusts in damp air, but not in dry air. It dissolves readily in dilute acids. Iron is chemically active and forms two major series of chemical compounds, the bivalent Iron (II), or ferrous, compounds and the trivalent Iron (III), or ferric, compounds[32].

Iron is the most used of all the metals, including 95 % of all the metal tonnage produced worldwide. Thanks to the combination of low cost and high strength, it is indispensable. Its applications go from food containers to family cars, from screwdrivers to washing machines, from cargo ships to paper staples. Steel is the best known alloy of Iron, and some of the forms that Iron takes include: pig Iron, cast Iron, carbon steel, wrought Iron, alloy steels, Iron oxides[33,34].

Iron believed to be the tenth most abundant element in the universe. Iron also the most abundant (by mass, 34.6%) element making up the Earth; the concentration of Iron in the various layers of the Earth ranges from high at the inner core to about 5% in the outer crust. Most of this Iron found in various Iron oxides, such as the minerals hematite, magnetite, and taconite. The earth's core believed to consist largely of a metallic Iron-nickel alloy. Iron is essential to almost living things, from microorganisms to humans[35].

A more common problem for humans is Iron deficiency, which leads to anemia. A man needs an average daily intake 7 mg of Iron and a woman 11 mg ; a normal diet will generally provide all that is needed [36] .

## (1-7) Solvent extraction

Solvent extraction is a mature technique in that extensive experience has led to a good understanding of the fundamental chemical reactions. At the same time, compared to many other chemical separation processes like precipitation, distillation, or pyro metallurgical treatment. New reagents continually developed, spurred on by computer modeling, and efficient contacting equipment is coming into use.

Considering such factors as demands for higher product purity, less pollution, and the need for recovering substances from more complex matrices and more dilute resources, the efficiency and high selectivity of solvent extraction should make it an increasingly competitive separation process both in research and in Industry[37].

The term solvent extraction refers to the distribution of a solute between two immiscible liquid phases in contact with each other, a two-phase distribution of a solute. Selective transport of mater in micro amounts to macro quantities between two solvent that don't immiscible; extraction based on differences in solubility; selectivity achieved by acidity control and complex formation[38].

It can described as a technique, resting on a strong scientific foundation. Scientists and engineers are concerned with the extent and dynamics of the distribution of different solutes - organic or inorganic and its use scientifically and industrially for separation of solute mixtures[37].

Liquid-liquid extraction as defined above is a two-phase ternary system; it therefore follows from Gibb's phase rule, namely (1-1):-

$$P + V = C + 2 \quad \ldots (1\text{-}1)$$

Where P is the number of phases, V the number of degree of freedom, and C the number of components, that at constant temperature and pressure, a three-component system has only one degree of freedom .Thus if the concentration of the solute in one phase is constant, the concentration of the solute in other phase is also fixed. According to the distribution, law proposed by Berthlot and Jung fleisch and developed by Nernst[39].Nernst distribution isotherm which derived as:

Chemical potentials of species A in organic and aqueous phases are represented by equation (1-2) and (1-3)

$$\mu_1 = \mu_1^o + RT \ln [A]_o \ldots (1\text{-}2)$$

$$\mu_2 = \mu_2^o + RT \ln [A]_{aq} \ldots (1\text{-}3)$$

When the distribution equilibrium is attained, $\mu_1 = \mu_2$ is held, and the next relation is derived as (1-4)

$$[A]_o / [A]_{aq} = \exp\{(\mu_2^o - \mu_1^o)/ RT\} = K_D \ldots (1\text{-}4)$$

Where

$K_D$ : is the distribution constant or the partition coefficient.

$\mu_1, \mu_2$ : The chemical potential of solute A in organic and aqueous phase

$\mu_1^0, \mu_2^0$: The standard chemical potential of solute A in organic and aqueous phase

$[A]_o, [A]_{aq}$: The molar concentration of solute A in organic and aqueous phase

T: Absolute temperature

R: Gas constant

## (1-8) Principle of Extraction

Extraction or separation of dissolved chemical component X from liquid phase A is accomplished by bringing the liquid solution of X into contact with a second phase, B, given that phases A and B are immiscible. Phase B may be a solid, liquid, gas, or supercritical fluid. A distribution of the component between the immiscible phases occurs. After the analyte is distributed between the two phases, the extracted analyte is released and/or recovered from phase B for subsequent extraction procedures or for instrumental analysis. The theory of chemical equilibrium leads us to describe the reversible distribution reaction as

$$\mathbf{X_A} \rightleftarrows \mathbf{X_B} \ldots\ldots\ldots \ (1\text{-}5)$$

and the equilibrium constant expression, referred to as the Nernst distribution law(1), is

$$KD = \frac{[X]B}{[X]A} \quad \text{-------------} \ (1\text{-}6)$$

Where the brackets denote the concentration of X in each phase at constant temperature (or the activity of X for non-ideal solutions). By convention, the concentration extracted into phase B appears in the numerator of equation (1-6). The equilibrium constant is independent of the rate at which it was achieved. The analysts function is to optimize extracting conditions so that the distribution of solute between phases lies far to the right in equation (1-5) and the resulting value of KD is large, indicating a high degree of extraction from phase A into phase B. Conversely, if KD is small, less chemical X transferred from phase A into phase B. If KD is equal to 1, Equivalent concentrations exist in each phase[40]**.**

A separation can made more efficient by adjustment of the proportions of organic and aqueous phases. The optimum ratio for the best separation is given by the Bush-Densen equation (1-7) [38]

$$\mathbf{V_o/V_{aq} = (1/D_AD_B)^{1/2}} \ldots\ldots\ldots \text{(1-7)}$$

## (1-9) The Percent of Extraction

The Percent of extraction depends on the values of D and on the comparative volumes of the solvents[38]. The percentage of separation in equation (1-8)

$$\mathbf{E\% = 100D / [D + (V_{aq}/V_o)]} \ldots\ldots\ldots \text{(1-8)}$$

Where $V_{aq}$ and $V_o$ are the volumes of the aqueous and organic phases respectively (1-9), or

$$\boldsymbol{E}\% = \frac{\mathbf{100}\boldsymbol{D}}{(\boldsymbol{D}+\mathbf{1})} \quad \ldots\ldots\ldots\ldots\ldots \text{(1-9)}$$

When the volume of solvents is equal. If the distribution ratio is large ($>10^2$), one extraction process may affect the virtually quantitative transport of the solute, while with smaller values of D more than one process of separation will be done. The quantity of solute that remains in the water phase readily studied for any times of separation with similar volumes of solvent that are immiscible from the equation (1-10)

$$\mathbf{(C_{aq})_n = C_{aq}[V_{aq}/(DV_o+V_{aq})]^n \ldots\ldots\ldots\ldots (1\text{-}10)}$$

When (C aq)n is the contain of solute reduced in the water layer, volume V aq after n separation with volumes Vo of the organic layer, and C aq is the contain of solute primarily existent in the water layer. If the amount of D is known, equation (1-10) is helpful for calculating the optimum conditions for transport quantity[38].

## (1-10) Extraction method [38]

The requisite matter for a salute to being separate from an aquatic solution is that it must be don't has a charge or can form a fraction of an uncharged ionic overall. Charge neutrality decreases the electrostatic reaction between the matter and water and hence lowers its aquatic solubility. Separation into a nonpolar organic solvent occurs if the kind not hydrated, or if mad coordinating groups such as big organic molecules simply separate the coordinated water. There are three kinds of chemical compounds, which can fulfill one or more of these requirements:

(1) Covalent, neutral molecules e.g. iodine, germanium tetrachloride and benzoic acid.

(2) Uncharged reagent e.g. mineral complex of acetylacetone, 8hydroxyquinoline, diphenylthiocarbazone, etc.

(3) Ion-combination group e.g. $(C_6H_5CH_2)_3NH^+$ , $GaCl_4^-$ , Fe(O-phenanthroline)$_3^{+2}$ , $2ClO_4^-$ , $[(C_2H_5)_2O]_3H^+$ , $FeCl_4^-$

The division of all three kinds must conform to the Nernst equation, however, in most cases; the focus of separated forms affected by chemical balance including them and other components of the system. This should be occupied with calculation when determining the best conditions for quantitative separation.

## (1-11) Extraction systems [38]

Batch separation is the simple and ultimate useful method, the two-layer being shaken with each other in a separatory funnel until the balance is reached and then allowed to break into two phases. If (D) values are large, a solute possibly transports quantitatively in one separate, on the other hand, several may be, requisite. If multi extractions are wanted, it is useful to be solvent density more than water, e.g. carbon tetrachloride or chloroform, so that the water layer can remain in the separatory funnel while the procedure is complete.

Continued separation consists of distilling the organic solvent from a reservoir flask, condensing it, and allow it to pass into the aquatic layer previously retreat to the reservoir flask to be recycled. The process is especially helpful when the (D) values are small ($D < 1$), and wherever the number of batch separation required for quantitative transport would be inconveniently large.

Disconnected countercurrent apportionment is a process devised by Craig that enables matter with the same (D) values to extract. The process involves a chain of single separate perfect spontaneously in specially designed systems. This consists of multi-times (50 or more) corresponding interlocking glass extraction units mounted in a frame that is rocked and titled automatically to mix and extract the layer during each extraction stage. At first, the same volumes of the extracting solvent, which must be the heavier phase, placed in either of the extraction units. This can be named the stationary phase as each part remains in the same unit anywhere the steps.

## (1-12) Selection of solvents [41]

The selectivity and efficiency of LLE is critically governed by the choice of the two immiscible solvents. Often the organic solvent for LLE is chosen because of its:

**1-** Low solubility in the aqueous phase (typically <10%).

**2-** High volatility for solvent evaporation in the concentration stage.

**3-** High purity (directly linked to the solvent evaporation process) which could pre-concentrate any impurities within the solvent.

**4-** Compatibility with the choice of chromatographic analysis.

**5-** Polarity and hydrogen-bonding properties that can enhance compound recovery in the organic phase.

## (1-13)Sequential extraction:-

In order to separate more, carefully labile (inorganic and organic) from remained phases and to allow more insight into particulate speciation, a sequential extraction method has been advanced. These processes are set up on a combination of fixed separation often used by soil scientists. Sequential separation technique may also be used, together with in situ and in vitro studies of commutation processes, to supply useful data for layout the hazards resulting from the pollution of aqueous residue. Such models require information on conditional engaged constants. Sequential separation methods are a perfect tool for the fulfillment of the processes responsible for the lessening in particulate trace metal, concentricity observed in different estuaries for many transition metals[42].

To determine the fractions of the elements, a sequential extraction method was used[43] , However, various complicated sequential extraction procedures were used to provide more detailed information regarding different metal phase associations[44].

A novel sequential extraction method for evaluation of the mobilization behavior of rare earth elements in soils and mine tailings materials is presented , was studied[45].

Neng-min Zhu, etal , 2018 [46], were applied a sequential extraction analysis to Pb (II) recovery by zerovalent Iron-based particles, was a surface-mediated process and more than 85% of recovered Pb (II) was immobilized.

Sequential extraction of U (VI), Eu (III) and Am (III) has been performed from acidic aqueous solutions ($HNO_3$, $HClO_4$) into the ionic liquid and UV—Vis spectroscopy measurements were performed to characterize the extracted species[47].

## (1-14)Substoichiometric extraction:-

Substoichiometric extraction of metals involve the use of chelating agent, the quantity of which is so chosen as to extract only a part of the metal present. The rapidity, simplicity and high selectivity of this method make it very attractive[48].

Substoichiometric radiochemical solvent extraction method using a newly designed organic moiety, N-thioacetylbenzamide as extractant and chloroform as solvent at aqueous pH=4 has been successfully to extracted gold[49].

Determination of Iron (III) by substoichiometric extraction with 2-methyloxine into n-butanol is being reported. The method has been applied for the determination of the metal in several analyzed samples like Mn-bronze, Al-bronze and dolomite[50].

A rapid and sensitive substoichiometric radiochemical procedure has developed for the extraction of cobalt with potassium salts of ethyl, propyl, butyl, pentyl and benzyl xanthates. The relative extractabilities of the cobalt-xanthate complexes into chloroform and carbon tetrachloride studied. Substoichiometric quantification methods were developed in each case and utilized to determine the cobalt content present in standard solutions as well as biological samples[51].

## (1-15)Literature review

The most important methods for separating metals based on extraction. Manganese, cobalt, nickel and lithium were extracted by solvent extraction fractionation from Lithium-ion batteries[52].A simple and fast method for the determination of cobalt in vitamin $B_{12}$ and water samples was based on the pre concentration of the element using dispersive liquid-liquid micro extraction and subsequent detection by digital image calorimetry[53]. Zinc(II), Copper(II), Cadmium(II), Mercury(II) and Cobalt(II) were extracted by solid phase extraction using Azo-Dye Functionalized Resin[54]. In 2018, Elnaz Koosha ,etal[55], studied a rapid and selective technique for extraction, pre concentration and determination of trace amounts of cobalt in water and pharmaceutical samples by air-assisted liquid–liquid micro extraction combined with flame atomic absorption spectrometry is proposed, 1-Nitroso-2-naphthol is used as a complexing agent and 1- octanol as an extraction solvent.

Liquid phase micro extraction had been propose for the determination of cobalt in egg yolk and Vitamin $B_{12}$ at trace levels. N, N-Dimethyl benzyl amide used as a switchable solvent and converted to protonated DMBA form by the addition of dry ice. Cobalt was complexed with 1, 5- diphenyl carbazone and extracted into the DMBA phase[56].

Cobalt (II) forms well chloroform-extractable ternary complex with -4-(2-pyridylazo) resorcinol and Nitron. The complex could be regarded as an ion associate between an intensively colored anion [57].

After pinpoint all optimum conditions for extraction Cobalt (II) as ion pair association complex or chelated complex with complexing agent 1-[2-pyridyl azo] -2-naphthol which , dimonirtrate $\lambda_{max}$ for complex extracted was (446nm.) more stable complex formation was at pH= 7 and 60μg Co(II)/5ml with ($1\times10^{-4}$M) 1-[2-pyridyl azo] -2-naphthol dissolved in chloroform and shaking time is 10 minutes[58].

Hongyan Chen ,etal , 2018[59] , were separated Cobalt(II) and Nickel(II) by solvent extraction with trihexyl (tetradecyl) phosphonium chloride , This work successfully applies the flowsheet model to replicate the reported experiments. Single-stage batch extraction and multistage continuous extraction using ionic liquid to separate cobalt and nickel are simulated and the predictions shown to be in good agreement with experimental results.

Solvent extraction and separation of Cobalt(II) from Ni-rich leaching solution , the extraction and separation of cobalt and nickel from impurities-free chloride leaching solution was investigated in IS-RPB using P507 as the extractant diluted by kerosene[60].

Lihua Zhang , etal. , 2017 [61] ,were studied liquid-liquid extraction for the separation of Co (II) from Ni (II) with Cyanex 272 Using a pilot scale re-entrance flow micro reactor , in this study they found the micro reactor was be very effective in liquid-liquid extraction and separation processes and allowed using a wide range of flow rates up to 9 l/h . With high flow rates, the residence time could be minimized to achieve a high throughput with no decrease in extraction and separation efficiency.

Carlos A. Nogueira ,etal., 2009[62], reported a new solvent-extraction process for the separation of cadmium, cobalt، and nickel in sulphate solutions coming from the hydrometallurgical processing of spent Ni-Cd batteries.

Recovery of Cobalt from waste mobile phone batteries, by leaching with sulfuric acid and hydrogen peroxide was carried out with subsequent selective separation of cobalt by means of liquid–liquid extraction[63].

Liquid-liquid extraction of Cobalt (II) and Zinc (II) from aqueous solutions using novel ionic liquids as an extractant, was studied by Aneta Łukomska , etal., 2020 [64] , extraction efficiencies of Co (II) and Zn (II) from aqueous phase with new ionic liquids in comparison that already studied in literature , but without addition of acids and at low temperatures are presented, thus, the new, environmental-friendly method of extraction of metal ions is proposed.

A novel ammonium, benzyldimethyloctadecylammonium bis (2,4,4-trimethylpentyl)phosphinate،didecyldimethylammonium saccharinate, and didecyldimethylammonium acesulfamate، were synthesized and used for this extraction.

On other hand, a selective and sensitive solvent extraction with p-methylphenyl thiourea system was present, the selectivity of the separation and determination of Osmium (VIII), Ruthenium (III), and Iron (II) from synthetic mixtures. The separation of these metal ions was resolved by taking advantage of different acid concentrations[65]. The mode of action of Iron(III) uptake from sulfate solutions by the commercial extractant Cyanex 272, bis (2,4,4 trimethylpentyl)phosphinic acid, has been studied using conventional solvent extraction methods[66].

Iron(III) was extracted and determined with schiffbase 2-[(2-hydroxyphenylimino( methyl]-4-nitrophenol , extracts Fe (III) quantitatively (99.95%) into chloroform from an aqueous solution of pH range 4.0-6.0[67].

To recovery of Iron from Electric Arc Furnace smelter slags via hydrochloric acid leaching and solvent extraction was investigated with a view to developing a simple hydrometallurgical route for the recovery of Iron from secondary sources such as smelter slags[68].

Iron (III) ion removal from aluminum solutions to explore the basic data for the recovery of aluminum resources from coal spoil. Fe removal was greater than 97% under the conditions of reaction time exceeding 20 min, initial aqueous pH of 1.5–2, 1:1 phase ratio, and room temperature[69]. Removal of Iron and Boron by solvent extraction with ionic liquids and recovery of neodymium metal by direct electrodeposition, in this study, the mechanism of $Fe^{3+}$ ion extraction was investigated in the TBP/[P2225][TFSA] system. According to the performed analysis, the $Fe^{3+}$ extraction is based on cation exchange with ionic liquids[70].

Methyl Isobutyl Ketone and Methyl Phenyl Ketone presented as suitable agents for extraction of Fe (III) from concentrated hydrochloric acid solutions. The maximum removal percentages of Iron (III) ions using both solvents achieved within the first 20 min. The removal percentages of Fe (III) ions increase sharply by increasing solvent ratios up to 14 %[71].

The oximes of 1-(2-pyridyl) tridekane-1-one and (1 -4) -pyridyl) tridecane-1-one were used as model hydrophobic extractant for Iron (III) from a chloride media. Both studied pyridyl ketoximes have the ability to extract Iron (III) from chloride solutions. The highest degree of Iron (III) extraction was observed for 1-(2-pyridyl) tridecane-1-one oxime. During extraction with 4-pyridyl ketoxime, a precipitated complex was observed, which has a disadvantageous effect for the extraction process[72].Extraction technology of Fe(III) is important to the low grade ferrous ore processing and decontamination of industrial products such as waste printed circuit boards. The performance of extraction and stripping of Fe (III) from hydrochloric acid with N,N,N′,N′-tetra-2-ethylhexyldiglycolamide in different diluents was studied in order to understand the relationship between the nature of the diluents and their extraction of Fe (III)[73].

Use of N,N-tetra substituted malonamides such as N,N-dimethyl-N,N-diphenylmalonamide and N,N-dimethyl-N,N- diphenyl tetra decyl malon amide for the extraction of Iron (III) from acid chloride solutions is investigated, in order to evaluate the possibility of using this family of compounds to extract base metal cations, Therefore, for these two systems, the chemical structure of the malonamide derivative directly affects the type of the metal ion transfer reactions from the aqueous to the organic phase[74].

## (1-16)The aim of study:-

The aim of this study are to:-

1. Synthesis a new azo reagent that use to development the extraction process of metal ions. Where synthesis the reagent derivative (7-((4-(dimethylamino) phenyl) diazenyl) quinoline-8-ol) that symbolizes (DPDQ), and characterized by spectroscopic methods (UV-Vis., FT-IR, $^{1}$HNMR and $^{13}$CNMR).
2. Development a liquid – liquid extraction process by this new reagent to extraction Cobalt (II) and Iron (III) ions from aqueous solutions, in addition, Study the sequential extraction of Cobalt (II) and Iron (III) ions .
3. Study the optimum conditions for extraction process , that represented by factors effected on distribution ratio and the percentage of extraction , on the extract of Co (II) and Fe (III) ions from aqueous solution , such as acidity of medium , time of shaking , concentration of ion , temperature , polar of solvent that use in extraction , etc.
4. Study the stoichiometry of extracted complexes by using Jobs method, molar ratio and substoichiometric method, and calculate the stability of extracted complexes and determined the stereo shape for it.
5. Calculation the thermodynamic functions for the extracted complexes.
6. Preparation of the two solid complexes for Co (II) and Fe (III) ions with the new reagent.
7. Study development of a new method for determining the concentration of Co (II) and Fe (III) ions in the organic phase.
8. Applied the development method of extraction on biological and drug samples.

# Chapter Two

# Experimental

## (2-1) Apparatus:

The apparatus that used in this study listed in table (2-1).

**Table (2-1) Apparatus used**.

| No. | Instrument name | Type & origin | The work | Place |
|---|---|---|---|---|
| 1. | Digital balance | Sartorius BS-210 (Germany ) | Wight the materials | University of Kerbala – college of Science |
| 2. | Double beam UV-visible spectrophotometer | Cecil 7200, (England). | Record electronic spectrum | University of Kerbala – college of Science |
| 3. | FT-IR spectrophotometer | 8400, Shamadzu, (Japan) | Record FT-IR spectrums | University of Kerbala – college of Science |
| 4. | Mass spectrophotometer | 5975C VL MSD with Tripe-Axis Detector(Agilent Technologies) | Record mass spectrums | (Iran) |
| 5. | Molar conductivity meter | WTW-270-inolab, (Germany). | Record conductivity | University of Kerbala – college of Science |
| 6. | NMR spectrophotometer | (VARIAN) , 500 MHZ | Record $^{1}$HNMR ,$^{13}$CNMR spectrums | (Iran) |
| 7. | pH-Meter | Hanna, (Italy) | Adjust pH | University of Kerbala – college of Science |

| | | | | |
|---|---|---|---|---|
| 8. | Shaker | Gemmy Orbit VRN-480 (England) | Shaking | University of Kerbala – college of Science |
| 9. | Single beam visible spectrophotometer | Sp-300(Japan) | Record the absorbance | University of Kerbala – college of Science |
| 10. | Temperature control circulator | BS-11, (Korea) | Temperature controller | University of Kerbala – college of Science |

## (2-2) Reagent and chemical materials used

The chemical materials in this study shown in table (2-1).

**Table (2-2) the chemical materials used in this study**

| Name | Chemical structure | Purity | Molecular Wight (g/mol) | Manufactured by companies |
|---|---|---|---|---|
| 1-Butanol | $C_4H_{10}O$ | 98.0% | 74.12 | ( Merck ) |
| 1-propanol | $C_3H_8O$ | 99.0% | 60.10 | ( Merck ) |
| 2-propanol | $C_3H_8O$ | 98.0% | 60.10 | ( Merck ) |
| 4-Amino-N, N-dimethylanilindihydrochloride | $C_8H_{14}N_2Cl$ | 98.0% | 209.12 | ( Merck ) |
| 8-hydroxyquinoline | $C_9H_7NO$ | 98.0% | 145.16 | (Fluka) |
| Acetone | $C_3H_6O$ | 98.0% | 58.08 | ( Merck ) |

| | | | | |
|---|---|---|---|---|
| Acetonitrile | $C_2H_3N$ | 98.0% | 41.05 | (BDH) |
| Ammonium chloride | $NH_4Cl$ | 98.0% | 53.49 | (Fluka) |
| Ammonium thiocyanate | $NH_4SCN$ | 99% | 76.12 | (BDH) |
| Amyl alcohol | $C_5H_{12}O$ | 98.0% | 88.15 | ( Merck ) |
| Ascorbic acid | $C_6H_8O_6$ | 99.5% | 176.12 | (Carlo Erba) |
| Benzene | $C_6H_6$ | 98.0% | 78.11 | (BDH) |
| Cadmium nitrate tetra hydrate | $Cd(NO_3)_2 \cdot 4H_2O$ | 99.0% | 308.47 | (Fluka ) |
| Carbon tetrachloride | $CCl_4$ | 99.8% | 153.82 | (BDH) |
| Chloroform | $CHCl_3$ | 99.5 % | 119.38 | (GCC) |
| Chromium(III) nitrate nona hydrate | $Cr(NO_3)_3.9H_2O$ | 99.0% | 400.15 | (Fluka ) |
| Cobaltous nitrate hex hydrate | $Co(NO_3)_2.6H_2O$ | 99.5% | 291.04 | (BDH) |
| Copper(II) nitrate hydrate | $Cu(NO_3)_2$ | 99.0% | 232.59 | (Fluka ) |
| Dichloromethane | $CH_2Cl_2$ | 98.0% | 84.93 | (BDH) |
| DMF | $C_3H_7NO$ | 98.0% | 73.09 | (BDH) |
| DMSO | $C_2H_6OS$ | 98.0% | 78.13 | ( Merck ) |

| | | | | |
|---|---|---|---|---|
| Ethanol | $C_2H_5OH$ | Absolute | 46.07 | (GCC) |
| Ethyl acetate | $C_4H_8O_2$ | 96.0% | 88.11 | (BDH) |
| Ferric nitrate nonahydrate | $Fe(NO_3)_3.9H_2O$ | 99.0% | 404.00 | (BDH) |
| Hydrochloric acid | HCl<br>37% W/V% | Analar | 36.46 | (Thomas Baker) |
| Hydrogen peroxide | $H_2O_2$ | 98.0% | 34.01 | (GCC) |
| Lead nitrate | $Pb(NO_3)_2$ | 99.0% | 331.20 | (BDH) |
| Mercuric nitrate hydrate | $Hg(NO_3)_2.H_2O$ | 99.0% | 342.16 | (BDH) |
| Methanol | $CH_4O$ | 98.0% | 32.04 | (BDH) |
| n-Hexane | $C_6H_{14}$ | 98.0% | 86.18 | (BDH) |
| Nickel nitrate hexa hydrate | $Ni(NO_3)_2.6H_2O$ | 99.5% | 290.81 | (BDH) |
| Nitric acid | $HNO_3$<br>65% W/V% | Analar | 63.01 | (Fluka ) |
| Potassium bromide | KBr | 99.0% | 119.01 | ( Merck ) |
| Potassium carbonate | $K_2CO_3$ | 99.0% | 138.21 | ( Merck ) |
| Potassium chromate | $K_2CrO_4$ | 99.0% | 194.20 | (Fluka ) |
| Potassium dichromate | $K_2Cr_2O_7$ | 99.5% | 294.19 | (Fluka ) |
| Potassium iodate | $KIO_3$ | 99.0% | 214.00 | (Fluka ) |

| | | | | |
|---|---|---|---|---|
| Potassium sulphate | $K_2SO_4$ | 99.5% | 174.27 | ( Merck ) |
| Potassium thiocnate | KSCN | 99.0% | 97.18 | (Fluka ) |
| Silver nitrate | $AgNO_3$ | 99.0% | 169.88 | (Fluka ) |
| Sodium chloride | NaCl | 98.0% | 58.44 | (Fluka ) |
| Sodium hydroxide | NaOH | 99.0% | 40.00 | ( Merck ) |
| Sodium nitrate | $NaNO_3$ | 99.0% | 84.99 | (Fluka ) |
| Sodium nitrite | $NaNO_2$ | 98.0% | 69.00 | (Fluka ) |
| Sodium sulphate | $Na_2SO_4$ | 99.0% | 142.04 | (Fluka ) |
| Strontium nitrate | $Sr(NO_3)_2$ | 99.0% | 211.63 | (Fluka ) |
| Tin chloride hydrated | $SnCl_2.2H_2O$ | 99.0% | 225.63 | ( Merck ) |
| Toluene | $C_7H_8$ | 98.0% | 92.14 | (Fluka ) |

## (2-3) Preparation of the reagent (DPDQ).

Preparation of reagent (7-((4-(dimethylamino) phenyl) diazenyl) quinoline-8-ol) from diazonium salt pairs of the(4-Amino-N,N-dimethylanilindihydrochloride) with (8-hydroxyquinoline) in an alcoholic medium by dissolving (2.0912 g, 0.01 mol) of 4-Amino-N,N-dimethylanilindihydrochloride in a solution obtained by mixing (2 mL) of concentrated hydrochloric acid with (25 mL) deionized water. (0.69 g , 0.01 mol ) of sodium nitrite dissolved in (10 mL) of deionized water drop by drop , stirring keep the temperature below 5 °C , and left the solution stile for (30 minutes) to complete the a zonation process and obtain a solution of diazonium chloride. This salt solution added slowly with continuous stirring to a solution (1.4516 g ,0.01mol) from 8-hydroxyquinoline that dissolved in a mixture of ( 25 mL) of ethanol and (15mL) of sodium hydroxide (2.5M) , was observed to discolor the solution in a reddish orange color .

The solution was left over night ,and modified the acidic function to (pH=5-6) to obtain reddish orange precipitate .The precipitate was filtrated and washed with deionized water to remove the sodium chloride that produced from the pairs and neutralization process ,and it dried and recrystallization from ethyl alcohol [75] , the yield was 75%.

