Republic of Iraq
Ministry of Higher Education
and Scientific Research
University of Kerbala
College of Science
Department of Chemistry

Spectrophotometric Determination of Micro Amount of copper(ll) and mercury(ll) ions Using a new (Azo) Derivative, Study of Thermodynamic Functions and Their Analytical Application

A Thesis

Submitted to the College of Science University of Kerbala
in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Chemistry

By

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Superviser

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2021 AD 1442 AH

بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ

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Dedication…

To that smiling face, where the wrinkles marked the days for me. To the one who spent all his ambitions for the sake of my ambitions. If all the languages of the world had turned into a word of gratitude, it would not have spared your right.

To the mystery of the permanence of life and the sacred candle that shines the darkness of years into the cold shadows of the desertion of life, my dear mother.

To the title of brotherhood and the eminence of sincerity, my brothers.

To the abode of life and my help in my career, my dear wife.

To my esteemed professor, the owner of noble positions, Prof. Alaa Farak.

To those who dwelt in my heart and drew a smile in my heart, even while I was alone, to whoever was a brother in every sense of the word, Muhammad Habtar.

To my distinguished professors, who have kindly provided me with education and support.

To everyone who supported me, even with a smile. I present this dedication with my gratitude

Acknowledgments…

Praise be to God, the owner of hopes and the being of the connection, the suspicions do not realize him and do not notice him in the eyes of the eyes, starting with the acquisition of knowledge, the pen and the pen, and then the prayer and completed the blessing of the bright light in the darkness and the rainy clouds with the types of feats, my master, the Messenger of God upon him, the God of peace and harmony, and his guardian and his cousin Abba Al-Hassan and Al-Hussein, Commander of the Faithful, Ali Ibn Abi Talib, peace be upon him.

Thanking is a sign of gratitude and gratitude, so I present my sincerity and the sum of it to my professors, who throughout my career have stuck with me for their dedication and dedication to support, giving and the hard effort that aims for a product with a distinguished scientific perspective.

The gratitude compass and the sails of gratitude are directed towards those who provided me with his knowledge and my love with the capacity of his chest, and surrounded me with his experience and guidance, my professor and my supervisor, Prof. Dr. Alaa Farak Hussein, for his supportive efforts which contributed to the delivery of my research results to what he is..so my words are strengthened in appreciation and gratitude to him..

My parents you are the light that shone the darkness of the maze and the release of patience to complete the task and the call of the grab with the acquisition of determination and the sustainability of life with the light of tranquility, the source of tenderness, and the origin of all safety, the first unconditional love, the inexhaustible giving, and the symbol of loyalty that is impossible find it with others, for you words are dwarfed and with your welcome the alphabets falter ...

Researcher: Mustafa Hamid Atiyah

Abstract

The study included the preparation and diagnosis of the new ligand 4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole (BMTI), which is one of the Azo compounds using the traditional nitrogenation method by duplicating the diazonium salt of the m-toluidine compound with the amidazole derivative and conducting a preliminary study with (9) Metallic ion to determine the two ions copper and mercury. The maximum absorpation of the reagent dissolved in ethanol (λ_{max}= 446.5nm), and the formation of the copper(II) and mercury(ll) complexes formed with the reagent, in addition to that, the best conditions for the reaction of these two ions with the reagent were studied, such as the acidity function, the concentration of the reagent and duration of time For the stability of the two complexes. The temperature, the order of addition of the reaction components, the calibration curves for each of these two ions were shown with the reagent, it was raound that Beer׳s law over the range of the copper(II)complex within the concentration ranges ($3.149x10^{-7}$ - $1.889x10^{-5}$M) with the linearity coefficient (R^2 = 0.9989) and the absorbance value. The molar absorptivity (ε) is equal to ($1.110x10^{4}$L.moL^{-1} .cm^{-1}) and Sandel's sensitivity is equal to (0.00588 μg/cm^2), while mercury (ll) is within the range of concentrations ($1.994x10^{-7}$-$8.973x10^{-6}$M) and with a coefficient of linearity (R^2 = 0.9988). value of the molar absorptivity (ε) = ($1.310x10^{4}$L.moL^{-1}.cm^{-1}) sandel sensitivity equal (0.00153 μg/cm^2) .The equivalence of the two complexes was studied by finding the ratio of the metal ion to the reagent (M: L) using the continuous changes method and the molar ratio and the Mollard method for the copper(II) and mercury(ll) complexes .

The stability constant (K_{stab}) for copper and mercury complexes were ($K = 2.649x10^{10}$) and ($K = 1.460x10^{9}$) repectively. In addition, the thermodynamic functions (ΔH , ΔG and ΔS) were calculated for both complexes, where the results indicated that the reaction of forming the copper(II) complex is exothermic and the mercury(ll) complex is endothermic. The study demonstrated that interferance of the presence of a number of cations and anions ions as potential interactions when estimating copper(II) and mercury(ll) ions, and the addition of appropriate masking agents was studied, as it was found that these ions interact to varying degrees depending on the nature and concentration of the interfering ion, and some of them were not show any effect. Remarkably, the charge of dissolved complexes was determined by measuring the conductivity of the two complexes, so the used complexes were not charged. The accuracy and precision of the analytical method was determined using three different concentrations for each ion, so the values of the percentage of relative standard deviation for the copper(II) ion ranged between (0.720-2.110%) and the relative recovery ranged between (95.829% -103.930%) for the mercury(ll) ion values ranged between (0.710-1.420%) and the relative recovery ranging between (97.703% - 99.197%), through which the detection limit was calculated for the copper(ll) ion ($3.590x10^{-8}$M), equivalent to (0.0114 µg /mL). The mercury(ll)ion is equal to ($1.435x10^{-7}$M), equivalent to (0.0288µg / mL), which indicates the sensitivity of the spectral method using this reagent (BMTI).The sediments of the reagent and the two complexes have also been studied by determining some of their physical characteristics such as melting point, solubility, molar conductivity. The method was applied to standard laboratory prepared

solutions as it was applied to samples of tea leaves and tap water to determine the concentrations of copper (II) and a model of dental filling to determine the concentrations of copper(II) ion. Also, the method was applied to samples of well water to determine the concentration of mercury. The method was found a high in sensitivity and accurcy.

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Symbol	Meaning
DMF	Dimethyl formamide
EDTA	Ethylene dianime tetra acetic acid
DMSO	Dimethyl sulfoxide
BMTI	4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole
RSD%	Relative standard deviation
L.O.D	Detection Limit
L.O.Q	Limit of quantification
Rec%	Recovery%
S.D	Standard deviation
ε	molar absorptivite
x'	mean
λ_{max}	Maximum wavelength
Am	Maximum absorption
As	Slow absorption
Vm	volume of the metal
VL	volume of the reagent
E%	Relative error
Abs	Absorption
r^2	Coefficient of determination

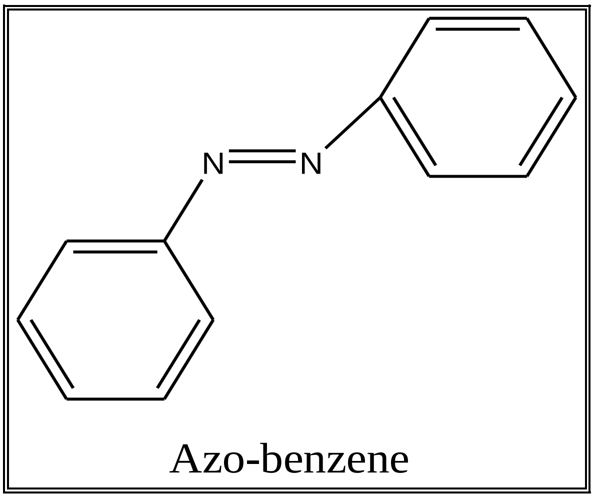
Chapter One
introduction

(1-1) Coordination Chemistry.

Coordination chemistry is one of the most important scientific discoveries since the discovery of the compound ($CoCl_3.6NH_3$) and it has gained a wide area in chemistry due to its great development in the practical side in the discovery of a large number of organic compounds. Coordination compounds also play an important role in developing the fields of medicine, agriculture and industry, also are widely used in analytical chemistry[1,2]. Coordination chemistry has been used to prepare a large number of metal ion complexes, the purpose of preparing these complexes is to estimate the metal ions in the compounds by selective processes such as masking agents and changing the pH[3]. It can be said that there are several methods in analytical chemistry to quantify elements in different models, including the electrical method, the thermal method, the optical method, the method of chromatographic analysis, the method of extraction, the method of ablation by flame, and the spectroscopic method [4]. Classical coordination chemistry is focused on the concept of a monatomic and cationic central metal atom bound to Lewis-base ligands with a specific coordination number and a polyhedral structure.16 Intersected with other disciplines, the development of coordination chemistry has encompassed the three dimensions of breadth, depth and applications,the modern coordination chemistry as more broadly defined only requires that distinct species are formed through metalfunctional group binding interactions. In addition, the development of powerful spectroscopic analytical techniques, such as X-ray absorption fine structure (XAFS) spectroscopy, further uncovers the roles of coordination chemistry [5]. Speciation studies are vital in coordination chemistry because in a metal–ligand system normally a wide variety of species are present in equilibrium. For example, in pharmaceutical applications one of the species is the active agent while the other is neutral or may even be poisonous. However, not only is the equilibrium speciation crucial but the duration time in which the system reaches the equilibrium is also important. The knowledge on the dynamics of metal complexes is critical in pharmaceutical or in environmental research because the toxic metal ions in very dilute solution lose the protective ligands eventually but the duration of it, luckily, sometimes lasts very long [6].

(1-2) Azo Dye.

Azo dyes represent a large part of the volume of production for dyes chemistry in previous years, and its relative importance may increase in the future due to its development, increased selective sensitivity and lower cost, as it plays an important role in managing the dye and printing market, these dyes are manufactured by nitrogenation of aromatic compounds, where different methods and modifications are developed to obtain properties that give multiple colors and increase the productivity to form these required compounds [7]. Azo dyes are the most used dyes and they account for more than 60% of the total pigments [8,9]. Azo dyes are used in a wide range of industries, including the textile and food industries, where they include large quantities and represent about 70% of the dye production at the global level, what distinguishes these colored compounds is that they contain one or more Azo bonds (N = N) as a chromophore group associated with aromatic (organic) compounds with functional groups such as OH and SO_3H, and other substituting compounds[10,11]. In the period of 1994, the statistics of the global production of dyes of various uses was about one million tons, with Azo dyes accounting for more than 50% of them [12]. Dyes in general have harmful aspects for humans and aquatic life. Many organizations have raised urgent calls to treat liquid wastes containing dyes and Azo dyes to eliminate them or convert them into a useful and safe product, because increased pollution from these compounds may lead to a human disaster[13,15]. Azo dyes for heterocyclic compounds are considered one of the most important compounds because they are very effective for the rest of the staples, such as chemical complexes for the various elements of the periodic table. Which was represented by a number of chemical bonds of the elements, this type of compound is known to be important in biological fields due to the presence of a number of highly effective elements that are associated with these compounds, and these elements are oxygen, nitrogen and sulfur [16,17]. The compounds azo imidazole and thiazolyl azo are a very important part of the manufacture of Azo compounds and a large number of other compounds that enter into various fields as they have been used in science and technology, and the results obtained from these compounds have great importance in life [18]. The use and characterization of compounds prepared from Azo depends on the chemical composition and the method of application that is specific to them, as they are used in general and widely in processes including dyeing cotton [19]. Wool [20]. Silk [21]. Rubber [22]. Plastic [23]. And in the manufacture of a large number of drugs, including it is used to inhibit the growth of germs [24-25]. The osmotic groups form large when associated with the Fatiya group, giving the formula (R− N = N - R) and called Azo fibrous compounds, which are not widely distributed in various fields because they are unstable, due to their rapid decomposition into nitrogen. If the link is in an aromatic group, as for the compounds with the formula (Ar - N = N - Ar), they are called aromatic Azo compounds, such as Azo-benzene, which are more stable and common examples of these compound show in following figures (1-1) [26].



Figure(1-1) Azo-aromatic compounds.

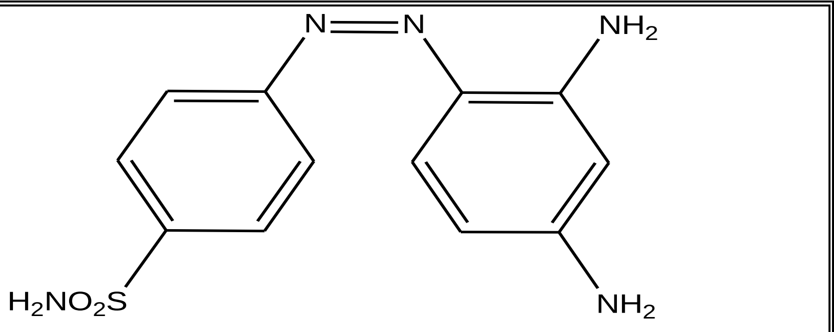
There are some Azo compounds, which contain electron evolution groups called groups that develop color, such as (Br, - SH, - CH_3, Cl, -OH, -NH) which have a major and essential role in increasing the sensitivity and selectivity of these compounds, which in turn increases Color density and thus affects the stability of these compounds and their complexes, and these groups are considered important because their uses are in several fields, including industrial, due to the high sensitivity and selectivity of these compounds, as well as their high stability, speed and ease of use, for this reason they have been widely used in the field of analytical chemistry, especially In the field of quantitative and qualitative estimation, using different techniques [27].

(1-3)Classification of Azo compound.

The classification of Azo compounds depende on type of rings associated to the end of the Azo Bridge group.

(1-3-1)Homocyclic Azo compounds [28].

In this method of compound the aromatic cycle linked on both sides of the Azo group are homogeneous , shown in the figure (1-2)**.**

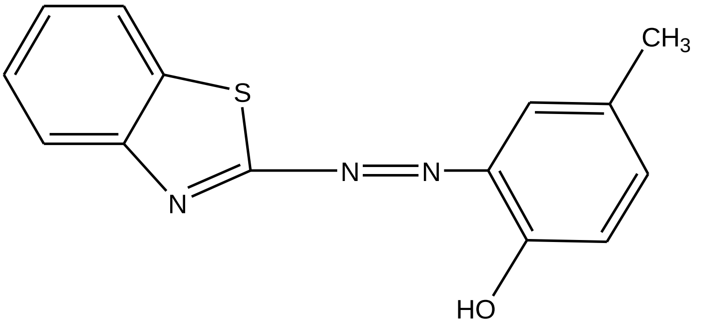


4-[1-(2,4-Diamino phenyl)azo]-1-aminosulpha benzene(DAPAB)

Figuer (1-2) **Homocyclic Azo compounds.**

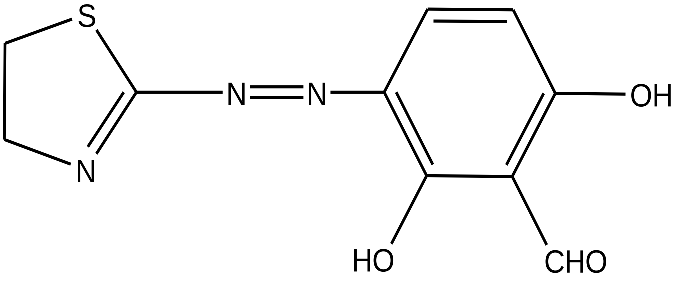
(1-3-2) Heterogeneous Azo compounds [29].

They are compound containing hetrocyclic rings located at one of the bridge Azo group as in the following figure(1-3) and figure(1-4).



2-(2-Benzo Thiazolyazo)-para cresol (BTAC)

Figure (1-3) Heterogeneous Azo compounds.



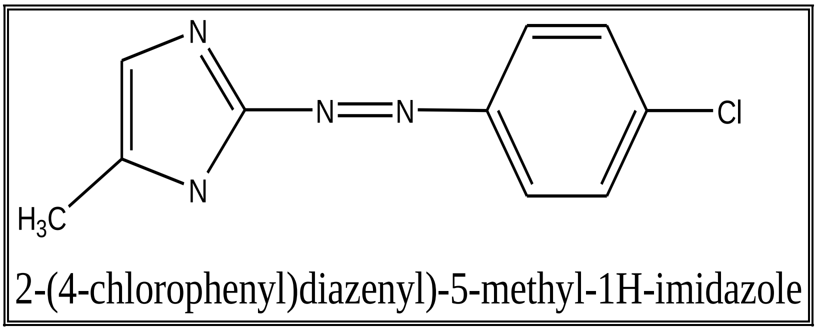
4-(2'-Thiazolylazo) formal resorcinol (TAFR)

Figuer(1-4) Azo compounds with a heterogeneous five-membered ring.

(1-4) Classification of azo dyes according to the number of azo groups.

(1-4-1) Mono Azo compound [30,31].

They are organic compounds consisting of two organic groups that are linked through coupling reactions with the Azo group to give colored compounds, it is called by this name because of its possession on the chromophore group (- N = N-), which can be related to the alkyl group or Ariel and form The pigment is more stable when attached to the Ariel group, and due to the possibility of preparing different types of these dyes because of the flexibility in their preparation and in their use and their possession of various properties due to the availability of amine substitutes that are used in their preparation and are considered one of the most important types of dyes at all, mono pigments can be schematically represented by the following formula: Z-N = N – W, shown in figure (1-5).

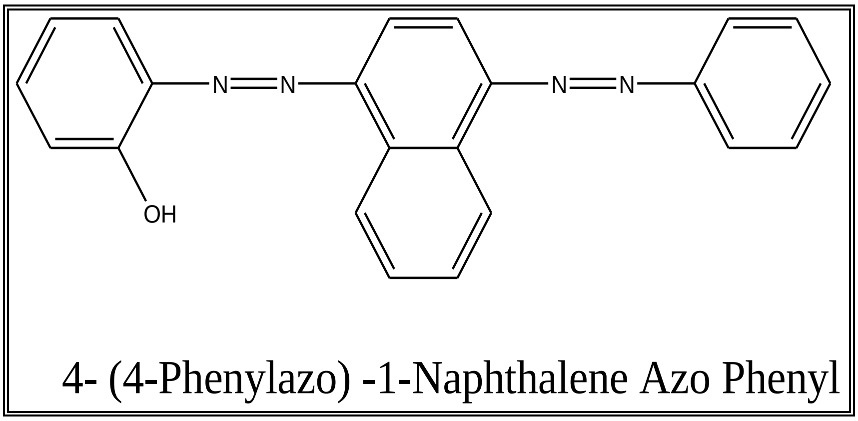


2-(4-chlorophenyl)diazenyl)-5-methyl-1H-imidazole

Figuer(1-5) Mono Azo compound.

(1-4-2) Bis Azo compound [32].

These compounds contain two Azo groups connected to each other by means of Azo groups, as they have connected rings at the ends of the Azo groups that make the Bis compounds, we explain these type in the following figures (1-6).

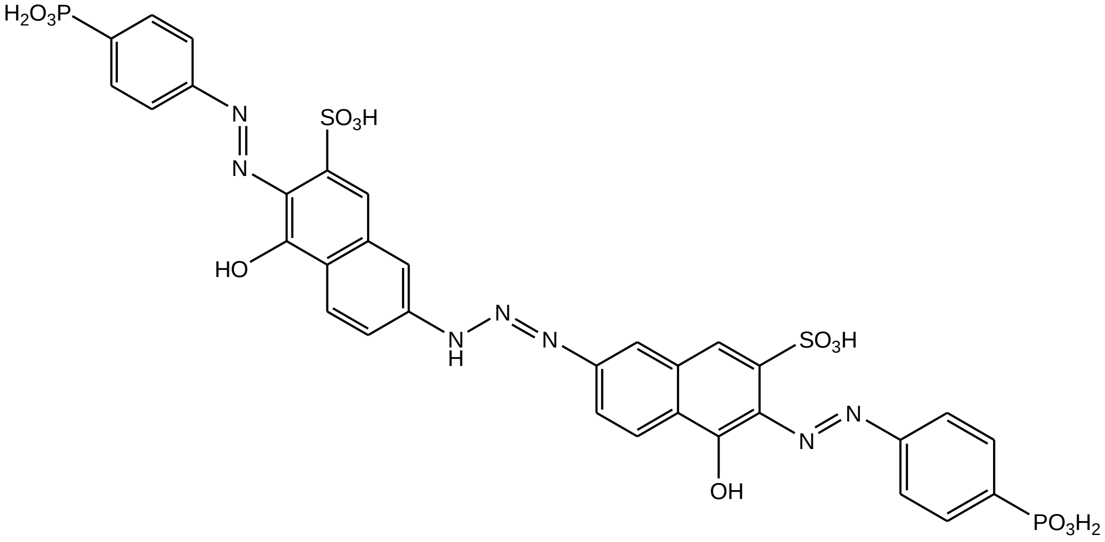


4- (4-Phenylazo) -1-Naphthalene Azo Phenyl

Figuer(1-6) Bis Azo compound.

(1-4-3)Tri Azo compoundes [33].