## (2-4) Determination of the Ionization Constant of the Reagent (DPDQ): -

The value of the dissociation constant is determinate for the reagent (DPDQ) mentioned above and the range of the acidic function ranged between (pH =2-12). Where a set of volumetric flask of (5ml) capacity was taken and each of them contained (2.5 ml) of deionized water after adjusting the acid function of it Then, add the same volume (2.5ml) of the reagent solution prepared with concentrated ($1\times10^{-4}$ M) with stirring.

By scanning the maximum wavelength ($\lambda_{max}$) of the reagent has been determined formally, the form acidic (HIn) and the basic (In-), then the absorbance of the reagent solutions mixed with deionized water was measured at each maximum wavelength ($\lambda_{max}$) which was determined during the scanning process. Accordingly, graphs were drawn between the acidic function values on the x-axis and the absorbance on the y-axis, with noting that the values at the two wavelengths are drawn in the same figure, thus obtaining the dissociation point of the reagent(pKa), (it represents the point where the half of the reagent is in a basic form and the other half in its acidic form and is called a similarity point or the absorption symmetry (Isopiestic point) or (Isoabsorptive point) using the following relationship .

$$pKa = pH + log\frac{[HIn]}{[In-]} \quad \ldots\ldots\ldots\ldots(\ 2\text{-}1\ )$$

Since the solution contains equal concentrations of (HIn) and (In-) at the intersection point the value of pH is equivalent to a value of pKa of the weak acid (reagent).

$$pka = pH \quad \ldots\ldots\ldots\ (2\text{-}2)$$

## (2-5) Preparation of standard solutions

### (2-5-1) Preparation of standard solution of Cobalt (II) ion (1mg/mL).

Prepared by dissolving (0.4938g) of Co $(NO_3)_2.6H_2O$ in deionized water and the volume completed to 100 mL with deionized water in a volumetric flask. Dilute Co (II) ion solutions were ready by dilute this standard solution through the necessary size of water.

### (2-5-2) Preparation of standard solution of Iron (III) ion (1mg/mL).

Prepared by dissolving (0.7236g) of Fe $(NO_3)_3.9H_2O$ deionized water and the volume completed to 100 mL with deionized water in a volumetric flask. Dilute Fe (III) solutions were ready by diluting this standard solution through the necessary size of water.

### (2-5-3) Preparation of the reagent solution (DPDQ) (0.1% W/V)

Prepared by dissolving (0.1g) of (DPDQ) in Chloroform and the volume was completed to (100 mL) with Chloroform in a volumetric flask.

### (2-5-4) Preparation of ascorbic acid solution (2% W/V)

Prepared by dissolving (2g) of $(C_6H_8O_6)$ in deionized water and the volume was completed to (100 mL) with deionized water in a volumetric flask.

### (2-5-5) Preparation of Ammonium Thiocyanate solution (50% W/V)

Prepared by dissolving (50g) of $NH_4SCN$ in deionized water and the volume was completed to (100 mL) with deionized water in a volumetric flask.

### (2-5-6) Preparation of Hydrochloric acid solution (1 M)

Prepared by diluting(8.818mL) concentrated hydrochloric acid (37%,1.18g/cm$^3$) in 100 mL volumetric flask by deionized water. Dilute HCl solutions were ready by diluting this standard solution through the necessary size of water.

### (2-5-7) Preparation of sodium hydroxide solution

Prepared of NaOH solution (0.1M) by dissolving suitable weight of NaOH in deionized water.

### (2-5-8) Preparation of cation solutions.

Prepared solution 1000 µg of cations ($Pb^{2+}$, $Ag^{1+}$, $Cu^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Cr^{3+}$,$Hg^{2+}$ & $Sr^{2+}$) nitrate salt , dissolved their salts depending on the molecular weight of salt which were used for these elements in (25mL) of deionized water.

### (2-5-9) Preparation of anions solutions

Prepared solution 500µg and 1000µg of anions ($Cr_2O_7^{=}$, $Br^{-}$, $SO_4^{=}$, $CrO_4^{=}$, $SCN^{-}$, $IO_3^{-}$ and $CO_3^{=}$) potassium salt, dissolved their salts depending on the molecular weight of salt that were used for these elements in (25mL) of deionized water.

### (2-5-10) Preparation of $SnCl_2.2H_2O$ solution (1 M)

Prepared by dissolving (5.6407g) of $SnCl_2.2H_2O$ in (1mL) of hydrochloric acid and the volume was completed to (25 mL) with deionized water in a volumetric flask.

### (2-5-11) Preparation of $NH_4Cl$ solution (1 M)

Prepared by dissolving (1.3375 g) of $NH_4Cl$ in double deionized water and the volume was completed to (25 mL) with double deionized water in a volumetric flask.

### (2-5-12) Preparation of NaCl solution (1 M)

Prepared by dissolving (1.461 g) of NaCl in double deionized water and the volume was completed to (25 mL) with double deionized water in a volumetric flask.

### (2-5-13) Preparation of $Na_2SO_4$ solution (1 M)

Prepared by dissolving (3.551 g) of $Na_2SO_4$ in double deionized water and the volume was completed to (25 mL) with double deionized water in a volumetric flask.

### (2-5-14) Preparation of $NaNO_3$ solution (1 M)

Prepared by dissolving (2.1247 g) of $NaNO_3$ in double deionized water and the volume was completed to (25 mL) with double deionized water in a volumetric flask.

## (2-6) Construction of calibration curve of Co (II) and Fe (III) ions

Calibration curves were prepared for Co(II) & Fe(III), separately, according to colorimetric method by thiocyanate complex [76]. To measure the absorption of standard solutions of Co (II) and Fe (III), separately, the processes as follows: -

(5 mL) of solutions containing different concentrations of ions, ranged from ($2.002\times10^{-4}$M – $2.2715\times10^{-3}$ M) equivalent to (59 μg- 800μg) and from ($3.581 \times 10^{-6}$M – $2.50693 \times 10^{-4}$M) equivalent to (1 μg- 70 μg.) for Co (II) & Fe(III), respectively, were taken. To each solution of Cobalt(II) (0.5mL) of (0.5M) hydrochloric acid solution was added,2mL of Ammonium thiocyanate

(50%w/v) was added, (1mL) of ascorbic acid solution was added then added (1.5 mL) from acetone. The absorbance measured at ($\lambda_{max}$ = 620nm) against a reagent blank solution. Using (1cm) cell. The relationship between the absorbance and concentration was constructed to the calibration curve.

To each solution of Iron(III) (2mL) of (20%w/v) ammonium thiocyanate and (1mL) nitric acid (0.5M) was added then complete the volume with deionized water to the mark in (10mL) volumetric flask. The absorbance measured at ($\lambda_{max}$ = 480nm) against a reagent blank solution. Using cell absorption (1cm) after that the relationship between the absorption and concentration was drew for the calibration curve.

## (2-7) Extraction of Co (II) and Fe (III) ions by using reagent (DPDQ)

A solution containing (2mL) (200µg) of Co (II) adjusted to (pH=10) complete to (5ml) by deionized water poured into a separate funnel as aqueous phase. The pH of the solution is adjust by using diluted $HNO_3$ or NaOH solutions. The aqueous phase is equilibrated with (5mL) of reagent (DPDQ) (0.05%w/v) dissolved in chloroform for (10) minutes. The aqueous and the organic phase allowed separating. Co (II) set on spectrophotometric after separation in an aqueous phase with thiocyanate[76]. An aliquot of the water layer in the cells for absorbance measurements at ($\lambda_{max}$ = 620 nm). The absorption measured in the same steps used in calibration curve. The difference in metal concentration between the initial and final aqueous solution used to calculate the concentration of metal in the organic phase.

A solution containing (2mL) (200µg) of Fe (III) adjusted to (pH=7) with diluted nitric acid complete to (5mL) by deionized water poured into a separate funnel as aqueous phase. The pH of the solution adjusted by using diluted $HNO_3$ (0.1 M) or NaOH (0.1 M) solutions. The aqueous phase is equilibrated with (5mL) of reagent (DPDQ) (0.1%w/v) dissolved in chloroform for (15) minutes. The aqueous and the organic phase were allows to separate. Co (II) determined spectrophotometrically after extraction in aqueous phase with thiocyanate[76]. An aliquot of the aqueous phase in the cells for absorbance measurements at ($\lambda_{max}$ = 480 nm). The absorption measured in the same steps used in calibration curve. The difference in metal concentration between the initial and final aqueous solution used to calculate the concentration of metal in the organic phase.

## (2-8) Calculation of distribution ratio.

Distribution ratio had found by the following considering the concentration of ions in the organic phase represents the difference between primary concentrations and concentration after extraction in the aqueous phase. Because it’s easily dealing with the aqueous phase and used the following relationship to calculate the distribution ratio[38]: -

$$\mathbf{D = \frac{\text{Total concentration of ion in organic phase}}{\text{Total concentration of ion in aqueous phase}}}$$

$$\mathbf{D = \frac{[M]_{org.}}{[M]_{aq.}}}$$

**Where [M] = Molar concentration of ion**

## (2-9) Study effect of different parameters on the extraction.

To reach the best conditions of extraction, the effects of the following factors in the (D) values studied, represented by –

### (2-9-1) The Effect of (pH) on extraction

The pH function ranged from (2 to 12) organized by installing the concentration of Co (II) and Fe (III) ions , separately, in the aqueous phase by using different amounts of nitric acid solution (0.1M) and/ or sodium hydroxide solution (0.1M) using the pH-meter then added the organic phase , the values of distribution ratios followed up to find the appropriate pH for the extraction of Co(II) and Fe(III) ions, separately, with the reagent.

### (2-9-2)The effect of shaking time on extraction

Shaking times effect between (organic and aqueous) phase were studied under experimental conditions for extraction of Co (II) and Fe (III) ions, individually, with reagent (DPDQ) to study it's effect on (D) value.

### (2-9-3)The effect of solvent polarity on extraction

The effect of different solvents polarity of organic phase on (D) value studied under experimental condition to extract Co (II) and Fe (III), separately.

### (2-9-4)The effect of the presence of some anions as interfering ions

The effect of some anions on (D) value were studied under optimum condition for extraction of Co(II) and Fe(III) ions , separately , with reagent (DPDQ) by addition of (500µg) and (1000µg ) of some anion, separately , such as ($Cr_2O_7^{=}$, $Br^{-}$, $SO_4^{=}$, $CrO_4^{=}$, $SCN^{-}$, $IO_3^{-}$ & $CO_3^{=}$).

### (2-9-5) The effect of the presence of some cations as interfering ions

The effect of some cations on(D) value were studied under optimum condition for extraction of Co(II) and Fe(III) ions, separately , with reagent (DPDQ) by addition of (200μg) of some cations, separately , such as ($Pb^{2+}$, $Ag^{1+}$, $Cu^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Cr^{3+}$, $Hg^{2+}$ & $Sr^{2+}$).

### (2-9-6)The effect of oxidation and reduction reagent on extraction

Effect of addition (1mL) hydrogen peroxide solution (35%) as oxidant agent and (1mL) solution of tin chloride (1M) as reducing agent, separately, studied for extraction of the Co (II) and Fe (III) ions, separately, with reagent (DPDQ) under optimum conditions.

### (2-9-7)The effect of enrichment extraction (Volume concentration technique)

The effect of different volumes of aqueous phase ranged from (5-25mL) for Co (II) and Fe (III) ions, individually, with (5mL) reagent (DPDQ) in chloroform on (D) values in extraction studied under optimum conditions.

### (2-9-8)The effect of metal concentration on extraction

The effect of concentration of Co (II) and Fe (III) on (D) values between two phases studied, separately, by installing the optimum conditions of extraction.

### (2-9-9)The effect of salting on extraction

The extraction studies performed by addition (1mL) ammonium chloride, Sodium chloride, Sodium sulphate, Sodium nitrate solutions (1M) as salting factor on extraction of Co (II) and Fe (III) ions, separately, with reagent (DPDQ) under optimum condition.

### (2-9-10)The effect batch method extraction

Batch extraction process of Co (II) and Fe (IIII) ions, individually, by reagent (DPDQ) under optimum condition studied. Extraction had done in three stages partition of organic phase to three volumes and calculate the (D) value after ending third part of extraction process.

### (2-9-11)The effect of temperature on extraction and determination of thermodynamic functions

To determine the effect of temperature on (D) value, Co (II) and Fe (III) ions, were extracted individually in different temperatures ranged from (20-45)°C with reagent (DPDQ) by thermostatic circulator under optimum conditions.

## (2-10)The stoichiometry of the extracted complexes

The metal to reagent ratio studied under optimum conditions by mole ratio method, Job’s method (continuous variations) and substoichiometric extraction.

### (2-10-1) Mole ratio method: -

This method is done by mixing known constant concentration of Co (II) and Fe (III) ions, separately, with increasing concentrations and proportionate of reagent (DPDQ) in chloroform. After conducting the extraction process for each concentration, the absorption measured for organic phase for each concentration at the greatest wavelength, the relationship between the absorption and mole ratio (M / L) plotted in the result.

### (2-10-2) Job’s method (Continuous variations): -

This method is done by mixing different volumes of solutions that have equal concentrations of Co(II) and Fe(III) ions. Separately, with reagent (DPDQ) in chloroform, absorption is measured for organic phase for each concentration and at the greatest wavelength. The relationship between the absorption and volume ratio is drew.

### (2-10-3) Substoichiometric extraction:-

To study the stoichiometry of the extracted complex of Cobalt , (2.0 mg) of (DPDQ) reagent, taken in (5mL) chloroform, was used for the extraction of increasing amounts of Cobalt (II) ion (from 25 μg to 400 μg at pH= 10). The D values of extraction plotted against the amount of ion taken.

On other hand, the stoichiometry of the extracted complex of Iron , (3.1mg) of (DPDQ) reagent, taken in (5mL) chloroform, was used for the extraction of increasing amounts of Iron (III) ion (from 25 μg to 400 μg at pH= 7). The D values of extraction plotted against the amount of ion taken.

## (2-11) Spectrophotometric studies

### (2-11-1) Study of UV – Visible spectra.

Absorption of UV-visible spectra for solutions plotted for each solution: -

1) Absorption spectrum of complex Co (II) with thiocyanate.
2) Absorption spectrum of complex Fe (III) with thiocyanate.
3) Absorption spectrum of reagent solution (DPDQ) dissolved in chloroform.
4) Absorption spectrum of organic phase after extraction of Co (II) by using (DPDQ) as reagent.
5) Absorption spectrum of organic phase after extraction of Fe (III) by using (DPDQ) as reagent.

## (2-11-2) Study of FT-IR spectra: -

FT- IR spectra recorded for the compounds: -

1. Infrared spectrum of (8-hydroxyquinoline) and (4-Amino-N, N-dimethylanilindihydrochloride) as starting materials for (DPDQ) syntheses.
2. Infrared spectrum of reagent (DPDQ).
3. Infrared spectrum of extracted complex for Co (II).
4. Infrared spectrum of extracted complex for Fe (III).

## (2-11-3) Study of $^{1}$HNMR spectra: -

It has been diagnosed the number of hydrogen atoms by NMR spectrum by using the solvent (DMSO).

## (2-11-4) Study of $^{13}$CNMR spectra: -

It has been diagnosed the number of carbon atoms by NMR spectrum by using the solvent (DMSO).

## (2-11-5) Study of mass spectra: -

Use the Mass spectrometry to determine the molecular weight of the reagent based on the ablation technique.

## (2-12) Preparation of the Cobalt (II) and Iron (III) complexes in the solid-form

### 1. The solid Cobalt (II) complex.

The solid Cobalt (II) complex was prepared from the reaction of the reagent (DPDQ) with the ion in a ratio of (1: 2) by taking (10 mL) (0.500 mmole) from the reagent dissolved in ethanol with (10 mL) (0.250 mmole) of Cobalt (II) ion dissolved in deionized water. The Cobalt (II) ion solution is placed in a round bottom flask with continuous stirring by magnetic stirrer, then the reagent solution is added gradually so that stirring continues for a period of (30 min.) with the acidic function adjusted at (pH = 10).

For a period of (24hr) at room temperature, a dark red precipitate was observed after the ethanol solvent dried, then filtered and washed with deionized water and recrystallization with ethanol and left to dry in the air.

### 2. The solid Iron (III) complex.

The solid Iron (III) complex was prepared from the reaction of the reagent (DPDQ) with the ion in a ratio of (1: 3) by taking (10 mL) (0.750 mmole) from the reagent dissolved in ethanol with (10 mL) (0.250 mmole) of Iron (III) ion dissolved in deionized water. The Iron (III) ion solution is placed in a round bottom flask with continuous stirring by magnetic stirrer, then the reagent solution is added gradually so that stirring continues for a period of (30 min.) with the acidic function adjusted at (pH = 7). For a period of (24hr) at room temperature, a dark red precipitate was observed after the ethanol solvent dried, then filtered and washed with deionized water and recrystallization with ethanol and left to dry in the air.

## (2-13) Determination of some physical properties for the complexes: -

### (2-13-1) Melting point

Melting point for reagent (DPDQ) and the complexes extracted after dry it in room temperature were measure by using melting point apparatus.

### (2-13-2) Electrical conductivity

The values of electrical conductivity for extracted complexes at room temperature studied on the concentration ($1\times10^{-3}$ M).

## (2-14) Study development of a new method for determining the concentration of Co (II) and Fe (III) ions in the organic phase

A new method has been developed for the determination of cobalt (II) and Iron (III) in organic phase .Different concentrations of cobalt (II) ion were extracted, ranging from ($1.6967\times10^{-4}$M – $23.7558\times10^{-4}$M), which is equivalent to (50µg-700µg) , and different concentrations of Iron (III) ion ranged between ($3.5813\times10^{-5}$M–$21.4880\times10^{-4}$M), which is equivalent to (10µg-600µg) by (5mL) of the (DPDQ) reagent (0.1%) , after separating the organic layer from the aqueous layer, (5mL) was transferred from the organic layer to a volumetric flask (25mL) and completed the volume to the mark with chloroform, and the absorption of the two complexes was measured at ($\lambda_{max}$ = 521.5nm) and ($\lambda_{max}$ = 505.5 nm), respectively.

## (2-15) Applications: -

Samples of Hair and Vitamin B12 were used in the application of the technique extraction of Cobalt ion& a sample of drugs to extract Iron ion.

### (2-15-1) Hair Sample

Sample of human hair from a head taken, a sample of hair weight (1g) washed it by acetone (2mL) then with deionized water (1mL) two times, then dried for (20 min.) in room temperature. The sample digested by (1mL) concentrated nitric acid, then the sample was transport to (50mL) volumetric flask and completed to the mark with deionized water. ( 5mL) of the solution adjusted to pH=10 to extract Co(II) by ( 5mL) reagent (DPDQ) [77].

### (2-15-2) Vitamin $B_{12}$ Sample

Vitamin $B_{12}$ ampule (1000µg/4mL) cyanocobalamin (43.481µgCo$^{2+}$/4mL) was taken, shaking good them take a (4mL) from Vit.$B_{12}$ solution to dried beaker , added (8mL) nitric acid (1:1) and heated until dry , add (8mL) hydrochloric acid (1:1) and heated a gain near dried , Colling the sample , added deionized water and transfer the sample to (10mL) volumetric flask and complete the volume to the mark with deionized water. Then take ( 5mL) to extract Co(II) by ( 5mL) from the reagent (DPDQ) [77].

### (2-15-3) Drug Samples contain Iron: -

A sample of two drugs tablet-containing Iron used. Referum tablet (dextriferron (100 mg Fe$^{3+}$/tablet), Ferrous Sulfate tablets (65mgFe$^{2+}$/tablet) one tablet of each drug was taken were weighed and transferred in to 250cm$^3$ volumetric flask, deionized water was added up to the mark to dissolve into solution[78].

After samples prepared, Iron (III) ion (0.5 mL) (200µg) & (130µg) respectively was diluted to (5mL) and pH=7 , extracted by (DPDQ) reagent that dissolved in chloroform.

### (2-16) Sequential extraction process: -

To extraction Co (II) & Fe (III) ions sequentially, mixed the sample of Co (II) (200µg) & Fe (III) sample (200µg) together adjusted the acidity of mixture to (pH=2) shaking with reagent (DPDQ) that dissolved in chloroform for fifteen minutes , after this time separated the aqueous phase ( that contain Fe (III) ion & low percent of Co (II) ) about organic phase ( contain Co (II) ion & low percent of Fe (III) ) , the aqueous phase adjusted to (pH=2 ) and mixed with reagent (DPDQ) again , shaking for ( 15 minutes ) , the aqueous phase contain Iron (III) after this time elapsed . The organic phase from first separation was striping by acidic media (pH=1.5) and shaking for (30 minutes), the aqueous phase contains Cobalt (II) ion. Repeat these processes three times.

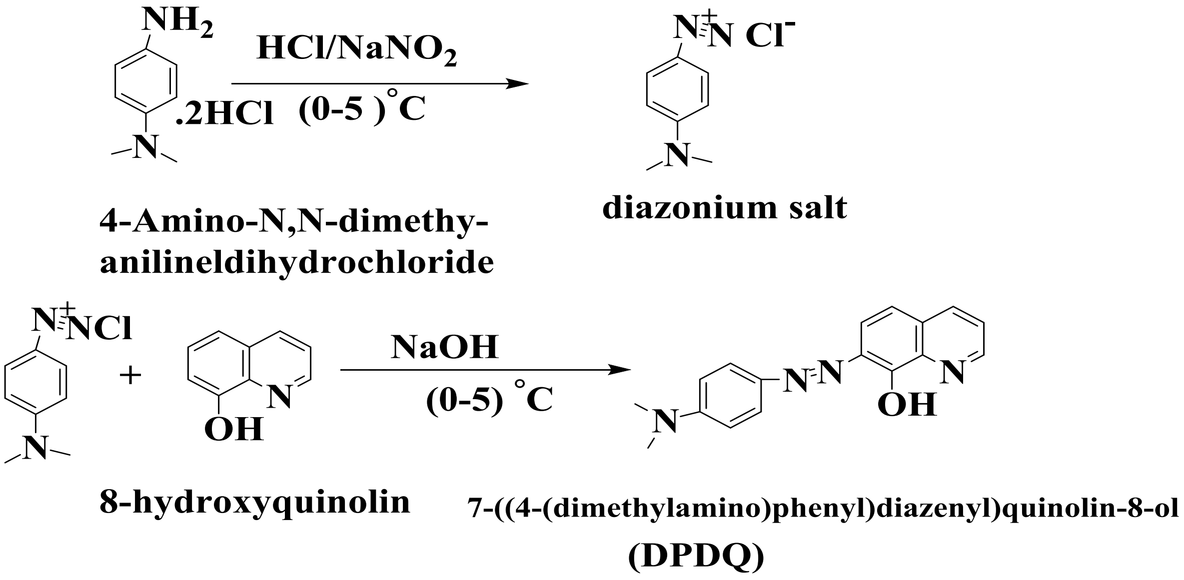
# Chapter Three

# Results & Dissection

## (3-1)Preparation of the Reagent: -

The preparation of reagent (DPDQ) from diazonium salt pairs of the (4-Amino-N,N-dimethylanilindihydrochloride) with (8-hydroxyquinoline) in an alcoholic medium by dissolving 4-Amino-N,N-dimethylanilindihydrochloride in a solution obtained by mixing of concentrated hydrochloric acid with deionized water, sodium nitrite dissolved in deionized water drop by drop.

Stirring keep the temperature below 5 °C, and left the solution stile to complete the azonation process and obtain a solution of diazonium chloride. This salt solution added slowly with continuous stirring to a solution of 8-hydroxyquinoline that dissolved in a mixture of ethanol and sodium hydroxide, to get the reagent (DPDQ) with a color reddish orang, the reaction steps can be explained as Scheme (3-1) :-



**Scheme (3-1): Steps of preparation of (DPDQ)**

The reaction steps have montane has been by a thin layer chromatography (TLC) technique using ethanol as a solvent(eluent), where a reddish orang precipitate was given and the retention or retardation factor (Rf) was calculated by measuring the distance travelled by the compound spot in relative to the distance travelled by the eluent.

$$Rf = \frac{distance\ travelled\ by\ the\ compound\ in\ solute}{distance\ travelled\ by\ the\ compound\ in\ solvent} \quad \text{........ (3- 1)}$$

By compensation resulting:
Rf = 0.95

## (3-2)The solubility of reagent (DPDQ): -

The solubility of reagent studied in many solvents and the result shown in table (3-1).

**Table (3-1): The solubility of the reagent in different solvents.**

| Solvent | Result | Solvent | Result |
|---|---|---|---|
| $H_2O$ | - | Chloroform | + |
| $CCl_4$ | + | DMF | + |
| Methanol | + | DMSO | + |
| Ethanol | + | Acetone | + |
| 1-Propanol | + | Dichloromethane | + |
| 2-Propanol | † | Acetonitrile | † |
| 1-Butanol | + | n-Hexane | - |

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

## (3-3) The Physical properties of (DPDQ): -

The physical properties shown in table (3-2)

**Table (3-2): The Physical Properties of the Prepared Reagent**

| Compound | Formula | Molecular weight (g/mol) | Melting pointe ( ˚C) | Colour |
|---|---|---|---|---|
| DPDQ | $C_{17}H_{16}N_4O$ | 292.1324 | 164-166 | Reddish-orang |

## (3-4) Determination of the Ionization Constant for the (DPDQ):

The ionization constants of weak electrolytes (acids or bases) can be determined in many ways. Including the method that depends on measuring electrical conductivity[79], spectral method and potentiometric titration method and other methods mentioned[80–86] .

Where the spectral method was used to specify the ionization constant of the reagent (DPDQ) in our study due to that the reagent contains (OH) group and the spectral method summarizes by measuring the absorbance values of series of reagent solutions (DPDQ) with deionized water at different values of the acidic function (pH= 2-12) and the figures(3-1),(3-2) which appears changing of the absorption of the reagent solution, where observed in these figures that the absorption increases at the wavelength (476 nm) with the increase in the values of the acidic function while the absorption decreases at (507 nm), and it is also noticed that these curves intersect at an almost combined point (ionization point of reagent).

The reagent as HIn is dissociate according to the following equations:

$$HIn \rightleftharpoons H^{+} + In^{-}$$ ………..(3-2)

Ka = [H$^+$] + [In$^-$ ] / [HIn]...................... ( 3-3 )

[H$^+$] = Ka [HIn] / [In$^-$ ] ....................... ( 3-4 )

By taking the logarithm of both parties

Log [H$^+$] = log Ka [HIn] / [In$^-$ ]................(3-5)

Log [H$^+$] = log Ka + log [HIn] / [In$^-$ ] .......... (3-6)

By multiplying both sides by (-1) result:

-Log [H$^+$] = -log Ka - log [HIn] / [In$^-$ ] ..........(3-7)

Whereas:

pKa = - log Ka and pH = - log [H$^+$]

Whether a given acid loses a proton in an aqueous solution depends on both the pKa of the acid and pH of the solution. The relationship between the two was given by the Henderson–Hassel Balch equation (3-8)[87].