There are compounds that contain in their composition three bridge Azo groups that are related to each other by different aromatic rings and they contain acid or base compensators and also vary in the compensation sites for these compensators on the aromatic rings and there are quadruple and pentagonal or multiple Azo compounds depending on the number of Azo groups involved in the composition of these compounds It is mentioned here that the colors of these compounds increase in intensity with the increase in the number of Azo groups linking the rings, examples of these compound show in following figures (1-7) **.**

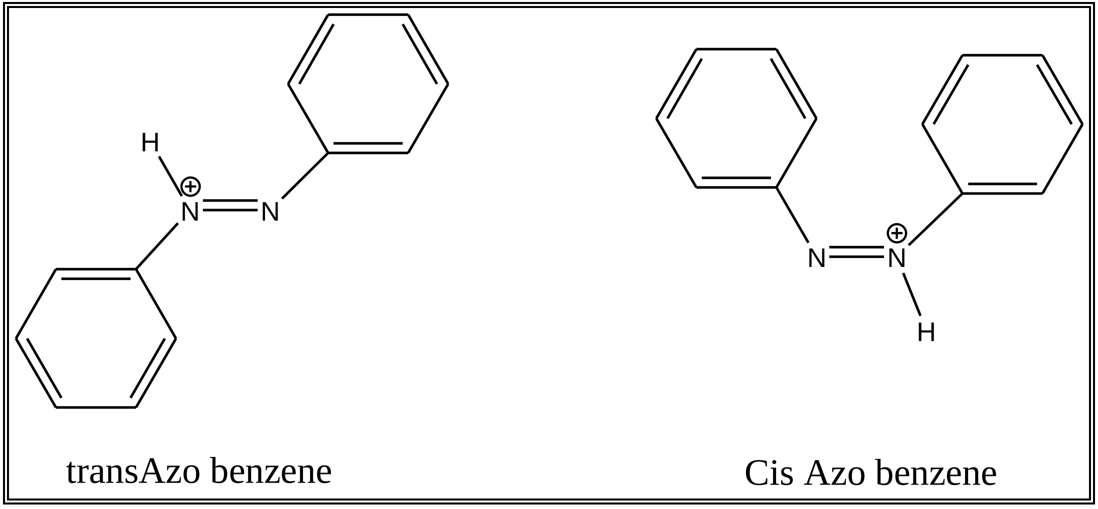


4-hydroxy-7-(3-(5-hydroxy-6-((E)-(4-phosphonophenyl)diazenyl)-7-sulfonaphthalen-2-yl)triaz-1-en-1-yl)-3-((E)-(4-phosphonophenyl)diazenyl)naphthalene-2-sulfonic acid

Figuer(1-7) Tri Azo compound

(1-5) Azo dyes Isomerism [34-36].

Isomers can be made from Azo dyes. Isomers are a term given to chemical compounds that have more than one synthetic formula but have a fixed molecular formula. In some molecules and under certain conditions, isomerization occurs spontaneously, as it occurs in some compounds, and interestingly for Azo benzene is the isomerization of the Azo bond between the more thermally stable E formation and the unstable form Z in an acidic medium, the Trans and Cis forms of azobenzenes cause the formation of different formed conjugate acids, the figuer (1-8) shows that.



Figure(1-8)Cis and trans of Azo-benzene.

(1-6) Applications of azo compound.

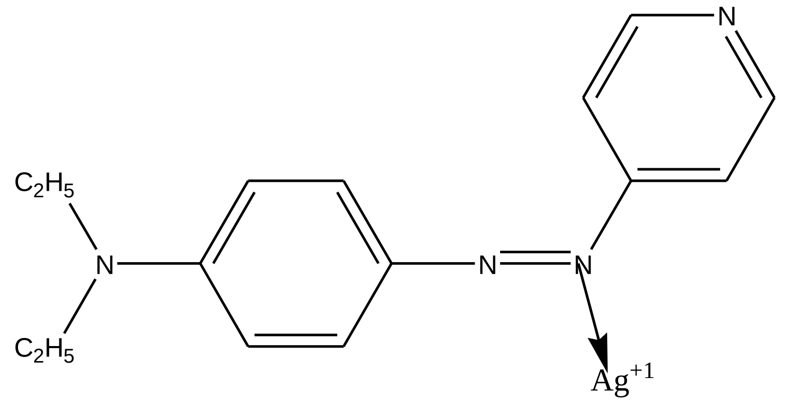
Dyes are the most versatile group of all synthetic dyes (N = N) and have been widely used in the fields of pharmacology, plastics, medicine, live cell cancer, pharmacological [37], biological [38], thermal transfer printers, phototherapy [39], also sensitive to solar cells [40], mineral markers, textile dye [41], and used in consmetics cosmetics [42], these dyes are involved in a number of biological reactions such as inhibition of DNA, RNA, protein synthesis, cancer generation and nitrogen fixation [43]. They are used in applications of optical properties [44,45], and have entered into many applications such as liquid crystals and nanotubes [46,47], and functional dyes containing heterocyclic aromatic compounds. Good manufacturing and dyeing performance [48]

(1-7) The Chelating Behavior for Azo compound.

Azo compounds are divided into three types in terms of how they bind to metal ions.

1- Mono dentate reagent [49].

Any reagents that participate in the formation of a single harmonic bond with the atom or the metal ion that gives one pair of electrons such as the nitrite ion (NO_2) and it may be a negative ion such as chloride (Cl^-) and the fluoride ion (F^-) or a group of neutral atoms and carry a pair of free electrons such as water (H_2O) and ammonia, NH_3: and CH_3 , meaning that they contain a single coordinate side for bonding with metal atoms when forming metal complexes, as shown in the following figure(1-9).

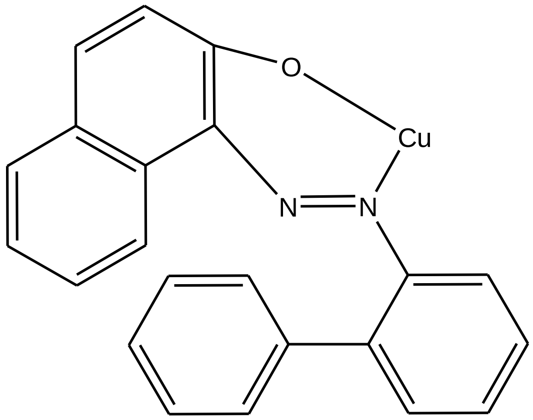


Diethyl-[4-(pyridin-4-ylazo)-phenyl]-amine

Figure(1-9) Mondentate reagent.

2- Bidentate reagent [50 - 52].

They are the reagents that co-ordinate with the metal ions by means of the nitrogen atom, the heterocyclic ring or any substituted group on the ring on the one hand, and the nitrogen atom of the iso group far from the ring on the other hand, so that the azo group is within a total ring. Examples of these reagents are shown in the following figure(1-10).

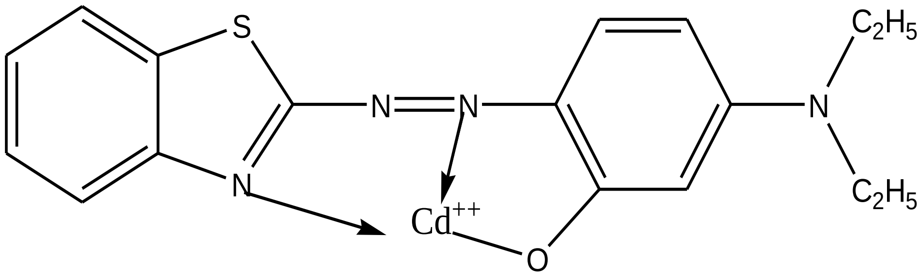


p-cymene Cu(II)(biphenylazo)phenolate

Figure(1-10) Bidentate reagent.

3- Tridentat reagent [53].

In this type the metal ion is linked with the reagent through three sites: the first is the nitrogen atom of the heterocyclic ring. The second is the nitrogen atom of the Azo group far from the heterogeneous ring, as for the third symmetry site it is represented by a basic or acid group at the ortho site relative to the bridge Azo group having the ability to Losing its proton. This link leads to the formation of a pentagonal ring, and in this case, the complexes formed have high stability compared to their counterparts in the first and second types, and among the most prominent reagents of this type are shown in the figure(1-11).



2-(2-Benzothiazolyl azo)-5-dimethyl amino phenol (BTADAP)

Figure(1-11) Tridentat reagent.

(1-8)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, 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 [54,55]. 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 [56,57]. 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 [58-60]. In recent years, Azo compounds have entered many electronic applications including the manufacture of electronic absorbable chips and other electronic manufacturing [61]. 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 [62]. Azo compounds have both emission and absorption properties, terefore, they have entered many industries, including the manufacture of laser pigments [63-65].

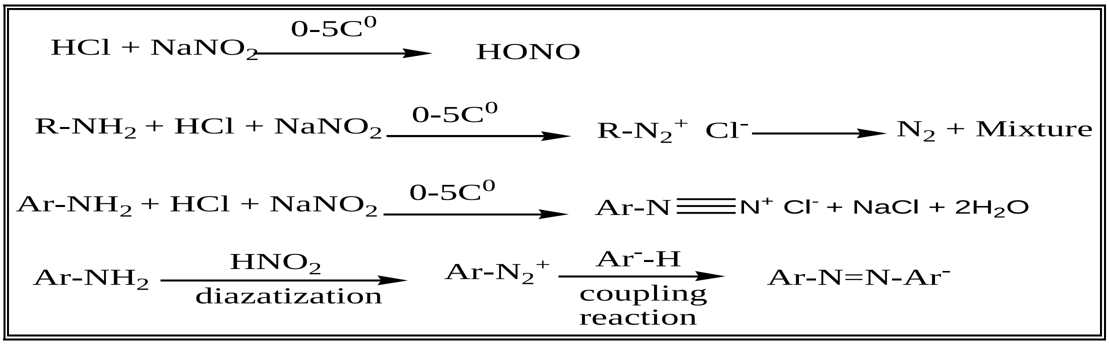
(1-9) Imidazole and Azo Imidazole Ligand.

Amidazole is a heterocyclic pentagonal ring containing an amine group, where it is considered a crystalline solid with a melting point of 90 ° C, amidazole was prepared from the reaction of cyclosal with ammonia. The imidazole ring contains strong sites that enable it to bind to form azo-imidazole prepared from diazonium salts of amidazole in the basic medium [66]. During the past years, imidazole has been used as alternative ionic liquid ingredients with a new approach to green chemistry and to quantify some effects of metal ions, especially the transition elements, imidazol azo compounds are based on the chemical composition and method of application in some drugs, including bacteria growth [67,68]. Medicines derived from Azo imidazole play an important role in industries and resulting from the diversity of compounds as a result of the development of harmonic chemistry due to the formation of stable complexes containing most of the transition metals [69-71].

Azo imidazole derivatives are a very important class of chemical compounds that are concerned with the development of scientific research, the azo-imidazole bonds and their mineral complexes are characterized by high colors and have been used as dyes and over time, compounds containing Azo have been used in dyeing processes [72], cotton[73], wool, silk[74], rubber, plastic, and printing [75]Azo imidazole derivatives are known as excellent analytical reagents in the spectral identification of most transitional metal ions, Imidazole derivatives show various pharmaceutical activities such as antivirals, anti-inflammatory, anti-depressant, anti-cancer[76]. The imidazole molecule has contributed to the preparation of several ligand that are anti-MDA aerobic pathogens that isolated bacteria from burn patients[77,78].

(1-10) Preparation of Azo dyes [79].

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^0)to give easily soluble salts in water called diazonium salts. , as shown in the following chemical equations.



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

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

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

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

Scheme (1-1) for preparing azo dyes.

the second step: the conjugation step (synthesis of azo dyes), which included the conjugation of the aromatic diazonium ion with active aromatic compounds in alkaline conditions, where the diazium 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.

(1-11) Chemistry of Copper.

Copper is a metallic element of the transition elements, the molecular weight (63.53 gm/mol) and its atomic weight (29), where copper possesses the electronic arrangement $3d^{10}$, copper possesses the ability of methods, clouds and electrical conductivity [80]. Copper is used as a feed additive to prevent diseases and promote animal growth. It is widely used in modern livestock [81]. Copper is readily available and a cost-effective material, but copper has weak mechanical properties, especially at high temperatures [82]. Copper has been widely used in engineering and electronic applications [83]. The coordination chemistry of copper is very rich in its biological roles and has a variety of practical applications, such as catalysts, fungicides and pesticides [84]. Copper is a basic non-ferrous mineral with a medium concentration in the earth's crust, about 50 parts per million, Copper is found naturally in all plants and animals, as it is an essential element for all known living organisms. Copper metal has a distinctive reddish brown color, with a metallic luster, however, it rapidly oxidizes in air, a feature of all base minerals. Copper deposits are found throughout the world in a variety of geological environments. Porphyry copper deposits are currently the world’s main source of copper (50--60% of world production) [85]. The copper atom consists of a positively charged nucleus containing 29 protons and 34 to 36 neutrons surrounded by 29 electrons. The electrons are arranged in a structure described with the symbol $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$, important physical properties, including its high electrical conductivity, chemical stability and reddish color, in the crystalline metallic copper, as with other metals, the 4s electron does not remain bound to any particular atom but becomes part of an electron cloud that dominates the crystal lattice. Copper has a high compressibility. When the crystal temperature is raised, the density of copper varies from 8.90 to 8.95 g/cm^3, depending on the mineral's thermomechanical history, the intensity initially decreases as the scores increase [86,87]. Excessive quantities of copper in the environment can have assets such as effluents from septic tanks and municipal wastewater, discharges from power plants as well as leaching from paints, the appreciation of copper by its azo pigments has received a great deal of attention in the past few decades due to its simplicity, flexibility and high productivity [88]. Copper and azo dyes were prepared as complexes on a wide range, as the formation of such complexes possesses high thermal stability which is useful in optical recording methods [89-91].

(1-11-1) Spectrophotomtric determination of copper.

In this study, some of the previous spectrophotometric methods used for determination of copper are present, as show in the table (1-1).

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

Seq	Method	Reagents	Results	Ref
1	Spectrophotometric	(2,2[O-Tolidine-4,4-bis azo]bis[4,5-diphenyl imidazole	conc.(5.00-80.00 µg/ml) , R^2=0.9995 , pH=5 , ε=(0.127x10^4L.mol^{-1}.cm^{-1}) ,λ_{max}= 409 nm , Sandell's Sensitiv= (0.040µg/cm^2), L.O.D=(1.924µg/mL) , , determine copper (II) ion in dental filling.	[92]
2	spectrophotometric	3-(4-Antipyriyl -azo)-1-Nitroso-2-naphthol (APANN)	conc.=0.1– 2.5µg /mL^{-1} ε= 1.83 x10^4 L.mol^{-1}.cm^{-1} pH=8.5 , λ_{max}=430.5nm , Sandell's sensitivity = 0.00349 µg/cm^2 , It estimate the copper in tea leaves.	[93]
3	Spectrophotometric	2-(benzyliminomethyl)-6-methoxy-4-(4-methoxyphenyl-azo) phenol	conc.2x10^{-6} - 5x10^{-2}M, D.O.L=5.9x10^{-7} slope (29.26±0.91), Measuring copper in mineral water samples.	[94]
4	Spectrophotometric	3-(3-phenylpyrazylazo)2,7-naphthalendiol (3PPA)	conc. =1.25 –10. 0 µg. ml^{-1} ε = 9.5x10^3 L.mol^{-1}.cm^{-1}, pH=3.4 , λ_{max}=516nm , (RSD=0.206%) ,(Rt=1.14%) , Ksp= 5 x10^{10} , , The method was applied to green tea leaves.	[95]
5	Spectrophotometric	2,3,4-trihydroxyacetophe nylhydrazone	conc. = 0.04-0.64µg.mL^{-}, pH=3.4 , λ_{max}=385nm Ɛ=1.0053×10^5 L.moL^{-1}.cm^{-1} S.D=0.0024 , , RSD%=0.47 , Sandell's Sensitivity =0.0006265 µg.cm^{-2}, estimating copper in models from the alloys	[96]

			And models of food and medicinal herbs volume_up content_copy share star_border	
6	spectrophotometric	Cefixime immediately in 1,4-dioxan-distilled water medium	Conc.= 1.015-8.122(μg / mL) , Ɛ = 8.29×10^{3}L / .mol.cm , Sandell's sensitivity = 0.008μg / cm^{-2} , L.O.D = 3.19 x 10^{-2}μg / mL L.O.Q = 9.65 x 10^{-2}μg / mL	[97]
7	Spectrophotometric	4-(4-chlorobenzylideneimino)-3-methyl-5-mercapto-1, 2, 4-triazole	pH = 4.2, λ_{max}=414nm, Ɛ= 0.33813 × 10^{4}L.mol^{-1}.cm^{-1} ,S = 0.01996μg. cm^{-2} and RSD% = 0.42 Copper (II) was quantified in samples from food	[98]
8	Spectrophotometric	5,5- dimethyl-2-(2- hydroxy-3,5-disulfophenylhydrazo)cyclohexane-1,3-dione (H2L)	Conc.=0.23-2.56 mg. mL^{-1} λ_{max}=467nm , pH=345nm Ɛ=2.50 x 10^{-4} L.Mol^{-1}.cm^{-1}, determination of copper(II) in soils polluted by oil,seawater, igneous rock,	[99]
9	Spectrophotometric	N,N-bis[(E)-(4-fluorophenyl)methylidene]thiocarbonohydrazide [bis(4-fluoroPM)TCH]	conc. 2.0 -14 μg mL^{-1} , λ_{max}=375nm, pH=2.5 -5 Sandell's sensitivity= 0.0014 μg/cm^{2}, (R.S.D.) = 0.13% , , Analysis of copper(II) from pharmaceutical allopathic samples , homeopathic pharmaceuticals	[100]
10	Spectrophotometric	3,3-(1,3-propanedyldiimine)bis-[3-methyl-2-butanone]dioxime (PnAO)	Conc.=0.5–350 μg/mL λ_{max}=524nm pH= 4–10, L.O.D=10 μg/mL , L.O.Q=40 μg/mL , , Ɛ = 2.95 × 10^{4}L.mol^{-1}.cm^{-1}, Slope= 0.002946 , 2 r^{2} =0.999 , (R%)= 0.74	[101]

11	Spectrophotometric	Morpholine-4-dithiocarbamate	Conc.=0.2-15 µg/mL , λ_{max}=443.5nm pH=4-7 , Ɛ =2.467 × 10^4L.mol^{-1}.cm^{-1} Sandell's sensitivity =0.00255 µg/cm^2 , , Samples were estimated from biological and pharmaceutical samples.	[102]
12	Spectrophotometric	poly[allylamine-co-N-4-(8-aminoquinolyl-5-azo)benzylidene allylamine](PAPPQ)	Conc.=0.1-25 µg/mL λ_{max}=440nm, pH =3.3 Ɛ =5.15 × 10^4 L.mol^{-1}.cm^{-1} applied for blood sera	[103]
13	Spectrophotometric	1-(2,4-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol	Conc. = (20-70µg/mL) λ_{max}=645nm Ɛ =0.87 × 10^3 L.mol^{-1}.cm^{-1} Sandell's sensitivity =0.072 µg.cm^{-2} , Copper (II) has been quantified in alloy, pharmaceutical, and biological samples	[104]
14	Spectrophotometric	2-(4-methoxy-phenyl) azo [5,4-diphenyl imidazole] (MPAI)	Conc. (1.2598x10^{-5} - 1.2598x10^{-4} M) λ_{max}= 507nm , pH=8 Ɛ =0. 71 × 10^4 L.mol^{-1}.cm^{-1} RSD%= 0.534 -2.903% R^2 = 0.9989 ,L.O.D=0.642 µg , applied for copper determination inTea leaves and dental filling.	[105]
15	flame atomic absorption spectrometry	2-[2-(6-methyl-benzothiazolylazo)]-4-bromophenol (Me-BTABr)	Conc.=1.08-100µg L^{-1}, pH=7.5, L.O.D=1.08 µg. L^{-1} L.O.Q= 3.60 µg .L^{-1} Precision (Cu 50 µg L^{-1}, n=7),%, RSD 2.6 Calibration function A = 8.4 x 10^{-3} + 2.2 x 10^{-3} C	[106]

16	flame atomic absorption spectrometry	6-(2-naphthyl)-2,3-dihydro-as-triazine-3-thione (NDTT)	Conc.= 0.22-100 ng.ml^{-1} , pH = 8.5 ,r^2 =0.998 , L.O.D= 0.22 ng.ml^{-1} , R.S.D = 2.1% , determination copper in water samples	[107]
17	In this study	4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole	Conc.= 0.1 - 6.0 µg/mL , λ_{max} (573nm), pH=8 Ɛ =1.11x10^{4}L.moL^{-1} .cm^{-1} (r^2) = (0.9989) , L.O.D= 0.0114 µg/mL L.O.Q= 0.0376µg/mL	

(1-12) Chemistry of Mercury.

Mercury is a strong toxic substance that affects humans and public health as well as the environment, although the danger coming from mercury to humans and wildlife at high levels may be toxic and this usually occurs through the consumption of contaminated food [108,109]. Most mercury pollution is a result of human activities, and there is another source in the atmosphere and enters into ecosystems through atmospheric deposits. Mercury oxidizing compounds have a more local effect than elemental mercury [110]. Mercury (Hg) undergoes - in nature - a variety of complex transitions and cycles between the interconnected atmospheric, ocean and Earth systems. While elemental mercury (metallic, Hg0) is aqueous, it quickly dissipates into a dangerous vapor form. Mercury has the ability to bond with other elements (Such as chlorine, sulfur, or oxygen), which leads to the formation of inorganic mercury (Hg^{1+}) and mercury salts (Hg^{2+}); and inorganic mercury can be changed to organic mercury by bacterial activity. Toxicity, the important organic form of mercury is methylmercury. Humans are primarily exposed to mercury through food with consumption of fish and seafood being the primary source [111-114]. In recent times, experiences have intensified for estimating and studying mercury, and that is because of the importance of estimating in terms of minimizing the harm of this element and increasing the benefit from it [115].

(1-12-1) Spectrophotomtric determination of mercury.

In this study, some of the previous spectrophotometric methods used for determination of mercury are present, as show in the table (1-2).

Table(1-2) the methods used to estimate mercury ion.

Seq	Method	Reagents	Note	Ref
1	Spectrophotometric	methyl phenyl] thiazolyl azo]-3-methyl-4-methoxy-2-naphthol	conc. (0.05-10ppm) λ_{max}= 497nm , pH=9 L.OD=0.041ppm , $R^2 = 0.9994$ $y = 0.0438x + 0.0267$, Mercury estimated in soil, water, vegetables, meat, and fruits.	[116]
2	Spectrophotometric	5-[(hydroxyl phenyl)azo]-4,6-di hydroxyl-2-mercapto (primidine)]	Conc.= 0.1—1.3 µg/ml, λ_{max}=524nm, pH =5.5—7 $\varepsilon = 4.01x10^4$, Ksp=$0.14x10^8$ $L^2.mol^{-2}$, Rer%= 1.42 Sand ell's sensitivity ($5x10^{-3}$µg/ cm^2) Estimation of mercury in the bacterial activity.	[117]
3	Spectrophotometric	3-[5-hydroxy-3 -6,6 trimethylclohexa 2,4-dienyl)diazenyl]	Conc.=$1\ x10^{-5}$-$9\ x10^{-5}$ λ_{max}= 300nm, pH=7 $y = 0.0278X + 0.0144$ $R^2 = 0.9982$ estimate mercury wastewater from	[118]

		phenol	Rustumiya city in Iraq.	
4	Spectrophotometric	5-amino-2-(phenyldiazenyl) phenol (I)	Conc. 2.5 – 200 ng ml^{-1} ε =8.81 x 10^{8} and 9.57 x 10^{8} L mol^{-1} cm^{-1}) , λ_{max}= 626 and 649 nm L.O.D= 0.75 and 2.37 ng RSD 1.45 and 1.34% ,ml^{-1} Mercury was estimated in a gunshot.	[119]
5	Spectrophotometric	4-(2-thiazolylazo) resorcinol (TAR)	Conc.=0.1–2.0 µg mL^{-1}, λ_{max}= 547nm , , R^2 =0.997 , L.O.D = 0.024 µg mL^{-1} , L.O.Q =0.081 µg mL^{-1} , determine mercury while eliminating ionic interference in water samples.	[120]
6	Spectrophotometric	7-(6-Bromo 2-benzothiazolyl azo)-8-Hydroxyquinoline	Conc.= 8-500 ng mL^{-1} λ_{max} =640nm , pH=7 , L.O.D = 7.4 ng mL^{-1} , recovery 100.43±1.23 , determination of mercury in some fish samples with satisfactory results.	[121]
7	Spectrophotometric	1-[(2,4-Dimethyl phenyl) Azo-2-Nephthol	Conc.=1.473x10^{-5} M–10.313x10^{-5}M λ_{max}= 626nm , pH=7 , L.O.D= 5.235x10^{-7} M, ε 0.339x10^{4} L. mol^{-1}.cm^{-1} , R^2 = 0.9952 ,	[122]
8	spectrophotometric	[methyl phenyl thiazolyl azo]-3-methyl-4-methoxy-2-naphthol (MPTAN)	y = 0.0438x + 0.0267 λ_{max}=497nm , pH = 9, R^2 = 0.9994 , RSD%=0.0745ppm , ε =2.11x10^{4} (L. mol^{-1}.cm^{-1}) Sandell's sensitivity = 9 x 10^{-9} µg/cm^2 , L.O.D = 0.041ppm , This method increases the extraction efficiency by	[123]

			the presence of electrolyte salts in aqueous solutions	
9	spectrophotometric	Diphenylthiocarbazone (dithizone)	linear=1.12 – 1.36µg.ml^{-1} Conc.=0.1 – 25 µg.ml^{-1} λ_{max}=488nm ,RSD=0-2.5% , Sandell's sensitivity = 2.5 x 10^{4} µg/cm^{2} , L.O.D = 20 ng .mL^{-1}, determination mercury in biological ,waters samples ,soils, plant samples.	[124]
10	spectrophotometric	o-carboxy phenyl diazoamino p-azobenzene	Conc.=0.08 - 0.8 µg.ml^{-1} λ_{max}=488nm , pH=11.3 Sandell's sensitivity= 2.22×10^{5} mol^{-1} cm^{-1}, , Beer's law =2–20 µg ,RSD=2.23% determination of mercury in air, water, soil and fungicide samples	[125]
11	Spectrofluorometric	2-hydroxy-1-naphthaldehydene-8-aminoquinoline (HNAAQ)	linear =0 - 16 µg.L^{-1} λ_{max}=445nm , , pH=8 , L.O.D =0.056 µg L^{-1}, determination of mercury in wastewater and prawns	[126]
12	spectrophotometric	5-[(hydroxyl phenyl)azo]-4,6-di hydroxyl-2-mercapto primidine)	Beer's law = 0.1—1.3 µg/ml) , λ^{max}=524nm, pH =5.5—7 ε =4.01x10^{4} L. mol^{-1}.cm^{-1}, Ksp =0.14 x 10^{8} , RSD=1.42% , Sand ell's sensitivity =0.005 µg/cm^{2} , The above newly synthesized compounds were investigated for their antibacterial.	[127]

13	spectrophotometric	3-amino-1,2,4-triazole azodye	Beer's law = 0.001—12.04 µg/ml . λ_{max}=490nm , pH = 9 , ε =3.31x10^{4} L. mol^{-1}.cm^{-1} , determination of mercury(II) in tap water seawater and synthetic seawater samples	[128]
14	atomic absorption spectrometry	2-(2-benzothiazolylazo)-p-cresol (BTAC)	Conc.=0.055–0.200 µg.L^{-1} pH= 8 L.O.D= 0.011 µg. L^{-1}, L.O.Q = 0.038 µg. L^{-1}, precision =0.50% , , determination of mercury in human saliva () seafood collected in Brazil	[129]
15	UV.detection	1-(2-pyridylazo)-2-naphthol	linear = 1-1,000 µg.L^{-1} pH=6.5 L.O.D= 0.62 µg. L^{-1}, , R^{2}=9991 , RSD= 4.1% , , determination of mercury in water samples.	[130]
16	In this study	4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole	Conc.= 0.2 - 9.0µg/mL λ_{max} =538nm , pH=10 Ɛ= 1.310x10^{4}L.moL^{-1}.cm^{-1}, R^{2} =0.9988, L.O.D=0 .00153 µg/mL L.O.Q= 0.00505 µg/mL	

(1-13) The importance of thermodynamic functions [131].

The thermodynamic functions (ΔG, ΔH, ΔS) are one of the most important characteristics that must be studied during chemical reactions, because they show the possibility of reactions occurring automatically or not automatically. Also, these functions are included in the study of random interactions (entropy). It is usual for the values of stability constants to be expressed in terms of their logarithms values. Moreover, the value in terms of its logarithms (LogK) is proportional to the value of the free energy of the reaction (G),the thermodynamic functions are calculated through the following equations.

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots\dots\dots (1-1)$$

$$\Delta G = - RT \ Ln \ K \quad \dots\dots\dots\dots\dots \quad (1-2)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \dots\dots\dots\dots..\dots (1-3)$$

(1-14) The aim of study.

The main objectives .

1-Perparation of a new reagent from an Azo derivative isolate and purify in the solid state then charactraization by ^{1}H.NMR ,^{13}C.NMR and mass spctrum methods, the prepared new reagent are used for the determination of trace amounts of copper(ll) and mercury(ll) ions, in different samples .

2-Studying the optimum conditions for the determination of (Cu^{+2}, Hg^{+2}) ions with the prepared reagent such as (Temperature, pH function, time effect, and sequence of addition, Limitation of optimum value of reagent) and concentration obey lambert-Beer law were also assigned each ions.

3-Study the nature of the link between ligand and ion by finding the ratio between ion and reagent using a method, molar ratios method, Job method and Mullard method.

4-The study also included identification of solid complexes and identification of some physical characteristics. Diagnosis of ligand and prepared complexes by means of techniques of the UV-vis and FT-IR, the atomic absorption spectrum of ions and complexes and then the proposed synthetic formulation of complexes.

5-An applied study of the method for the determination of ions on some laboratory standard samples and samples from Dental filling, well water and tap water samples.

Chapter Two
Experimental part

(2-1)Apparatus.

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

No.	**Instrument name**	**Type**
1	FT-IR Spectrophotometer	FTIR – 8400S Shimadzu (Japan). At the University of Kerbala.
2	Dual-beam UV Vis Spectrophotometer	[Double Beam Uv-Visible Spectrophotometer - 1800, Shimadzu, (Japan)]. At the University of Kerbala.
3	Single-beam visible-ray Spectrophotometer	[Single Beam UV- visible Spectrophotometer Sp-300 (Japan)]. At the University of Kerbala.
4	Sensitive balance	Sartorius(Germany). At the University of Karbala.
5	Acidic function measuring Instrument	pH-meter-WTW-720-inoLab (Germany). At the University of Kerbala.
6	Water bath	BS-11 JEIO TECH (Korea). At the University of Kerbala.
7	Melting point measuring Instrument	Type Melting point Apparatus (England). At the University of Kerbala.
8	Electric heater	IKA RH Basic2(Korea). At the University of Kerbala.
9	Conductivity measuring Instrument	Digital conductivity Meter- WTW -720 –inoLab (Germany) At the University of Kerbala.
10	Flame atomic absorption spectrometry	SHIMADZU AA-7000 In Uscience laboratory in Diwaniyah
11	Mass spctrum	Manufacturer Company: Agilent Technologies 1. MS Model: 5975C VL MSD with Tripe-Axis Detector In Iran
12	^{1}HNMR and ^{13}CNMR spctrum	Instrument : inova spectrometer frequency=499.47 In Iran

(2-2)Chemical Materials.

Table (2-2) All chemicals and reagent are used with out further purification.

No	Subject Name	Chemical formula	Company Name	Purity
1	bis(4-methoxyphenyl) -1,2 ethane-1,2-dione	$C_{16}H_{14}O_4$	Fluka	99.9%
2	Hexamethylenetetramine	$C_6H_{12}N_4$	Fluka	99.8%
3	m-toluidine	C_7H_9N	Fluka	99.9%
4	Glacial acetic acid	CH3COOH	GCC	98.0%
5	Sodium nitrite	$NaNO_2$	E.M.Darmstadt	99.0%
6	Ammonium hydroxide	NH_4OH	(B.D.H)	97.0%
7	Glacial Acetic acid	CH_3COOH	GCC	99.6%
8	Ammonium acetate	NH_4CH_3COO	GRIFFIM	99.8%
9	Iron(III)nitrate.9-hyrate	$Fe(NO_3)_3.9H_2O$	(B.D.H)	99.0%
10	Cobalt(II)nitrate.6-hyrate	$Co(NO_3)_2.6H_2O$	(B.D.H)	99.0%
11	Nikel(II)nitrate.6-hydrate	$Ni(NO_3)_2.6H_2O$	(B.D.H)	99.0%
12	Cupper(II)nitrate.3-hydrate	$Cu(NO_3)_2.3H_2O$	(B.D.H)	99.0%
13	Chromium(III) nitrate.9-hydrate	$Cr(NO_3)_3.9H_2O$	Fluka	99.0%
14	Cadumium(II)nitrate.4-hydrate	$Cd(NO_3)_2.4H_2O$	E.Merck,Darmstadt	99.0%
15	Mercury(II)nitrate.1/2-hydrate	$Hg(NO_3)_2.1/2H_2O$	GCC	99.0%
16	Lead (II)nitrate	$Pb(NO_3)_2$	HIAMEDIA	99.0%
17	Barium (II)nitrate	$Ba(NO_3)_2$	Poisin	99.0%
18	Potassium dichromate	$K_2Cr_2O_7$	Riedel	99.0%
19	Potassium Sulfate	K_2SO_4	Merck	99.0%
20	Potassium carbonate	K_2CO_3	(B.D.H)	99.0%
21	Potassium thiocyannate	KSCN	ANALAR	99.4%
22	Potassium cyannate	KCN	(B.D.H)	99.0%
23	Potassium bromide	KBr	NANIWA	99.0%
24	Potassium chloride	KCl	GCC	99.0%
25	Potassium Fluoride	KF	Fluka	99.0%
26	acetic acid	CH_3COOH	GCC	98.0%

27	Ascorbic acid	$C_6H_8O_6$	(B.D.H)	99.5%
28	Citric acid	$C_6H_8O_7$	Scharlou	99.0%
29	Tartaric acid	$C_4H_6O_6$	AAG	99.0%
30	Thiourea	CH_4N_2S	Scharlou	99.0%
31	formaldehyde	CH_2O	Scharlou	99.0%
32	Sodium hydroxide	NaOH	(B.D.H)	99.0%
33	Hydrochloric acid	HCl 36w/v%	HIAMEDIA	Analar
34	Ethanol	C_2H_5OH	Haymankimian	99.9%
35	Nitric acid	HNO_3 65w/v%	E.Merck,Darmstadt	Analar
36	Sodium nitrate	NaNO3	Fluka	98.0%

(2-3)Preparation of the organic reagent:

1-Preparation of the compound 4,5-dimer (4-methoxyphenyl) imidazole.

In a 500mL round flask, (2.70g, 0.01mol) of the benzyl derivative and (0.256g, 0.005mol) of hexamethylene tetraamine were mixed with (6.0g, 0.23mol) of ammonium acetate followed by adding (40ml) of glacial acidic acid, and the solution was sublimated for a period of (90min) and after cooling the reaction product, (400g) of Groats Althel were added to mixture, then the ammonium hydroxide solution was added by drop to modify the acid function and obtain the imidazole derivative in the form of a white precipitate. The precipitate was filtered, and washed by distillid water to get rid of the remnants of the base and salts, and the product was dried and recrystallized by ethanol to obtain white crystals, dried and the melting point was measured (73-74C^0), yield percentage was (84%).

2-Synthesis of Ligand 4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole (BMTI).

Synthesis of Ligand 4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole (BMTI). The new isoamidazole was prepared from the diazonium salt pairs of the tlodine derivative with the derivative Imidazole in an alcoholic medium by dissolving (1.08 ml, 0.01 mol) of methaldodine in a solution obtained by mixing (3 ml) hydrochloric acid with (50 ml) distilled water. 0.7 gm, 0.01 mol) of sodium nitrite dissolved in (10 ml) of distilled water drop by drop, taking into account stirring and maintaining the temperature below 5 C°, after which the solution was left to settle for a period of (30 minutes) to complete the nitrogenation process and obtain a solution Diazanium chloride. This salt solution was added gradually with continuous stirring to a solution (2.80 g, 0.01 mol) from the base pairs 5,4-dimethyl (methoxyphenyl) amidazole dissolved in a mixture of (150 ml) of ethyl alcohol and (15 ml). The sodium hydroxide solution (1 M) was observed to discolor the solution in an orange color. The solution was left for the 24 hours, and the acidic function was modified down to (pH = 6) to obtain a reddish orange precipitate. The precipitate was filtered and washed with deionized water to get rid of the sodium chloride resulting from the pairs and neutralization process, and it was dried and recrystallized from ethanol to obtain the reagent in its pure form. Intial test for the prepared new reagent, melting point of reagent (174 – 178 C^{o}) and Molecular weight (399 gm/mol).

(2-4) Preparation of the Standard Solution.

1- Reagent Solution BMTI ($2.50x10^{-3}$M).

The reagent Prepard by dissolving (0.1 g) of (BMTI) Molecular weight (399 gm/mol) in ethanol and the volume was completed to (100 mL) with ethanol in volumetric flask.

2-Prepration of the standard solution of copper(ll) (1mg /mL).

The standard solution of copper (ll) ion was prepared at a concentration of (1 mg/mL), equivalent($1.574x10^{-2}$ M) from dissolving (0.3802 g) of copper nitrate $Cu\ (NO_3)\ _2.3H_2O$ in (100 mL) deionized water. From this standard solution other standard solutions were prepared by sequential dilution with deionized water.

3- Prepration of the standard solution of mercury(ll)(1mg/mL).

The standard solution of a mercury (ll) ion was prepared at a concentration of (1 mg/mL), equivalent ($4.977x10^{-3}$ M) from dissolving (0.166 g) of mercury nitrate $Hg(NO_3)_2.1/2H_2O$ in (100 mL) deionized water and from this standard solution the other standard solutions were prepared by squential dilution with deionized water.

4- prepration of Sodium hydroxide solution (0.1 M).

The sodium hydroxide solution was prepared at a concentration of (0.1 M) by dissolving (0.400 g) of it in a certain volume of deionized water, then the solution was diluted to (100 mL) by deionized water.

5- prepration of nitric acid solution (0.1 M).

A solution of nitric acid was prepared at a concentration of (0.1 M) by transferring (0.694 mL) of concentrated acid (65 w/v%) in a certain volume of deionized water, then diluting the solution to (100 mL) by deionized water.

6- Preparation of Cationic solutions.

Cationic ions solutions were prepared at a concentration of (1 mg/mL) from the elemental nitrate salts by dissolving the calculated weights there of in (100 mL) of deionized water. From these standard solutions, others were prepared by sequential dilution with deionized water. As installed below.

Table (2-3) Shows the amount of weights used to prepare the cation solutions.

Seq	Substance	Weight(g)
1	$Fe(NO_3)_3.9H_2O$	0.721
2	$Cr(NO_3)_3.9H_2O$	0.769
3	$Co(NO_3)_2.6H_2O$	0.493
4	$Ni(NO_3)_2.6H_2O$	0.495
5	$Cd(NO_3)_2.4H_2O$	0.274
6	$Cu(NO_3)_2.3H_2O$	0.380
7	$Hg(NO_3)_2.1/2H2O$	0.166
8	$Pb(NO_3)_2$	0.159
9	$Ba(NO_3)_2$	0.190

7- Preparation of anions solutions.

Anions solutions were prepared at a concentration of (1 mg/mL) from the elemental potassium salts by dissolving the calculated weights there of in (100 mL) of deionized water. From these standard solutions, others were prepared by sequential dilution with deionized water. As installed below.

Table (2-4) Shows the amount of weights used to prepare the anions solutions.

Seq	Substance	Weight(g)
1	$K_2Cr_2O_7$	0.136
2	K_2SO_4	0.181
3	K_2CO_3	0.230
4	KSCN	0.167
5	KCN	0.250
6	KBr	0.161
7	KF	0.305
8	KCl	0.210

8-Preparation of standard solutions at different concentrations for the purpose of studying the effect of ionic strength.

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

A solution of sodium sulfate (0.5 M) was prepared by dissolving (1.780 g) from sodium sulfate in a (5 mL) deionized water and the solution was transferred to a volumetric flask (25 mL) capacity and the volume was completed to (25 mL) with deionized water. The concentrations were prepared ($5.\ 00\text{x}10^{-2}$, $5.\ 00\text{x}10^{-3}$,$5.\ 00\text{x}10^{-4}$ M) by sequential dilution of the standard solution.

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

A solution of sodium nitrate(0.5 M) was prepared by dissolving (1.063 g) from sodium nitrate (NaNO3) in a (5 mL) deionized water and transferred to a volumetric flask (25 mL) and completed to (25mL) with deionized water. The concentrations were prepared ($5.00x10^{-2}$, $5,00x10^{-3}$,$5,00x10^{-4}$M) by sequential dilution of the standard solution.

9-Preparation of buffer solutions [132].

1-Preparation of a buffer solution of citric acid pH (8,10).

A solution (0.1 M) of citric acid ($C_6H_8O_7$) was prepared by dissolving (1.921 g) of it in (100 mL) of deionized water, then gradually adding a solution of (0.1 M) of NaOH until the pH is reached Required.

2- Preparation of a buffer solution of Ascorbic acid pH (8,10).

A solution (0.1 M) of Ascorbic acid ($C_6H_8O_6$) was prepared by dissolving (1.760 g) of it in (100 mL) of deionized water, then gradually adding a solution of (0.1 M) of NaOH until the pH is reached Required.

3- Preparation of a buffer solution of Acetic acid pH (8,10).

A solution (0.040 N) of Acetic acid (CH_3COOH), then gradually adding a solution of (0.1 M) of NaOH until the pH is reached Required.

10- Preparation of masking agent solutions.

Masking agent solutions were prepared with a volume of (25 mL) by dissolving a specific weight of each substance in a (5 mL) deionized water and transferring the resulting solution to a volumetric flask of (25 mL) capacity and completing the volume to the mark with deionized water.

Table (2-5) Shows the masking factors used in this study.

Seq	Substance	Weight(g)	Molar concentration	Final Volume(mL)
1	Tartaric acid	0.375	0.1	25
2	Citric acid	0.480	0.1	25
3	Thiourea	0.190	0.1	25
4	KCl	0.052	0.1	25
5	Ascorbic acid	0.440	0.1	25
6	Formaldehyde	0.075	0.1	25

(2-5)Procedure.

(2-5-1) Preliminary tests for the reaction of the reagent with a Variables metal ions.

A set of test tubes were taken and in each individual of them we placed (1 mL) of metallic ion solutions (about ten) ions Concentrated (40 µg/mL), then to (1.0 mL) when added to it of the reagent solution at a concentration ($2.50x10^{-3}$ M) gradually with shaking, where it was evident that A new color or precipitate was formed during the addition process, and after this step the solution is divided into two parts, one of which was added drops of (0.1 M) solution of NaOH, while the other was added to the other drops of (0.1 M) of HNO_3 solution to see the effect of the acidic function in the reaction and record the results obtained.

(2-6) Study the absorption spectra of the reagent(BMTI) and its complexes formed with copper (II) and mercury (II) ions.

(2-6-1)Study of the absorption spectrum of the reagent(BMTI) in the ultraviolet - visible region.

The spectral scanning of the reagent (BMTI) at a concentration of ($2.50x10^{-3}$ M) in the bounded area between (190-1100 nm) versus ethanol as a comparable solution (Blank) was taken using a dual-beam UV-visible spectrphotometer and using quartz cells with a light path of (1 cm) thickness., And (λ_{max} =498 nm) was determined at the highest absorbance value for the reagent.

(2-6-2) Study of the absorption spectra of both copper (II) and mercury (II) complexes in the ultraviolet - visible region.

The metal ions that interact with the reagent were well defined in paragraph (2-5-1), taken two volumetric flasks (10 mL) were taken and one of them put (5 mL) of copper (II) ion solution at a concentration of ($1.259x10^{-4}$ M) equivalent to (40 µg). /5 mL) and also in the second volumetric flask, (5 mL) of mercury (II) ion solution was added at a concentration of ($3.988x10^{-5}$ M), equivalent to (40 µg/5 mL), and (1.0 mL) of the reagent solution was added to each volumetric flask at a concentration of ($2.50x10^{-3}$ M). The volume was completed to the mark with ethanol, and the comparative solution (Blank) was prepared in the same way, with the exception of adding copper (II) and mercury (II) ions.

A spectrophotometric survey of the complex solutions prepared in the above paragraph was conducted in the area between (190-1100 nm) and the values of (λ_{max}) were determined. For complexes in this region at the highest value of absorption against the reagent solution being a comparative solution (Blank) except for the addition of ions.

(2-7) Study the optimum conditions for the formation of copper (II) and mercury (ll) complexes with the BMTI reagent.