$pH = pKa + log \frac{[In-]}{[HIn]}$ …………… (3-8)

Since it is at the absorption symmetry point, [HIn]=[In$^-$]

$\therefore pKa = pH$

$\therefore pKa = 9$

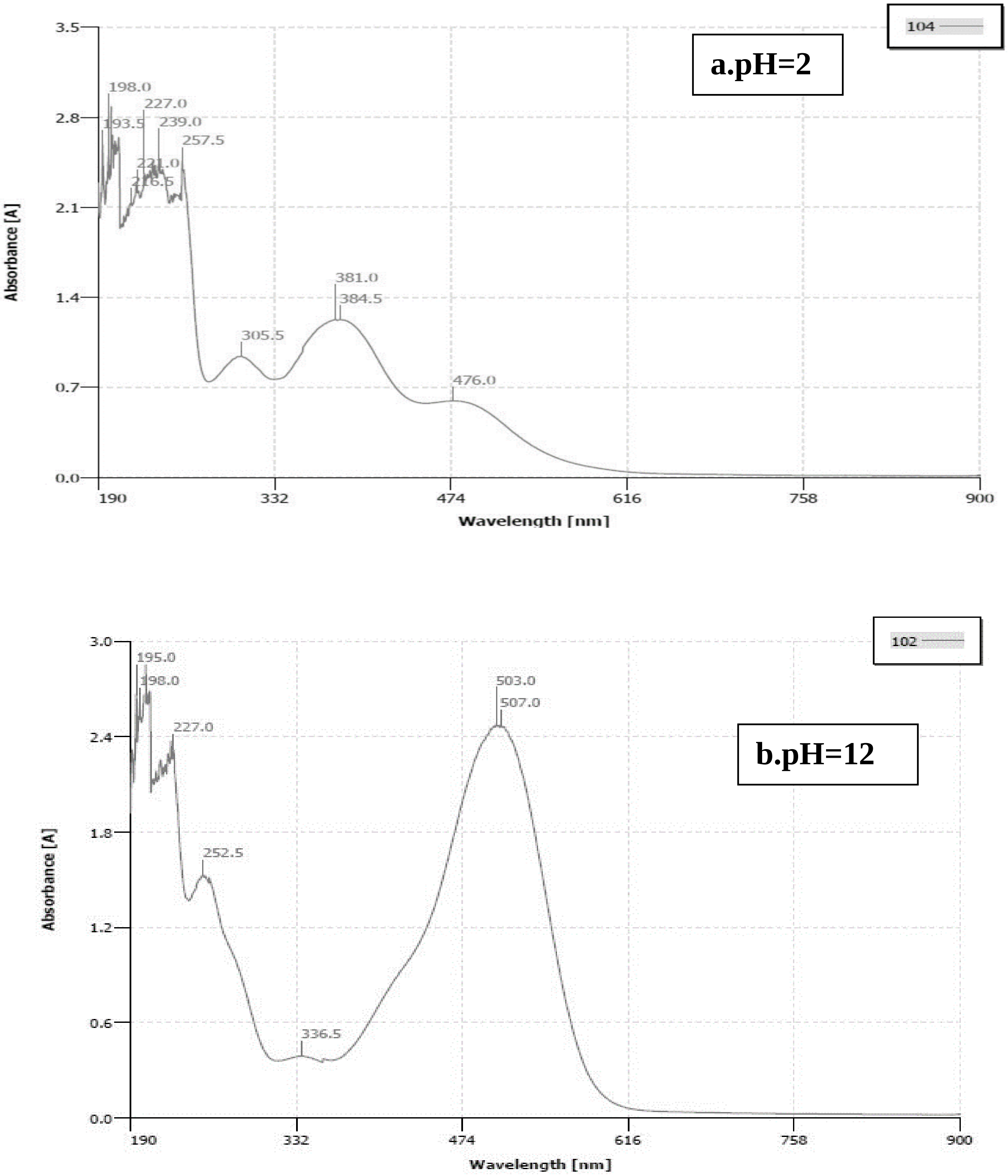


**Figure (3-1): Changing the absorption curves of (DPDQ) in acidic and basic medium ( a.pH=2 , b.pH=12 ) .**

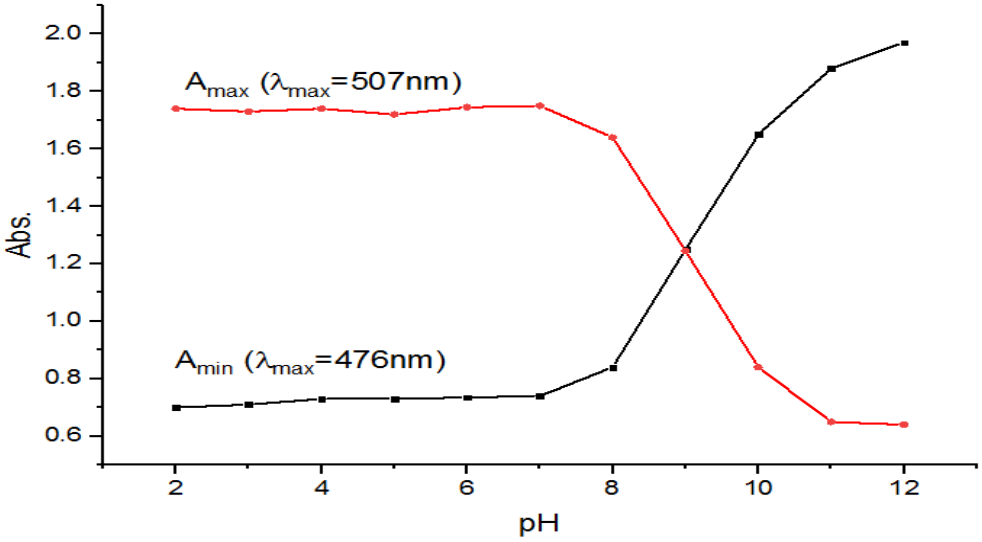


**Figure (3-2): the absorption curve of (DPDQ) by changing the values of pH at ($\lambda_{max}$ = 476nm and 507nm).**

## (3-5) Spectroscopic studies of reagent (DPDQ): -

### (3-5-1) (UV-Vis.) spectrum for the reagent: -

The (UV-Vis) spectrum for the reagent (DPDQ), figure (3-3) exhibits a high intense absorption peak at (244.0nm), (260.5nm), (324.5nm) and (442.5nm) which assigned to (π→π*), (π→π*), (π→π*) and (n→π*) transition respectively.

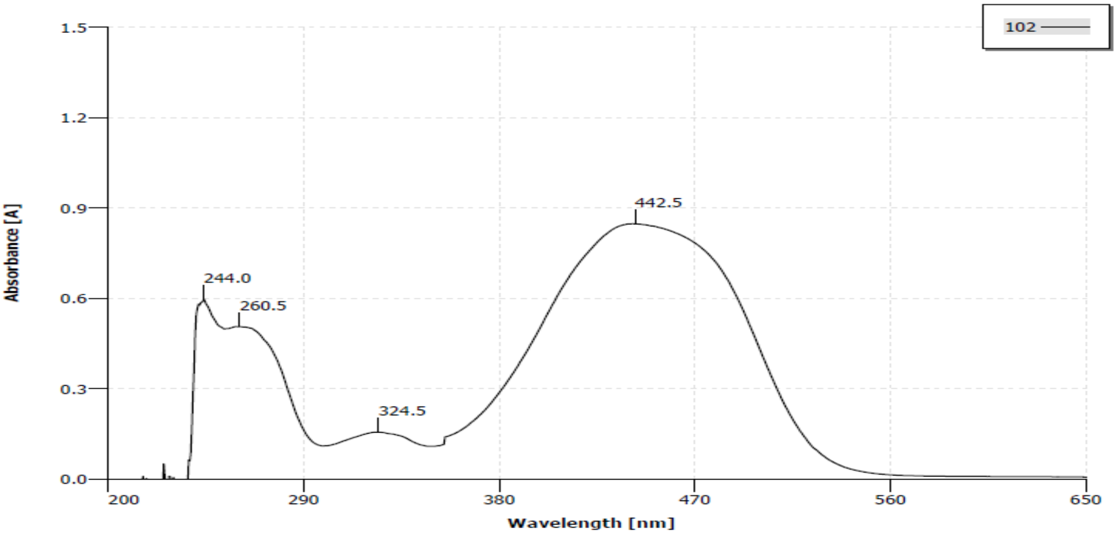


**Figure (3-3) Electronic spectrum data of the reagent.**

## (3-5-2) FT.IR spectra for the reagent & row materials: -

FT.IR spectroscopy is one of the common methods of diagnosing and studying the composition of reagents and their complexes. The prepared heterogeneous azo reagent and its complexes had studied with infrared spectroscopy in the form of potassium bromide disk and within the range (400-4000) cm$^{-1}$ and the results are as follows.

a. **FT.IR spectrum of 8-hydroxy quinoline: -**

Figure (3-4) shows the spectrum of 8-hydroxyquinoline by FT.IR Spectroscopy.

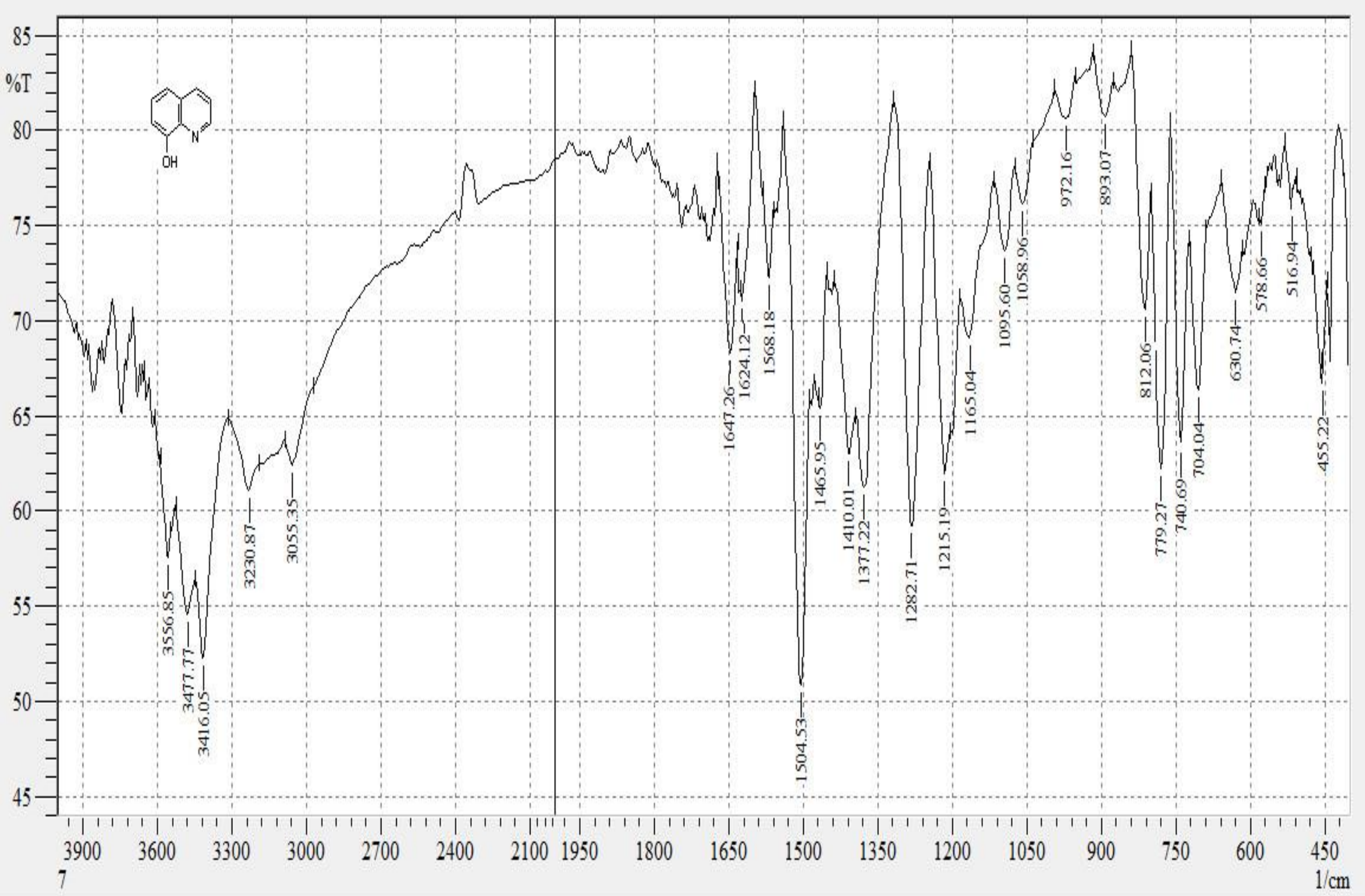


Figure (3-4) FT.IR spectrum of 8-hydroxy quinoline

### b. FT.IR spectrum of 4-Amino-N, N-dimethylaniline dihydrochloride: -

Figure (3-5) shows the spectrum of 4-Amino-N, N-dimethylaniline dihydrochloride by FT.IR Spectroscopy.

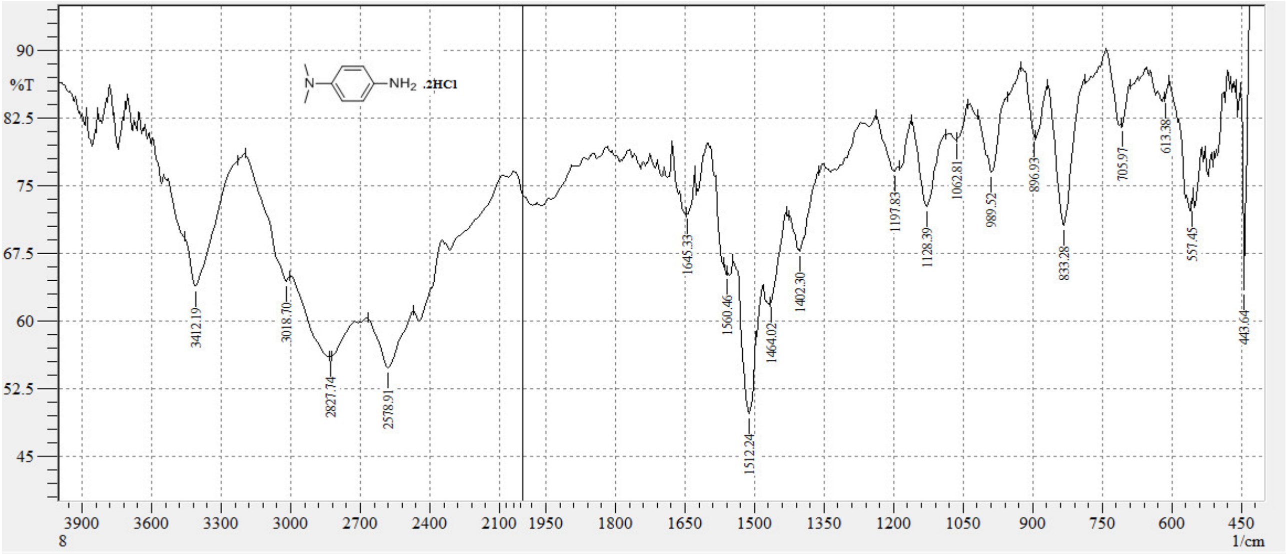


**Figure (3-5) FT.IR spectrum of 4-Amino-N, N-dimethylaniline dihydrochloride**

### c. FT.IR spectrum of reagent (DPDQ): -

Figure (3-6) shows the spectrum of reagent (DPDQ) by FT.IR. spectroscopy.

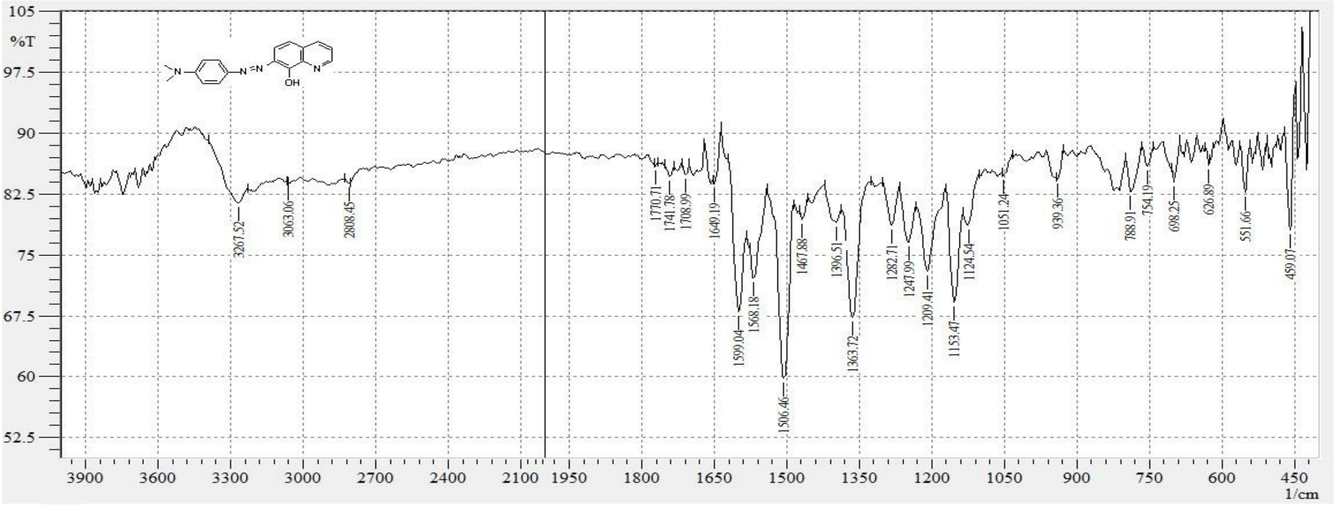


**Figure (3-6) FT.IR spectrum of reagent (DPDQ)**

**Table (3-3) show the main data of FT.IR spectrums of reagent & it's row materials. [88-90]**

| Bond | 8-hydroxyquinoline | 4-Amino-N, N-dimethylaniline dihydrochloride | (DPDQ) reagent |
|---|---|---|---|
| **St. (C=N)** | 1647.26 | --- | 1599.04 |
| **St. (C-N)** | 1377.22 | 1402.30 | 1363.72 |
| **St. (C=C) Aromatic** | 1568.18 | 1560.46 | 1568.18 |
| **St. (C-H) Aromatic** | 3055.35 | 3018.70 | 3063.06 |
| **St. (N=N)** | --- | --- | 1506.46 |
| **St. (O-H)** | 3416.05 | --- | 3267.52 |
| **St. (C-H) Aliphatic** | --- | 2827.74 | 2808.45 |
| **St. (C-O)** | 1282.71 | --- | 1282.71 |

## (3-5-3) NMR spectrums for the reagent: -

Figures (3-7) & (3-8) shows the spectrum of reagent (DPDQ) by $^{1}$HNMR & $^{13}$CNMR spectroscopy respectively.

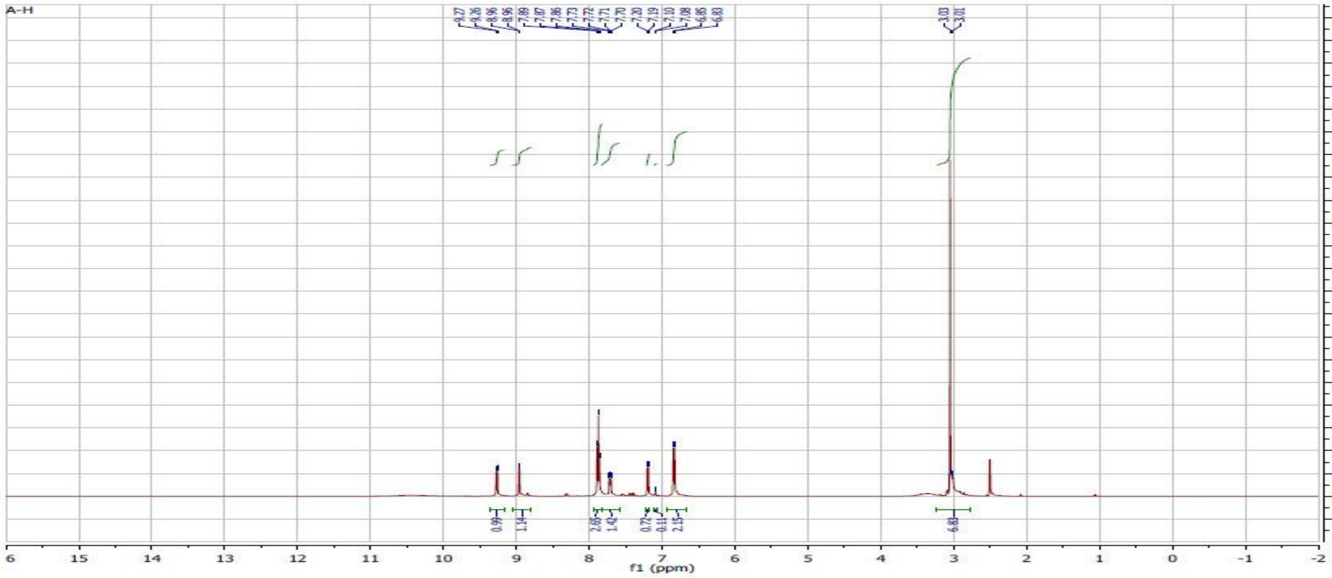


Figure (3-7) $^{1}$HNMR spectrum of reagent (DPDQ)

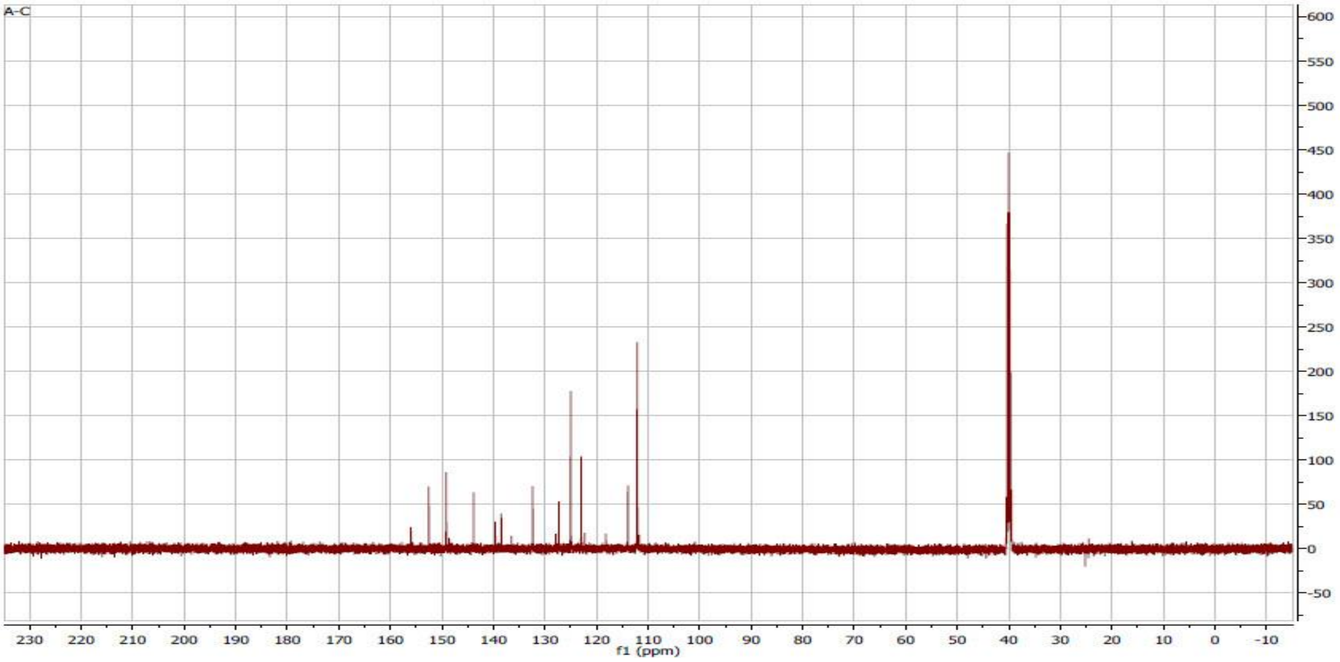


Figure (3-8) $^{13}$CNMR spectrum of reagent (DPDQ)

Proton nuclear magnetic resonance spectrometry ($^1$HNMR) is an excellent tool to check the purity of the organic compounds, the $^1$HNMR and $^{13}$CNMR spectrums of the ligand (L) was diagnosed in (DMSO-d6) as a solvent and at laboratory temperature.

## (3-5-4) Mass spectrum for the reagent:

Figure (3-9) shows the spectrum of reagent (DPDQ) by Mass spectroscopy, from the figure it is clear that the theoretically calculated molecular weight (292.1324g/mole) is identical to the practical result.

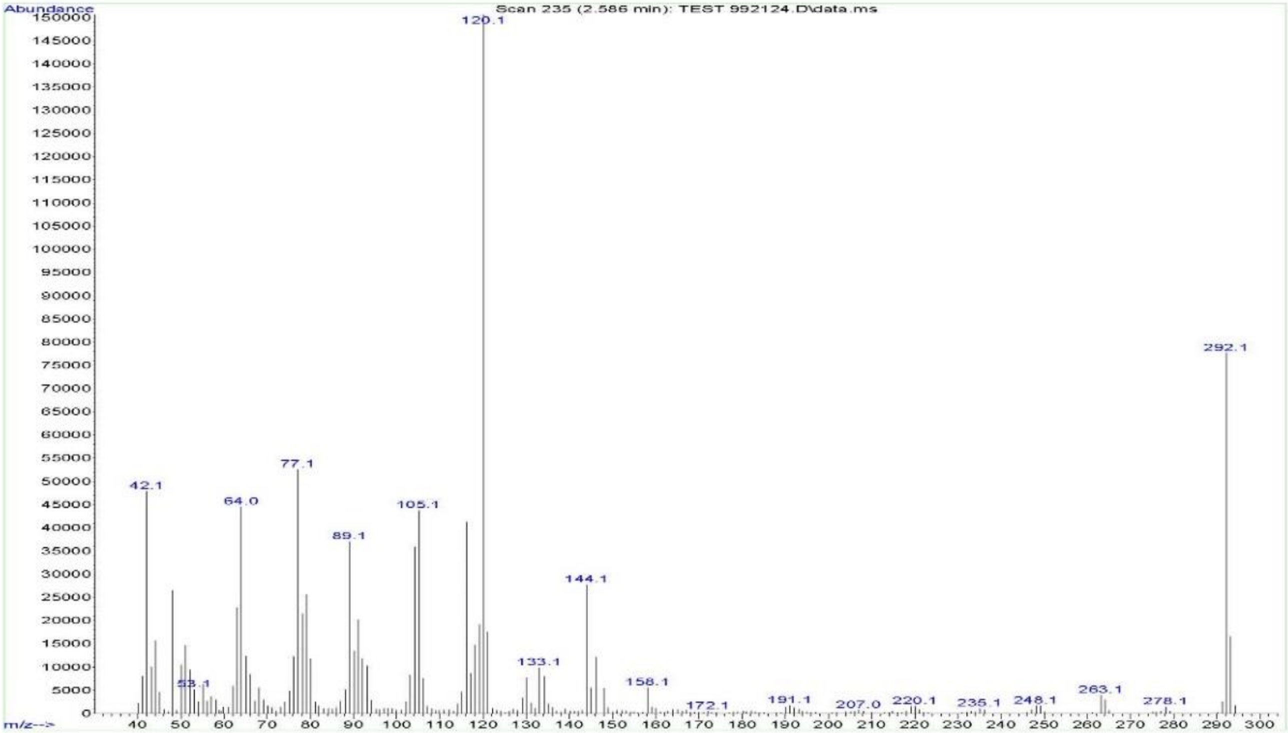


Figure (3-9) Mass spectrum of reagent (DPDQ)

## (3-6) Calibration curves of Cobalt (II) and Iron (III) ions.

After confirmation from the main site of absorption ($\lambda_{\mathbf{max}}$) of Co (II) & Fe (III) complexes, separately, with thiocyanate solution and by spectra scan of absorption for complexes in UV. – Visible figures (3-10) & (3-11) respectively. These complexes had the greatest absorption at ($\lambda_{\mathbf{max}}$ = 620 nm) for Cobalt (II) ion & ($\lambda_{\mathbf{max}}$ = 480 nm) for Iron (III) ion. This came in line with those reported previously in the literature[76].

Different concentrations of Co(II) and Fe (III) ions, individually, were prepared within the range (50µg/5mL- 800µg/5mL) for Co(II) ion, and within the range (1µg/5mL- 70µg/5mL) the absorption of each concentration of Co (II) and Fe (III) ions, separately, were recorded at ($\lambda_{\mathbf{max}}$=620 nm) & ($\lambda_{\mathbf{max}}$ = 480 nm) respectively. By plotting the relationship between the absorption and concentration a linear relationship between absorption and concentration had been obtained as illustrated in Figures (3-12) and (3-13).