After determining the maximum absorption (λ_{max}) for each of the complexes in paragraph (2-6-2), which is (573 nm,538 nm) for each of the copper (II) and mercury (ll) complexs, respectively, the following experiments were conducted to determine the opimum conditions for the formation of the two complexes by the spectrophotometric method, in order to reach High sensitivity and selectivity in the estimation process of ions.

(2-7-1)Limitation of optimum value of reagent.

1-A group of volumetric flask(10 mL) was taken and added to each of them (5 mL) of copper (II) ion solution at a concentration of ($6.299x10^{-5}$ M), equivalent to (20 µg / 5 mL), and then added to them in sequential different volumes of the reagent solution at a concentration of ($2.50x10^{-3}$ M), where it ranged between (0.2-0.9 mL), then the acidity function was modified at (pH = 8) followed by the volume completion to the mark in ethanol and the absorption record at the greatest wavelength of the copper complex (λ_{max} = 573 nm) for each solution versus the reagent solution as it is a comparative solution With the exception of adding the ion to all the measured solutions.

2-A set of volumetric flask(10 mL) was taken and added to each of them (5 mL) of the mercury (II) ion solution at a concentration of ($3.988x10^{-5}$ M), equivalent to ((40 µg /5 mL), and then added to them, sequential, different volumes of the reagent solution at a concentration of ($2.50x10^{-3}$ M), where it ranged between (0.2-1.0 mL), then the acidity function was modified at (pH = 10), followed by the volume completion to the mark with ethanol and the absorption record at the greatest wavelength of the mercury complex (λ_{max} = 538 nm) for each solution versus the reagent solution for being a comparable solution except for addition Mercury ion and for all measured solutions.

(2-7-2) Effect of pH.

1-Study the effect of the acidic function of copper (II) complex.

A series of solutions of copper (II) ions were prepared at a concentration of ($6.299x10^{-5}$ M) equivalent to (20 µg / 5 mL) by mixing (5 mL) copper ion (ll) with (0.6 mL) of the reagent solution at a concentration of ($2.50x10^{-5}$ M). and adjust the acidic function of the compound with different values within the range (1.0-10.0), then transfer the mixture to volumetric flasks (10 mL) and complete the volume to the mark with ethanol. The comparative solution used in the spectroscopic measurements of the group above was prepared by transferring (5 mL) From deionized water, then adding (0.6 mL) of reagent solution at a concentration of (2.50×10^{-3} M) with the adjustment of the acidic function and transferred to a volumetric flask(10 mL) and Complete the volume to the mark using ethanol. The absorption was recorded at the maximum wavelength of the copper compound. (λ_{max} = 573 nm) .

2- Study the effect of the acidic function of mercury (II).

A series of solutions of mercury (II) ions were prepared at a concentration of (3.988×10^{-5} M) equivalent to (40 µg/5 mL) by mixing (5 mL) copper ion (ll) with (0.6 mL) of the reagent solution at a concentration of (2.50×10^{-5} M). and adjust the acidic function of the compound with different values within the range (1.0-10.0), then transfer the mixture to volumetric flasks (10 mL) and complete the volume to the mark with ethanol. The comparative solution used in the spectroscopic measurements of the group above was prepared by transferring (5 mL) of deionized water, then adding (0.6 mL) of reagent solution at a concentration of (2.50×10^{-3} M) with the adjustment of the acidic function and transferred to a volumetric flask (10 mL) and Complete the volume to the mark using ethanol. The absorption was recorded at the maximum wavelength of the mercury compound (λ_{max} = 538 nm).

(2-7-3) Effect of temperature.

1-Study the temperature effect of copper (II) complex.

The temperature effect of the copper complex was studied by taking a group of volumetric flask (10 mL) and placing (5 mL) of copper (II) ions in each of them with a concentration of (6.299×10^{-5} M) equivalent to (20 µg /5 mL) and then adding to each of them (0.6 mL) from the reagent at the best concentration, then adjusting the optimal acidic function at (pH = 8), then transferring to a volumetric flask (10 mL) and completing the volume with ethanol to the mark and then placing these flask in a water bath with a range of temperatures between (10 - 60 C^0) after which the absorption measurement at the maximum absorption wavelength of the complex versus the comparator solution prepared in the same way without adding copper ion.

2- Study the temperature effect of the mercury complex (II).

The effect of the mercury compound temperature was studied by taking a group of volumetric flask (10 mL) and placing (5 mL) mercury (II) ions in each of them at a concentration of ($3.988x10^{-5}$ M) equivalent to (40 µg /5 ml). Then add to each of them (0.7 mL) of the reagent at the best concentration, then set the optimum acidic function at (pH = 10), then move to a volumetric flask (10 mL) and complete the volume with ethanol to the mark and then put these bottles in a water bath temperature ranges between (10 - 60 ° C) and after that the absorption is measured at the maximum absorption wavelength of the compound against the comparison solution was prepared in the same way without adding the mercury ion.

(2-7-4) The effect of time on the complex stability.

The illustrate the effectof time factor on the stability of the copper (II) and mercury (II) complexex. The follow-up of the absorption measurement was studied for the two prepared complexes at different time intervals at the specified wavelenth (λ_{max}) for the two complexes.

1- Study the effect of time on copper (II) complex absorption.

The copper (II) complex was prepared by mixing (5 mL) of copper (II) ion solution at a concentration of ($6.299x10^{-5}$ M) equivalent to (20 µg / 5mL) with (0.6 mL) of the reagent solution at a concentration of ($2.50x10^{-3}$ M) with adjusting the value of the optimum acidic function at (pH = 8) Then the volume is completed to (10 mL) with ethanol. Then the absorption of the prepared complex was measured at (λ_{max}=573 nm) for the complex versus the comparative solution (Blank) and for time periods ranging from the moment of the reaction to (48hr).

2- Study the effect of time on the absorption of mercury (II).

The mercury (II) complex was prepared by mixing (5 mL) of mercury ion solution at a concentration of (3.988 x10^{-5} M) equivalent to (40µg / 5mL) with (0.7 mL) of the reagent solution at a concentration of (2.50x10^{-3} M) with adjusting the value of the optimum acidic function at (pH = 10) Then the volume is completed to (10 mL) with ethanol. Then the absorption of the prepared complex was measured at (λ_{max}=538 nm) for the complex versus the comparative solution (Blank) and for time periods ranging from the moment of the reaction to (48hr).

(2-7-5) Effect of addition sequential.

This study included changing the order of additives and work in terms of addition of ion, reagent and measurement (pH) as shown below.

a- copper(ll)ion complex.

1- Addition sequential includes an addition (5mL) of copper(ll) ion solution at a concentration of (6.299x10^{-5} M) equivalent to (20 µg /5 mL) and the acidity function was modified (pH = 8) and then addition (0.6 mL) of the reagent solution at a concentration of (2. 50x10^{-3} M) and the volume was completed by Ethanol in a volumetric flask (10 mL) to the extent of the mark. As for the comparative solution, it was prepared by mixing the solutions with the same previous steps, with the size of the copper (II) ion replaced by deionize water. Then the absorption of the prepared complex was measured at(λ_{max}=573 nm).

2- Addition sequential includes an addition (5 mL) of copper(ll) ion solution at a concentration of (6.299×10^{-5} M), equivalent to (20 µg /5 mL) and then addition (0.6 mL) of the reagent solution at a concentration of (2.50×10^{-3}M) and adjusting the pH (pH = 8), then complete the volume by ethanol in a volumetric flask (10) mL to the mark. As for the comparative solution, it was prepared by mixing the solutions with the same previous steps, with the volume of copper (II) ion replaced by deionized water. Then the absorption of the prepared complex was measured at (λ_{max} = 573 nm)**.**

3- Addition sequential includes an addition (0.6 mL) of the reagent solution at a concentration of (2.50×10^{-3} M) to (5mL) of the copper(ll) solution at a concentration of (6.299×10^{-5}M), equivalent to (20 µg/5 mL) and adjusting the pH (pH = 8), then complete the volume by Ethanol in a volumetric flask (10 mL) to the limit of the mark. As for the comparative solution, it was prepared by mixing the solutions in the same previous steps with the volume of copper (II) ion replaced by deionize water. Then the absorption of the prepared complex was measured at (λ_{max} = 573 nm**).**

b- Mercury(ll) ion complex.

1- Addition sequential includes an addition (5 mL) of the mercury (ll) solution at a concentration of (3.988×10^{-5} M) was, equivalent to (40 µg /5 mL), and the acidity function was modified (pH = 10) and then addition (0.7mL) of the reagent solution at a concentration of (2.50×10^{-3} M) and the volume was completed by Ethanol in a volumetric flask (10 mL). As for the comparative solution, it was prepared by mixing the solutions with the same previous steps, with compensating the size of the mercury ion (II) by deionized water. Then the absorption of the prepared complex was measured at (λ_{max} = 538 nm).

2- Addition sequential includes an addition (5 mL) of mercury(II) solution at a concentration of (3.988×10^{-5} M) that is equivalent to (40 µg/5 mL) to (0.7 mL) of the reagent solution at the best concentration and adjust the acidic function at (pH = 10) then complete the volume with ethanol in a volumetric flask (10mL) limit the mark. As for the comparative solution, it was prepared by mixing the solutions with the same previous steps, with the size of the mercury ion(II) being compensated by deionized water. Then the absorbance of the prepared complex was measured at (λ_{max} = 538 nm).

3- Addition sequential includes an addition (0.7 mL) of reagent solution at a concentration of (2.50×10^{-3} M) to (5 mL) of mercury(II) solution at a concentration of (3.988×10^{-5}M) equivalent to (40 µg/5mL) and the acidity function was modified (pH = 10), then the volume was completed by Ethanol in a volumetric bottle (10 mL) to the limit of the mark. As for the comparative solution, it was prepared by mixing the solutions in the same previous steps with the volume of mercury (II) ion replaced by deionized water. Then the absorption of the prepared complex was measured at (λ_{max} = 538 nm).

(2-8) Effect of ionic strength.

The ions of different ionic forces have an effect on the degree of solubility of the reactants and the speed of their reaction, as well as on the sensitivity of the estimation. Therefore, it is important to study this influencing factor. This was explained through the following steps.

1- A set of volumetric flask(10 mL) were taken and added to it (5 mL) of a copper (II) ion solution at a concentration of ($6.299x10^{-5}$m), equivalent to (20 µg/5 mL), and then added to it (1 mL) of sodium nitrate solutions and sodium sulfate Both separately at different concentrations There concentration ranged between ($0.5-5.0x10^{-4}$ M) separately, then added to each of them (0.6 mL) of reagent solution at a concentration of ($2.50x10^{-3}$ M) and the volume was completed to the mark with ethanol after the optimal acidic function was modified to form the copper (II) complex. The absorption at the maximum wavelength of the complex (λ_{max} =573 nm) was recorded against the reagent solution prepared in the same way as it is a comparable solution (Blank) except for the addition of the ion and for all the measured solutions.

2- The same method was reproduced for the determination of the mercury(II) ion complex.

(2-9) Effect of buffer solution on the optimal acidic function of each complex.

1-Three volumetric flasks (10 mL) were taken and transferred to each of them (5 mL) of copper (II) ion solution at a concentration of ($6.299 x 10^{-5}$ M) equivalent to (20 µg/5 mL) and then addion to each of them (0.6mL) of the reagent solution at a concentration of ($2.50 x 10^{-3}$M) and the optimal acidic function of the copper(II) complex was modified at (pH=8) using the buffer solutions prepared in paragraph (2-4), after which the volume was completed to the mark with ethanol and the absorption record at the maximum wavelength of the complex (λ_{max} =573 nm) versus a solution. The prepared reagent in the same way as it is a comparable solution (Blank) with the exception of adding the ion and for all the measured solutions [133].

2-Three volumetric flasks (10 mL) were taken and of the mercury(II) ion were transferred to each of (5 mL) solution at a concentration of ($3.988 x 10^{-5}$M) equivalent to (40 µg/5 mL) and then addtion to each of them (0.7 mL) of the reagent solution at a concentration of ($2.50 x 10^{-3}$ M) and the optimal acidic function of the mercury (II) complex was modified at (pH = 10) using the buffer solutions prepared in paragraph (2-4), after which the volume was completed to the mark with ethanol and the absorption record at the maximum wavelength of the complex (λ_{max} =538 nm) versus a solution. The prepared reagent in the same way as it is a comparable solution (Blank) with the exception of adding the ion and for all the measured solutions [133].

(2-10) Calibration curves .

(2-10-1) Calibration curve for the copper(II) complex.

Were taken group of volumetric flask (10 mL) and addtion to it (5 mL) from copper (II) ion solution different concentrations ranging between ($1.574x10^{-6}$ - $9.448x10^{-5}$ M), equivalent to (0.1 µg/mL - 6.0 µg/mL). Then (0.6 mL) of the reagent solution was added to it at a concentration of ($2.50x10^{-3}$ M) and the pH was modified (pH = 8) with following the other optiumum conditions reached in this study, then the volume was completed with ethanol to the of mark. Prepared by the same complex preparation method, compensating for the volume of a copper (II) ion solution with an equivalent volume of deionized water. Measured the absorption of all solutions at (λ_{max}) of the complex, the relationship between absorption versus concentration.

(2-10-2) Calibration curve for the mercury (II) complex.

Were taken group of volumetric flask (10 mL) and addtion to it (5 mL) from mercury (II) ion solution different concentrations ranging between ($9.970x10^{-7}$- $4.486x10^{-5}$ M), equivalent to (0.2 µg/mL-9.0 µg/mL). Then (0.6 mL) of the reagent solution was added to it at a concentration of ($2.50x10^{-3}$ M) and the pH was modified (pH = 8) with following the other optimum conditions reached in this study, then the volume was completed with ethanol to the extent of the mark. Prepared by the same complex preparation method, compensating for the volume of a mercury (II) ion solution with an equivalent volume of deionize water. Measured the absorption of all solutions at (λ_{max}) of the complex, the relationship between absorption versus concentration.

(2-11) The Stoichiometry of the complexes.

The metal to ligand ratio (M : L) is studied under optimum condition by both mole ratio method , Job method (continuos variations)and Mollard method .

(2-11-1) Continuous variation (Job's) Method [134].

1- copper(II) ion complex.

This method involves preparing two solutions that have the same concentration for both metal ion and the reagent for copper and mercury complexes at conc. (1.0×10^{-5} M) and (3.988×10^{-5} M) respectively then this solution are reacted with different volumetric proportions with equal final volume every time , then the curve is drawn between the absorbance and the volumetric ratio at the appropriate meximum wavelenth for each complex where the ratio (VL/Vm) as (vm the volume of the metal ion (cu) solution , VL the volume of the reagent solution) which represents the mole ratio of the complex formed.

(2-11-2) Mole Ratio Method [135].

1- copper(II) ion complex.

In this method, a group of volumetric flasks (10 mL) were taken and each of them placed a fixed and known concentration of the copper (II)ion (3.147×10^{-5} M) with increasing and proportional concentrations of the reagent (1.573×10^{-5}—1.101×10^{-4} M) and the acidity function was modified. At (pH = 8), the optimum conditions that were reached in the formation of the complex were followed and the volume was completed with ethanol to the limit of the mark. The comparison solutions were prepared in the same way as the complex preparation with the volume of the copper (II) ion solution replaced with an equivalent volume of deionized water. Absorption of all solutions at ($λ_{max}$=573 nm) for the complex.

2- mercury (II) ion complex.

In this method, a group of volumetric bottles (10 mL) were taken and each of them placed a fixed and known concentration of the mercury (ll)ion ($3.988x10^{-5}$ M) with increasing and proportional concentrations of the reagent ($1.994x10^{-5}$—$1.395x10^{-4}$ M) and the acidity function was modified. At (pH = 10), the optimum conditions that were reached in the formation of the complex were followed and the volume was completed with ethanol to the limit of the mark. The comparison solutions were prepared in the same way as the complex preparation with the volume of the mercury (II) ion solution replaced with an equivalent volume of deionized water. Absorption of all solutions at ($λ_{max}$=538 nm) for the complex **.**

(2-11-3) Mollard Method [136].

1- copper(II) ion complex.

a- Mixed in volumetric flask (5 mL) of copper (II) ion solution a concentration of ($2.00x10^{-5}$ M) with an increase of the reagent solution at a concentration of ($2.50x10^{-3}$ M) and the acidity function was adjusted at (pH = 8) and the volume was completed to (10 mL) by ethanol. Absorption was measured at ($λ_{max}$ = 573 nm) against the comparator solution .

b- Mixed in volumetric flask (5 mL) of copper (II) ion solution a concentration of (3.149×10^{-3} M) with low concentration of the reagent solution at a concentration of (2.00×10^{-4} M) and the acidity function was adjusted at (pH = 8) and the volume was completed to (10 mL) by ethanol. Absorption was measured at (λ_{max} = 573 nm) against the comparator solution .

2-mercury (II) ion comples.

a- Mixed in volumetric flask (5 mL) of mercury(II) ion solution a concentration of (3.988×10^{-5} M) with an increase of the reagent solution at a concentration of (2.50×10^{-3} M) and the acidity function was adjusted at (pH = 10) and the volume was completed to (10 mL) by ethanol. Absorption was measured at (λ_{max} = 538 nm) against the comparator solution.

b- Mixed in volumetric flask (5 mL) of mercury (II) ion solution a concentration of (1.99×10^{-4} M) with low concentration from reagent solution at a concentration of (3.988×10^{-5} M) and the acidity function was adjusted at (pH = 10) and the volume was completed to (10 mL) by ethanol. Absorption was measured at (λ_{max} = 538 nm) against the comparator solution.

(2-12) Calculation of the degree of dissociation, stabilit constant, and thermodynamic functions of the two formed complexes [137].

1- copper(II) ion complex.

Taken two volumetric flask (10 mL) and placed in the first volumetric flask (5 mL) of copper (II) ion at a concentration of (9.448×10^{-5} M), then adding (1 mL) of the reagent solution at a concentration of (1.815×10^{-4} M) then the acidity function was modified at (pH = 8) and complete the volume to the point of the mark with ethanol, then put in the second volumetric flask (5 mL) of copper(II) ion at a concentration of (9.448×10^{-5} M), then add to it (1 mL) of the reagent solution at a concentration of (3.630×10^{-4} M) then the function was modified pH at (pH = 8) Complete the volume to the mark with ethanol. Then the two volumetric flask were placed in an waterbath in a temperature range between (10 – 35 C^0) after which the absorption of the solutions was measured at the wavelength of the greatest absorption of the complex at each temperature versus the comparator solution. The absorption value was expressed for the first volumetric flask (As) and for the second volumetric flask (Am), from which the dissociation constant was calculated .

2- mercury (II) ion complex.

Two volumetric flasks were taken(10 mL) and placed in the first volumetric flask (5 mL) of mercury (II) ion at a concentration of (3.988×10^{-5} M), then adding (1 mL) of the reagent solution at a concentration of (1.500×10^{-4} M) then the acidity function was modified at (pH = 10) and complete the volume to the mark with ethanol, then put in the second volumetric flask (5 mL) of mercury (II) ion at a concentration of ($3.988x10^{-5}$ M), then add to it (1 mL) of the reagent solution at a concentration of ($3.000x10^{-4}$ M) then the function was modified pH at (pH = 10) Complete the volume to the mark with ethanol. Then the two volumetric flask were placed in an waterbath in a temperature range between ($10 – 35\ C^0$) after which the absorption of the solutions was measured at the wavelength of the greatest absorption of the complex at each temperature versus the comparator solution. The absorption value was expressed for the first volumetric flask (As) and for the second volumetric flask (Am), from which the dissociation constant was calculated.

(2-13) The effect masking agents[137].

(2-13-1) Optimum masking agents.

1- copper(II) ion complex.

The effect of the masking agents prepared in paragraph (2-4) on the absorption of the complex under study was studied by taking a group of volumetric flasks (10 mL) and placed in (5 mL) of copper (II) ion solution at a concentration of (20 µg /5 mL), then (1 mL) of the different masking agent solutions were added to it separately, then the best volume (0.6 ml) of the reagent solution was added to it at a concentration of ($2.50x10^{-3}$ M) and the volume was completed to the mark with ethanol after the acidity function was modified at (pH = 8) For the formation of the Cu (II) complex, the absorption was scored at (λ_{max} = 573 nm) versus the comparator solution (Blank). After it was determined that the masking agents no effect on the absorption of the copper (II) complex, a study was conducted that included determining the optimum masking agent and its size for each of the ions interfering with the copper (II) ion.

2- mercury (II) ion complex.

The effect of the masking agents prepared in paragraph (2-4) on the absorption of the complex under study was studied by taking a group of volumetric flasks (10 mL) and placing (5 mL) of mercury (II) ion solution at a concentration of (40 µg/5 mL), then (1 mL) of the different masking agent solutions were added to it separately, then the best volume (0.7 ml) of the reagent solution was added to it at a concentration of (2. 50x10^{-3} M) and the volume was completed to the mark with ethanol after the acidity function was modified at (pH = 10) For the formation of the mercury (II) complex, the absorption was scored at (λ_{max} = 538 nm) versus the comparator solution (Blank). After it was determined that the masking agents no effect on the absorption of the mercury (II) complex, a study was conducted that included determining the optimum masking agent and its size for each of the ions interfering with the mercury(II)ion.

(2-13-2) The effect of anions and cations ions interference.

1-Determenation copper (II) ions with some interference anions and cations ions.

In this study, the copper(II) ion was determined after adding solutions of metal ions that could interfere with the ions under study by taking a set of volumetric flask(10 ml) and added to it (5 ml) of a copper(II) ion solution at a concentration of (20 µg/5 ml) followed by the addition of (1 ml) of metallic ion solutions (40 µg/5 ml, 20 µg/5 ml) (, Ni^{+2}, Ba^{+2}, Pb^{+2}, Fe^{+3}, Co^{+2}, Cr^{+3}, Cd^{+2}) which can be interfered with the copper(II) ion separately and then added to it (0.6 mL) of reagent solution at a concentration of ($2.50x10^{-3}$ M). The volume was completed to the mark with ethanol after the acidic function was modified at (pH = 8) to form a Cu (II) complex and the absorption scored at (λ_{max} = 573 nm) versus the comparison solution (Blank). The same way is repeated for anione.

2-Determenation ion mercury (II) ions that there are some interference cations and anions ions.

In this study, the mercury(II) ion was determined after adding solutions of metal ions that could interfere with the ions under study by taking a set of volumetric flask (10 ml) and added to it (5 ml) of a mercury(II) ion solution at a concentration of (40 µg /5 ml) followed by the addition of (1ml) of metal ion solutions (80 µg/5 ml, 40 µg/5 ml) (, Ni^{+2}, Ba^{+2}, Pb^{+2}, Fe^{+3}, Co^{+2}, Cr^{+3}, Cd^{+2}) which can be interfered with the mercury (II) ion separately and then added to it (0.7mL) of reagent solution at a concentration of ($2.50x10^{-3}$M). The volume was completed to the mark with ethanol after the acidic function was modified at (pH = 10) to form a Hg(II) complex and the absorption scored at (λ_{max} = 538nm) versus the comparison solution (Blank). The same way is repeated for anions.

(2-13-3) Use of a better masking agent to determine the copper(II)ion and mercury(II) ion in the presence of cations interferers.

1- copper(II)ion complex.

Taken group volumetric flask(10 mL) and placed in all volumetric flask (5 mL) of copper (II) ion at a concentration of ($6.299x10^{-5}$ M), then addtion (1 mL) cations ion at a concentration of (20 µg) and addtion (1 mL) masking agent (0.1 M) Finally, an addition (1 mL) of the reagent at a concentration ($2.50x10^{-3}$ M) solution then the acidity function was modified at (pH = 8) and complete the volume to the point of the mark with ethanol, Absorption was measured at (λ_{max} = 573 nm) against the comparator solution.

2- **mercury(II) ion complex**.

Taken group volumetric flask(10mL) and placed in all volumetric flasks (5 mL) of mercury(II) ion at a concentration of ($3.988x10^{-5}$ M), then addtion (1 mL) cations ion at a concentration of (40 µg) and addtion (1 mL) masking agent (0.1 M) Finally, an addition (1 mL) of the reagent at a concentration ($2.50x10^{-3}$ M) solution then the acidity function was modified at (pH = 10) and complete the volume to the point of the mark with ethanol, Absorption was measured at (λ_{max} = 538 nm) against the comparator solution.

(2-14)Statistical treatment of the results.

1- Precision[138].

Determiniy the precision of the analytical methodis by finding the standard deviation (S.D) and the percentage relative standard deviation (RSD%) for four replicates and for three different concentrations of each metal ion with fixing the best conditions for each ion after which the absorption was measured at λ_{max} for each complex against the comparator solution prepared under the same conditions**.**

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

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

S.D= standard deviation
R.S.D= Relative standard deviation
X= Value
X'= mean
N= Number of values

2- Accuracy[139].

The control of the method used to estimate these metal ions was determined by the prepared reagent by applying the best conditions for the calibration curves obtained from previous experiments. The percentage error (Ere%) was calculated from the relationship.

$$Er\% = \frac{E}{Xt} \times 100 ....(2\text{-}3)$$

$$E = Xi - Xt ....(2\text{-}4)$$

$$Re\% = 100 \mp Ere \times 100 ....(2\text{-}5)$$

E= The difference between analytical reading and truth.
Xt= The real value.

(2-15) Preparation of the solid complex of copper(II) and mercury(II) ions.

1-The solid copper(II) complex.

The solid Copper (II) complex was prepared from the reaction of the reagent (BMTI) 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 copper (II) ion dissolved in deionized water. The copper (II) ion solution is placed in a circular flask with continuous stirring by instrument, then the reagent solution is added gradually so that stirring continues for a period of (two hours) with the acidic function adjusted at (pH = 8). For a period of (48hr) at room temperature, a dark red precipitate was observed after the ethanol solvent dried, Then filltered and washed with deionized water and recrystalization with ethanol and left to dry in the air.

2- The solid mercury(II) complex.

The solid mercury (II) complex was prepared from the reaction of the reagent (BMTI) 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 mercury (II) ion dissolved in deionized water. The mercury (II) ion solution is placed in a circular flask with continuous stirring by instrument, then the reagent solution is added gradually so that stirring continues for a period of (two hours) with the acidic function adjusted at (pH = 10). For a period of (48hr) at room temperature, a dark red precipitate was observed after the ethanol solvent dried, Then filltered and washed with deionized water and recrystalization with ethanol and left to dry in the air.

(2-16) Determine the melting point of the reagent, copper(II) complex, and mercury(II) complex.

For the purpose of comparison between the melting point of the reagent and the melting point of the two complexes copper(II) and mercury(II) ion prepared in paragraph (2-15), their melting point has been determined and the purpose of determining the melting point is to ensure the formation of the two complexes through a difference between the melting point of the reagent and the copper(II) and mercury(II)complexes [140].

(2-17) Measurement of molar conductivity of the, copper(II) complex, and mercury(II) complex.

The preparation of a copper(II) complex solution at a concentration of (1×10^{-3} M) by dissolving (0.008 g) of the complex precipitate in (10 mL of ethanol), after which the molar conductivity was measured at room temperature and the same previous work method was repeated for the mercury (II) complex at a concentration of (1×10^{-3} M) by dissolving (0.010 g) of mercury (II) complex precipitate in (10 mL) of ethanol and molar conductivity was measured at room temperature [140].

(2-18) Estimation spectroscopy and atomic elements.

1-UV-Vis Spectrophotometer.

The UV-visible spectrum of the reagent and its dissolved complexes was measured by using a device Double Beam Uv-Visible Spectrophotometer - 1800, Shimadzu and Single Beam UV- visible Spectrophotometer -300

2-Study of the infrared spectra (FT.IR).

The infrared spectra were recorded for the reagent, copper(ll) complex, and mercury(ll) complex.

1-Reagent (BMTI) It has been measured in a disk transfer method by means of the model holder (KBr).

2-Copper(II) complex It has been measured in a disk transfer method by means of the model holder (KBr).

3- mercury (ll) complex It has been measured in a disk transfer method by means of the model holder (KBr).

3- Atomic Absorption Spectrophotometer.

A Atomic Absorption Spectrophotometer device to identify the ion atoms in the complex.

4-Nuclear Magnetic Resonance Spectroscopy (^{1}H.NMR , ^{13}C.NMR).

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

5-Mass spectrum.

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

(2-19) Application.

The spectroscopic method used to determine the copper (II) and mercury (II) ions was applied in laboratory prepared samples, samples from tea leaves, a sample of dental filling , tap water and samples from well water from different regions to find the concentration of ions in these models.

(2-19-1) Determination of copper(II) ions in samples from tea leaves [141] .

a- Digestion of tea leaves.

1- A weight (1.00 g) of tea was weighed, the sample was heated for half an hour at a temperature of 250 C^0.

2- The samples were burned in an oven with a temperature ranging between (700-750) C^0. Then it was noticed that the sample turned into ash after an 3 hour had passed.

3- The ash was wetted by adding (2 mL) of deionized water to it, followed by the addition of (10 mL) of concentrated hydrochloric acid. The solution is filtered and then transferred the filtrate into a volumetric bottle of (25 mL) capacity, then the volume was completed to the mark with deionized water.

4- That the sample was ready for the ion estimation by process using UV-visible spectrophotometer using the reagent (BMTI) and flame atomic absorption spectroscopy.

5- The results of the atomic absorption were compared with the results obtained from the spectrophotometer method used for ion estimation. Copper (II) with the reagent (BMTI) is under study using the best conditions that have been reached for each complex, after the ion has been determined by spectrophotometric method according to the following.

b- Determination the copper ion in the tea sample.

Taken a volumetric flask(10 mL) and put (5 mL) of the filtrate in paragraph (2-19-2) in the first stage and added to it (0.6mL) of the reagent solution at a concentration of ($2.50x10^{-3}$ M), then completed the volume to the mark with ethanol with the function adjustment The best acidity of the complex was at (pH = 8), then the absorption at the greatest wavelength was recorded at (λ_{max} = 573 nm) versus the comparative solution (Blank).

(2-19-2) Determination the copper ion in the tap water.

Volumetric flask(10 mL) were taken and put (5 mL) from the tap water and added to it (0.6 mL) of the reagent solution at a concentration of ($2.50x10^{-3}$ M), then completed the volume to the mark with ethanol with the function adjustment The best acidity of the complex was at (pH = 8), then the absorption at the greatest wavelength was recorded at (λmax = 573 nm) versus the comparative solution (Blank).

(2-19-3) Determination of the copper (II) ion in a dental filling.

The copper was determined in a sample of dental fillings by dissolving (0.100g) of dental filling using (10 mL) of concentrated nitric acid (HNO_3) (65%) and after the completion of the reaction the solution was filtered. The filtrate is kept in a volume flask (100 mL) opaque, as for the sediment The solution resulting from the filtration was taken and (3 M) of hydrochloric acid was added to it to get rid of the silver(I) ion interference, as a white precipitate was obtained from silver chloride after that, the solution was filtered to obtain the filtrate and the precipitate was neglected. (10 mL) and put (2 mL) of the filtrate in it to estimate the copper (II) ion, and it was determined spectrophotometrically using the spectral method described in this study under the best conditions [141].

(2-19-4) Determination of mercury(II) ion in samples from wells water and tap water.

A number of well water samples were collected From different places such as Ain Al-Tamr and Western Creek in Karbala, and after treating the samples with a centrifuge, the mercury(II) ion concentration in the samples was estimated by taking a set of volumetric bottles (10 mL) and (5 mL) of each sample was placed in a volumetric flask, after which the optimal volume of the reagent was added (0.7 mL) at a concentration of ($2.50x10^{-3}$ M) After adjusting the acid function at (pH = 10), then measure the absorbance at the greatest wavelength (λ_{max} = 538 nm) against the comparator solution (Blank).

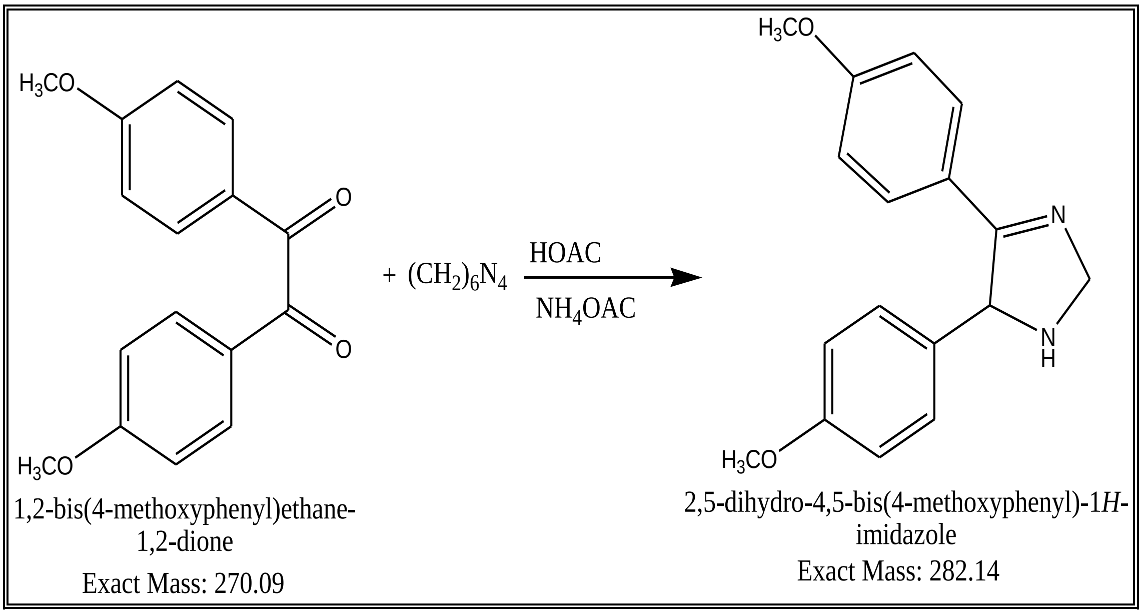
Chapter Three

Results and Discussion

(3-1) preparation of Reagent.

(3-1-1) Preparation of the compound 4,5-dimer (4-methoxyphenyl) imidazole.

The preparation of imidazole is shown in the diagram (3-1) below.



scheme (3-1) Preparation 4,5-dimer (4-methoxyphenyl)imidazole.

-FT.IR spectrum of the imidazole.

IR spectrum of the prepared imidazole that gave a beam at site 3433 cm^{-1} representing NH, a beam at site 3100 cm^{-1} representing C-H aromatic, a beam at site 2866-2942 cm^{-1} representing C-H alphatic, and a beam at site, site 1616 cm^{-1}, site 1522 cm^{-1}, and site 1234 cm^{-1} which represents, C = N, C = C, and C-O respectively[145] shown in the Figure (3-1).

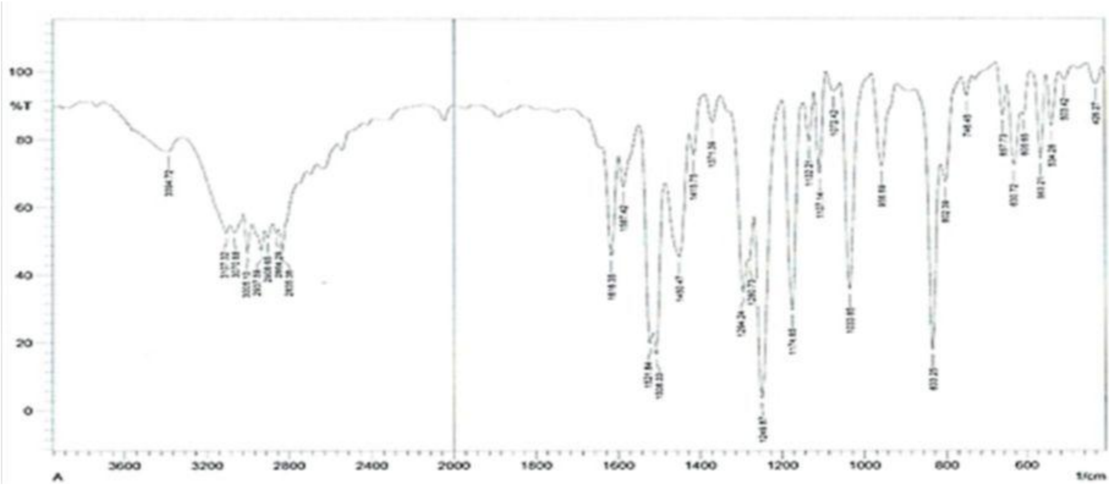
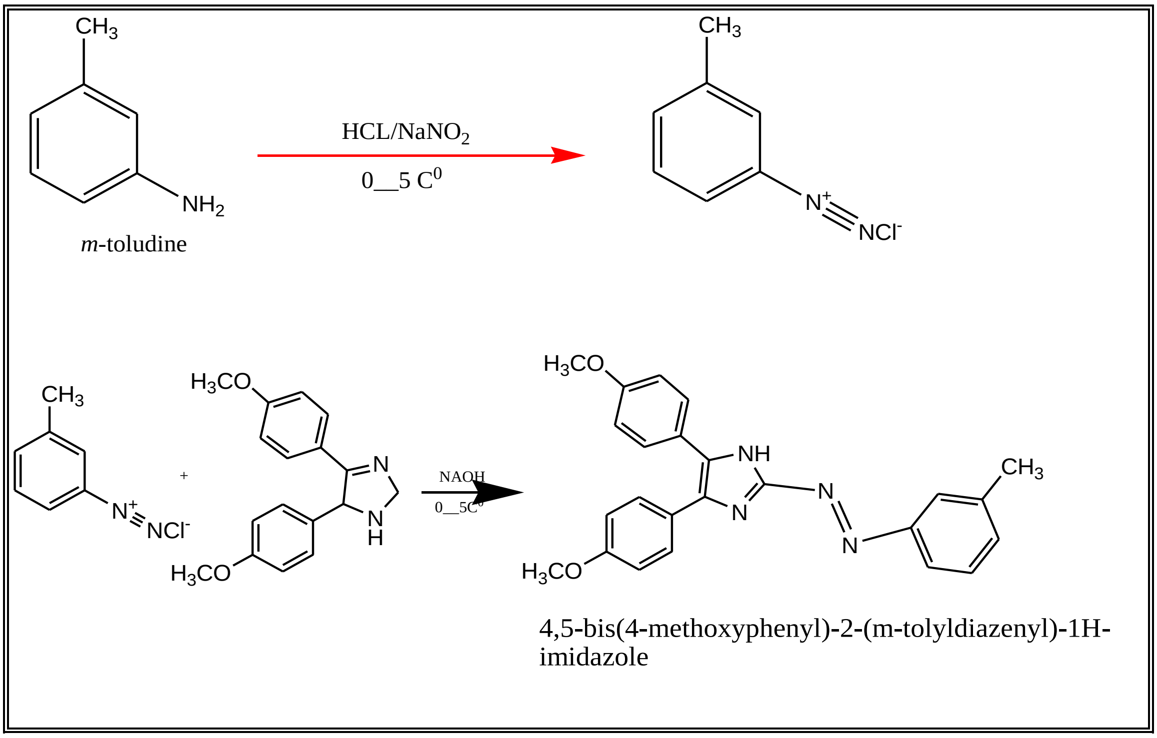


Figure (3-1). FT-IR spectrum of imidazol

(3-1-2) Synthesis of Ligand 4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole (BMTI).

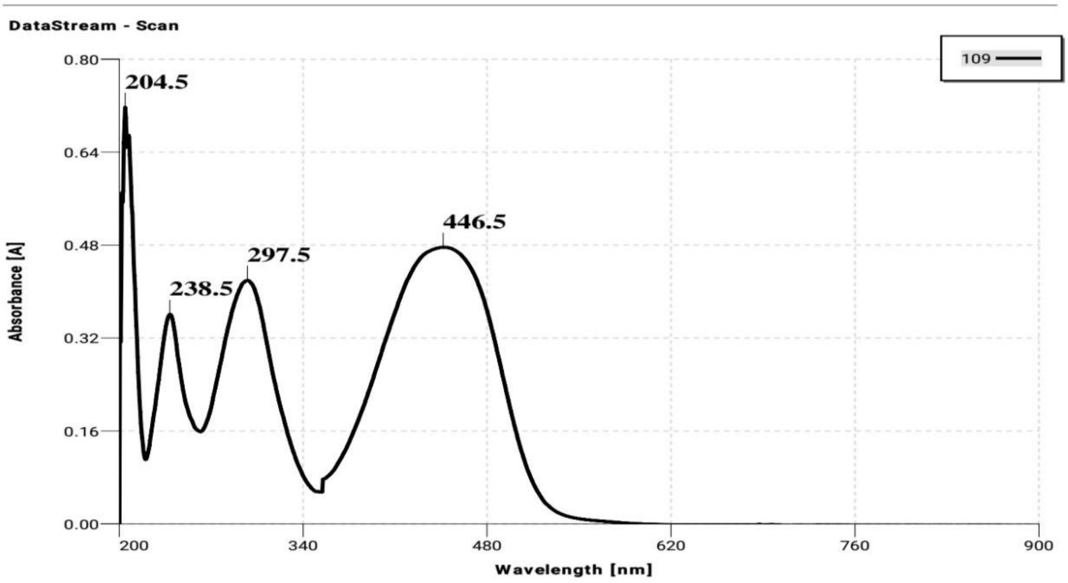
The preparation of ligand is shown in the diagram (3-2) below.



scheme (3-2) Synthesis of Ligand (BMTI).

(3-2) UV- Visible spctrum of the reagent .

Figure (3-2) shows the absorption spectrum of the reagent. It showed a two peaks in the visible region of the reagent (BMTI) at a maximum wavelength (446.5 nm) Which represents the electronic transmission (n⇾π*) these transitions return to atoms that have the ability of electronic donation, such as the bridge azo group and wavelength (297.5) Which represents the electronic transmission (π⇾π*)which return to the heterogeneous ring that is associated with the bridge azo group[142] shown in the Figure(3-2).



Figure(3-2):- UV-vis spctrum (BMTI).

(3-3) Infrared spectra of reagent.

It shows the IR spectrum of the prepared ligand that gave a beam at site 3443 cm^{-1} representing NH, a beam at site 3001 cm^{-1} representing C-H aromatic, a beam at site 2835-2931 cm^{-1} representing C-H alphatic, and a beam at site 1465 cm^{-1}, site 1610 cm^{-1}, site 1523-1506 cm^{-1}, and site 1249 cm^{-1} which represents N = N, C = N, C = C, and C-O respectively [145] shown in the Figure(3-3).