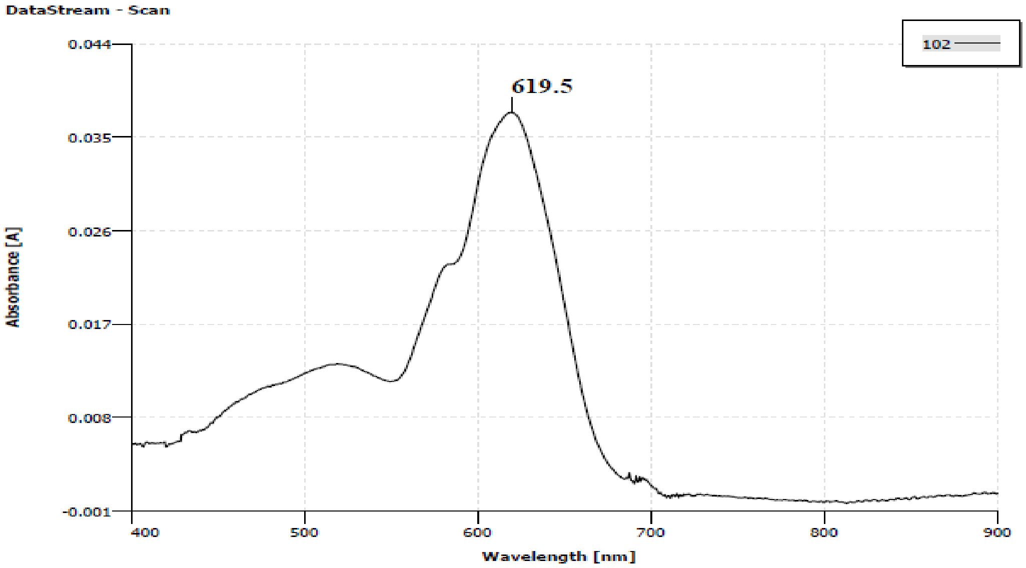


Figure **(3-10) Electronic spectrum of Co (II) complex with thiocyanate.**

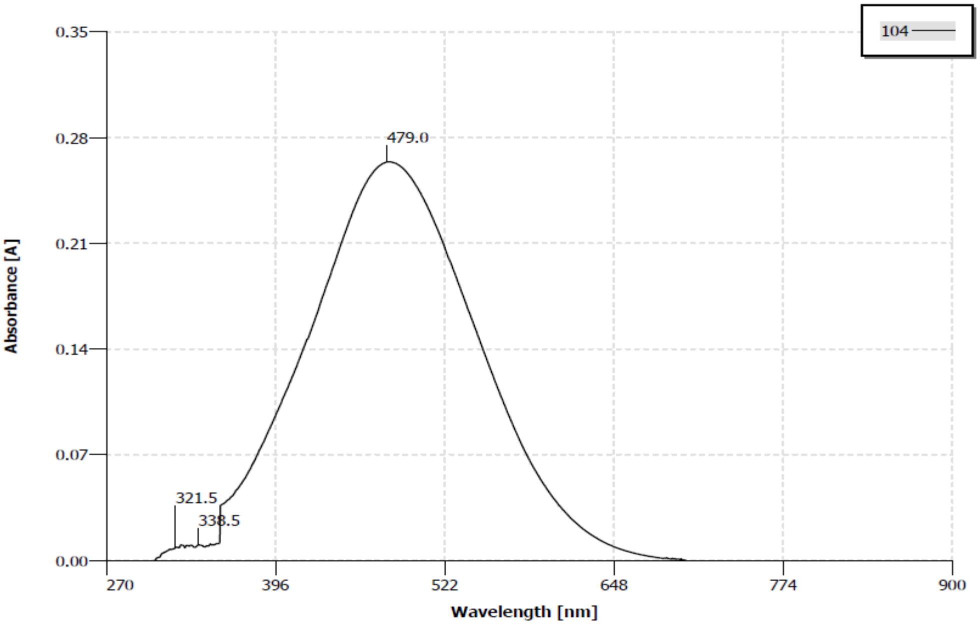


**Figure. (3-11) Electronic spectrum of Fe (III) complex with thiocyanate**.

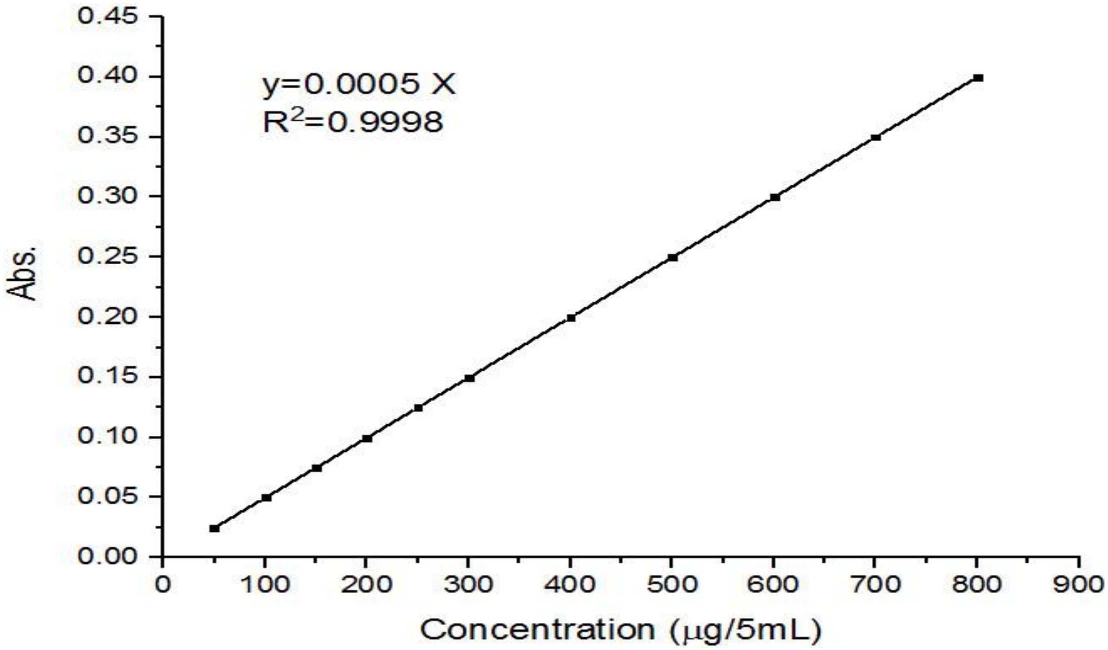


**Figure (3-12) Calibration curve for the determination of Co (II) ion with thiocyanate.**

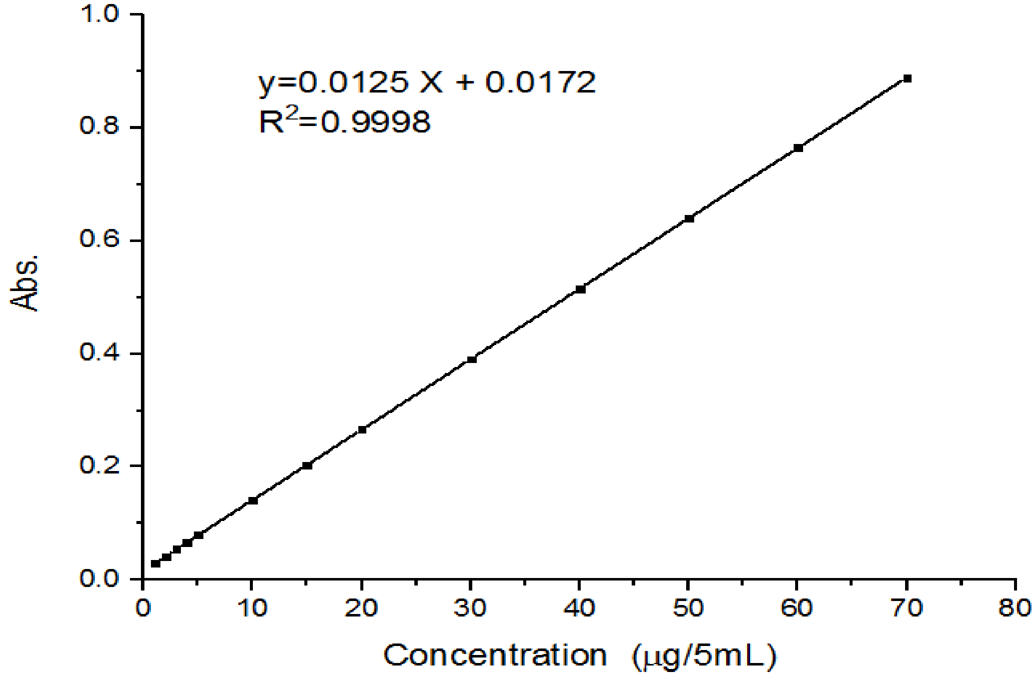


**Figure (3-13) Calibration curve for the determination of Fe (III) ion by thiocyanate.**

## (3-7) Study The Effect of Different Parameters on The Extraction.

Some of chemical and physical parameters such as pH, shaking time, temperature.... are examined in order to get the best results in the extraction process and access to the best chemical equilibrium at which the free energy would be equal for the dissolved substance in both immiscible phases had examined in the following factors: -

### (3-7-1)The effect of pH on the extraction.

The effect of this factor was determined by calculating (D) values to extract constant concentration of Co (II) solution (200µg), ($6.7873\times10^{-4}$M) in (5mL) and of Fe (III) solution (200µg) ($7.1626\times10^{-4}$M) in (5mL), separately, in different pH from (2-12) of Co (II) and Fe (III). Separately, with 5mL of (0.1%) (DPDQ) solution dissolved in chloroform as organic phase. The results illustrated in tables (3-4) and (3-5).

**Table: (3 -4)The effect of pH on the extraction of Co (II) ion by using (DPDQ) dissolved in chloroform.**

| pH | D | E% |
|---|---|---|
| 2.00 | 1.001 | 50.030 |
| 3.00 | 1.273 | 56.007 |
| 4.00 | 1.577 | 61.200 |
| 5.00 | 1.795 | 64.222 |
| 6.00 | 2.109 | 67.831 |
| 7.00 | 2.333 | 70.000 |
| 8.00 | 2.032 | 67.022 |
| 9.00 | 2.126 | 68.010 |
| **10.00** | **4.952** | **83.200** |
| 11.00 | 4.001 | 80.004 |
| 12.00 | 2.233 | 69.070 |

**Aqueous phase: - (5 mL) solution of Co (II) ion concentration** (200μg),
**($6.7873 \times 10^{-4}$M) in different pH.**
**Organic phase: - (5mL) of (0.1%) (DPDQ) solution dissolved in chloroform.**
**Equilibrium time: - (10) min.**
**Temperature: - (20 ± 2) °C.**

**Table: (3 -5) The effect of pH on the extraction of Fe (III) ion by using (DPDQ) dissolved in chloroform**

| pH | D | E% |
|---|---|---|
| 2.00 | 0.118 | 10.528 |
| 3.00 | 0.270 | 21.288 |
| 4.00 | 0.673 | 40.222 |
| 5.00 | 2.245 | 69.188 |
| 6.00 | 5.365 | 84.288 |
| **7.00** | **20.177** | **95.278** |
| 8.00 | 9.622 | 90.586 |
| 9.00 | 7.530 | 88.277 |
| 10.00 | 6.512 | 86.688 |
| 11.00 | 3.034 | 75.208 |
| 12.00 | 2.950 | 74.684 |

**Aqueous phase: - (5 mL) solution of Fe (III) ion concentration (200µg), (7.1626x$10^{-4}$M) in different pH.**

**Organic phase: (5mL) of (0.1%) (DPDQ) solution dissolved in chloroform.**

**Equilibrium time: - (15) min.**

**Temperature: - (20± 2) °C.**

The results in tables (3-4) & (3-5) indicated variation in (D) and (E %) with pH values. Thus, it could be due to the nature of the properties of organic reagent used in the solvent extraction process and it's impact on pH.

### (3-7-2)The effect of shaking time on the extraction

Change in (D) values for extraction Co (II) and Fe (III) ions, separately, calculated by using (DPDQ) as a function of time of equilibrium phases for different times ranged between (2-30) minutes. The results shown in table (3-6), (3-7) and figures (3-14), (3-15).

**Table (3-6): The effect of time equilibrium in the extraction of Co (II) ion by using (DPDQ) dissolved in chloroform.**

| Time | D | E% |
|---|---|---|
| 2 | 3.003 | 75.020 |
| 5 | 3.608 | 78.300 |
| **10** | **4.951** | **83.195** |
| 15 | 3.205 | 76.220 |
| 20 | 2.336 | 70.021 |
| 30 | 1.818 | 64.520 |

**Aqueous phase: - (5 mL) solution of Co (II) ion concentration** (200μg), **($6.7873x10^{-4}$M) pH=10.**

**Organic phase: - (5mL) of (0.1%) (DPDQ) solution dissolved in chloroform.**

**Equilibrium time: - (X) min.**

**Temperature: - (20 ± 2) C°.**

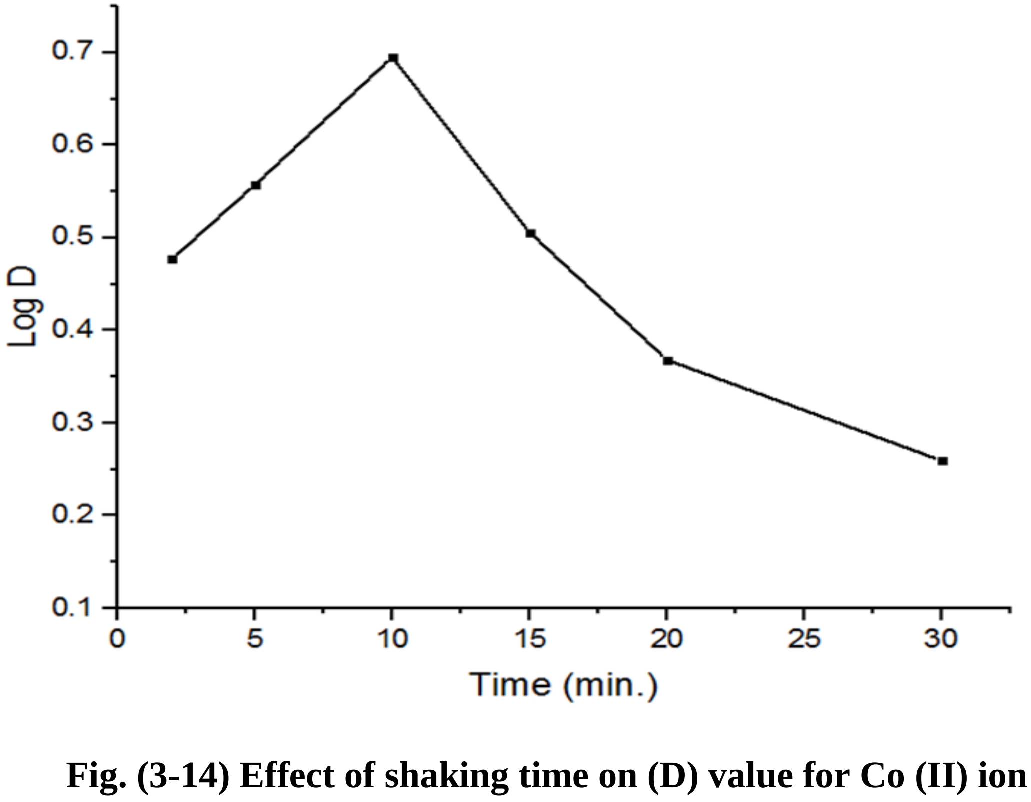


**Fig. (3-14) Effect of shaking time on (D) value for Co (II) ion extraction.**

**Table (3-7): The effect of time equilibrium in the extraction of Fe(III) ion by using (DPDQ) dissolved in chloroform.**

| Time | D | E% |
|---|---|---|
| 2 | 5.818 | 85.333 |
| 5 | 7.843 | 88.692 |
| 10 | 15.358 | 93.887 |
| **15** | **20.169** | **95.276** |
| 20 | 11.481 | 91.988 |
| 30 | 7.256 | 87.888 |

**Aqueous phase: - (5 mL) solution of Fe (III) ion concentration** (200μg), **($7.1626x10^{-4}$M) at pH=7.**

**Organic phase: (5mL) of (0.1%) (DPDQ) solution dissolved in chloroform.**

**Equilibrium time: - (X ) min.**

**Temperature: - (20± 2) °C.**

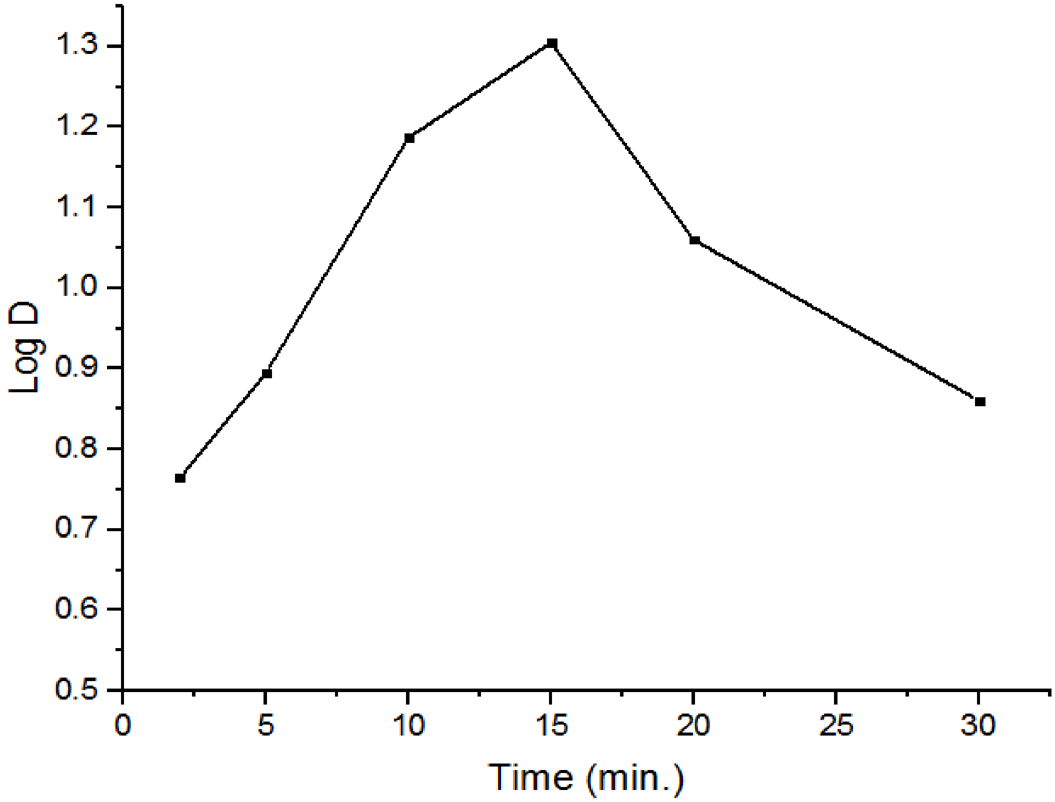


**Fig. (3-15) Effect of shaking time on (D) value for Fe (III) ion extraction.**

From the results in tables (3-6), (3-7) and figures (3-14), (3-15) the best time to extract Co (II) and Fe (III) were (10) and (15) minutes, respectively, by using (DPDQ), then (D) values of start decline with increasing in the shaking time.

Increasing in the shaking time lead to increase the contact between organic and aqueous phase, which mean increasing the surface area between the phases that differ in the free energy initially depending on the different components of each phase. And shaking process in this case is accelerate the access to equilibrium between phases. while decreasing in (D)value after the maximum value when exceeding the shaking time may be due to several reasons, including destroying the complex formed and deviation the equilibrium to the aqueous phase or formation third phase. These results are in agreement with the previous study[91].

### (3-7-3)The effect of organic solvent on the extraction.

The nature of organic diluents substantially affects the Cobalt (II) and Iron (III) extraction efficiency. To clarify the effect of diluents on the extraction of Cobalt (II) & Iron (III) with compound, (D) values measured for selected diluents of varying dielectric constant under experimental conditions.

A number of organic solvents which had different dielectric constant had been selected to study (D) values to extract a fixed amount of Co(II) ($6.7873x10^{-4}$ M) , (200µg/5mL) and Fe(III) ($7.1626x10^{-4}$ M),(200µg/5mL) ions, separately, by (5 mL),(0.1 %DPDQ) solution under the experimental conditions, After each extraction process and separation of the aqueous phase from organic phase, the amount of ions in the aqueous phase were determined by colorimetric method[76] and calculated the amount of metal ions in the organic phase as described earlier and then calculated the (D) values for ions with (DPDQ). The results in tables (3-8), (3-9) and figures (3-16), (3-17).

**Table (3-8): The effect of polar organic solvent to extract Co (II) ion by using (DPDQ) dissolved in different solvents.**

| Organic Solvent | ε (farad/ meter) | 1/ε | D | E% |
|---|---|---|---|---|
| **Toluene** | 2.24 | 0.446 | 3.673 | 78.600 |
| **Benzene** | 2.28 | 0.438 | 1.564 | 61.000 |
| **Chloroform** | **4.90** | **0.204** | **4.619** | **82.202** |
| **Ethyl acetate** | 6.02 | 0.166 | 2.333 | 70.000 |
| **Dichloromethane** | 9.10 | 0.109 | 3.630 | 78.402 |
| **Amyl alcohol** | 15.80 | 0.063 | 2.733 | 73.210 |

**Aqueous phase: - (5 mL) solution of Co (II) ion concentration** (200μg), **($6.7873 \times 10^{-4}$M) at pH=10.**

**Organic phase: - (5mL) of (0.1%) (DPDQ) solution dissolved in different solvents.**

**Equilibrium time: - (10) min.**

**Temperature: (20 ± 2) °C.**

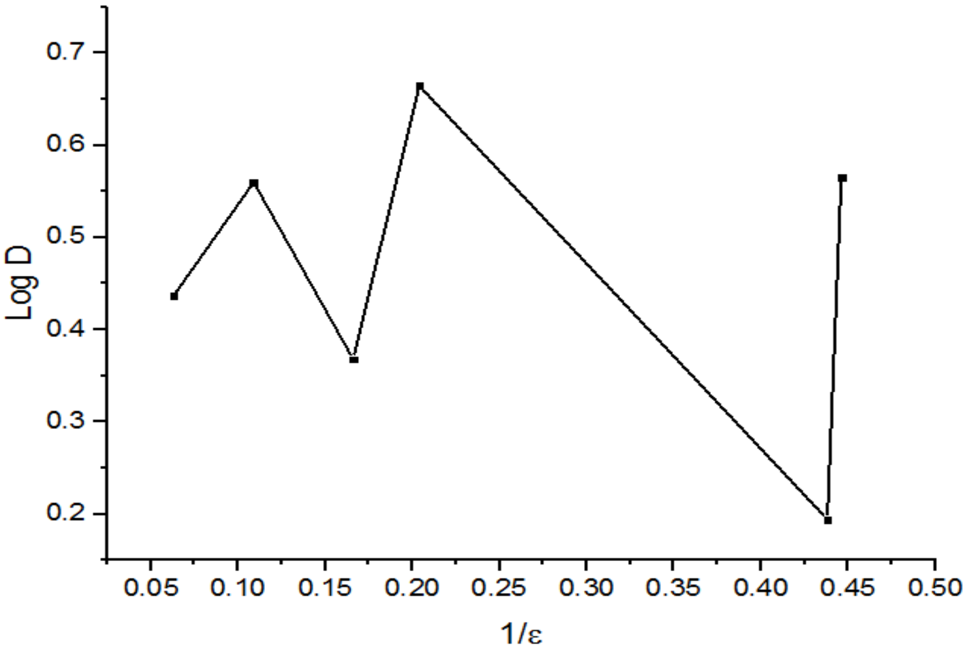


**Fig. (3-16)The effect of polar organic solvent to extract Co (II) ion by using (DPDQ).**

**Table (3-9): The effect of polar organic solvent to extract Fe (III) ion by using (DPDQ).**

| Organic Solvent | ε | 1/ε | D | E% |
|---|---|---|---|---|
| **Toluene** | 2.24 | 0.446 | 3.419 | 77.368 |
| **Benzene** | 2.28 | 0.438 | 6.046 | 85.808 |
| **Chloroform** | **4.90** | **0.204** | **20.133** | **95.268** |
| **Ethyl acetate** | 6.02 | 0.166 | 1.878 | 65.248 |
| **Dichloromethane** | 9.10 | 0.109 | 2.225 | 68.988 |
| **Amyl alcohol** | 15.80 | 0.063 | 1.748 | 63.608 |

**Aqueous phase: - (5 mL) solution of Fe (III) ion concentration** (200μg), **(7.1626x$10^{-4}$M) at pH=7.**

**Organic phase: (5mL) of (0.1%) (DPDQ) solution dissolved in different solvents.**

**Equilibrium time: - (15) min.**

**Temperature: - (20± 2) °C.**

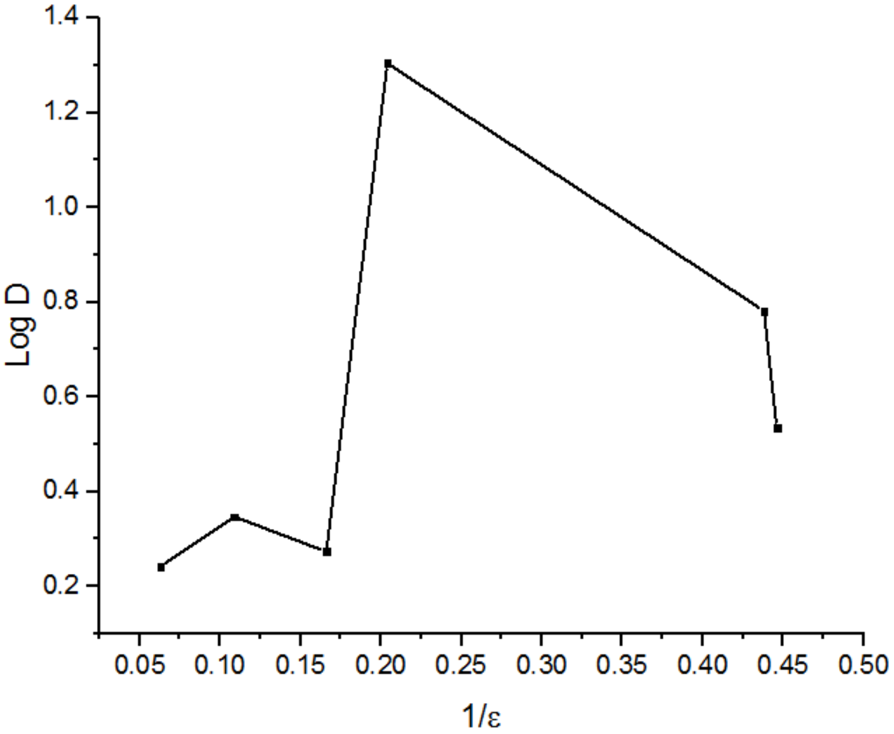


**Figure (3-17) The effect of polar organic solvent to extract Fe (III) ion by using (DPDQ)**

Results in tables (3-8), (3-9) and figures (3-16), (3-17) demonstrate the non-linearity of the relation between distribution ratio (D) and the dielectric constant (ε) of the organic solvent.

The organic solvents such as toluene, benzene, chloroform, ethyl acetate, dichloromethane & amyl alcohol were tested. Chloroform, which owns a fixed dielectric constant equal to (4.90) where (D) values were (4.619) & (20.133) with (DPDQ). It found the best solvent for the quantitative extraction of Co (II) & Fe (III), which had the highest (D) value and (E%). This is contrary to what is indicated by the Bourne relationship represented by the following equation

$$\Delta G = \frac{Z^2}{2r}\left[\frac{1}{\varepsilon_w} - \frac{1}{\varepsilon_o}\right] \quad \text{-----------(3-9)}$$

Where Z: is the ion charge.

r: the radius of the ion.

$\varepsilon_w$, $\varepsilon_o$ : dielectric constant of water and organic solvent, respectively.

$\Delta G$: free energy to move the ion.

The (D) values of amyl alcohol solvent which is the highest fixed dielectric constant (2.733) for Co (II) and (1.748) for Fe (III), separately, with (DPDQ) , while The (D) values of with toluene solvent which had the lower fixed dielectric constant (3.444) for Co (II) and (3.4185) for Fe (III), separately, with (DPDQ) and this confirms that there is no linear relationship between the (D) values and the dielectric constant of the solvents.

This demonstrated that the system of extraction in this study cannot be controlled by the dielectric constant of the solvent and the reason was attributed to the extracted complexes were no charge chelate. Many factors affect these types of complexes including the solubility of the extracted complex or geometry of organic solvent and if the solvent contains oxygen atom or not. This supported the role of organic solvent composition to achieve the best extraction away from the polar organic solvent that used to have a role in creating the best extraction, but its role was not a major, it does not exclude the possibility of participation of organic solvent in the process of extraction, the results of this study are in agreement with the previous studies[92].

### (3-7-4)The effect of foreign ions

### (3-7-4-1) Effect of some anions on the extraction

The values of distribution ratio to extract (200 μg/5mL) ($6.7873x10^{-4}$M) of Co (II) and (200 μg/5mL) ($7.1626x10^{-4}$ M) Fe (III) ions, separately from aqueous solutions were calculated under the optimum conditions by addition of different concentrations of some anions of potassium salts using the reagent (DPDQ) dissolved in chloroform.

**Table (3-10)The effect of adding some anions to extract Co (II) ion by using (DPDQ).**

| Anions | 500μg/mL | | 1000μg/mL | |
|---|---|---|---|---|
| | D | E% | D | E% |
| **----** | **4.627** | **82.228** | **4.627** | **82.228** |
| $Br^-$ | 1.941 | 66.000 | 1.000 | 50.000 |
| $SCN^-$ | 1.857 | 65.000 | 2.333 | 70.000 |
| $SO_4^=$ | 2.030 | 67.000 | 1.326 | 57.000 |
| $Cr_2O_7^=$ | 2.125 | 68.000 | 0.887 | 47.000 |
| $CrO_4^=$ | 2.333 | 70.000 | 1.632 | 62.000 |
| $CO_3^=$ | 1.500 | 60.000 | 0.724 | 42.000 |
| $IO_3^-$ | 0.818 | 45.000 | 2.030 | 67.000 |

Aqueous phase: - (2 mL) solution of Co (II) ion concentration (200 μg), + (1 mL) (500µg/mL & 1000μg/mL), from some of the anions+ (2mL) deionized water, at (pH =10).

Organic phase: - (5mL) (DPDQ) dissolved in Chloroform.

Equilibrium time: - (10) minutes.

Temperature: - (20± 2) °C .

**Table (3-11): The effect of adding some anions to extract Fe (III) ion by using (DPDQ).**

| Anions | 500µg/mL | | 1000µg/mL | |
|---|---|---|---|---|
| | D | E% | D | E% |
| ---- | **20.177** | **95.278** | **20.177** | **95.278** |
| $Br^-$ | 12.676 | 92.688 | 10.748 | 91.488 |
| $SCN^-$ | 7.538 | 88.288 | 9.297 | 90.288 |
| $SO_4^=$ | 8.423 | 89.388 | 7.840 | 88.688 |
| $Cr_2O_7^=$ | 13.680 | 93.188 | 4.913 | 83.088 |
| $CrO_4^=$ | 8.513 | 89.488 | 7.538 | 88.288 |
| $CO_3^=$ | 9.625 | 90.588 | 10.888 | 91.588 |
| $IO_3^-$ | 3.482 | 77.688 | 0.508 | 33.688 |

Aqueous phase :-( 2mL) solution of Fe (III) ion concentration (500µg), + (1mL) (500µg/mL&1000µg/mL) from some of the negative ions & (2mL) deionized water at (pH = 7).

Organic phase: - (5 mL) (DPDQ) dissolved in chloroform. Equilibrium time: - (15) min. Temperature: - (20 ± 2) °C.

The results in the tables (3-10) and (3-11) show that the presence of some anions have disparity influence on the extraction of Co (II) and Fe (III) ions, separately, depending on the nature of the anions added.

### (3-7-4-2)The effect of some cations on the extraction

Number of cations were selected to study the influence of the extraction of Co (II) and Fe (III), separately, ions using (DPDQ), (D) values and (E%) were calculated to extract (200 µg/5mL), ($6.7873x10^{-4}$M) of Co (II) and (200µg5mL),($7.1626x10^{-4}$M) of Fe (III) ions, separately, under optimum conditions in the presence of (1000µg) of some cations by (DPDQ) dissolved in chloroform. Table (3-12) and (3-13) shows the results for this study.

## Table (3-12): The effect of some cations on the extraction of Co (II) ion with (DPDQ).

| **Cations** | **D** | **E%** |
|---|---|---|
| **---** | **4.618** | **82.200** |
| **$Pb^{2+}$** | 3.115 | 75.700 |
| **$Ag^{1+}$** | 2.577 | 72.040 |
| **$Cu^{2+}$** | 3.352 | 77.020 |
| **$Ni^{2+}$** | 0.767 | 43.400 |
| **$Cd^{2+}$** | 2.572 | 72.005 |
| **$Cr^{3+}$** | 2.356 | 70.200 |
| **$Hg^{2+}$** | 1.919 | 65.736 |
| **$Sr^{2+}$** | 2.209 | 68.841 |

**Aqueous phase :-( 2mL) solution of Co (II) ion concentration (200µg), + (1mL) (200µg/mL) from some of the positive ions & (2mL) deionized water at (pH = 10).**

**Organic phase: - (5 mL) (DPDQ) dissolved in chloroform.**
**Equilibrium time: - (10) min.**
**Temperature: - (20 ± 2) °C**

**Table (3-13): The effect of some cations in the extraction of Fe (III) ion with (DPDQ).**

| Cations | D | E% |
|---|---|---|
| --- | **20.133** | **95.268** |
| **$Pb^{2+}$** | 9.855 | 90.788 |
| **$Ag^{+}$** | 14.451 | 93.528 |
| **$Cu^{2+}$** | 11.639 | 92.088 |
| **$Ni^{2+}$** | 9.625 | 90.588 |
| **$Cd^{2+}$** | 14.547 | 93.568 |
| **$Cr^{3+}$** | 11.031 | 91.688 |
| **$Hg^{2+}$** | 12.904 | 92.808 |
| **$Sr^{2+}$** | 13.468 | 93.088 |

**Aqueous phase :-(2mL) solution of Fe(III) ion concentration(200µg), +(1mL) (200µg/mL) from some of the positive ions&(2mL) deionized water at (pH = 7).**
**Organic phase: - (5 mL) (DPDQ) dissolved in chloroform.**
**Equilibrium time: - (15) min.**
**Temperature: - (20 ± 2) °C.**

From table (3-12) the results show that the extraction of Co (II) ions in presence of some cations leads to disparity results, since the presence ($Ni^{2+}$, $Cr^{3+}$, $Hg^{2+}$ and $Sr^{2+}$) were working to reduce (D) value. The reason attributed to competition cations with Co (II) ion to coordinate with (DPDQ) to form complexes[93].

Also table (3-12) shows that a little effect on the values of distribution ratios for Co (II) ion extraction with (DPDQ) in the presence of $Pb^{2+}$ & $Cu^{2+}$ .

From table (3-13) the results show that the extraction of Fe (III) ion in presence of some cations leads to a little effect on the values of distribution ratios. The reason was attributed to the possibility that these ions may be absorpted at the same ($\lambda_{max}$) of complex or decrease hydration energy for ions lead to increase E% [92].

## (3-7-5)The effect of the oxidation agents and reduction agents on the extraction.

The effect of the oxidation was examined by adding (1mL) from 35 % (W/V) of hydrogen peroxide solution as an oxidant agent in extraction of Co (II) and Fe(III) ions, separately, with (DPDQ), under the optimum conditions. Distribution ratios of Co (II) and Fe (III) ions with (DPDQ) calculated after separating aqueous phase from organic phase. The amount of remained ions in aqueous phase were, calculated by colorimetric method[76].

The influence of the reducing agent on (D) value to extract Co(II) and Fe(III) ions, separately, with (DPDQ) were studied by adding (1mL) from (1M) of $SnCl_2.2H_2O$ solution to the aqueous phase and by following the same method used with the studying of the influence of oxidizing agent. Results were illustrated in the tables (3-14) and (3-15).

**Table (3-14): The effect of oxidation - reduction factors in the extraction of Co (II) ion with (DPDQ).**

| Extraction | D | E% |
|---|---|---|
| **Co (II) with (DPDQ)**<br>**In absence of oxidation-reduction factors** | **4.556** | **82.000** |
| **Co (II) with (DPDQ)**<br>**In presence of oxidation factors** | 1.862 | 65.060 |
| **Co (II) with (DPDQ)**<br>**In presence of reduction factors** | 2.334 | 70.005 |

**Table (3-15): The effect of oxidation - reduction factors in the extraction of Fe (III) with (DPDQ)**

| Extraction | D | E% |
|---|---|---|
| **Fe (III) with (DPDQ)**<br>**In absence of oxidation-reduction factors** | **20.088** | **95.258** |
| **Fe (III) with (DPDQ)**<br>**In presence of oxidation factors** | 3.365 | 77.088 |
| **Fe (III) with (DPDQ)**<br>**In presence of reduction factors** | 19.695 | 95.168 |

The results of this study show that the extraction processes were incompetent in the presence of oxidizing agent because of it's effect on the reagent. It probably works on the oxidation and changes the nature of chelating reagent. The oxidation of Co (II) and Fe (III) ions were also expected that distortion of the system of complex formation extracted. Therefore, affect the process of extraction, because the Co (II) and Fe (III) not extracted efficiently by (DPDQ). While the results of reducing agent show that distribution ratios were increased when extracted Fe (III) because of increasing in stability of trivalent oxidation state Fe (II) , while decreasing in extraction of Co (II) , Separately, because Co (II) ion was not reduced by using $SnCl_2.2H_2O$ and Co (I) is not stable.

### (3-7-6)The effect of enrichment extraction (Volume concentration technique) on the extraction.

The values of distribution ratios for the extraction of Co (II) and Fe (III) ions, separately, were calculated from volumes ranging from (5-25) mL for Co(II) and Fe(III), separately, of aqueous phase by using (5) mL of organic phase. Under the optimum conditions Tables (3-16) and (3-17) show the results.

**Table (3-16): The effect of enrichment method to extract Co (II) ion by using (DPDQ).**

| Volume of aqueous phase (mL) | Volume of organic phase (mL) | D | E% |
|---|---|---|---|
| **5** | **5** | **4.615** | **82.190** |
| 10 | 5 | 2.333 | 53.846 |
| 15 | 5 | 0.587 | 16.372 |
| 20 | 5 | 0.136 | 3.297 |
| 25 | 5 | 0.053 | 1.042 |

**Aqueous phase: - (XmL) of a solution of Co (II) ion concentration (200 µg), at (pH=10).**
**Organic phase: - (5 mL) (DPDQ) dissolved in Chloroform.**
**Equilibrium time: - (10) min.**
**Temperature: - (20±2) ˚C.**

**Table (3-17): The effect of enrichment method to extract Fe (III) using (DPDQ).**

| Volume of aqueous phase (mL) | Volume of organic phase (mL) | D | E% |
|---|---|---|---|
| 5 | **5** | **20.164** | **95.275** |
| 10 | 5 | 17.776 | 89.887 |
| 15 | 5 | 10.182 | 77.242 |
| 20 | 5 | 9.972 | 71.372 |
| 25 | 5 | 4.301 | 46.240 |

**Aqueous phase: - (XmL) of a solution of Fe (III) ion concentration (200 µg), at(pH=7).**
**Organic phase: - (5 mL) (DPDQ) dissolved in chloroform.**
**Equilibrium time: - (15) min.**
**Temperature :-( 20±2) ˚C.**

The results of the tables (3-16) and (3-17) show the possibility to extract Co(II) and Fe (III) ions, separately, by the reagent(DPDQ) from large volumes of aqueous phase, but in low distribution ratios and thus being (E%) were an efficient. The results of this study approved with recent studies[94].

The results indicate that a preferred (aqueous/organic) phase ratio in this study found to be (5:5). This is evident from the sharp increase in the separation efficiency as well as the distribution ratio of Co (II) and Fe (III) when phase ratio (A/O) changed from (25:5) to (5:5) for Co (II) and Fe (III), respectively ; This may simply be due to the unavailability of reagent for metal extraction and so a crowding effect occurs at low phase ratio[95].

## (3-7-7)The effect of concentration of Co (II) and Fe (III) ions on the extraction.

Co(II) and Fe(III) ions are extracted from aqueous solution which contain increasing concentrations of these ions ranged from (50 µg/5mL to 350µg / 5mL), ($1.6968x10^{-4}$ M to $1.18778x10^{-3}$ M) for Co(II) and (25 µg/5mL to 350µg/ 5mL), ($8.9533x10^{-5}$ M to $1.25346x10^{-3}$ M) for Fe(III), separately, with (5 mL), (0.1%DPDQ) solution under the optimum conditions. Results of this study described in tables (3-18), (3-19) and figures (3-18), (3-19).

**Table (3-18): The effect of concentration of Co (II) ion by using (DPDQ) on extraction.**

| **$[M]x10^{-4}$** | **Log[M]** | **D** | **E%** |
|---|---|---|---|
| 1.697 | -3.770 | 1.784 | 64.082 |
| 3.394 | -3.469 | 2.910 | 74.427 |
| 5.091 | -3.293 | 3.688 | 78.667 |
| **6.787** | **-3.168** | **4.743** | **82.588** |
| 8.484 | -3.071 | 3.470 | 77.631 |
| 10.018 | -2.999 | 3.286 | 76.667 |
| 11.889 | -2.925 | 2.889 | 74.286 |

**Aqueous phase: - (5 mL) solution of Co (II) ion in different concentration with (at (pH= 10).**

**Organic phase: - (5mL) (DPDQ) dissolved in Chloroform.**

Equilibrium time: - (10) min.

Temperature: - (20 ± 2) °C.

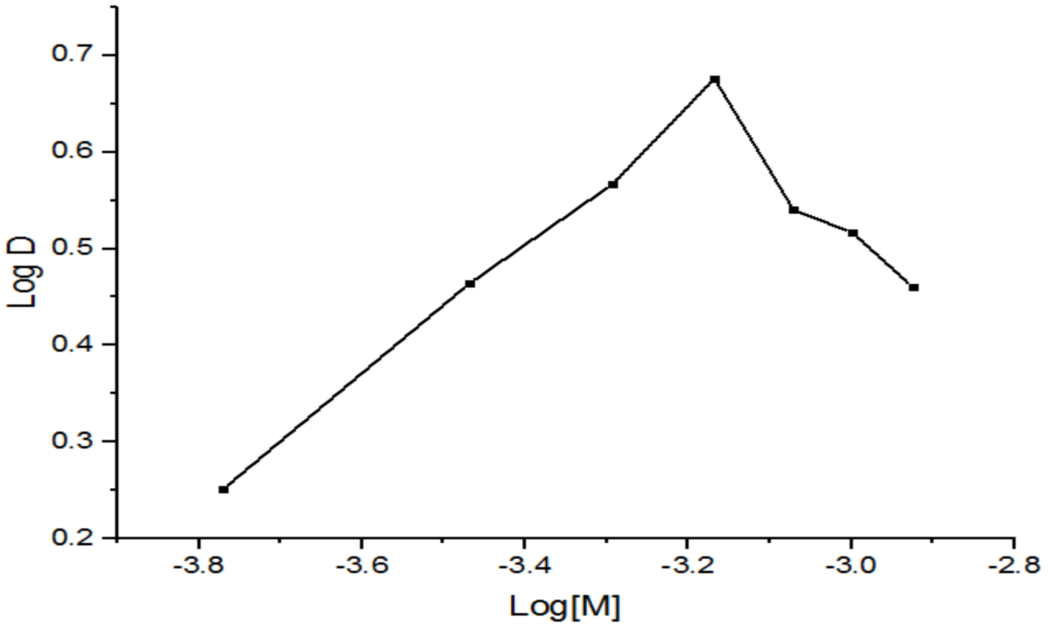


**Fig. (3-18)The effect of different concentration of Co (II) ion by using (DPDQ) on the extraction.**

**Table (3-19): The effect of concentration of Fe (III) ion by using (DPDQ) on extraction.**

| **$[M]x10^{-4}$** | **Log [M]** | **D** | **E%** |
|---|---|---|---|
| 0.895 | -4.048 | 5.298 | 84.121 |
| 1.791 | -3.747 | 6.433 | 86.546 |
| 3.581 | -3.446 | 7.865 | 88.720 |
| 5.372 | -3.270 | 13.665 | 93.181 |
| **7.163** | **-3.145** | **20.124** | **95.266** |
| 8.953 | -3.048 | 13.837 | 93.260 |
| 10.744 | -2.969 | 6.952 | 87.425 |
| 12.535 | -2.902 | 4.118 | 80.461 |

**Aqueous phase: - (5 mL) solution of Fe (III) ion in different concentration with at (pH= 7).**

**Organic phase: - (5mL) (DPDQ) dissolved in Chloroform.**

Equilibrium time: - (15) min.

Temperature: - (20 ± 2) °C.

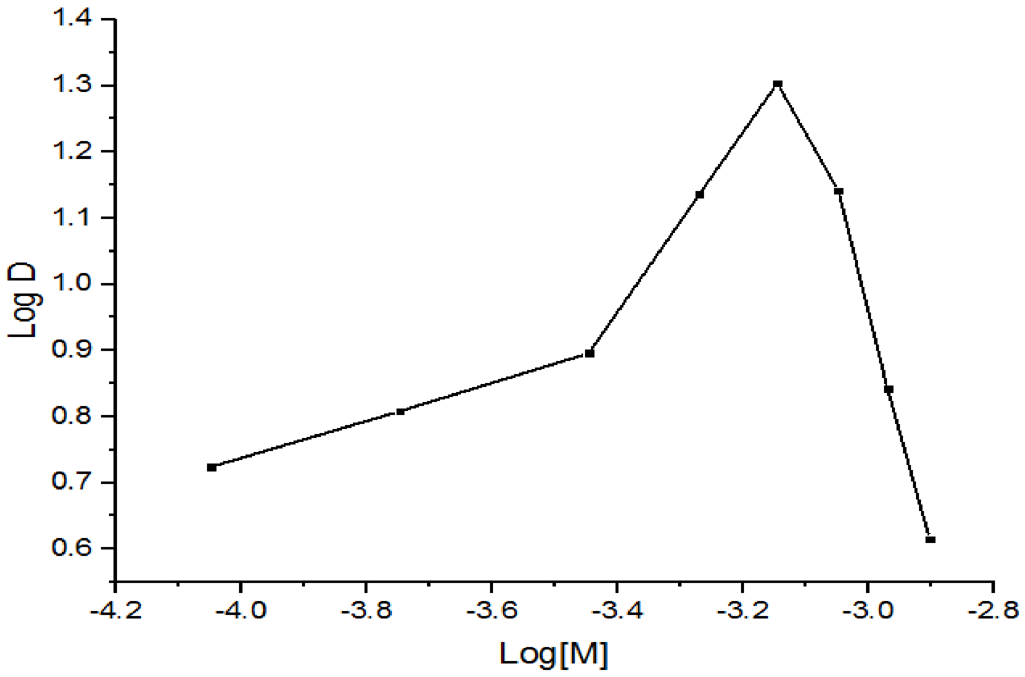


**Fig. (3-19)The effect of different concentration of Fe (III) ion by using (DPDQ) in the extraction.**

From the result in tables (3-18), (3-19) and figures (3-18), (3-19). The relationship between the (D) value with concentration of Co (II) and Fe (III) ions was not linear, when extracted by (DPDQ).

## (3-7-8)The effect of salting out on the extraction

To study the effect of the salting, Ammonium chloride, Sodium chloride, Sodium sulphate & Sodium nitrate chosen for this purpose, because these salt was not extracted from organic phase. It can be stripped and destroyed if we need to do that, so it is favorite as salting agent[96].

The values of distribution ratios were calculated to extract (200µg/5mL), ($6.7873 \times 10^{-4}$ M) of Co(II) and (200µg/5mL), ($7.1626 \times 10^{-4}$ M) Fe (III) ions, separately, with (0.1%)(DPDQ) dissolved in chloroform in the presence of (1mL of 1M ) of ammonium chloride, Sodium chloride, Sodium sulphate & Sodium nitrate solutions under the optimum conditions.

**Table (3-20) The effect of salting process to extract Co (II) ion with (DPDQ).**

| Salt | D | E% |
|---|---|---|
| --- | **4.616** | **82.195** |
| $NH_4Cl$ | 2.704 | 73.000 |
| NaCl | 2.226 | 69.000 |
| $Na_2SO_4$ | 2.448 | 71.000 |
| $NaNO_3$ | 2.030 | 67.000 |

**Table (3-21): The effect of salting process to extract Fe (III) ion with (DPDQ).**

| Salt | D | E% |
|---|---|---|
| --- | **20.133** | **95.268** |
| $NH_4Cl$ | 2.464 | 71.128 |
| NaCl | 3.701 | 78.728 |
| $Na_2SO_4$ | 3.547 | 78.008 |
| $NaNO_3$ | 4.941 | 83.168 |

From the results in table (3-20) & (3-21) the (D) values to extract Co (II) & Fe (III) ions with (DPDQ) decreased in the presence of salting factor. The reason for this could attributed to the behavior of negative ion as masking agent, which decrease the coordinate linkage of (DPDQ) with ions. The reason for this could be attributed to the possibility that salting process decreases hydration energy for Co (II) and Fe (III) ions extracted and this leads to facilitate the replacement of water molecules with reagent molecules.

### (3-7-9) Effect of batch method on the extraction

The effect of using batch extraction to extract (200µg/5mL), ($6.7873 \times 10^{-4}$ M) of Co (II) and (200µg/5mL), ($7.1626 \times 10^{-4}$ M) of Fe (III) ions, separately, with (DPDQ) was studied. Extraction held in three stages after partition of organic phase (5mL) into three volumes. Equal volume for each extraction stage had been part of this phase. The values of distribution ratios calculated after the end of part three of extraction process, tables (3-22) and (3-23) shows the results of this study.

**Table (3-22): The effect of batch method on the extraction of Co (II) ion with (DPDQ).**

| Extraction Technique | D | E% |
|---|---|---|
| Co(II) with (DPDQ)<br>Continuous extraction | 4.618 | 82.200 |
| Co(II) with (DPDQ)<br>Batch extraction | 4.507 | 81.840 |

**Temperature: - (20±2) ˚C.**

**Table (3-23): The effect of batch method on the extraction of Fe (III) ion with (DPDQ).**

| Extraction Technique | D | E% |
|---|---|---|
| Fe(III) with (DPDQ)<br>Continuous extraction | 20.177 | 95.278 |
| Fe(III) with (DPDQ)<br>Batch extraction | 20.066 | 95.253 |

**Temperature: - (20±2) °C.**

The results of the tables (3-22) and (3-23) show a little change in (D) values and (% E) for Co(II) and Fe(III) ions, separately, extraction with (DPDQ), which means that the possibility of using a continuous extraction to save effort and time[94].

### (3-7-10)The effect of temperature on the extraction and determination of some thermodynamic functions.

The values of distribution ratios for extraction of Co(II) and Fe(III) ions, separately, by (DPDQ) dissolve in chloroform at different temperatures ranged from (20-45) °C under the optimum conditions were calculated. Tables (3-24) and (3-25) shows the results of this study.

**Table: (3-24) The values of distribution ratios for the extraction of Co (II) ion by using the reagent (DPDQ) at different temperatures.**

| T( K ) | (1/T)x10$^{-3}$ | D |
|---|---|---|
| 293 | 3.413 | 4.556 |
| 298 | 3.356 | 4.263 |
| 303 | 3.300 | 3.348 |
| 308 | 3.247 | 3.000 |
| 313 | 3.195 | 2.704 |
| 318 | 3.145 | 2.333 |

**Aqueous phase: - (5mL) solution of Co (II) ion concentration (200µg) at (pH = 5).**

**Organic phase: - (5mL) (DPDQ) dissolved in Chloroform.**

**Equilibrium time: - (10) min.**

**Temperature: - ranged from (20-45) °C.**

**Table: (3-25)The values of distribution ratios for the extraction of Fe (III) ion by using the reagent (DPDQ) at different temperatures.**

| T( K ) | (1/T)x10$^{-3}$ | D |
|---|---|---|
| 293 | 3.4130 | 21.163 |
| 298 | 3.3557 | 13.061 |
| 303 | 3.3003 | 9.130 |
| 308 | 3.2468 | 4.221 |
| 313 | 3.1949 | 3.800 |
| 318 | 3.1447 | 3.506 |

**Aqueous phase: - (5mL) solution of Fe (III) ion concentration (200 µg) , at (pH = 7).**

**Organic phase: - (5mL) (DPDQ) dissolved in Chloroform.**

**Equilibrium time: - (15) min.**

**Temperature: - ranged from (20-45) °C.**

By using Vant-Hoff Equation (3-1): [97]

$$2.303 \text{ Log } D = \frac{-\Delta H}{RT} \text{-------} (3\text{-}1)$$

In addition, by drawing the relationship between the Log D versus 1/T, the two figures (3-20), (3-21) obtained, and the value of enthalpy ($\Delta H_{ex}$) calculated.

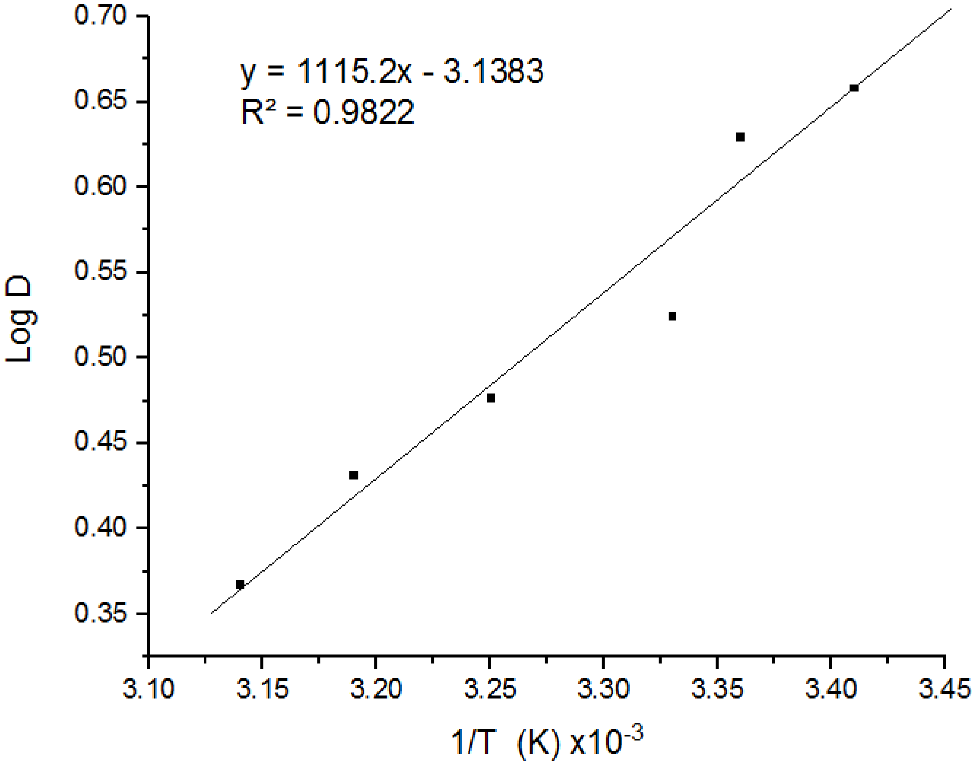


**Fig. (3-20)The effect of temperature to extract Co (II) ion by using (DPDQ).**

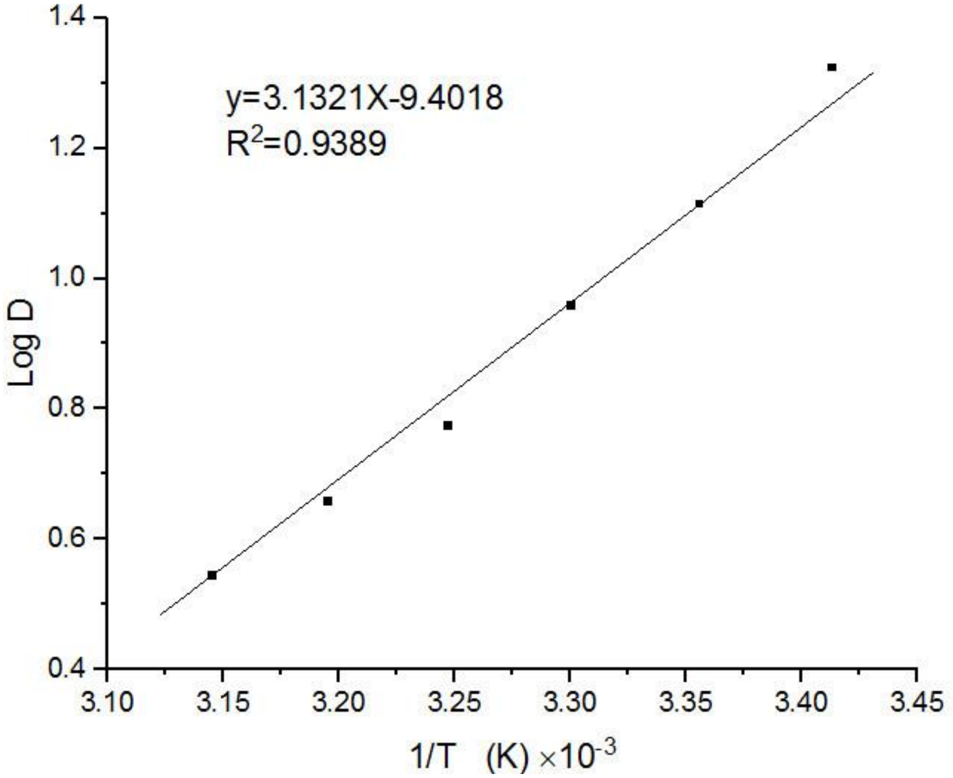


**Fig. (3-21)The effect of temperature to extract Fe (III) ion by using (DPDQ).**

Values of ($\Delta G_{ex}$), ($\Delta S_{ex}$) were calculated by using the Gibbs equations described below[97]: -

$\Delta G_{ex} = \Delta H - T\Delta S$ ………… (3-2)

$\Delta G_{ex} = -RT \ln D$ ………… (3-3) where $\text{Log } D = \text{Log } K_{ex}$,

**Table (3-26) The values of thermodynamic functions to extract Co (II) ion by using (DPDQ)**

| T (K) | $\Delta H_{ex}$(kJ.Mol$^{-1}$) | $\Delta G_{ex}$(kJ.Mol$^{-1}$) | $\Delta S_{ex}$(J.K$^{-1}$.Mol$^{-1}$) |
|---|---|---|---|
| 293 | -18.4 | -3.6944 | -0.05018 |
| 298 | | -3.5931 | -0.04968 |
| 303 | | -3.0444 | -0.05067 |
| 308 | | -2.8137 | -0.05060 |
| 313 | | -2.5887 | -0.05051 |
| 318 | | -2.24053 | -0.05081 |

**Table (3-27) The values of thermodynamic functions to extract Fe (III) ion by using (DPDQ).**

| T (K) | $\Delta H_{ex}$(kJ.Mol$^{-1}$) | $\Delta G_{ex}$(kJ.Mol$^{-1}$) | $\Delta S_{ex}$(J.K$^{-1}$.Mol$^{-1}$) |
|---|---|---|---|
| 293 | -57.2585 | -7.4366 | -0.1700 |
| 298 | | -6.3675 | -0.17077 |
| 303 | | -5.5721 | -0.17058 |
| 308 | | -3.6885 | -0.1739 |
| 313 | | -3.4748 | -0.17183 |
| 318 | | -3.3173 | -0.1696 |

The results in tables (3-24), (3-25) and figures (3-20), (3-21) show that the (D) values for the extraction of Co(II) and Fe(III)ions, separately, with reagent (DPDQ) decreases with increasing temperature. From tables (3-26) and (3-27) the negative sign of the values of enthalpy show that the reaction between Co(II) and Fe(III) ions, separately, with (DPDQ) were exothermic and these means decrease in the possibility of formation complex that extract with increasing temperature, in general for this type of reaction reagent.