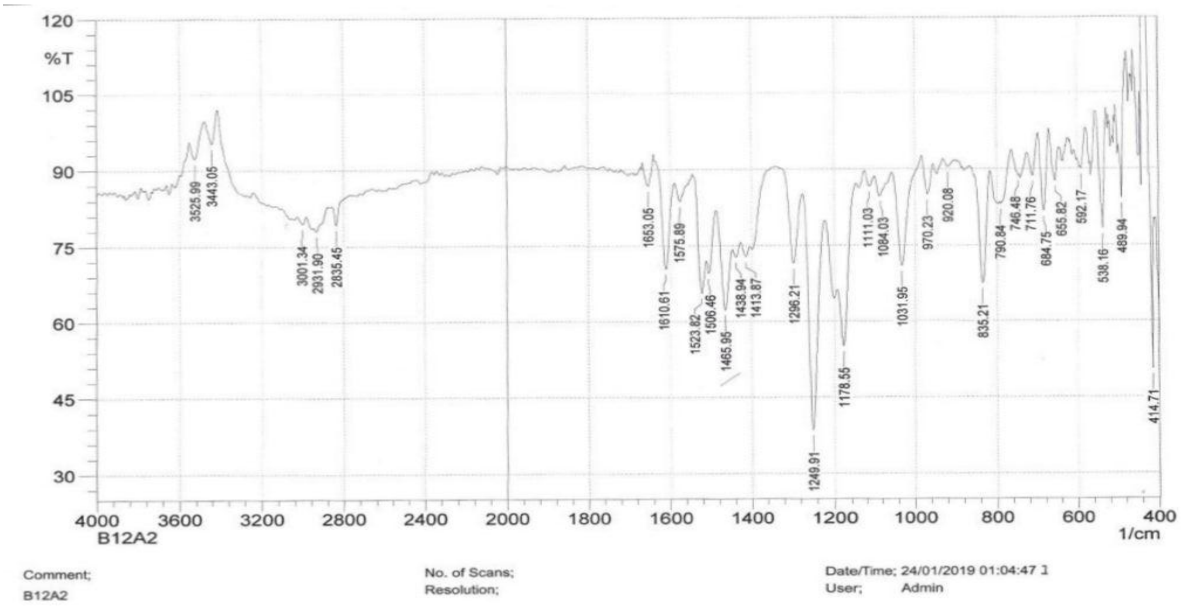
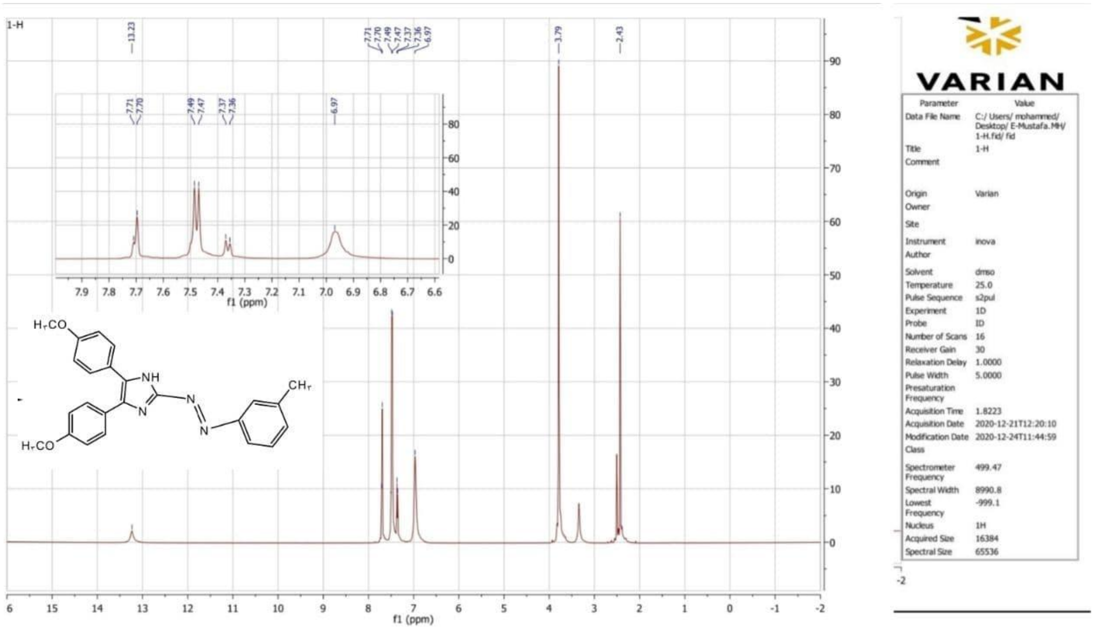


Figure (3-3). FT-IR spectrum of reagent.

(3-4) Nuclear Magnetic Resonance spectrum (NMR).

1-^{1}H.NMR.

Proton nuclear magnetic resonance spectrometry (1H-NMR) is an excellent tool to check the purity of the organic compounds, the ^{1}H NMR spectrum of the ligand (L) was diagnosed in (DMSO-d6) as a solvent and at room temperature. The azo dye ligand displayed a signal singlet at 13.23 ppm (s, 1H, Ar-NH) is due to N-H in imidazole ring, and the tow signals (doublet,doublet) due to eight aromatic protons for tow rings of imidazol due it is equivalent (m, 8H, Ar-H) have resonated in the region (7.37 , 7.49 ppm) , and the signals that are located in the region (6.97 , 7.70 , 7.71) revert to the protons of the toluene ring ,while a proton resonated at (3.79 ppm) as singlet may be assigned to methoxy group at (s,6H,2× OCH_3) Another singlet observed at (2.43 ppm) (s, 3H, CH3) , corresponds to methyl protons attached to the organic ring. Finally, the solvent signal appeared at (2.40 ppm) (DMSO). that shown in Figure (3-4).



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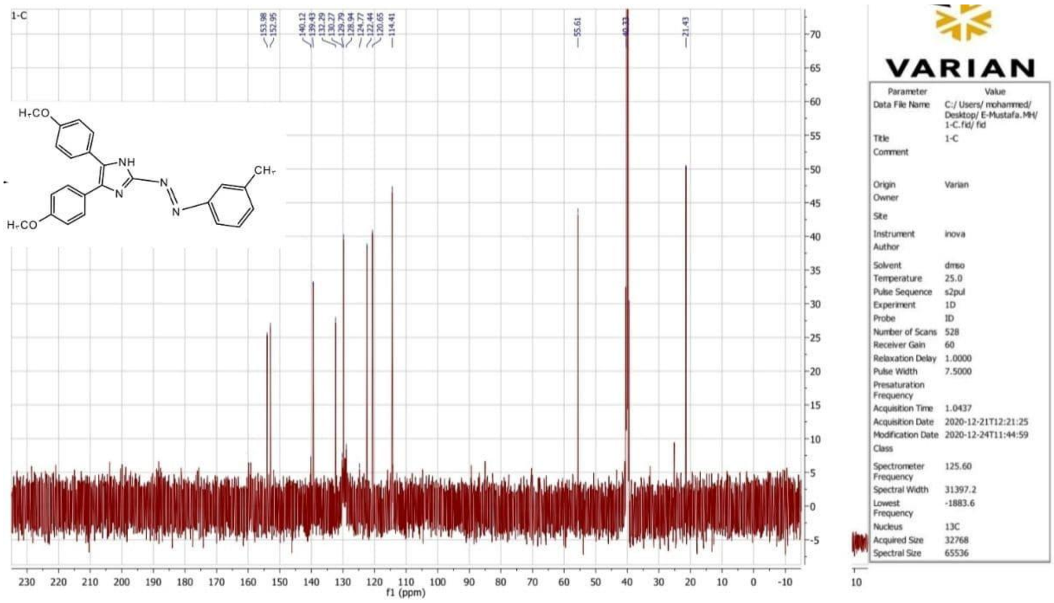
Lowest Frequency	-999.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

Figure(3-4):- ^{1}H.NMRspectrum (BMTI).

2-^{13}C.NMR.

The NMR spectrum of carbon showed one signal at 22 ppm revert to the methylene group and another signal at 55 ppm revert to the methoxy group. As for the carbon atoms in the triple ring, it showed two signals at 129 ppm, 140 ppm. The vinyl ring associated with the iso group showed six signals at 120 ppm, 122 ppm, 124 ppm, 132 ppm, 139 ppm, 152 ppm. The two phenyl groups of the amidazole derivative together with the methoxy group showed four signals at 114 ppm, 128 ppm, 130 ppm, and 153 ppm. It is noticeable that the magnetic and stereo carbon atoms gaive a single signal in the spectrum. Which shown in Figure (3-5).



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Nucleus	13C
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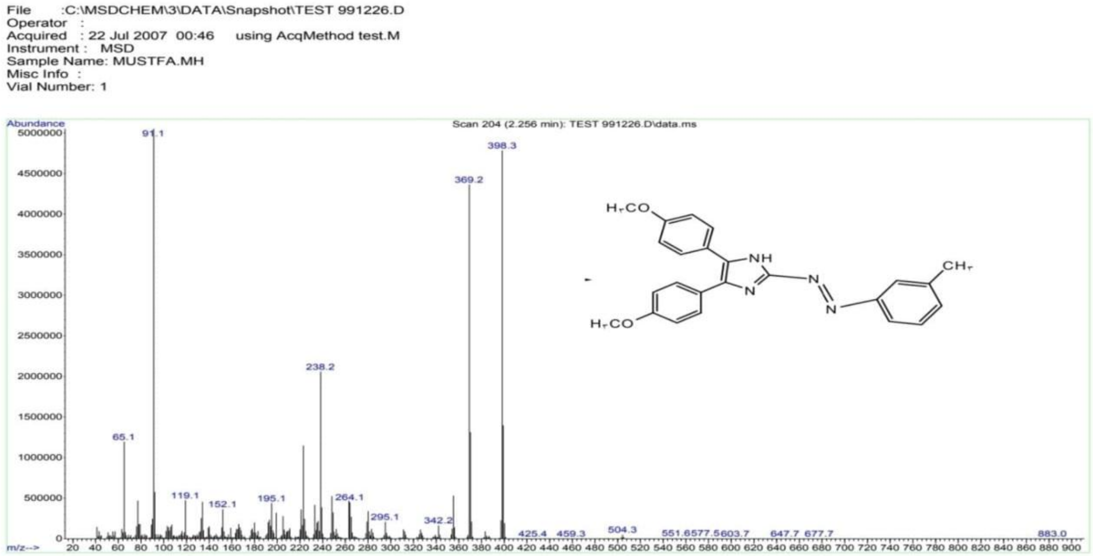
Spectral Size	65536

Figure(3-5):- ^{13}C.NMRspctrum (BMTI).

(3-5) Mass spctrum.

When fragmented, the AZO compounds take one of the following three paths: the first pathway is the loss of a nitrogen molecule from the parent molecule. The second and third pathways involve a homogeneous or heterogeneous refraction of the AZO group .The diamond spectrum of the prepared ligand shows that the base peak of the compound is at 398.3 m/z, which represents the molecular weight of the compound and the relative abundance of this fragment (100%) indicates its high stability. The fragments visible at 368 m/z, 280 m/z, 91 m/z indicate the loss of the N_2 molecule before the compound fragments were broken off to form the toluene molecule and the molecule of amidazole.



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Sample Name: MUSTFA.MH
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Vial Number: 1
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Figure(3-6):- mass spctrum (BMTI).

(3-6) Preliminary tests for the reaction of the reagent (BMTI) with some metal ions and determine the best ions to interact with the reagent.

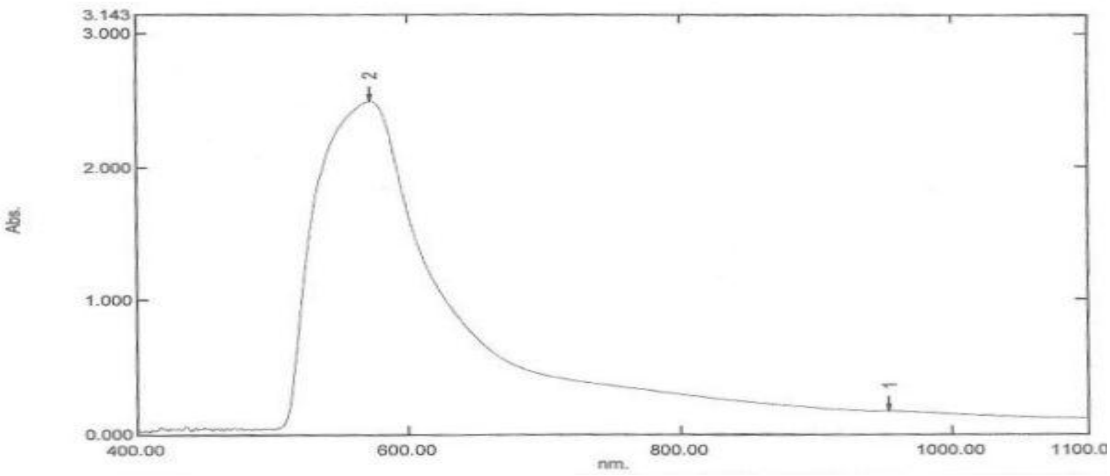
Several tests were Conducted to study the possibility of the reagent interacting with (9) metal ions, noting the color change associated with adding the reagent solution to the solutions of metal ions, and it became clear that the reagent interacts with these ions, namely (Fe^{+3}, Co^{+2}, Hg^{+2}, Ba^{+2}, Pb^{+2}, Cr^{+3}, Ni^{+2}, Cd^{+2}, Cu^{+2}) and colored solutions indicating that the reaction between the reagent and these ions occurred. Copper (II) and mercury (ll) ions were selected from among these ions for study and spectrophotometric determination , as Table (3-1) shows the results of the initial tests for the reaction reagent with Copper(II) and Mercury (ll) ions.

Table (3-1) The results of the preliminary test for the reaction of the reagent with the copper(II) and mercury(ll) ions.

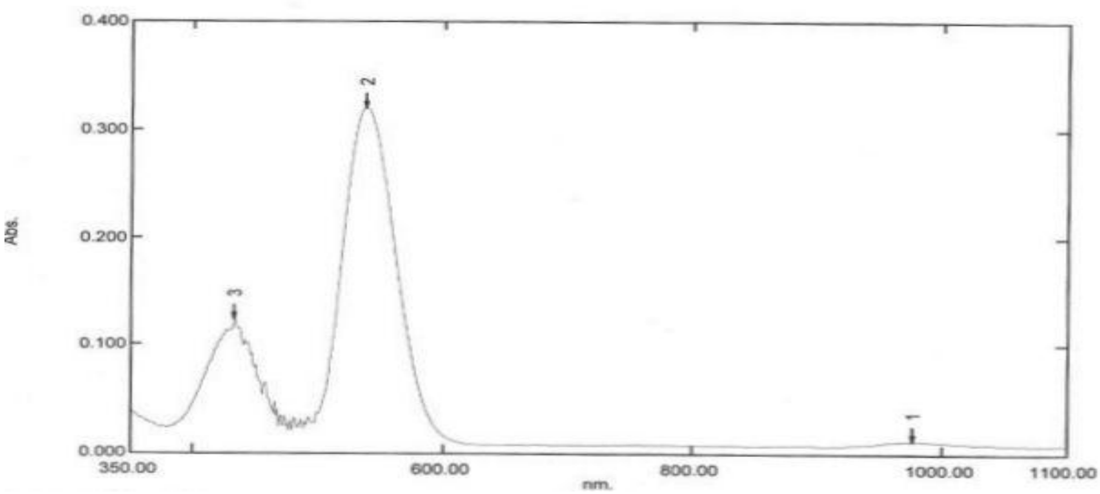
No.	Ion	Solved color	Complex color	color base medium	color acid medium
1	Cu(ll)	light green	purple	purple	yellow
2	Hg(ll)	Color less	light red	light red	Light orange

(3-7) Study of the Absorption spectra of the prepared complexes.

Figures (3-7) and (3-8) show the absorption spectra of both copper(II) and mercury(ll) complexes with the reagent respectively where the copper (II) absorption spectrum was recorded in a range of (400-1100 nm) wavelengths. The spectrum of the complex showed a red shift due to the electronic transmission ($\pi \rightarrow \pi^*$), as the complex solution showed a maximum absorption peak at the wavelength (λ_{max} = 573 nm) versus the comparative solution, and the absorption spectrum of the mercury complex (ll) in a range of wavelengths (350-1100nm), the complex spectrum showed a red shift due to the electronic transmission ($n \rightarrow \pi^*$) and ($\pi \rightarrow \pi^*$) as the complex solution showed a maximum absorption peak at the wavelength (λ_{max} = 434 nm) and (λ_{max} = 538 nm) Respectively versus the comparator solution, and when comparing the absorption spectrum of the reagent with the absorption spectrum of the two complexes, we notice a clear difference in the values of (λ_{max}) for both the reagent and the two complexes formed, and the occurrence of a red shift towards the longer wavelength is an indication of the occurrence of the coordination process between the metal ion and the reagent and the two complexes [142].



Figure(3-7) UV-visible spectrum of copper(II) complex.



Figure(3-8) UV-visible absorption spectrum of mercury (II) complex.

(3-8) FT.IR spectrum of copper(II) and mercury(II) complexes.

The study of infrared spectroscopy is an important method in diagnosing the absorption beams resulting from the active groups that are likely to be Coordination with metal ions The difference in the intensity, shape and location of absorption beams in the spectrum of complexes towards lower or higher frequencies compared to their locations in the spectrum of the reagent alone is an indication of how the link between the metal ion and the donor atoms in the reagent occurs.

The infrared spectra were recorded for copper(II) and mercury(ll) complexes in ranges ranging from (190-4000 cm^{-1}) as shown in the figures (3-9)(3-10) respectively, there is a marked change in the complexity spectra from the reagent alone spectrum in terms of the shape, intensity and location of these beams, in addition to the emergence of new beams that were not present in the reagent alone as a result of the Coordination between the reagent and the metal ions under study. The IR spectrum indicates the presence of a band at 1 (3423-3444 cm^{-1}) and this band refers to the Absorbency frequencies of the (N-H) amino group of the amidazole ring that appears in the spectra of both the reagent and its complexes. The reagent spectrum also showed a weak intensity absorption beam that is located at the frequency (3001 cm^{-1}) due to the vibration of the aromatic (C-H) band stretch and the aliphatic (C-H) absorption beam at the frequency (2931-2835 cm^{-1}) as the reagent spectrum showed a medium intensity beam at the frequency (1523-1506 cm^{-1}) It is due to the vibration of the bundle stretch υ (C = C) of the amidazole ring. As the reagent spectrum showed a medium intensity beam at the frequency (1610 cm^{-1}) It is due to the vibration of the bundle stretch υ(C = N) of the amidazole ring. The reagent spectrum also showed a beam of medium intensity at the frequency (1465 cm^{-1}) related to the frequencies of the bridging iso group υ(N = N). It was observed that this beam was suffering a shift towards a lower frequency of the two complexes formed in the mercury(ll) complex the beam appeared at the frequency (1465 cm $^{-1}$) As for the copper (II) complex, it appeared at the frequency (1462 cm^{-1}) due to its participation in the process of coordination with the metal ion and forming a υ(M-N) cluster through the free electronic duplex of one of the atoms of this group. Bands appeared in the spectra of the two complexes confined between (532 – 540 cm^{-1}) and (474 - 491 cm^{-1}), such as the elastic frequencies υ(M-N) and υ(M-O), respectively, which is the result of the formation of symmetric bonds between the donor atoms (N, O) with The central metal ion[143].

Table (3-2) Demonstrates the important beams in the infrared spectra of the complexes prepared in it is measured in units (cm^{-1}).

Compound	Cu[BMTI]	Hg[BMTI]
(N-H)	3444 w	3423w
(C-H)Ar	3003 w	3001w
(C-H)	2812w	2933-2837w
(N=N)	1462m	1465m
(C=N)	1610m	1610m
(C=C)	1519m	1518m
(C-O)	1251 s	1253 s
(M-O)	474 w	491w
(M-N)	532 w	540 w

m=medium , w= weak ,s=strong

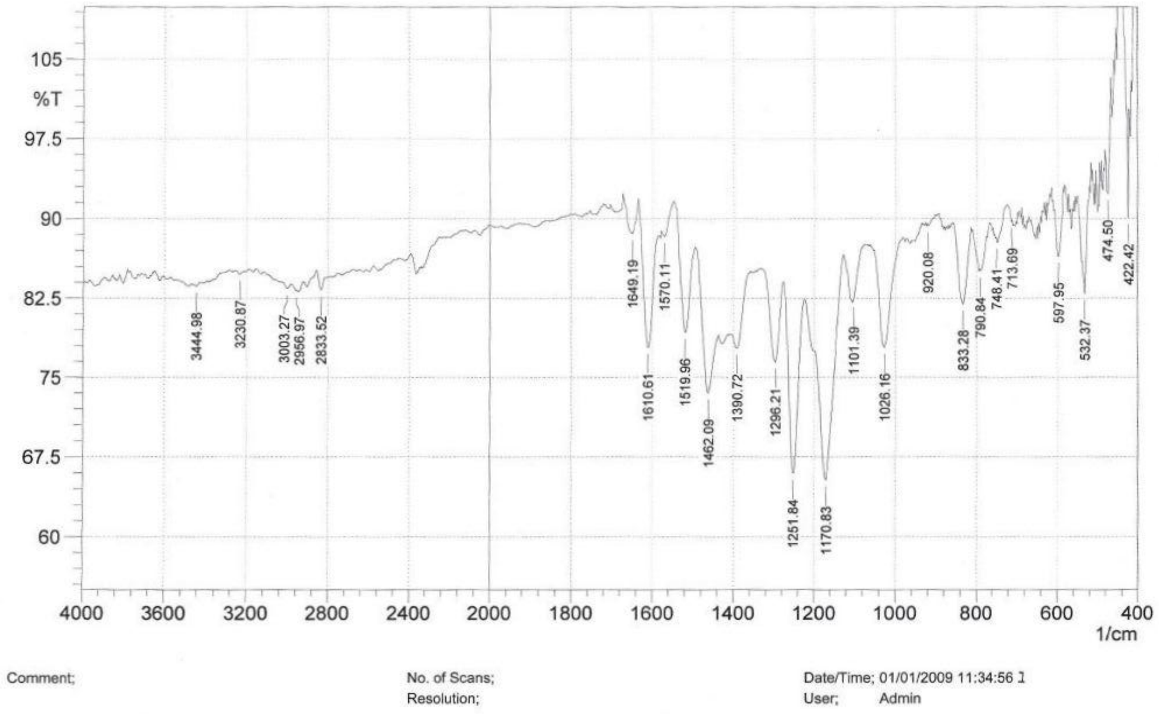


Figure (3-9). FT-IR spectrum of Cu(ll) complex.