The negative sign of the free energy for the extraction of Co (II) and Fe (III) ions, respectively, with reagent (DPDQ) indicate the reactions are spontaneously. Transfer of ions from aqueous phase to organic phase are spontaneous and this is favorite thermodynamically in low temperature and lead to increase the distribution ratio with decrease the temperature. The values of entropy approach to zero and each other demonstrated to the spontaneous reaction (less random) and stability of complex that extracted, these study are in agreement with a previously studies[91,98,99] with other reagents.

## (3-8) Stoichiometry of the extracted complexes

The stoichiometry of the extraction complex (M: L) was determined by different methods to determine the more probable structure of chelate complexes.

### (3-8-1) Job's method (Continuous variables)[100]

This method done by mixing different volumes of solutions of equal concentrations ( $6.7873x10^{-4}$ M) of Co (II) and ($7.1626$ $x10^{-4}$ M) of Fe (III) ions , with (DPDQ) so that the final volume equal to (10mL) , under the optimum conditions After the extraction , the organic phase separate from the aqueous phase and the absorption of organic phase (which contains the extracted complex) were measured at ($\lambda_{max}$ = 521.5nm) for Co (II) complex & ($\lambda_{max}$=505.5nm) for Fe (III) complex , tables ( 3-28) , (3-29) and Figures ( 3-22) and (3-23) shows the results of this method.

**Table (3-28): The results of Job's method (continuous variables) for the Co (II) ion by using (DPDQ) dissolved in chloroform.**

| $V_M/(V_M+V_L)$ | Abs. |
|---|---|
| 0.1 | 1.85 |
| 0.2 | 2.123 |
| 0.3 | 2.448 |
| 0.4 | 2.050 |
| 0.5 | 1.750 |
| 0.6 | 1.470 |
| 0.7 | 1.150 |

**Table (3-29): The results of Job's method (continuous variables) for the Fe (III) ion by using (DPDQ) dissolved in chloroform.**

| $V_M/(V_M+V_L)$ | Abs. |
|---|---|
| 0.9 | 0.907 |
| 0.8 | 1.238 |
| 0.7 | 1.504 |
| 0.6 | 1.760 |
| 0.5 | 2.078 |
| 0.4 | 2.274 |
| 0.3 | 2.528 |
| 0.2 | 2.438 |
| 0.1 | 2.009 |

Drawing Abs. against ($V_M$ / ($V_M$ + $V_L$)), where ($V_M$) refers to the volume of the metal and ($V_L$) refers to the volume of organic reagent, the figures (3-22) and (3-23) will obtained.

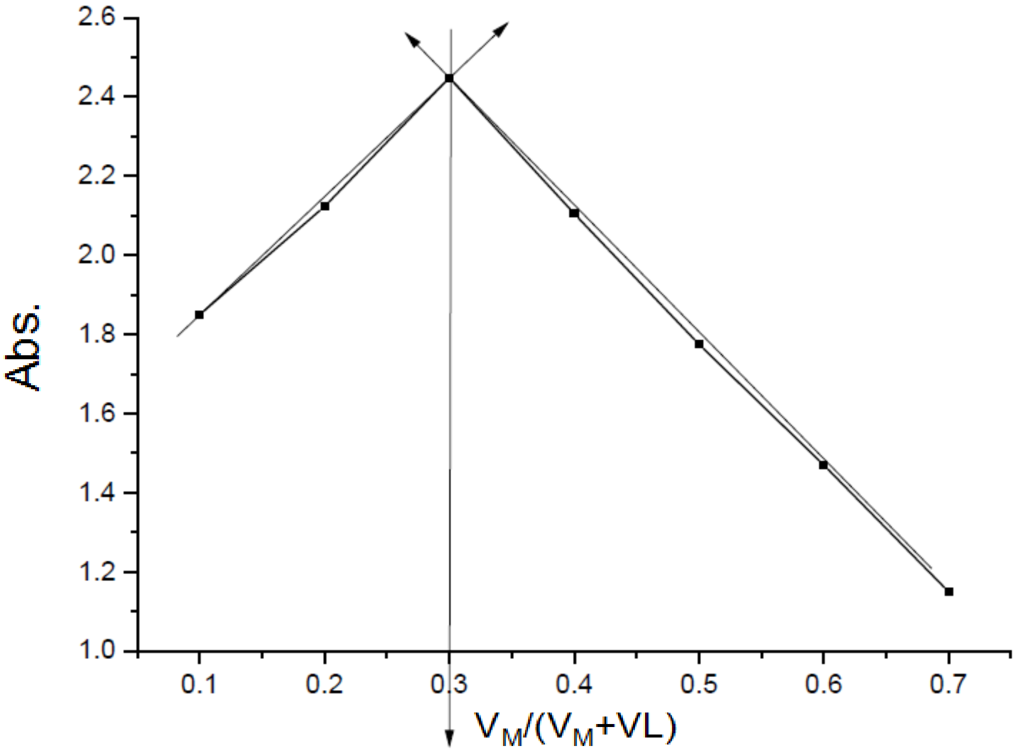


Fig. (3-22) Job's method (continuous variables) for the Co (II) ion with (DPDQ) dissolved in chloroform.

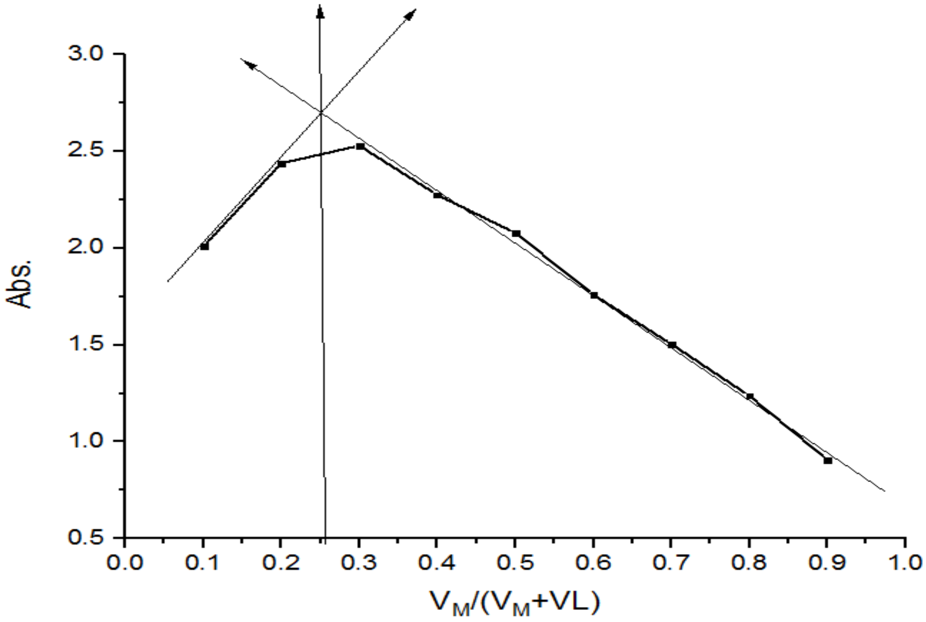


Fig. (3-23) Job's method (continuous variables) for the Fe III) ion With (DPDQ) dissolved in chloroform.

The results in the tables (3-28), (3-29) and figures (3-21), (3-22) show that the stoichiometry of the complexes are ($ML_2$) for Co (II) complex and ($ML_3$) for Fe(III) complex.

## (3-8-2) Mole ratio method[101]

The values of distribution ratios are calculated to extract fixed concentration ($6.7873x10^{-4}$ M) of Co (II) and ($7.1626\ x10^{-4}$ M) of Fe (III) ions, with proportionate and increasing concentration from (DPDQ) under optimum conditions. Tables (3-30), (3-31) and figures (3-24), (3-25) show the results of this method.

**Table (3-30): Mole ratio to extract Co (II) ion by using the reagent (DPDQ) dissolved in chloroform.**

| $C_L/C_M$ | Abs. |
|---|---|
| 0.5 | 0.205 |
| 1.0 | 0.394 |
| 1.5 | 0.544 |
| 2.0 | 0.681 |
| 2.5 | 0.712 |
| 3.0 | 0.801 |
| 3.5 | 0.895 |

**Table (3-31): Mole ratio to extract Fe (III) ion by using the reagent (DPDQ) dissolved chloroform.**

| $C_L/C_M$ | Abs. |
|---|---|
| 0.5 | 1.788 |
| 1.0 | 1.947 |
| 1.5 | 2.125 |
| 2.0 | 2.307 |
| 2.5 | 2.482 |
| 3.0 | 2.531 |
| 3.5 | 2.587 |

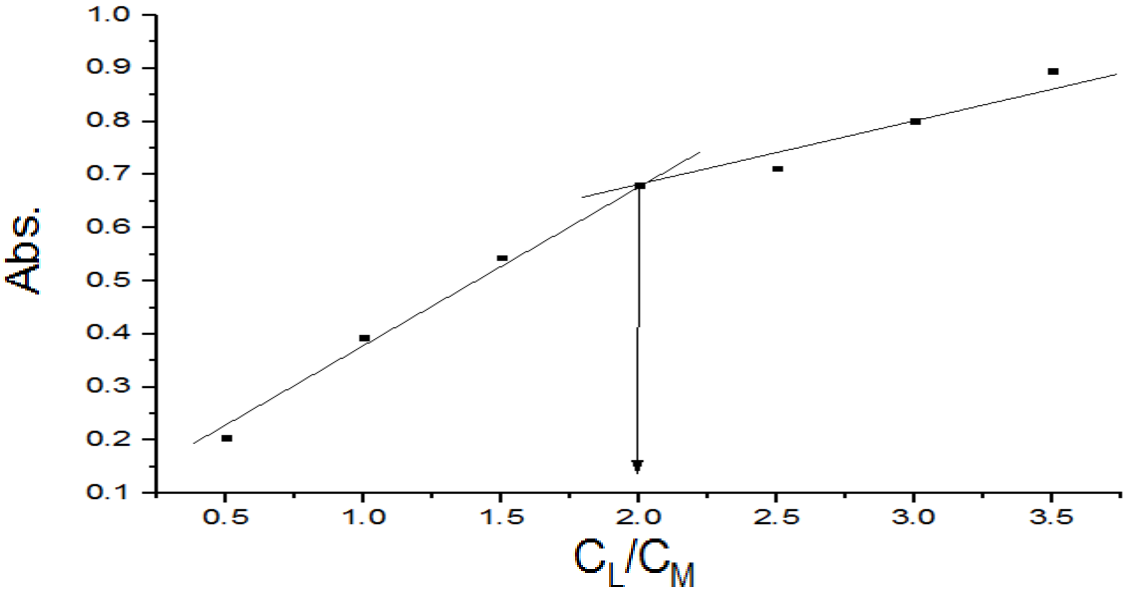


**Fig. (3-24)The mole ratio method to extract Co (II) ion by using (DPDQ).**

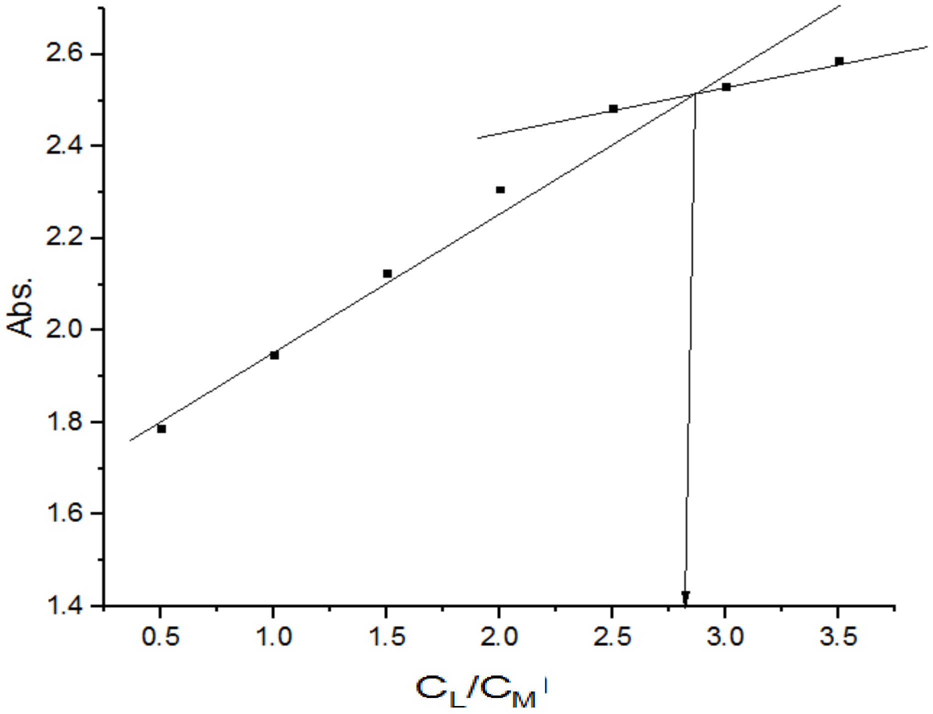


**Fig. (3-25) The mole ratio method to extract Fe (III) ion by using (DPDQ)**

The results of tables (3-30), (3-31) and figures (3-24), (3-25) confirm what came in the job's method (continuous variables) that showed the committed in the extracted complexes have been (1:2) (M: L) for Co(II) complex which means one mole of metal with two mole of reagent and this means that the empirical formula was ($ML_2$) & (1:3) (M: L), which means one that mole of metal with three mole of reagent ($ML_3$) for Fe(III) complex.

## (3-8-3) Substoichiometric Extraction

To study the stoichiometry of the extracted complex of Cobalt , 2.0 mg of (DPDQ) reagent, taken in 5mL chloroform, was used for the extraction of increasing amounts of Cobalt (II) ion (from 25 μg to 400 μg at pH= 10).

The D values of extraction plotted against the amount of ion taken Fig. (3-26).At the equivalence point, it seen that 2 mg reagent corresponded to 200 μg Co (II). Hence, the extracted species might have a molar ratio of metal: reagent = 1: 2.

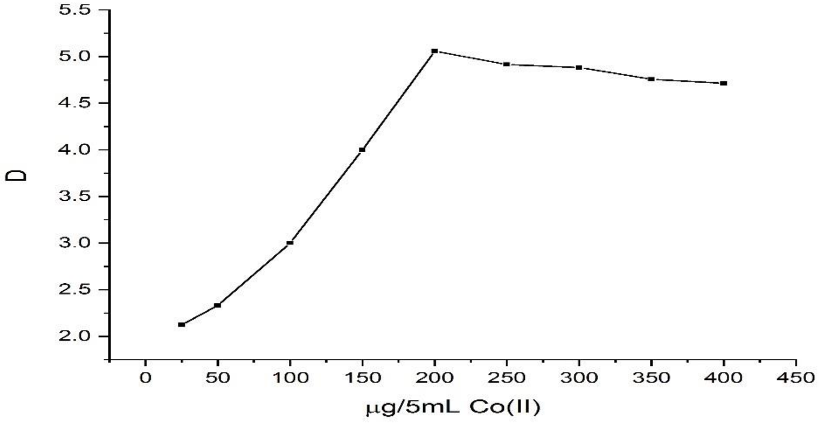


**Fig. (3-26) Reproducibility of Substoichiometric extraction of Co (II) ion using (DPDQ)**

On other hand, the stoichiometry of the extracted complex of Iron , 3.1mg of (DPDQ) reagent, taken in 5mL chloroform, was used for the extraction of increasing amounts of Iron (III) ion (from 25 μg to 400 μg at pH= 7). The D values of extraction plotted against the amount of ion taken Fig. (3-27).

At the equivalence point, it seen that 3.1 mg reagent corresponded to 200µg Fe (III). Hence, the extracted species might have a molar ratio of metal: reagent = 1: 3.

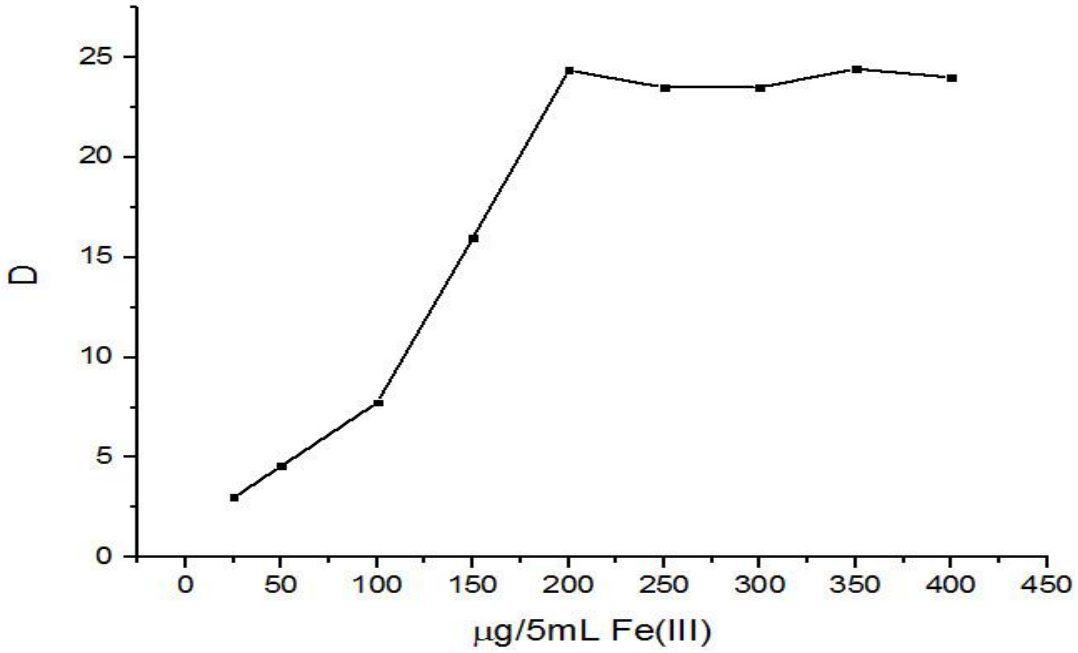


**Fig. (3-27) Reproducibility of substoichiometric extraction of Fe (III) ion using (DPDQ).**

## (3-9) Study the stability for the extracted complexes in organic phase.

The stability of the complex represented by the magnitude of an equilibrium constant representing its formation. Stability constant[102] of the two extracted complexes in the organic phase were calculated ($ML_2$) & ($ML_3$) by drawing the equilibrium reactions for extracted complexes.

$$\underset{\alpha C}{M^{2+}} + \underset{2\alpha C}{2L} \rightleftharpoons \underset{(1-\alpha)C}{ML_2}$$ (for cobalt (II) complex)

$$K = (1\text{-}\alpha)\ C) / \alpha C(2\alpha C)^2 \quad \text{-----------------(3-4)}$$

$$\alpha = \frac{Am - As}{Am} \quad \text{--------------- (3-5)}$$

**Where α: dissociation degree**

**C: Metal concentration**

**K: Stability constant**

**Am: The greatest absorption**

**As: The absorption at end point**

$$\begin{array}{cccc} M^{3+} + & 3L & \rightleftharpoons & ML_3 \\ \alpha C & 3\alpha C & & (1\text{-}\alpha)C \end{array}$$

(for Iron (III) complex)

K = (1-α) C / (αC (3αC) $^3$) .......... (3-6)

**Table (3-32) Data of dissociation constant and stability constant for extracted complexes.**

| Complex | A | $A_s$ | α | $K_{sta.}$ |
|---|---|---|---|---|
| $[Co(DPDQ)_2(H_2O)_2]$ | **0.895** | **0.681** | **0.2391** | **19.3333×10$^8$** |
| $[Fe(DPDQ)_3]$ | **2.587** | **2.482** | **0.0405** | **3.56675×10$^{13}$** |

## (3-10) Spectrophotometric studied

### (3-10-1) Study of UV –Visible Spectra of complexes

1. The (UV –Vis.) spectrum for the complex Co (II) ion with (DPDQ).

Figure (3-28) exhibits a high intense absorption peak at (521.5nm) which used to measure absorption of the complex. By comparing absorption spectrum of reagent, there is red shift for complex.

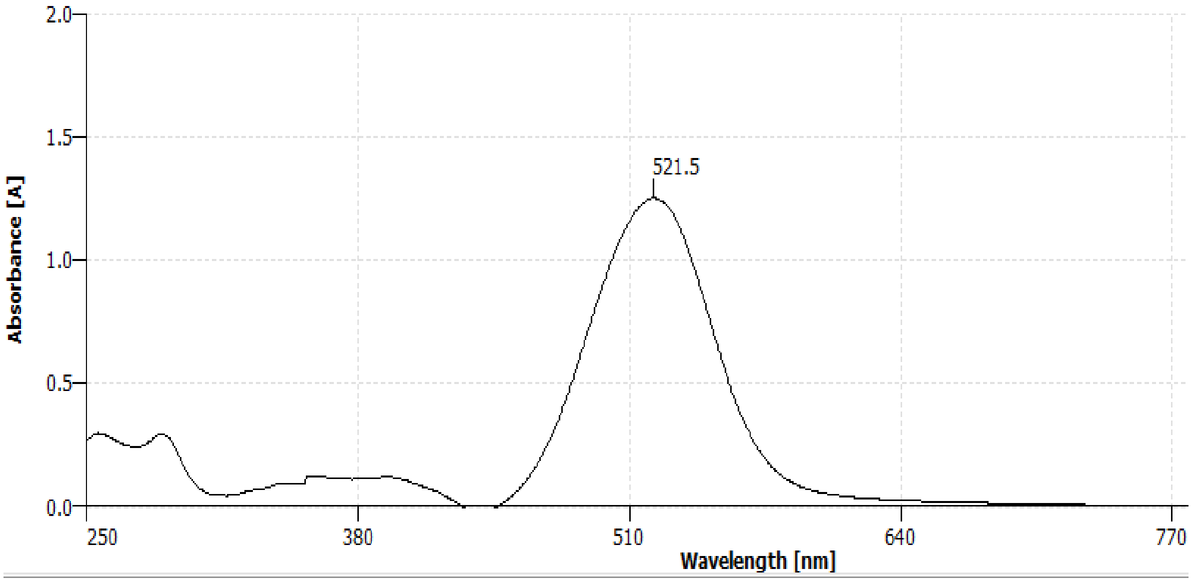


**Figure (3-28) UV –vis. spectrum for the Co (II) complex**

## 2. The (UV –Vis.) spectrum for the complex Fe (III) ion with (DPDQ).

Figure (3-29) exhibits a high intense absorption peak at (505.5nm) which used to measure absorption of the complex. By comparing absorption spectrum of reagent, there is red shift for complex.

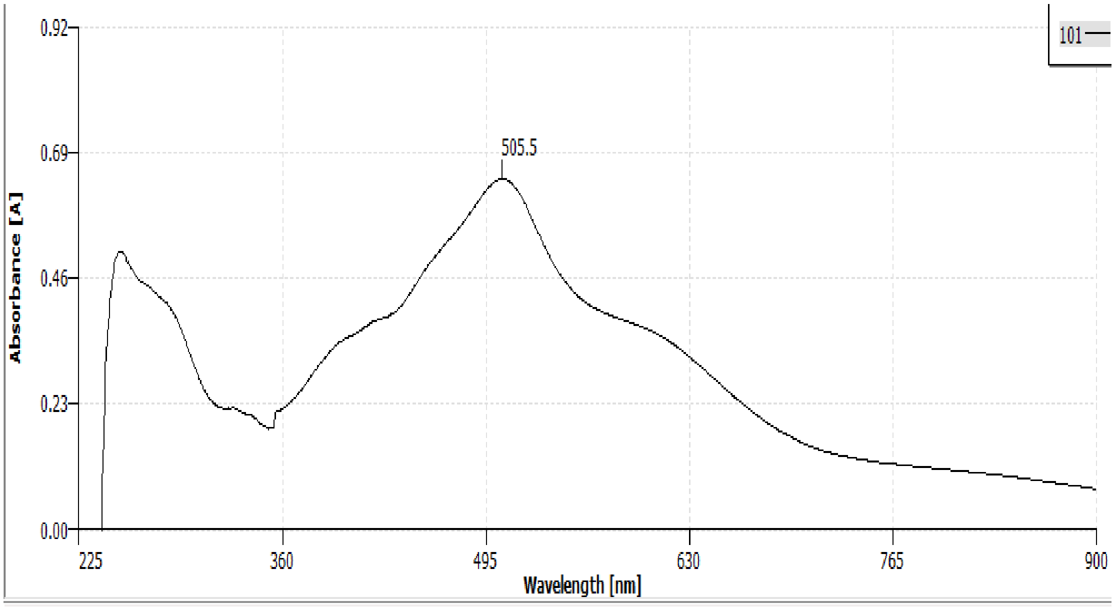


**Figure (3-29) UV –Vis. Spectrum for the Fe (III) complex**

## (3-10-2) Study of FT.IR spectra of complexes: -

FT.IR spectra was recorded for complexes explains as shown in figures (3-30) & (3-31), the data of FT.IR. Spectra listed in table (3-33): -

**Table (3-33) Typical FT-IR absorption frequencies for reagent and complexes in** (cm$^{-1}$) [84-86]

| Bond | Reagent | Cobalt complex | Iron complex |
|---|---|---|---|
| St.(C=N) | 1599.04 | 1581.68 | 1597.11 |
| St.(C-N) | 1363.72 | 1359.86 | 1361.79 |
| St.(C=C)Aromatic | 1568.18 | 1568 | 1568.18 |
| St.(C-H)Aromatic | 3063.06 | 3063 | 3063 |
| St.(N=N) | 1506.46 | 1494.88 | 1494.88 |
| St.(O-H) | 3267.52 | --- | --- |
| St.(C-H)Aliphatic | 2808.45 | 2802.66 | 2804.59 |
| St.(M-N) | --- | 418.57 | 493.19 |
| St.(M-O) | --- | 518.87 | 615.31 |

can explain the results as blow:-

1- The stretching vibration of the (C=N)group has shifted from (1599.04cm$^{-1}$) in the ligand to (1581.68 cm$^{-1}$) in Cobalt (II) complex and to (1597.11 cm$^{-1}$) in Iron (III) complex , which suggests that the electron pairs on N group is not involved in bonding .
2- The absorption in (2808.45-2802.66 cm$^{-1}$) is due to stretching vibration for (C-H) aliphatic in reagent and complexes.

3- The absence of any broad band between (2854 and 3300 cm$^{-1}$) in the Cobalt and Iron complexes, indicates the absence of ν(O-H) thus the possibility of forming a coordinate link to metal through the oxygen of (O-H) group.
4- The stretching vibration of the (N=N)group has shifted from (1506.46 cm-1) in the ligand to (1494.88 cm-1) in both Cobalt (II) complex and Iron (III) complex , which suggests that the electron pairs on N group is involved in bonding.
5- The presence of bands in the (418.57 , 493.19 cm$^{-1}$) region and (518.87 , 615.31 cm$^{-1}$) typical of metal-ligand (M-N)(M-O), suggests that the bonding of the metal to the ligand is through the oxygen atoms and the pairs of electron for nitrogen in both complexes of Cobalt (II) and Iron (III) .

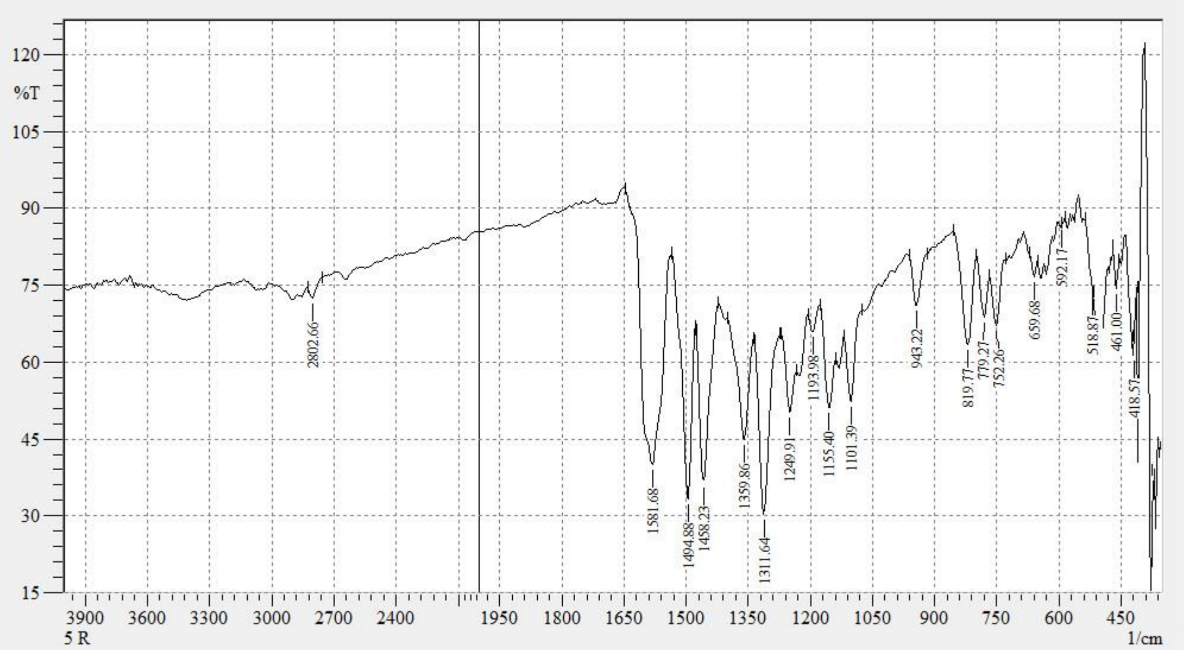


Figure (3-30) FT-IR spectrum of cobalt (II) complex

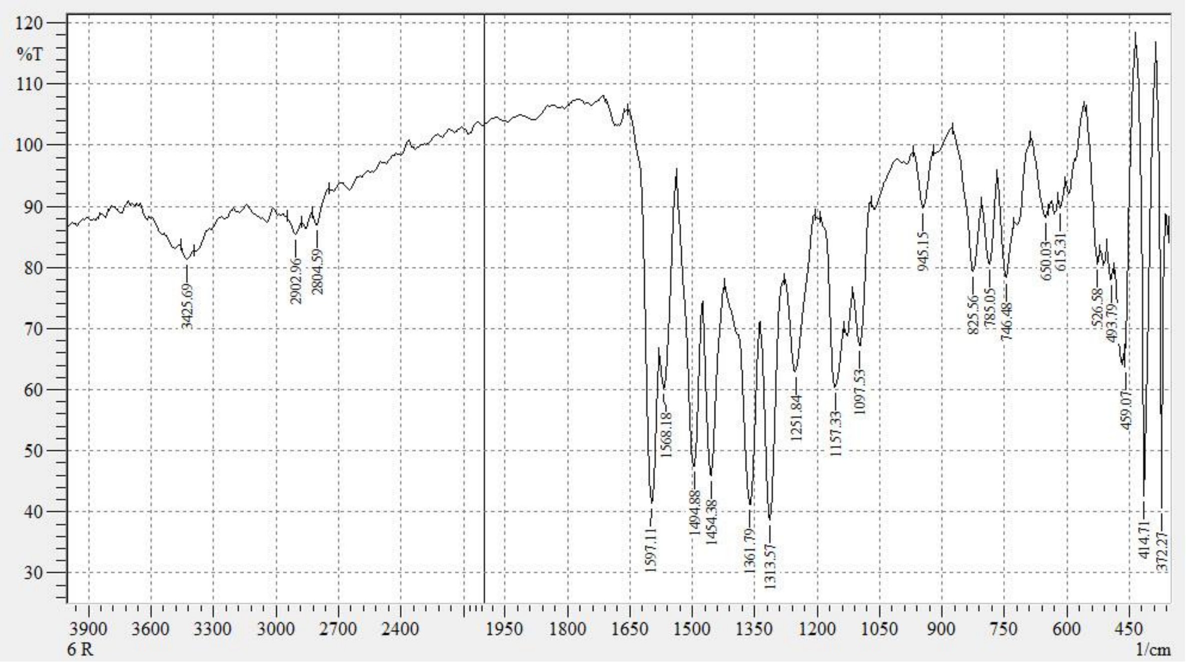


**Figure (3-31) FT-IR spectrum of Iron (III) complex.**

## (3-11) Determination of some physical properties of the complexes

### (3-11-1) Melting point

Melting point of extracted complexes and reagent (DPDQ) measured.

Table (3-34) shows the results.

Table (3-34) melting points

| Material | Melting point ˚C |
|---|---|
| Reagent | 164-166 |
| Cobalt complex | 295-298 |
| Iron complex | 301-304 |

Table (3-34) shows that the complexes were thermal stable.

## (3-11-2) Electrical conductivity

The molar conductivity of the solutions of the solid complexes was measured at the concentration of ($1\times10^{-3}$M) dissolved in ethanol at the laboratory temperature. The results are shown in the table (3-43), showing the absence of the ionic character of both complexes (uncharged)[103].

**Table (3-35) electrical conductivity**

| Material | Molar electrical conductivity Ω(μs/cm$^2$) |
|---|---|
| $Co(DPDQ)_2$ | 14 |
| $Fe(DPDQ)_3$ | 16 |

## (3-12) Study Development of a New Method for Determining the Concentration of Co (II) and Fe (III) Ions in the Organic Phase

The ions extracted in the organic layer are often estimated by the process of stripping. Although, it is characterized by accuracy sometimes, it requires effort and time with the possibility of losing some of the ions if the precautions are not sufficient for this purpose and for this the study aimed at the possibility of identifying cobalt (II) and Iron (III) Extracted by the reagent (DPDQ) individually in the organic phase and directly spectrophotometry, as shown below: -

1- The absorption spectrum of cobalt (II) and Iron (III) complex was studied with the (DPDQ) reagent in the organic layer, where the complexes in the organic phase (chloroform) showed greater absorption at the wavelength ($\lambda_{max}$ = 521.5 nm) and ($\lambda_{max}$ = 505.5 nm) respectively as in Figures (3-28) and (3-29) above.

2- Studying the calibration curve in the organic phase and knowing the extent to which the concentrations comply with (Lambert-Beer's law) and for this purpose, different concentrations of cobalt (II) ion were extracted, ranging from ($1.6967\times10^{-4}$M – $23.7558\times10^{-4}$M), which is equivalent to (50µg/ 5mL-700µg/5mL) , and different concentrations of Iron (III) ion ranged between ($3.5813\times10^{-5}$M – $21.4880\times10^{-4}$M), which is equivalent to (10µg/5mL-600µg/5mL) by (5mL) of the (DPDQ) reagent (0.1%) , after separating the organic layer from the aqueous layer, (5mL) was transferred from the organic layer to a volumetric flask (25mL) and completed the volume to the mark with chloroform, and the absorption of the two complexes was measured at ($\lambda_{max}$ = 521.5nm) and ($\lambda_{max}$ = 505.5 nm), respectively, the results were shown in Figures (3-32) and (3-33), respectively.

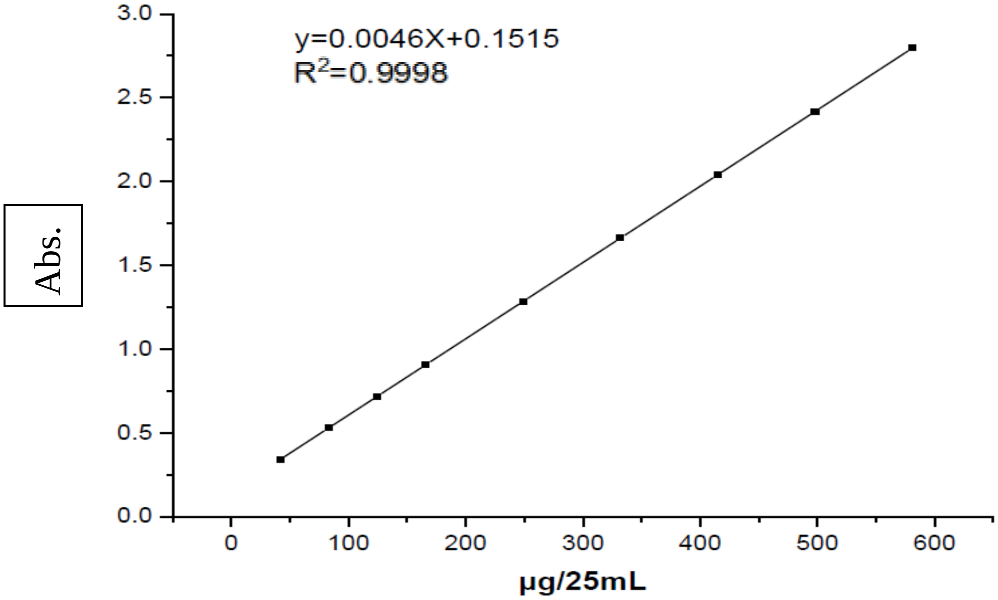


**Figure (3-32) Calibration Carve of Cobalt complex in Organic phase at ($\lambda_{max}$=521.5nm)**

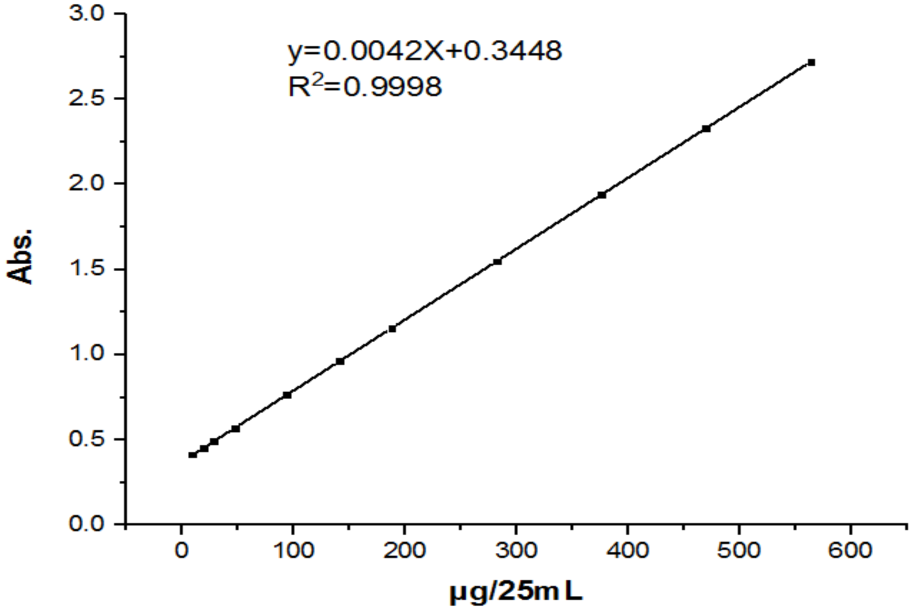


**Figure (3-33) Calibration Carve of Iron (III) complex in Organic phase at ($\lambda_{max}$=505.5nm)**

## (3-13)The suggested structures for complexes

From the results in this study, the stoichiometry of complexes (M: L) were found to be (1:2) & (1:3) for Cobalt (II) & Iron (III) respectively[104]. The suggested structures of complexes explained in figure (3-34).

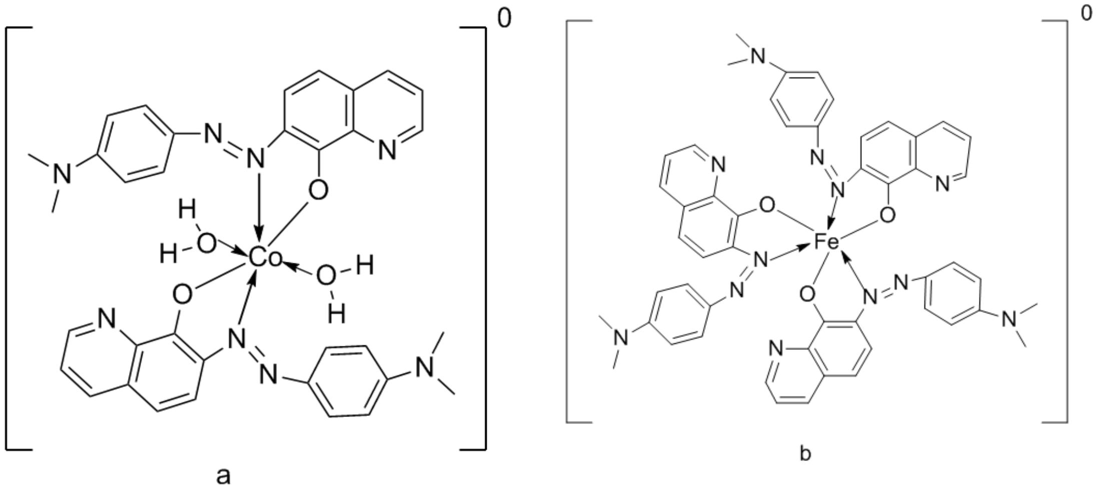


**Fig. (3-34)The suggested figure for the complexes (a.Cobalt (II) complex, b. Iron (III) complex)**

## (3-14) Applications

The applied study included determine each of the Cobalt (II) in the Hair sample using Atomic Absorption Spectroscopy, and Vitamin ($B_{12}$) that was relied on the concentration of Cobalt mentioned on the ampoule, as it is one of the products of the company (GERDA) and the Cobalt concentration was (43.481µg/4mL), The comparison of results obtained from the practical results of extracting the cobalt in the two samples with the reagent (DPDQ) with estimating the amount extracted in the organic phase, showing that the results for the Hair sample close to the Atomic Absorption method , and the practical results of vitamin ($B_{12}$) were also close to that mentioned on the ampoule.

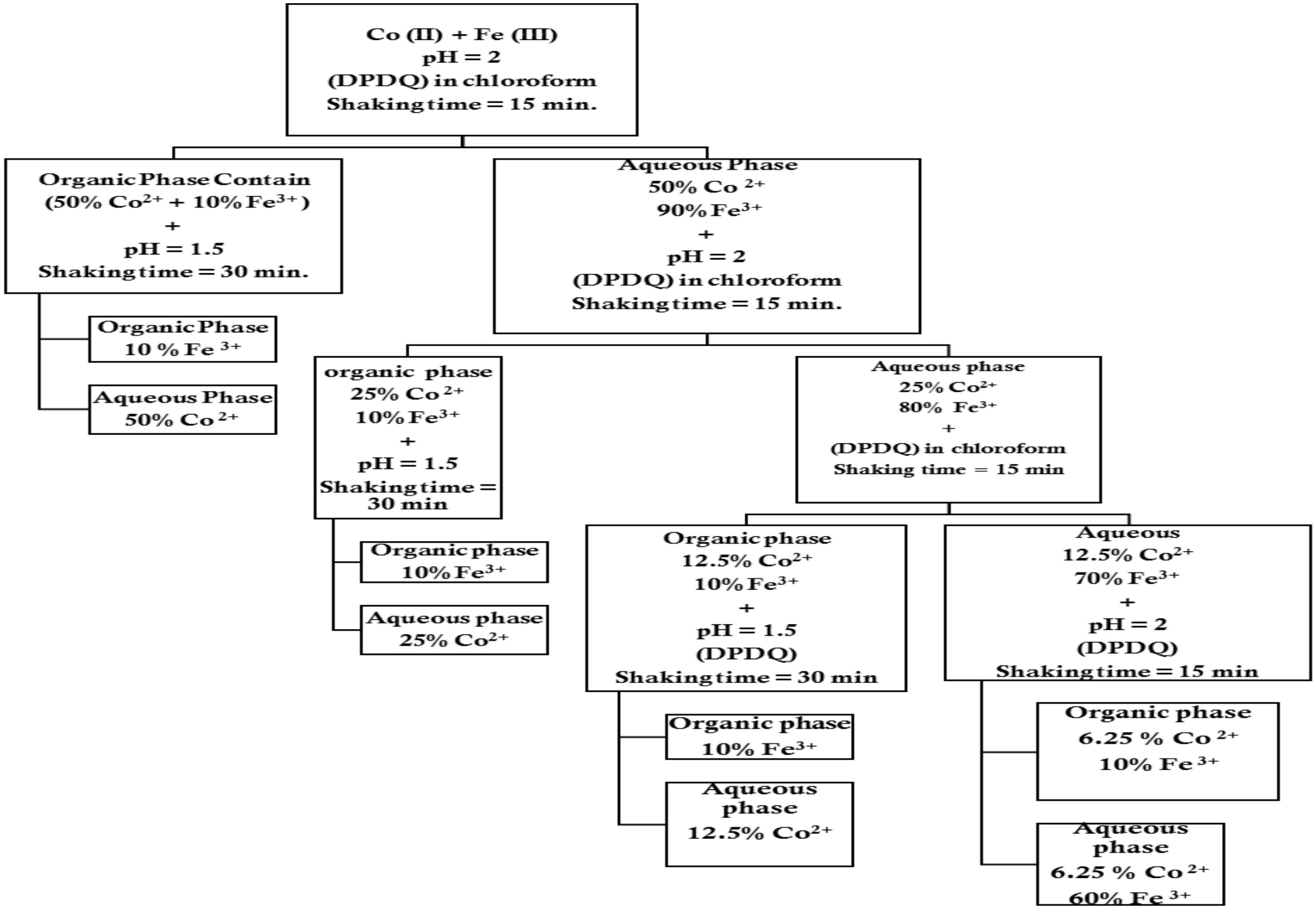
The applied study also included the determination of the Iron ions in samples of medical drugs, and it was based on the percentage of Iron ions mentioned on the drug, where the drug (Referum) which is one of the products of the company (Replek Farm) and contains (100mg Iron($Fe^{3+}$)/tablet), and the drug (Ferrous Sulfate Tablets) produced by the company (Actavis) that contain (65mg ferrous Iron/tablet) , the practical results were very close to what was mentioned on the two drugs. Table (3-36) shows the applied results for the extraction of cobalt and Iron ions.

**Table (3-36) Results of the Applications of Cobalt & Iron Extraction**

| | Sample | Extracted method | Atomic method | E% (error percentage) |
|---|---|---|---|---|
| Cobalt | Hair | 10.875 µg/g | 11.263 µg/g | 3.444 |
| | Vit.B12 | 41.731 µg/10ml | | 4.024 |
| Iron | Referum tablet | 191µg/5mL | | 4.500 |
| | Ferrous Sulfate tablets | 123.5 µg/5mL | | 5.010 |

## (3-15) Sequential extraction

The sequential separation of Cobalt (II) and Iron (III) ions carried out based on the tables (3-4), (3-5), where (200 µg) of both ions mixed. Then extracted with the reagent (DPDQ) .Scheme (3-2) shows diagram illustrates this process.



**Scheme. (3-2)The Sequential extraction of Cobalt (II) & Fe (III) ion**

## (3-16) Statistical Treatment

Relative standard deviation dependent as a measure for precision of data in all experiments. For this purpose, extraction Co (II) ($6.7873x10^{-4}$M), ($10.1810x10^{-4}$M) and Fe (III) ($7.1626x10^{-}4$M), ($10.7440x10^{-4}$M), separately, by using (5 mL) of (DPDQ) dissolved in chloroform. The results obtained in tables (3-37) & (3-38) respectively.

**Table (3-37) The absorption and RSD for extraction of two concentration of Co (II) ion with (DPDQ) dissolved in chloroform.**

| **Exp.*NO.*** | **Abs. (**$6.7873x10^{-4}$M) | **Abs. (**$10.1810x10^{-4}$M) |
|---|---|---|
| 1 | 0.026 | 0.024 |
| 2 | 0.025 | 0.023 |
| 3 | 0.025 | 0.023 |
| 4 | 0.026 | 0.023 |
| **RSD%** | **2.2641** | **2.1505** |

**Table (3-38) The absorption and RSD for extraction of two concentration of Fe (III) ion with (DPDQ) dissolved in chloroform.**

| **Exp.*NO.*** | **Abs. (**$7.1626x10^{-4}$M) | **Abs. (**$10.7440x10^{-4}$M) |
|---|---|---|
| 1 | 0.097 | 0.195 |
| 2 | 0.097 | 0.195 |
| 3 | 0.096 | 0.195 |
| 4 | 0.097 | 0.194 |
| **RSD%** | **0.5167** | **0.2567** |

The tables show that (RSD) in permitted rang in the experimental

## (3-17) Conclusion

1. This study synthesized a new azo derivative from 8-hydroxy quinoline by nitrogen method, and characterization of it by spectroscopic methods such as UV-Vis., FT-IR, $^{1}$HNMR and $^{13}$CNMR.
2. The maximum wavelength ($\lambda_{max}$) was (442 nm) in a chloroform as a best solvent for the reagent and the melting point was (164-166°C).
3. The synthesized reagent use to extract Cobalt (II) and Iron (III) ions from an aqueous solution.
4. The study included parameters that affected this extraction process such as acidity, time extraction, temperature.
5. The study of pH effected on extraction explain that the optimum acidity media was (10, 7) to extracted Cobalt (II) and Iron (III) respectively.
6. The extraction process give a good results at low temperatures because the study of thermodynamic functions ($\Delta H$, $\Delta G$, $\Delta S$) that the process was exothermic and spontaneously.
7. The extracted complex has a red shift in UV-Vis. Spectrum against the reagent.
8. The extracted complexes have a lower electrical conductivity that explains NO effect of the dielectric constant of solvents on extraction process for these ions.
9. Each complex has an octahedral shape.
10. The new reagent could be used to extracted Cobalt (II) & Iron ions from biological and drug samples with a good result.
11. There is no linear proportion between the solvent polarities and (D) value for Cobalt & Iron ions, thus; indicates that the extracted complexes are neutral.

12. The distribution ratio and E% decrease in presence of certain cations and anions and increase in presence of another certain cations and anions for Cobalt & Iron ions being investigated.
13. The batch extraction technique enhanced the extraction but not much.
14. The new reagent successful in sequentially separation for cobalt (II) and Iron (III) ions.

## (3- 18) Recommendations

1- Possibility to use the newly synthesized reagent to extract an other metal ions.

2- Use an other azo derivative of 8-hydroxy quinoline as a reagent to extracted Co (II) and Fe (III) ions.

3- Possibility to use the newly synthesized reagent in quantitative spectroscopic for metal ions.

4- Use the newly synthesized reagent in the sequential separation of other metal ions.

5- Study the biological activity of the complexes of the newly synthesized reagent with metal ions.

# Appendixes

# Appendix (1)

## Calculation of RSD at ($6.7873x10^{-4}$M) of Co (II)

| No. Read | Abs.(Xi) | Mean ($\bar{X}$) | ( Xi-$\bar{X}$) | ∑( Xi-X)$^2$ | $S = \frac{\sqrt{\Sigma(\mathrm{xi}-\bar{\mathrm{x}})2}}{\mathrm{N}-1}$ | $RSD = \frac{S}{\bar{x}} \times 100$ |
|---|---|---|---|---|---|---|
| **1** | 0.026 | 0.0255 | 0.0005 | 1×$10^{-6}$ | 57.735×$10^{-5}$ | 2.2641 |
| **2** | 0.025 | | -0.0005 | | | |
| **3** | 0.025 | | -0.0005 | | | |
| **4** | 0.026 | | 0.0005 | | | |

## Calculation of RSD at ($10.1810x10^{-4}$M) of Co (II)

| No. Read | Abs.(Xi) | Mean ($\bar{X}$) | ( Xi-$\bar{X}$) | ∑( Xi-X)$^2$ | $S = \frac{\sqrt{\Sigma(\mathrm{xi}-\bar{\mathrm{x}})2}}{\mathrm{N}-1}$ | $RSD = \frac{S}{\bar{x}} \times 100$ |
|---|---|---|---|---|---|---|
| **1** | 0.024 | 0.02325 | -0.00075 | 75×$10^{-8}$ | 0.0005 | 2.1505 |
| **2** | 0.023 | | -0.00025 | | | |
| **3** | 0.023 | | -0.00025 | | | |
| **4** | 0.023 | | -0.00025 | | | |

# Appendix (2)

## Calculation of RSD at ($7.1626x10^{-4}$M) of Fe (III)

| No. Read | Abs.(Xi) | Mean ($\bar{X}$) | ( Xi-$\bar{X}$) | ∑( Xi-X)$^2$ | $S = \frac{\sqrt{\Sigma(xi-\bar{x})2}}{N-1}$ | $RSD = \frac{S}{\bar{x}} \times 100$ |
|---|---|---|---|---|---|---|
| **1** | 0.097 | 0.09675 | 0.00025 | $75\times10^{-8}$ | 0.0005 | 0.5167 |
| **2** | 0.097 |  | 0.00025 |  |  |  |
| **3** | 0.096 |  | -0.00075 |  |  |  |
| **4** | 0.097 |  | 0.00025 |  |  |  |

## Calculation of RSD at ($10.7440x10^{-4}$M) of Fe (III)

| No. Read | Abs.(Xi) | Mean ($\bar{X}$) | ( Xi-$\bar{X}$) | ∑( Xi-X)$^2$ | $S = \frac{\sqrt{\Sigma(xi-\bar{x})2}}{N-1}$ | $RSD = \frac{S}{\bar{x}} \times 100$ |
|---|---|---|---|---|---|---|
| **1** | 0.195 | 0.19475 | 0.00025 | $75\times10^{-8}$ | 0.0005 | 0.2567 |
| **2** | 0.195 |  | 0.00025 |  |  |  |
| **3** | 0.195 |  | 0.00025 |  |  |  |
| **4** | 0.194 |  | -0.00075 |  |  |  |

# References

## References

[1] G. S. Shankarling, P. P. Deshmukh, and A. R. Joglekar, “Process Intensification in Azo Dyes,” *Environ. Chem. Eng.*,vol.5,Iss.4, pp.3302-3308, **2017**.

[2] A. Gürses, M. Açıkyıldız, K. Güneş, and M. S. Gürses, “Classification of Dye and Pigments,” pp. 31–45, **2016**.

[3] M. Shah, “Effective Treatment Systems for Azo Dye Degradation: A Joint Venture between Physico-Chemical & Microbiological Process,” *Int. J. Environ. Bioremediation Biodegrad.*, vol. 2, no. 5, pp. 231–242, **2014**.

[4] M. Berradi, Rachid Hsissou, Mohammed Khudhair, Mohammed Assouag, Omar Cherkaoui, Abderrahim El Bachiri, Ahmed El Harf, “Textile finishing dyes and their impact on aquatic environs,” *Heliyon*, vol. 5, no. 11, **2019**.

[5] O. I. Lipskikh, E. I. Korotkova, Y. P. Khristunova, J. Barek, and B. Kratochvil, “Sensors for voltammetric determination of food azo dyes - A critical review,” *Electrochim. Acta*, vol. 260, pp. 974–985, **2018**.

[6] B. Said, R. Souad M’, and E. H. Ahmed, “classifications, recent synthesis and applications of textile dyes,” *Appl. J. Environ. Eng. Sci.*, vol. 3, pp. 311–320, **2017**.

[7] S. Benkhaya, S. M’ rabet, and A. El Harfi, “A review on classifications, recent synthesis and applications of textile dyes,” *Inorg. Chem. Commun.*, vol. 115, no. March, **2020**.

[8] R. F. M. Elshaarawy, T. M. Sayed, H. M. Khalifa, and E. A. El-Sawi, “A mild and convenient protocol for the conversion of toxic acid red 37 into pharmacological (antibiotic and anticancer) nominees: Organopalladium architectures,” *Comptes Rendus Chim.*, vol. 20, pp. 1–8, **2017**.

[9] S. Benkhaya , Brahim Achioub, Mohamed Ouammoub, Jamal Bennazhab, Saad Alami Younssib, Souad M’rabetc, Ahmed El Harfi, “Preparation of low-cost composite membrane made of polysulfone/polyetherimide ultrafiltration layer and ceramic pozzolan support for dyes removal,” *Mater. Today Commun.*, vol. 19, 2018, pp. 212–219, **2019**.

[10] S. Sandhya, “Biodegradation of Azo Dyes Under Anaerobic Condition: Role of Azoreductase,” no. February, pp. 39–57, **2010**.

[11] K. Xie, A. Gao, C. Li, and M. Li, “Sensors and Actuators B : Chemical Highly water-soluble and pH-sensitive colorimetric sensors based on a D – π – A heterocyclic azo chromosphere,” *Sensors Actuators B. Chem.*, vol. 204, pp. 167–174, **2014**.

[12] A. D. Wolela, “An Overview on Surface Modification of Cotton using Cationic Reagents for Salt-Free or Low Salt Dyeing,” *Curr Trends Fash. Technol Text. Eng*, vol. 5, no. 1, pp. 37–46, **2019**.

[13] S. Akhtar, A. A. Khan, and Q. Husain, “Potential of immobilized bitter gourd (Momordica charantia) peroxidases in the decolorization and removal of textile dyes from polluted wastewater and dyeing effluent,” *Chemosphere*, vol. 60, no. 3, pp. 291–301, **2005**.

[14] A. A. Mousa, “Synthesis and application of a polyfunctional bis(monochlorotriazine/sulphatoethylsulphone) reactive dye,” *Dye. Pigment.*, vol. 75, no. 3, pp. 747–752, **2007**.

[15] İ. Şener, N. Şener, and M. Gür, “Synthesis, structural analysis, and absorption properties of disperse benzothiazol-derivative mono-azo dyes,” *J. Mol. Struct.*, vol. 1174, pp. 12–17, **2018**.

[16] Ç. Karabacak Atay, M. Gökalp, S. Ö. Kart, and T. Tilki, “Mono azo dyes derived from 5-nitroanthranilic acid: Synthesis, absorption properties and DFT calculations,” *J. Mol. Struct.*, vol. 1141, pp. 237–244, **2017**.

[17] S. Crespi, N. A. Simeth, and B. König, “Heteroaryl azo dyes as molecular photoswitches,” *Nat. Rev. Chem.*, vol. 3, no. 3, pp. 133–146, **2019**.

[18] N. A. Simeth, S. Crespi, M. Fagnoni, and B. König, “Tuning the Thermal Isomerization of Phenylazoindole Photoswitches from Days to Nanoseconds,” *J. Am. Chem. Soc.*, vol. 140, no. 8, pp. 2940–2946, **2018**.