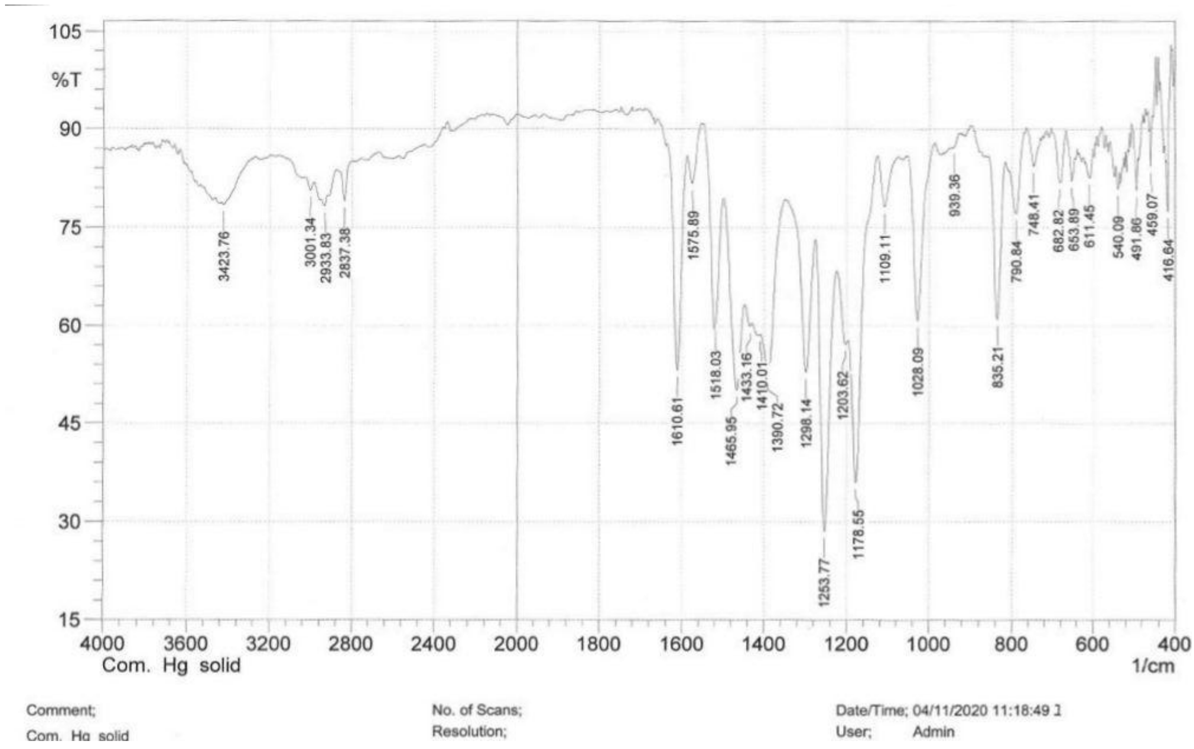
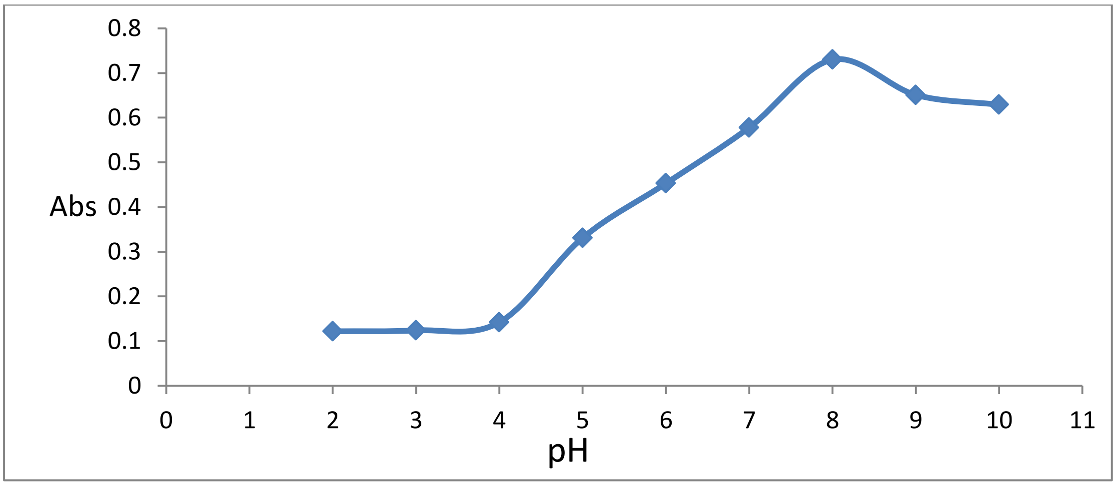


Figure (3-10). FT-IR spectrum of Hg(ll) complex

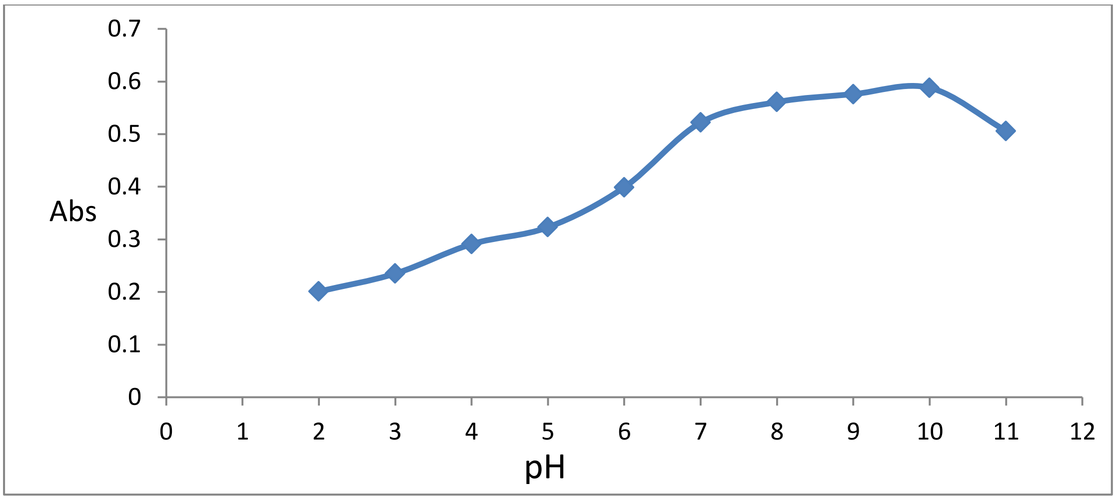
(3-9) Limitation of the optimum conditions for complexes solutions.

(3-9-1) Effect of (pH) value.

The effect of the acidic function on the absorption of solutions of copper (II) and mercury(II) complexes can be shown in Figures (3-11) and (3-12) respectively, as it was observed that the color intensity of the two complexes solutions gradually increased to reach its its max.abs at the acidic functions (8,10) respectively, then the absorbance value of the two complexes decreases when the acidic function increases more than previously mentioned, and this can be attributed to the precipitation of the two ions or to the formation of unstable complex ions [144].



Figure(3-11) Effect of pH on absorption of Cu(II) complex with reagent.



Figure(3-12) Effect of pH on absorption of Hg(II) complex with reagent.

(3-9-2) Effect of optimum value of reagent.

The effect studied volume of the reagent solution on the formation of copper(II) and mercury(II) complexes. It is evident from the results mentioned in the table (3-3)(3-4) that the absorption values of the two complexes increase to reach their peak when the reagent solution is added (0.6mL) and (0.7mL) for each of copper(II) and mercury (II), respectively. The reason is due to the interaction between the metal ion and the reagent in the direction of forming the complex and giving the best color intensity, then the absorption values begin to decrease when the size of the reagent increases, and it may be due to the fullness or sufficiency of the coordination fieled of the ion in reagent or the insolubility of the reagent with the solvent .

Table (3-3) Effect of reagent size on Cu(II)-BMTI.

Volume of reagent.	Abs.
0.2	0.451
0.3	0.491
0.4	0.554
0.5	0.649
0.6	0.711
0.7	0.670
0.8	0.666
0.9	0.656

Table (3-4) Effect of reagent size on Hg(II)-BMTI.

Volume of reagent	Abs.
0.2	0.313
0.3	0.338
0.4	0.352
0.6	0.514
0.7	0.523
0.8	0.515
1	0.482

(3-9-3) The Effect of time on stability was studies.

The effect of time on the stability of the prepared complexes was studied as an important factor in order to reach the best period of time during which the complex can maintain its stability, where the absorption values of the copper(II) and mercury(II) complexes are followed up with the reagent (BMTI) under the best conditions reached and the results shown in Tables (3-5), (3-6) . The results of this study indicate the stability of the copper (II) and mercury (ll) complex, as these complexes are very-stable (in terms of absorption values) for 48 hours from the start of formation with the copper compound and stable for 48 hours from the onset of the mercury(ll) complex formation. The results of this study enhance the ease of use of this reagent as one of the important reagents used to determine the amount of ionic copper(II) and mercury(ll) ions .

Table (3-5) Effect of time on Cu(II)-BMTI.

Time/Min.	Abs.
1	0.710
10	0.694
20	0.688
30	0.688
40	0.688
50	0.681
70	0.677
100	0.667
24h	0.633
48 h	0.631

Table (3-6) Effect of time on Hg(II)-BMTI.

Time/Min.	Abs.
1	0.522
10	0.520
20	0.515
30	0.514
40	0.511
60	0.508
70	0.502
100	0.498
24h	0.476
48h	0.472

(3-9-4) Effect of temperature .

The effect of temperature on the absorption of copper(II) and mercury (ll) complexes solutions has been studied, and the results of this study are shown in Tables (3-7), (3-8) where it is found that the absorption values of the copper(ll) complex and the mercury(ll) complex reach their peak and give the bestColor intensity at temperatures between (10-20 C^0) for copper(ll) complex and bestColor intensity at temperatures between (10-40 C^0) for mercury(ll)complex then the absorption values decrease with increasing temperature, and the reason may be due to a decrease in its stability or as a result of its dissolution at high temperatures .

Table (3-7) Effect of temperature on Cu(II)-BMTI.

Tem.C^o	Abs. Mnbb
10	0.708
15	0.712
20	0.711
30	0.615
40	0.601
50	0.574
60	0.558

Table (3-8) Effect of temperature on Hg(II)-BMTI.

Tem.C^o	Abs.
10	0.511
20	0.523
30	0.519
40	0.510
50	0.508
60	0.487

(3-9-5) Effect of sequence of addition.

The sequence of addition shown in Tables (3-9)(3-10) below showed each of the copper(ll) and mercury(ll) complexes an effect on the absorption.

Table (3-9) Effect of Sequence addition on Cu(II)-BMTI.

Sequence of number	Sequence of addition	Abs.of Cu(ll) complex
1	M+L+pH	0.711
2	L+M+pH	0.633
3	M+pH+L	0.433

Table (3-10) Effect of Sequence addition on Hg(II)-BMTI.

Sequence of number	Sequence of addition	Abs.of Hg(ll) complex
1	M+L+pH	0.523
2	L+M+pH	0.512
3	M+pH+L	0.425

M=metal
L=ligand

The results shown in the tables above showed that the best absorption occurs when adding the ion, then the reagent, and then limitation the pH, respectively.

(3-9-6) Effect of ionic strength.

This study was carried out by taking the sodium nitrate salt and the sodium sulfate salt and preparing them at different concentrations ranging between (0.0005-0.5 M) for each salt in order to demonstrate the effect of the ionic strength and its effect on the absorption of copper

(II) and mercury(ll) complexes, after adding (1mL) From solutions of these salts to complex copper (II), mercury (ll) .

Table (3-11) Effect ionic strength on Cu(II)-BMTI.

Added Salt	Conc(M).of add salt	Abs.	Added salt	Conc(M).of add Salt	Abs.
Na_2SO_4	0.5	0.933	$NaNO_3$	0.5	0.579
	0.05	0.631		0.05	0.619
	0.005	0.621		0.005	0.641
	0.0005	0.629		0.0005	0.629
Absorption before adding to the copper (II) complex 0.711					

Table (3-12) Effect ionic strength on Hg(II)-BMTI.

Added Salt	Conc(M).of add salt	Abs.	Added salt	Conc(M).of add salt	Abs.
Na_2SO_4	0.5	0.003	$NaNO_3$	0.5	0.448
	0.05	0.221		0.05	0.432
	0.005	0.262		0.005	0.413
	0.0005	0.436		0.0005	0.407
Absorption before adding to the mercury (II) complex 0.523					

The results shown in tables (3-11) and (3-12) respectively the results obtained indicate that all the concentrations mentioned in the tables do not significantly affect the absorption value, and we conclude from this that the ions do not affect the solubility, stability and sensitivity of the copper (ll)ion determination But there is an effect of sodium sulfate when concentrating 0.5M.The mercury estimation table, they give mixed results, evidence of instability of the mercury(ll) complex with added salts.

(3-9-7) Effect of the type of buffer solution.

Studied the effect of the type of buffer solution on the absorption of the copper(II) and mercury(ll) complexs, three types of buffer solutions were tested and to note the difference in the absorption values of the copper(II) and mercury(II) complexs with the reagent (BMTI) using the optimum conditions.

Table (3-13) Effect of buffer solution on Cu(II)-BMTI.

No.	Buffer Solution	Abs.
1	Ascorbic	0.350
2	Citric acid	0.192
3	Acetate	0.682
Absorption before adding to the copper (II) complex 0.711		

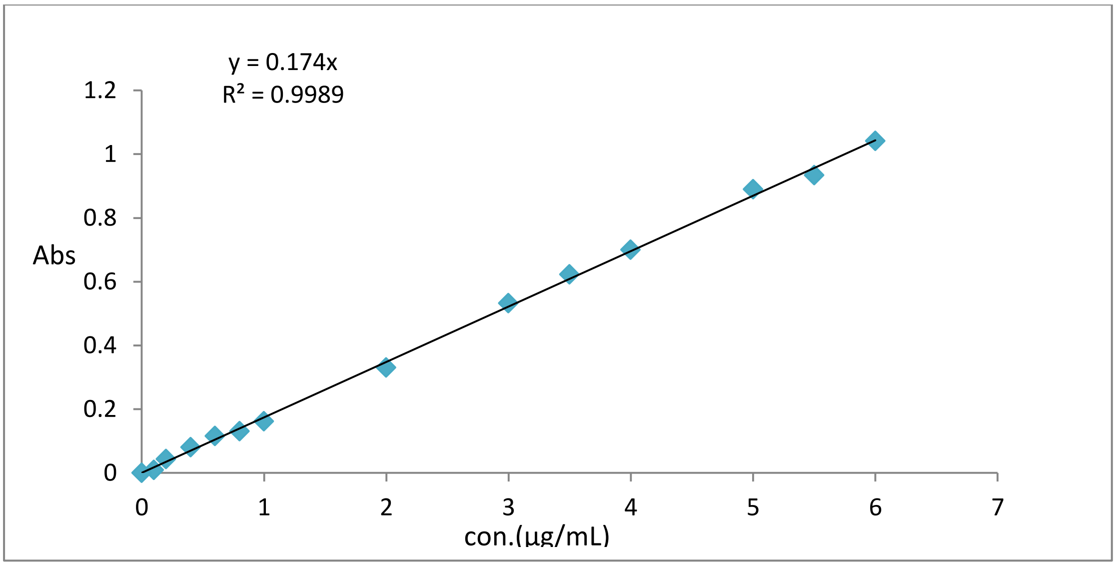
Table (3-14) Effect of buffer solution on Hg(II)-BMTI.

No.	Buffer Solution	Abs.
1	Ascorbic	0.428
2	Citric acid	0.522
3	Acetate	0.376
Absorption before adding to the mercury(II) complex 0.523		

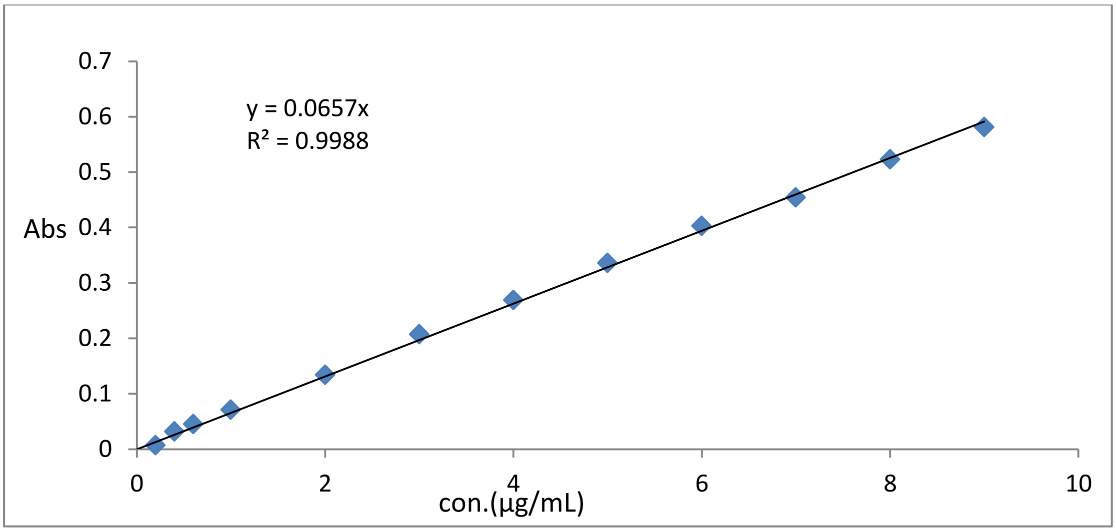
The results of using buffer solutions are shown in the tables (3-13) (3-14) which show results the buffer acetate solution in the copper(ll) complex gives a higher absorbency compared to the other buffer solutions. As for the mercury complex, the citric acid buffer solution gives the highest absorption compared to the other buffer solutions, however, the absorption of the copper(II) and mercury(II) complex in the presence of the buffer solution is lower. Than from the absorption obtained by using nitric acid and a dilute sodium hydroxide base, therefore the modification of the acidic function was limited to the use of the acid and the base only to obtain high sensitivity and accuracy for the determination of copper (II) and mercury(II) ions [133].

(3-10) Calibration curve for Cu(II) and Hg(II) complexes.

After knowing the optimum best condition an a reached, the Calibration curves for copper(II) and mercury(II) ions were prepared with the reagent (BMTI) dissolved in ethanol. The results of this study are shown in Fig. (3-13) and (3-14) for the copper(II) ionand the mercury(II) ion respectively.



Figure(3-13) Calibration curves of copper(II) complex.



Figure(3-14) Calibration curves of mercury(II) complex.

The results of Figure (3-13) show that the copper(II) ion obeys Lambert-Beer law in the range of concentrations ($3.149x10^{-7}$-$1.889x10^{-5}$ M), equivalent to (0.100 µg/mL- 6.0 µg/mL) at the wavelength for the maximum absorption (573nm), the molar absorption coefficient ($1.110x10^{4}$ $L.moL^{-1}.cm^{-1}$), the linearity coefficient (R^2= 0.9989) and the detection limit unit ($3.590x10^{-8}$ M) equivalent to (0.0114 µg/mL) and the quantitative limit ($1.184x10^{-6}$ M) equivalent to (0.0376 µg/mL).

Figure (3-14) shows that the mercury(II) ion obeys Lambert-Beer law in the range of concentrations ($1.994x10^{-7}$-$8.973x10^{-6}$ M) which is equivalent to (0.2 µg/mL- 9.0 µg/mL) at the wavelength of absorption The greatest (538 nm) is the molar absorption coefficient ($1.310x10^{4}$ $L.moL^{-1}.cm^{-1}$), linearity coefficient (R^2= 0.9988), detection limit ($1.435x10^{-7}$ M), equivalent to (0.0288 µg/mL), quantitative limit ($4.745x10^{-7}$ M, equivalent to (0.0952 µg/mL) and Sandel sensitivity was calculated from the following relationship .

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

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

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

ε = molar absorptivite
S = Sandel sensitivity
a= Specific absorption coefficient

The value of (S) for copper(II) ion is (0.00588 µg/cm^2), the value of (S) for mercury(II) ion is (0.00153 µg/cm^2), and these results indicate that the copper(II) and mercury(ll) ions particles are complex with the (BMTI) reagent It is strongly absorbed in the visual region, which enhances the possibility of estimating the low concentrations of both copper(II) and mercury(II) ions in this way. The negative deviation at high concentrations may be due to several reasons, including those related to the interference of the complex molecules with the solvent or the agglomeration of the complex molecules with Some [141]. Table (3-15) shows a summary of the results of the calibration curve.

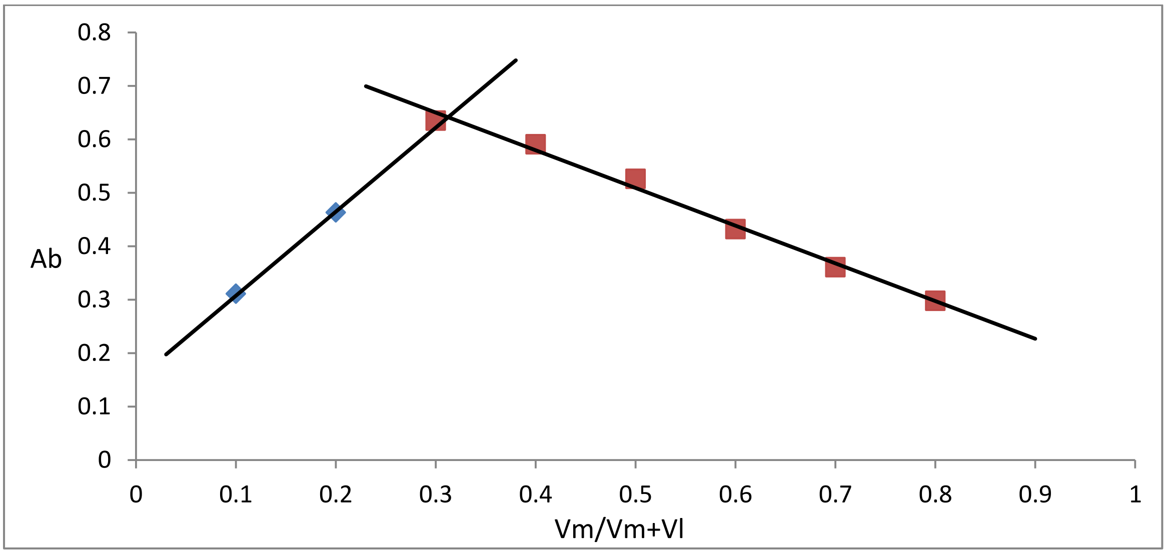
Table (3-15)Analytical data to determine copper(II) and mercury(ll) complexes.