[19] B. Derkowska-Zielinska, L. Skowronski, T. Kozlowski, V. Smokal, A. Kysil, A. Biitseva, O. Krupka, “Influence of peripheral substituents on the optical properties of heterocyclic azo dyes,” *Opt. Mater. (Amst).*, vol. 49, pp. 325–329, **2015**.

[20] E. Schab-Balcerzak, Henryk Flakus, Anna Jarczyk-Jedryka, Jolanta Konieczkowska, Mariola Siwy, Katarzyna Bijak, Anna Sobolewska, Joachim Stumpe, “Photochromic supramolecular azopolyimides based on hydrogen bonds,” *Opt. Mater. (Amst).*, vol. 47, pp. 501–511, **2015**.

[21] Y. H. Ebead, “Spectrophotometric investigations and computational calculations of prototropic tautomerism and acid-base properties of some new azo dyes,” *Dye. Pigment.*, vol. 92, no. 1, pp. 705–713, **2012**.

[22] U. Kurtan, M. Amir, A. Yildiz, and A. Baykal, “Synthesis of magnetically recyclable MnFe 2 O 4 @SiO 2 @Ag nanocatalyst: Its high catalytic performances for azo dyes and nitro compounds reduction,” *Appl. Surf. Sci.*, vol. 376, pp. 16–25, **2016**.

[23] L. H. Madkour, S. Kaya, C. Kaya, and L. Guo, “Quantum chemical calculations, molecular dynamics simulation and experimental studies of using some azo dyes as corrosion inhibitors for iron. Part 1: Mono-azo dye derivatives,” *J. Taiwan Inst. Chem. Eng.*, vol. 68, pp. 461–480, **2016**.

[24] A. B. Tathe and N. Sekar, “Red Emitting Coumarin—Azo Dyes : Synthesis, Characterization, Linear and Non-linear Optical Properties-

Experimental and Computational Approach," *J. Fluoresc.*, vol. 26, no. 4, pp. 1279–1293, **2016**.

[25] H. Motiei, A. Jafari, and R. Naderali, "Third-order nonlinear optical properties of organic azo dyes by using strength of nonlinearity parameter and Z-scan technique," *Opt. Laser Technol.*, vol. 88, no. September 2016, pp. 68–74, **2017**.

[26] N. O. Mahmoodi, S. Rahimi, and M. Pasandideh Nadamani, "Microwave-assisted synthesis and photochromic properties of new azo-imidazoles," *Dye. Pigment.*, vol. 143, pp. 387–392, **2017**.

[27] Y. K. Tsui, S. Devaraj, and Y. P. Yen, "Azo dyes featuring with nitrobenzoxadiazole (NBD) unit: A new selective chromogenic and fluorogenic sensor for cyanide ion," *Sensors Actuators, B Chem.*, vol. 161, no. 1, pp. 510–519, **2012**.

[28] D. J. Paustenbach, B. E. Tvermoes, K. M. Unice, B. L. Finley, and B. D. Kerger, "A review of the health hazards posed by cobalt," *Crit. Rev. Toxicol.*, vol. 43, no. 4, pp. 316–362, **2013**.

[29] L. A. National and C. Division, "Periodic Table of the Elements A," 2001.

[30] R. A. Goyer, T. W. Clarkson, and S. Ag, "Toxic Effects of Metals," in *British Medical Journal*, **2001**.

[31] G. F. Nordberg, B. A. Fowler, and M. Nordberg, *Handbook on the Toxicology of Metals*, vol. I. **2015**.

[32] Theeraphol Jatuponwiphat, "Reconstruction Of Core Iron-Associated Protein," Kasetsart University, **2017**.

[33] A. Babiker, Z. Elabdin, and M. Ahmed, "Determination of Some Metal Ions in Milk Powder using Graphite Furnace Atomic Absorption Spectrophotometer," University of Gezira, **2018**.

[34] V. Marimuthu, "Pollution Abatement By Activated Nano Materials Derived From Natural Plants And Minerals," Bharathidasan University, **2015**.

[35] T. Ganz, "Iron and infection," *Int. J. Hematol.*, vol. 107, no. 1, pp. 7–15, **2018**.

[36] M. J. Guzmán Llanos, J. L. Guzmán Zamudio, and M. J. LLanos de los Reyes-García, "Significance of anaemia in the different stages of life," *Enferm. Glob.*, vol. 15, no. 3, pp. 419–430, **2016**.

[37] J. Rydberg, M. Cox, C. Musikas, and G. R. Choppin, *Solvent Extraction Principles and Practice.*, Second Edi. **2004**.

[38] S. B. Hawthorne and J. W. King, *Principles and Practice of Analytical SFE*, Fifth Edit. **2000**.

[39] D. S. JIRI STARY, "The solvent extraction of metal chelates," p. 521, **1964.**

[40] J. K. Steehler, *Sample Preparation Techniques in Analytical Chemistry*, vol. 81, no. 2. **2003**.

[41] J. R. Dean, *Extraction Techniques In Analytical Sciences*, First edit. WILEY, **2009**.

[42] J. M. Martin, P. Nirel, and A. J. Thomas, "Sequential extraction techniques: Promises and problems," *Mar. Chem.*, vol. 22, no. 2–4, pp. 313–341, **1987**.

[43] V. Kumar., A. Sharma., and A. Cerdà., *Heavy Metals in Environment , Contamination and Remediation*. Elsevier, **2021**.

[44] H. K. Okoro and O. S. Fatoki, "A Review of Sequential Extraction Procedures for Heavy Metals Speciation in Soil and Sediments," *J. Environ. Anal. Toxicol.*, vol. 01, no. 3, pp. 1–9, **2012**.

[45] M. Mittermüller, J. Saatz, and B. Daus, "A sequential extraction procedure to evaluate the mobilization behavior of rare earth elements in soils and tailings materials," *Chemosphere*, vol. 147, pp. 155–162, **2016**.

[46] N. min Zhu, Y. sheng Xu, L. Dai, Y. fei Zhang, and G. quan Hu, "Application of sequential extraction analysis to Pb(II) recovery by zerovalent iron-based particles," *J. Hazard. Mater.*, vol. 351, no. Ii, pp. 138–146, **2018**.

[47] D. Ternova,Ali Ouadi,Valerie Mazan,Sylvia Georg,Maria Baltoeva,Vitaly Kalchenko,Stanislas Miroshnichenko,Isabelle Billard ,Clotide Gaillard , "New Ionic Liquid Based on the CMPO Pattern for the Sequential Extraction of U(VI), Am(III) and Eu(III)," *Journal of Solution Chemistry*, vol. 47, no. 8. pp. 1309–1325, **2018**.

[48] J. Dutta and S. Basu, "Determination of cerium by substoichiometric extraction with β-hydroxy naphthaldoxime," *J. Radioanal. Nucl. Chem.*, vol. 221, no. 1–2, pp. 221–223, **1997**.

[49] M. Bag, P. Chattopadhyay, and S. Basu, "Determination of gold by substoichiometric extraction with N-thioacetyl benzamide," *J. Radioanal. Nucl. Chem.*, vol. 290, no. 1, pp. 175–178, **2011**.

[50] M. Mandal, D. Pal, and S. Basu, "Substoichiometric extraction of iron by 2-methyloxine into n-butanol," *Radiochim. Acta*, vol. 94, no. 8, pp. 465–467, **2006**.

[51] P. Chandrasekhar Reddy, K. S. S. Prasad, and B. Rangamannar, "Substoichiometric extraction and quantification of cobalt with potassium salts of ethyl, propyl, butyl, pentyl and benzyl xanthates," *J. Radioanal. Nucl. Chem.*, vol. 241, no. 3, pp. 671–674, **1999**.

[52] G. Zante, A. Braun, A. Masmoudi, R. Barillon, D. Trébouet, and M. Boltoeva, "Solvent extraction fractionation of manganese, cobalt, nickel

and lithium using ionic liquids and deep eutectic solvents,” *Miner. Eng.*, vol. 156, no. March, p. 106512, **2020**.

[53] V. A. Lemos, I. V. S. Junior, L. B. Santos, J. A. Barreto, and S. L. C. Ferreira, “A New Simple and Fast Method for Determination of Cobalt in Vitamin B12 and Water Samples Using Dispersive Liquid-Liquid Microextraction and Digital Image Analysis,” *Water. Air. Soil Pollut.*, vol. 231, no. 7, pp. 1–8, **2020**.

[54] M. Chatterjee, B. Srivastava, M. K. Barman, and B. Mandal, “Combined cation-exchange and solid phase extraction for the selective separation and preconcentration of zinc, copper, cadmium, mercury and cobalt among others using azo-dye functionalized resin,” *J. Chromatogr. A*, vol. 1440, pp. 1–14, **2016**.

[55] E. Koosha, M. Ramezani, and A. Niazi, “Determination of cobalt by air-assisted liquid–liquid microextraction,” *Toxicol. Environ. Chem.*, vol. 100, no. 3, pp. 317–325, **2018**.

[56] Z. Tekin, S. Erarpat, A. Şahin, D. Selali Chormey, and S. Bakırdere, “Determination of Vitamin B12 and cobalt in egg yolk using vortex assisted switchable solvent based liquid phase microextraction prior to slotted quartz tube flame atomic absorption spectrometry,” *Food Chem.*, vol. 286, no. February, pp. 500–505, **2019**.

[57] P. V. Racheva, K. B. Gavazov, V. D. Lekova, and A. N. Dimitrov, “Complex Formation in a Liquid-Liquid Extraction System Containing Cobalt ( II ), 4- ( 2-Pyridylazo ) resorcinol , and Nitron,” *J. Mater.*, vol. 2013, **2013**.

[58] S. K. Jawad, F. A. Wannas, J. R. Maslim, and I. R. Ali, “Organic Solvent Effect, Thermodynamic Study and Synergism Behavior for Extraction Efficiency of Cobalt (II) Complex with1-[2-Pyridyl Azo] -2-Naphthol,” *Glob. J. Sci. Front. Res. B Chem.*, vol. 16, no. 1, **2016**.

[59] H. Chen, M. Jobson, A. J. Masters, M. Gonzalez-Miquel, and S. Halstead, “Flowsheet Simulation of Cobalt-Nickel Separation by Solvent Extraction with Trihexyl(tetradecyl)phosphonium Chloride,” *Ind. Eng. Chem. Res.*, vol. 57, no. 30, pp. 10049–10060, **2018**.

[60] J. Chang, F. Jia, K. A. Mumford, X. Yang, and Z. Xie, “Intensified solvent extraction and separation of cobalt from Ni-rich leaching solution in impinging stream-rotating packed bed contactor,” *Geosystem Eng.*, vol. 23, no. 5, pp. 251–264, **2020**.

[61] L. Zhang, V. Hessel, and J. Peng, “Liquid-liquid extraction for the separation of Co(II) from Ni(II) with Cyanex 272 using a pilot scale Re-entrance flow microreactor,” *Chem. Eng. J.*, vol. 332, no. Ii, pp. 131–139, **2018**.

[62] C. A. Nogueira, P. C. Oliveira, and F. M. Pedrosa, “Separation of cadmium, cobalt, and nickel by solvent extraction using the nickel salts of the extractants,” *Solvent Extr. Ion Exch.*, vol. 27, no. 2, pp. 295–311, **2009**.

[63] D. Quintero-almanza, Z. Gamiño-arroyo, L. E. S, and F. I. G, “Recovery of Cobalt from Spent Lithium-Ion Mobile Phone Batteries Using Liquid – Liquid Extraction,” *batteries*, vol. 5, no. 44, pp. 1–13, **2019**.

[64] A. Łukomska, A. Wiśniewska, Z. Dąbrowski, and U. Domańska, “Liquid-liquid extraction of cobalt(II) and zinc(II) from aqueous solutions using novel ionic liquids as an extractants,” *J. Mol. Liq.*, vol. 307, no. Ii, p. 112955, **2020**.

[65] S. R. Kuchekar, H. R. Aher, S. D. Bhumkar, and P. Ramasami, “Solvent extraction separation and spectrophotometric determination of ruthenium(III) with p-methylphenyl thiourea: sequential separation of ruthenium, osmium and iron,” *Sep. Sci. Technol.*, vol. 55, no. 14, pp. 2570–2582, **2020**.

[66] I. Carson *et al.*, “Co-extraction of Iron and Sulfate by Bis(2,4,4-trimethylpentyl)phosphinic Acid, CYANEX®272,” *Solvent Extr. Ion Exch.*, vol. 38, no. 3, pp. 328–339, **2020**.

[67] D. B. Mandhare and V. D. Barhate, “Development of extractive spectrophotometric method for the determination of Iron (III) with Schiff base 2-[(2-hydroxyphenylimino) methyl]-4-nitrophenol,” *Int. J. Curr. Pharm. Rev. Res.*, vol. 8, no. 4, pp. 89–91, **2016**.

[68] O. Sanda, A. C. Tinubu, and E. A. Taiwo, “Recovery of iron from EAF smelter slags via hydrochloric acid leaching and solvent extraction using trioctyl phosphine oxide,” *Sep. Sci. Technol.*, vol. 56, no. 6, pp. 1026–1034, **2020**.

[69] X. Sun, Y. Sun, and J. Yu, “Removal of ferric ions from aluminum solutions by solvent extraction , part I : Iron removal,” *Sep. Purif. Technol.*, vol. 159, pp. 18–22, **2016**.

[70] Y. K. & S. K. Masahiko Matsumiya, Takahiro Yamada, “Removal of iron and boron by solvent extraction with ionic liquids and recovery of neodymium metal by direct electrodeposition,” vol. 6299, no. August, **2016**.

[71] R. Farouq and Y. Selim, “Solvent extraction of iron ionS from hydrochloric acid SolutionS,” *J. Chil. Chem. Soc.*, vol. 2, pp. 60–62, **2017**.

[72] A. Parus, K. Wieszczycka, and A. Olszanowski, “Solvent Extraction of Iron ( III ) From Chloride Solutions in the Presence of Copper ( II ) and Zinc ( II ) Using Hydrophobic Pyridyl Ketoximes Solvent Extraction of

Iron ( III ) From Chloride Solutions in the Presence of," *Sep. Sci. Technol.*, vol. 46, pp. 87–93, **2011**.

[73] X. Cai, B. Wei, J. Han, Y. Li, Y. Cui, and G. Sun, "Solvent extraction of iron(III) from hydrochloric acid solution by N,N,N′,N′-tetra-2-ethylhexyldiglycolamide in different diluents," *Hydrometallurgy*, vol. 164, pp. 1–6, **2016**.

[74] M. C, A. Carvalho, A. Uryga, and A. P. Paiva, "Solvent Extraction of Iron(III) from Hydrochloric Acid Solutions Using N,N'-Dimethyl-N,N'-diphenylmalonamide and N,N0-Dimethyl-N,N'-diphenyltetradecylmalonamide," *Solvent Extr. Ion Exch.*, vol. 21, no. 5, pp. 653–686, **2003**.

[75] R. J. Mhessn, "Synthesis and Characterization of Azo Dye Para Red and New Derivatives," *E-Journal Chem.*, vol. 9, no. 1, pp. 465–470, **2012**.

[76] M. B. Zygmunt Marczenko, *Separation, Preconcentration and S pect ro p hotomet ry i n I norg an ic Analysis*, First edit. Elsevier B.V., **2000**.

[77] A. S. Ayodele, J. T. , Bayero, "Manganese and Cobalt Concentrations in Hair and Nail of Some Kano Inhabitants," *Int. J. Environ. Res*, vol. 4, no. 2, pp. 333–340, **2010**.

[78] M. A. Balarabe and A. Z. Folashade, "Determination of Iron in Some Selected Iron Containing Tablets Using Redox Titration," *World J. Appl. Chem.*, vol. 4, no. 3, pp. 42–44, **2019**.

[79] J. Reijenga, A. van Hoof, A. van Loon, and B. Teunissen, "Development of methods for the determination of pKa values," *Anal. Chem. Insights*, vol. 8, no. 1, pp. 53–71, **2013**.

[80] A. Doğan, N. E. Başcı, and M. B. Polat, "Spectrophotometry, potentiometry and HPLC in determination of acidity constant for Cabergoline and Tadalafil," *J. Res. Pharm.*, vol. 23, no. 2, pp. 177–186, **2019**.

[81] B. H. Pogostin, A. Malmendal, C. H. Londergan, and K. S. Åkerfeldt, "PKA determination of a histidine residue in a short peptide using Raman spectroscopy," *Molecules*, vol. 24, no. 3, pp. 1–12, **2019**.

[82] A. A. Shalaby and A. A. Mohamed, "Determination of acid dissociation constants of Alizarin Red S, Methyl Orange, Bromothymol Blue and Bromophenol Blue using a digital camera," *RSC Adv.*, vol. 10, no. 19, pp. 11311–11316, **2020**.

[83] T. Angelov and I. Hristov, "HPLC determination of pka value of 10-hydroxy-2-decenoic acid," *J. Liq. Chromatogr. Relat. Technol.*, vol. 41, no. 2, pp. 87–92, **2018.**

[84] T. Volná, K. Motyka, and J. Hlaváč, "RP-HPLC determination of dissociation constant using solely aqueous mobile phase," J. Pharm.

Biomed. Anal., vol. 134, pp. 143–148, **2017**.

[85] G. Rabah, “Determination of the Acid Dissociation Constant of a Phenolic Acid by High Performance Liquid Chromatography: An Experiment for the Upper Level Analytical Chemistry laboratory,” J. Chem. Educ., vol. 95, no. 2, pp. 310–314, **2018**.

[86] J. Savić, B. Marković, V. Vitnik, and S. Dilber, “Determination of ionization constants (PKA) of β-hydroxy-β-arylalkanoic acids using high-pressure liquid chromatography,” Kragujev. J. Sci., vol. 40, no. 40, pp. 103–111, **2018**

. [87] R. De Levie, “The Henderson-Hasselbalch equation: Its history and limitations,” J. Chem. Educ., vol. 80, no. 2, p. 146, 2003.

[88] J. R. V. Donald L.Pavia , Gary M. Lampman , George S. Kriz, Introduction to Spectroscopy, Fifth edit. Cengage Learning, 2015.

[89] D. J. K. Robert M.Silverstein , Francis X. Webster, Spectrometric Identification of Organic Compounds. John Wiley & Sons . INC, 2005

[90] M. B. B. Ern¨o Pretsch · Philippe, Structure Determination of Organic Compounds. Springer US, 2009.

[91] M. I. Saleh, F. Bari, and B. Saad, “Solvent extraction of lanthanum ( III ) from acidic nitrate-acetato medium by Cyanex 272 in toluene,” *Hydrometallurgy*, vol. 63, pp. 75–84, **2002**.

[92] M. A. A. Raghad Saad Hatam, Alaa Frak Husain, “Study of Liquid – Liquid Extraction of lanthanum ( III ) ion by derivative of amino acid N-Acetyl-cysteine,” *J. Kerbala Univ.*, vol. 10, no. 2, pp. 191–210, **2012**.

[93] G. Song *et al.*, “Extraction of selected rare earth elements from anthracite acid mine drainage using supercritical CO2 via coagulation and complexation,” *J. Rare Earths*, vol. 39, no. 1, pp. 83–89, **2021**.

[94] A. frak husain Abd-AL abbas S.T, “Study of Liquid – Liquid Extraction of Cobalt ( II ) by 2-[(6-Methoxy -2-benzthiazolyl) azo] -4-benzyl phenol (6-MBTABP),” *J. Kerbala Univ.*, vol. 3, no. 8, **2010.**

[95] S. Kuchekar, S. Pulate, V. Gaikwad, P. Dighe, P. Ramasami, and C. C. Group, “Solvent Extraction, Spectrophotometric Determination Of Selenium (Iv) At Microgram Level Using O-Methylphenyl Thiourea As A Sensitive Reagent: Analysis Of Pharmaceuticals, Synthetic Mixtures And Real Samples,” *World J. Pharm. Pharm. Sci.*, vol. 6, no. 4, pp. 1664–1685, **2017**.

[96] A. Y. Umar, “Synthesis, Characterization And Solvent Extraction Studies Of 3,5-Bis[(2-Hydroxy-Benzylidene)-Amino]-Benzoic Acid And Its Co(Ii) And Ni(Ii) Complexes,” **2014**.

[97] P. A. de Paula, *Atkins’ Physical Chemistry*, Eighth Edi. Great Britain by Oxford University Press, **2006**.

## References

[98] P. L. Zanonato, P. Di Bernardo, A. Bismondo, L. Rao, and G. R. Choppin, "Thermodynamic studies of the complexation between neodymium and acetate at elevated temperatures," *J. Solution Chem.*, vol. 30, no. 1, pp. 1–18, **2001** .

[99] A. N.AL-Shirify, Kassim H.Kadhim, Ahmed A. AL-Kriamy, "Liquid-Liquid Extraction of Palladium by Dibenzo-18-Crown-6 from salts Media," *Natinal J. Chem.*, vol. 20, pp. 521–528, **2005**.

[100] K. M. Elsherif1, A. Zubi, H. B. Shawish, S. A. Abajja, E. B. Almelah, "Spectrophotometric and Conductometric Study of Formation Constant and Stoichiometry of Co ( II ) -Salen Type Ligand Complex," vol. 07, no. 2, pp. 144–157, **2020**.

[101] U. B. Barache, A. B. Shaikh, T. N. Lokhande, G. S. Kamble, M. A. Anuse, and S. H. Gaikwad, "An efficient, cost effective, sensing behaviour liquid-liquid extraction and spectrophotometric determination of copper(II) incorporated with 4-(4′-chlorobenzylideneimino)-3-methyl-5-mercapto-1, 2, 4-triazole: Analysis of food samples, leafy vegetables, f," *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, vol. 189, no. Ii, pp. 443–453, **2018** .

[102] O. V. Ikpeazu, I. E. Otuokere , K. K.Igwe, "Determination of Stability Constants and Thermodynamic parameters of Cefotaxime –Fe(III) Complex at Different Temperatures," vol. 45, no. 4, pp. 663–669, **2020** .

[103] I. Ali, W. A. Wani, and K. Saleem, "Empirical formulae to molecular structures of metal complexes by molar conductance," *Synth. React. Inorganic, Met. Nano-Metal Chem.*, vol. 43, no. 9, pp. 1162–1170, **2013** .

[104] C. E. Housecroft and A. G. Sharpe, *Inorganic Chemistry*, Fourth edi. **2012**.

بِسْمِ اللّهِ الرَّحْمَنِ الرَّحِيمِ

(( وَيَسْأَلُونَكَ عَنِ الرُّوحِ ۞ قُلِ الرُّوحُ مِنْ أَمْرِ رَبِّي وَمَا

أُوتِيتُم مِّنَ الْعِلْمِ إِلَّا قَلِيلً ))

صدق اللہ العلي العظيم

سورة الاسراء ( الاية 85 )

# الملخص

تتضمن هذه الدراسة تخليق مشتق آزو جديد (7 - ((4- (ثنائي مثيل امينو) فينيل) ديازينيل) كينولين -8-أول) (DPDQ) من 8-هيدروكسي كينولين بطريقة الازوته ، وكان الكاشف مسحوق برتقالي محمر ، وتم تشخيصه باستخدام طرق التحليل الطيفي مثل مطيافية الاشعة فوق البنفسجية – المرئية و مطيافة الاشعة تحت الحمراء و مطيافية الرنين النووي المغناطيسي لنظيري الهيدروجين و الكاربون ، والوزن جزيئي للكاشف المحضر هو (292.1324 جم / مول).

كانت نقطة الانصهار للكاشف المحضر (166-164 درجة مئوية) ، و ذائب في العديد من المذيبات العضوية مثل رابع كلوريد الكربون ، ثنائي ميثيل فورماميد ، ثنائي ميثيل سلفوكسيد وكلوروفورم ، للكاشف طول موجي اعظم قدره (442.5 نانومتر) .

تضمنت الدراسة ايضا عملية استخلاص سائل-سائل لأيونات الكوبالت الثنائي والحديد الثلاثي كل على حدة بواسطة كاشف الازو الجديد المحضر ودراسة إمكانية إجراء الفصل التتابعي للأيونات قيد الدراسة .و قد أجريت دراسة لتوضيح تأثير العوامل المختلفة التي تؤثر على قيمة نسبة التوزيع (D) ونسبة الاستخلاص (E٪).

من دراسة تاثير الدالة الحامضية على عملية استخلاص للايونات قيد الدراسة اتضح ان الدالة الحامضية المثلى لاستخلاص ايوني الكوبلت الثنائي و الحديد الثلاثي كانت (10) و (7) على التوالي . و أفضل فترة زمنية للرج كانت (10) دقائق لايون الكوبالت الثنائي و (15) دقيقة لايون الحديد الثلاثي ، وأظهرت النتائج أن الكلوروفورم هو أفضل مذيب عضوي لاجراء عملية استخلاص كلا الايونين قيد الدراسة .

لتقييم تأثير تداخل الايونات الموجبة والسالبة على قيم ثابت التوزيع و نسبة الاستخلاص لايوني الكوبالت الثنائي و الحديد الثلاثي تم استخدام عدة ايونات لهذا الغرض ، و أشارت النتائج إلى وجود اختلاف في قيم (D) و (E٪) مع وجود تراكيز متغيرة من الايونات الموجبة والسالبة.

كما تم دراسة تأثير العوامل المؤكسدة والمختزلة على عملية الاستخلاص ، اذ يتضح من النتائج التي تم الحصول عليها من هذه الدراسة بوجود تفاوت في التاثير على عملية الاستخلاص باستخدام عامل مؤكسد ومتقارب باستخدام عامل الاختزال بالنسبة لايون الحديد الثلاثي مما يدل على امكانية استخدام الكاشف المحضر في استخلاص ايون الحديد الثنائي ايضا لثبات حالة التاكسد الثنائية للحديد ، على العكس من ايون الكوبالت اذا ان حالة الاكسدة الاحادية غير مستقرة .

تؤدي تقنية االاغناء الحجمي إلى انخفاض قيم (D) و (E٪). كما أوضحت النتائج أن قيم (D) و (E٪) تزداد مع زيادة تركيز الايونات قيد الدراسة ثم انخفاضها عند الوصول لتركيز محدد.

بدراسة تأثير درجات الحرارة على عملية الاستخلاص في هذه الدراسة ، اتضح ان قيم (D) و ( E% ) تنخفض بزيادة درجات الحرارة. و قد تم حساب قيم الدوال الثيرموديناميكية ( $\Delta H$ ، $\Delta G$ ،$\Delta S$ ) ، وأظهرت النتائج أن تفاعل كلا ايوني الكوبالت الثنائي و الحديد الثلاثي مع الكاشف المحضر هو تفاعل طارد للحرارة ( كانت قيمة الانثالبي لاستخلاص ايوني الكوبلت الثنائي و الحديد الثلاثي هي -18.4 ، -57.258 على التوالي ) .

تمت دراسة تأثير عملية التمليح الخارجي باستخدام عدة املاح ايونية ( كلوريد الأمونيوم وكلوريد الصوديوم وكبريتات الصوديوم وملح نترات الصوديوم ) ، وأظهرت الدراسة تأثر قيم (D) و (E٪) للأيونات بهذه العملية . عززت تقنية الاستخلاص المتقطع ( بشكل دفعات صغيرة من الطور العضوي ) عملية الاستخلاص.

تمت دراسة تكافؤية المعقدات المستخلصة للايونات قيد الدراسة بواسطة الكاشف الجديد المحضر لبيان نسبة ( الفلز:الكاشف ) باستخدام ثلاث طرق ( طريقة جوب للتغيرات المستمرة ، طريقة النسب المولية اضافة الى استخدام طريقة الاستخلاص دون نقطة التكافؤ ) و اظهرت النتائج ان نسبة ايون الكوبالت الثنائي الى الكاشف (DPDQ) كانت (1: 2) و (1: 3) بالنسبة لايون الحديد الثلاثي .

لاجراء تطبيقات لعملية الاستخلاص باستخدام الكاشف المحضر الجديد (DPDQ) ، تم استخدام العديد من العينات (الشعر ، فيتامين ب 12 ، وبعض الادوية التي تحتوي على الحديد) ، وأظهرت النتيجة أن الكاشف أعطى نتائج جيدة في هذه الدراسة ( حيث كان تركيز الكوبلت في كلا عينتي الشعر و فيتامين ب 12 هي 10.875 مكغم/غم ، 41.731 مكغم /10مل على التوالي ) وكان تركيز الحديد في نماذج الادوية المستخدمة في الدراسة هي 191 مكغم /5مل ، 123.5 مكغم /5مل على التوالي . نجح الكاشف في فصل أيونات الكوبالت (II) والحديد (III) في الفصل المتسلسل.

جمهورية العراق

وزارة التعليم العالي و البحث العلمي

جامعة كربلاء

كلية العلوم

# دراسة في الاستخلاص سائل - سائل لايوني الكوبلت الثنائي و الحديد الثلاثي باستخدام مشتق (الازو) - الفصل التتابعي وتطبيقاتها التحليلية

رسالة مقدمة الى

كلية العلوم / جامعة كربلاء

وهي جزء من متطلبات نيل درجة

الماجستير في علوم الكيمياء

من قبل

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باشراف

**الاستاذ الدكتور علاء فراك حسين**

2021 ميلادية

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