Analytical Data	**Value of Cu(ll)**	**Value of Hg(ll)**
linear equation	Y=0.174x	Y=0.657x
Linear range [µg/mL]	0.1-6.0	0.2 -9.0
Detection limit(µg/mL)	0.0114	0.0288
Limit of quantificationb (µg/mL)	0.0376	0.0950
Molar Absorpitivity (Lmol^{-1}cm^{-1})	1.11×10^4	1.31×10^4
linearity coefficient	0.9989	0.9988
Sandel sensitivity (µg/cm^2)	0.00588	0.00153
λ_{max}	573nm	538nm
Color of product	purple	prit red

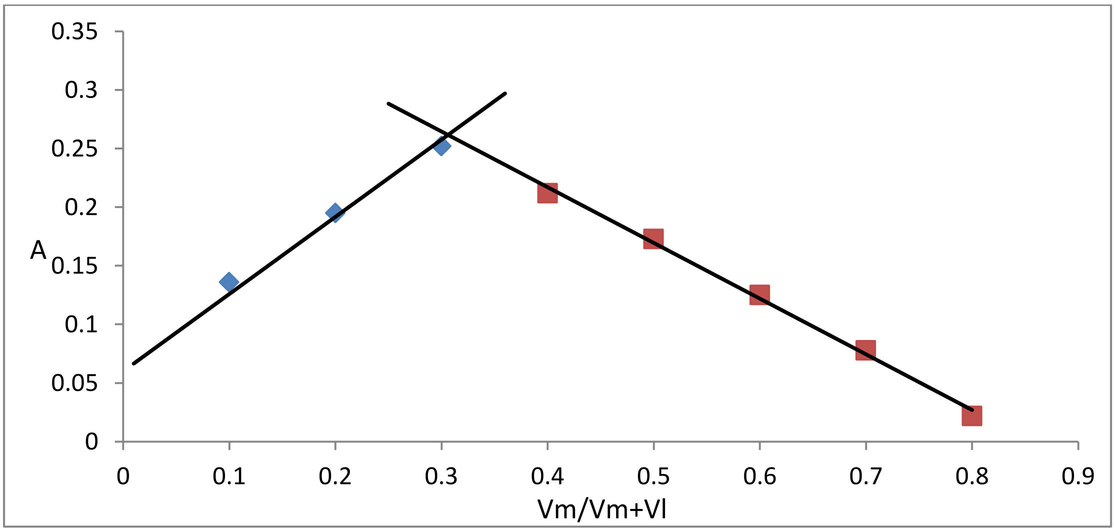
(3-11) The Stoichiometry of the complexes.

The metal to ligand ratio (M : L) is studied under optimum condition by both Mole ratio method , Job's method (continuos variations)and Mollard method.

(3-11-1) Job's Method.



Figure(3-15) Job's Method of copper(II) complex.



Figure(3-16) Job's Method of mercury(II) complex.

Figures (3-15) and (3-16) show that the bonding in the copper(II) and mercury(II) complexs is in the ratio (1 : 2) where the complex consists of two moles of the reagent to one mole of the ion.

(3-11-2) Mollard Method [136].

1-copper(II) ion complex.

$$mC_{M} + lC_{s} \rightarrow M_{M}L_{s} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3-4)$$

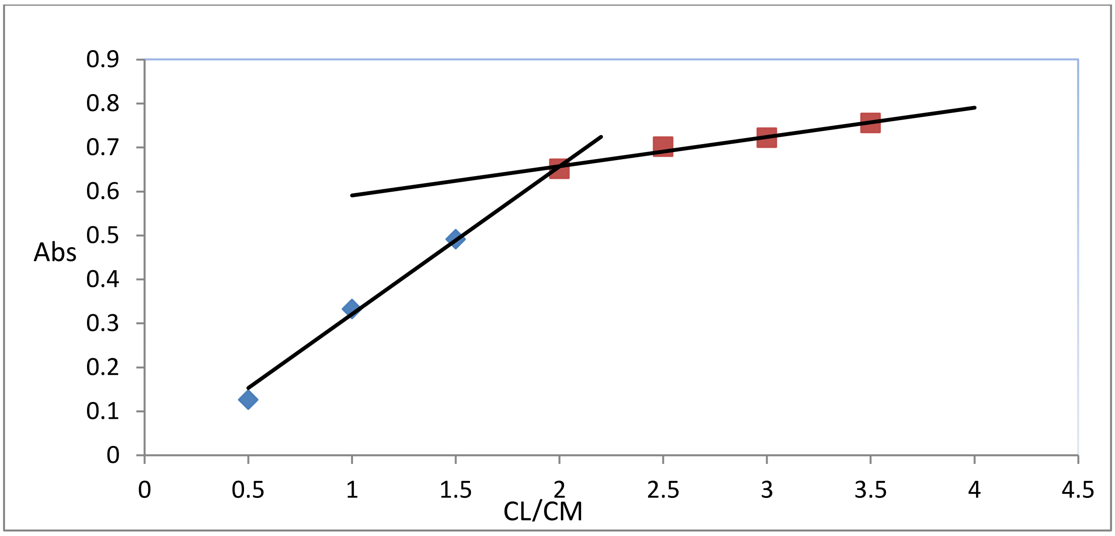
$$\frac{s}{m} = \frac{As}{Am} = \frac{0.399}{0.201} = 1.98$$

2- mercury(II) ion complex.

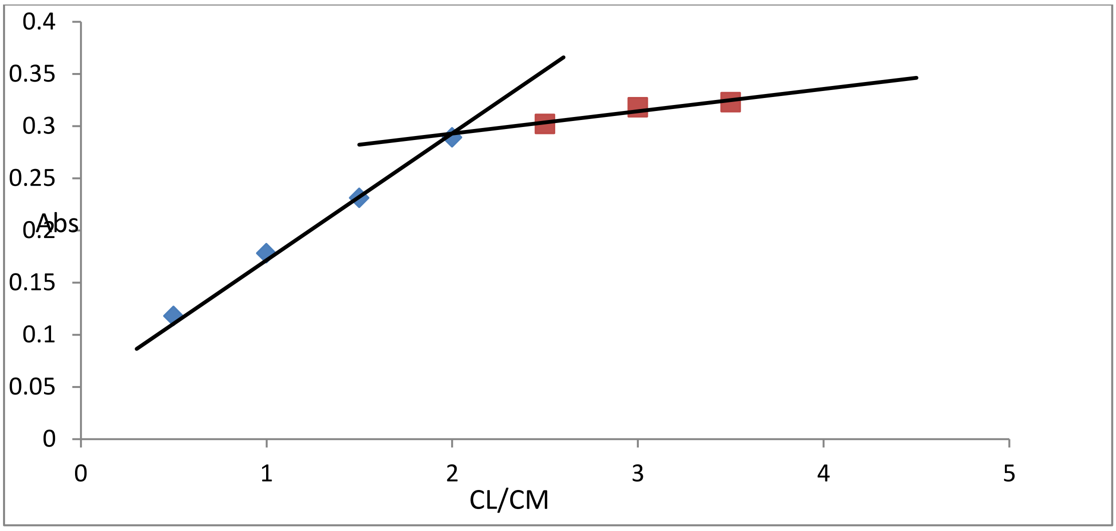
$$\frac{s}{m} = \frac{As}{Am} = \frac{0.511}{0.226} = 2.26$$

It can be seen from the previous results that the ratio of the reagent to metal (M: L) in the copper(II) and mercury(II) complexs is (1: 2), where two moles of the reagent are associated with one mole of the ions.

(3-11-3)Mole Ratio Method[135].



Figure(3-17) Mole Ratio of copper(II) complex.



Figure(3-18) Mole Ratio of mercury(II) complex.

Figures (3-17) and (3-18) show that the bonding in the copper(II) and mercury(II) complexs is in the ratio (1 : 2) where the complex consists of two moles of the reagent to one mole of the ion.

(3-12) Calculation the stability constant of complexes [142].

The stability constant of the copper(II) complex and the mercury(II) complex was calculated by adopting the absorption values obtained from the results of the molar ratios of the two complexes, which were discussed in Paragraph(3-11-2), as spectral methods can be used to calculate the stability constants of the complexes by using concentrations of copper and mercury ions in their solutions, especially if they are The complexes concerned are colored , and the aforementioned constants have been computed according to the following equations .

$$\boldsymbol{M^{+\mathrm{n}} + \mathrm{n}L \leftrightarrow MLn} \ldots\ldots\ldots\ldots\ldots\ldots (\mathbf{3-5})$$

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

$$\boldsymbol{K = \frac{[MLn]}{[M^{+n}][L]}} \ldots\ldots\ldots\ldots\ldots (\mathbf{3-6})$$

M^{+n}=ion

L = ligand

C = molar concentration

N = no.of mole

α = The degree of dissociation is calculated through the following equations

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

$$\boldsymbol{K = \frac{1\_\alpha}{n^{\text{n}}\alpha^{n+1}c^{n}}} \ldots\ldots\ldots\ldots\ldots . (\mathbf{3-8})$$

α = is calculated through the following equations.

$$\boldsymbol{\alpha = \frac{Am\_As}{Am}} \ldots\ldots\ldots\ldots\ldots (\mathbf{3-9})$$

Am = The greatest absorption with a complex.

As = The absorption of the complex at the equivalence point.

Table (3-16) Determine the stability constant of copper(II) and mercury(II) complexs.

The determination metal ion [M]	A_sValue	A_m Value	α	Stability Constant
Cu^{2+}	0.651	0.755	0.1377	$2.649x10^{10}$
Hg^{2+}	0.291	0.323	0.099	$14.60x10^{10}$

The table(3-16) shows the high stability of the formed complex, which increases the process of this complex.

(3-13) Calculation of the degree of dissociation, stability Constant , and thermodynamic functions of the two complexes [137].

1- The effect of temperature on the degree of dissociation and the stability constant for the two complexes.

The effect of temperature on the degree of dissociation and the stability constant of the copper (ll) and mercury (ll) complex is studied and the results of this study are shown in the two tables (3-17)(3-18).

Table (3-17) The effect of temperature difference on the values of the degree of stability and stability constant of the copper(ll) complex.

$T(C^0)$	T(K)	Am	As	α	$K*10^9$
10	283	0.211	0.249	0.1526	6.719
15	288	0.210	0.247	0.1495	7.127
20	293	0.203	0.238	0.1470	7.519
25	298	0.201	0.235	0.1447	7.904
30	303	0.199	0.232	0.1422	8.354
35	308	0.197	0.229	0.1397	8.835

Table (3-18) The effect of temperature difference on the values of the degree of dissociation and stability constant of the mercury(ll) complex.

$T(C^0)$	T(K)	Am	As	α	$K*10^{10}$
10	283	0.246	0.218	0.1138	9.454
15	288	0.215	0.189	0.1209	7.821
20	293	0.204	0.185	0.1274	6.635
25	298	0.186	0.161	0.1344	5.606
30	303	0.158	0.136	0.1392	5.010
35	308	0.143	0.122	0.1468	4.240

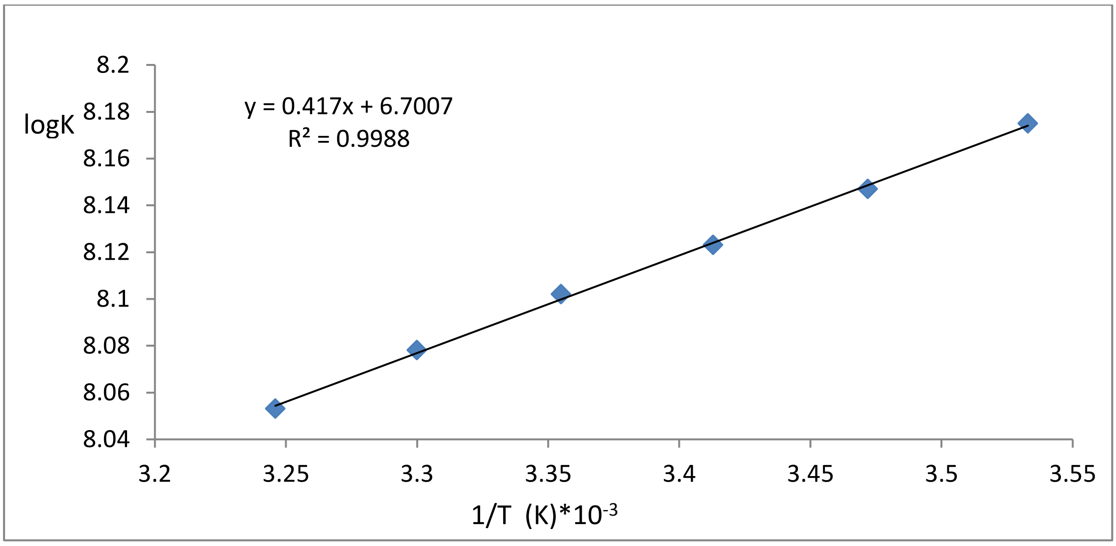
That the copper(II) mercury(ll) complexes formed has high stability, which enhances the possibility of using the reagent (BMTI) in the spectrophotometre determination.

2- Calculation of the thermodynamic functions of the two complexes.

The effect of temperature on the thermodynamic functions of copper (II) and mercury (II) complex under study was calculated through the results obtained from the previous paragraph, and through the equations mentioned in the first chapter, paragraph (1 -11), ΔH, ΔG, ΔS was calculated and the results of this study are shown in the table (3-19) with the figure (3-19) for the copper(ll) complex and in the table (3-20) with the figure (3-20) for the mercury(ll) complex.

Table (3-19) Effect of temperature difference on the thermodynamic functions values of copper(II) complex.

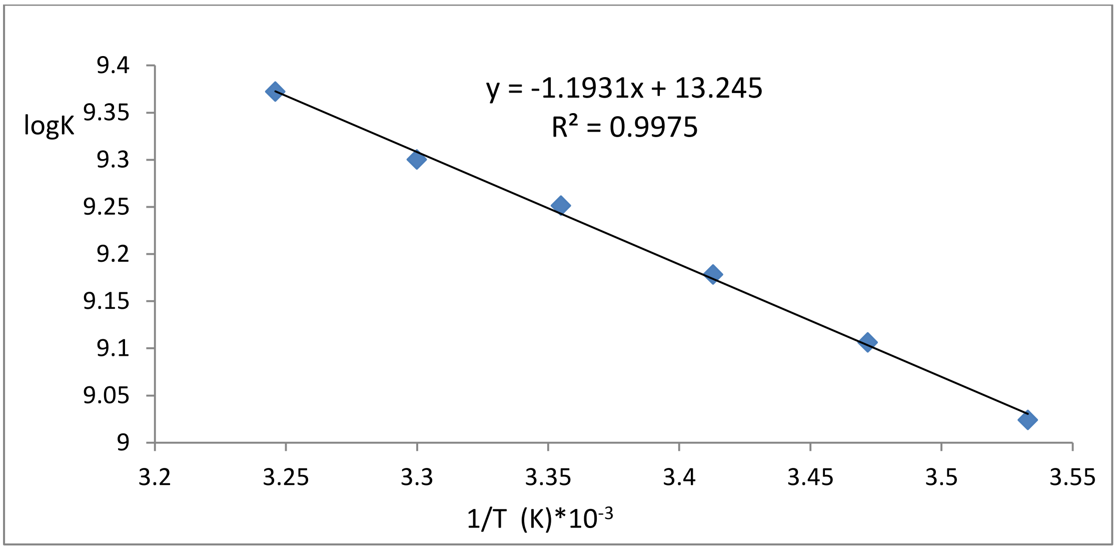
T(K)	1/T*10^{-3} (K^{-1})	log K	ΔH Kj.$mole^{-1}$	ΔG (K.J/mole)	ΔS (K.J/mole.K)
283	3.533	8.175	-7.984	-44.297	0.12831
288	3.472	8.147		-44.399	0.12644
293	3.413	8.123		-45.570	0.12827
298	3.355	8.102		-46.228	0.12833
303	3.3	8.078		-46.865	0.12832
308	3.053	8.053		-47.491	0.12826



Figure(3-19) The relationship between logK and 1/T values for copper(II) complex.

Table (3-20) Effect of temperature difference on the thermodynamic functions values of mercury(II) complex.

T(K)	$1/T*10^{-3}$ (K^{-1})	log K	ΔH Kj.$mole^{-1}$	ΔG (K.J/mole)	ΔS (K.J/mole.K)
283	3.533	9.024	22.844	-48.897	0.25350
288	3.472	9.106		-50.213	0.25367
293	3.413	9.178		-51.489	0.25369
298	3.355	9.251		-52.784	0.25378
303	3.3	9.300		-53.954	0.25345
308	3.053	9.372		-55.269	0.25361



Figure(3-20) The relationship between logK and 1/T values for mercury(II) complex.

It can be seen from Table (3-18) and Fig. (3-19) that the values of ΔH are negative for the copper(II) complex, indicating that the reaction is exothermic, and this means that the greater the interaction between the reagent with Lewis acid, the greater the amount of heat emitted from the reaction, and thus the resulting complex is more stable. As for Table (3-19) and Fig. (3-20), the values of ΔH are positive for the mercury(II) complex, indicating that the reaction is endothermic, and this arises from the positive effect of temperature through its effect on the hydrolysis shells around the mercury ion, which does not dissolve easily due to its concentration the shipment. The values of ΔG are negative, this indicates the spontaneity of the reaction for both ions, and that the more automatic reactions lose more energy, reaching more stable compounds. A slight increase in the ΔS values with increasing temperature is indicative of the positive interaction of both complexes [132].

(3-14) The effect of anions and cations ions interference on copper(II) and mercury(II) complexes.

1- Determenation copper (II) ions with some interference anions and cations ions.

The effect of the presence of interference of anions and cations ions was studied when estimating the copper(II) ion A number of ions were selected to see the effect of their interference on the absorbance of the copper(II) complex The results of this study are shown in Tables (3-21) and (3-22).

Table (3-21) Effect of cations interference with copper(II) complex.

Foreign Ions	Formula structure of ions	20µg/5mL		40µg/5mL	
		Absorption after addition of ions	Error %	Absorbance after addition of ions	Error%
	Absorbance without interferences	0.711			
Fe^{3+}	$Fe(NO_3)_3.9H_2O$	0.527	-25.88	1.322	85.93
Cr^{3+}	$Cr(NO_3)_3.9H_2O$	0.545	-23.34	0.939	32.06
Co^{2+}	$Co(NO_3)_2.6H_2O$	1.466	106.1	1.503	111.3
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	0.758	6.610	0.854	20.11
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	1.086	52.74	1.379	93.95
Ba^{2+}	$Ba(NO_3)_2$	0.611	-14.06	1.242	74.68
Pb^{2+}	$Pb(NO_3)_2$	0.599	-15.75	1.413	98.73

Table (3-22) Effect of anions interference with copper(ll) complex.

Foreign Ions	Formula structure of ions	30µg/mL Absorption after addition of ions	Error%	60µg/mL Absorption after addition of ions	Error %
	Absorbance without interferences	0.711			
$Cr_2O_7^{2-}$	$K_2Cr_2O_7$	0.638	-10.26	0.864	21.51
SO_4^{2-}	K_2SO_4	0.629	-11.53	0.930	30.80
CO_3^{2-}	K_2CO_3	0.691	-2.812	0.906	27.42
SCN^{1-}	KSCN	0.771	8.438	0.853	19.97
CN^{1-}	KCN	0.272	-61.74	0.173	-75.66
Br^{1-}	KBr	0.642	-9.704	0.833	17.15
Cl^{1-}	KCl	0.779	9.563	1.005	41.35
F^{1-}	KF	0.672	5.485	0.836	17.58

The results obtained in the above tables that most of the ions have an effect on the absorption values of the copper(ll) ion complex with the reagent, and this depends on the nature of the added ions and their concentration, and in general it can be seen that the cations ions decrease or increase the absorption and this is due the interference. The combination of these ions creates a complex with the reagent that reduces competition and increases the sensitivity of the method towards the copper(ll) ion. As for the decrease in the absorption that occurs in the presence of anions ions, it is attributed to their behavior as masking agents[133].

2- Determenation mercury(II) ions with some interference anions and cations ions.

The effect of the presence of interactions of anions and cations ions was studied when estimating the mercury(ll) ion A number of ions were selected to see the effect of their interference on the absorbance of the mercury(ll) complex The results of this study are shown in Tables (3-23) and (3-24).

Table (3-23) Effect of cations ions interference with mercury(ll) complex.

Foreign Ions	Formula structure of ions	40µg/5mL Absorption after addition of ions	Error %	80µg/5mL Absorbance after addition of ions	Error%
	Absorbance without interferences	0.523			
Fe^{3+}	$Fe(NO_3)_3.9H_2O$	0.398	23.90	0.351	32.88
Cr^{3+}	$Cr(NO_3)_3.9H_2O$	0.383	26.76	0.461	11.85
Co^{2+}	$Co(NO_3)_2.6H_2O$	0.054	89.67	0.028	94.64
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	0.015	97.13	-0.009	101.7
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	0.162	69.02	0.026	95.02
Ba^{2+}	$Ba(NO_3)_2$	0.409	21.79	0.476	8.986
Pb^{2+}	$Pb(NO_3)_2$	0.453	13.38	0.467	10.70

Table (3-24) Effect of anions ions interference with mercury(ll) complex.

Foreign Ions	Formula structure of ions	30µg/mL Absorption after addition of ions	Error%	60µg/mL Absorption after addition of ions	Error %
	Absorbance without interferences	0.523			
$Cr_2O_7^{2-}$	$K_2Cr_2O_7$	0.453	13.38	0.315	39.77
SO_4^{2-}	K_2SO_4	0.439	16.06	0.513	1.912
CO_3^{2-}	K_2CO_3	0.523	0.000	0.423	19.12
SCN^{1-}	KSCN	0.439	16.06	0.531	-1.529
CN^{1-}	KCN	0.167	68.06	0.105	79.92
Br^{1-}	KBr	0.161	69.21	0.614	-17.39
Cl^{1-}	KCl	0.511	2.294	0.494	5.544
F^{1-}	KF	0.469	10.32	0.333	36.32

The results obtained in the above tables that most of the ions have an effect on the absorption values of the mercury(ll) ion complex with the reagent, and this depends on the nature of the added ions and their concentration, and in general it can be seen that the cations ions decrease or increase the absorption and this is due to the interferance. The combination of these ions creates a complex with the reagent that reduces competition and increases the sensitivity of the method towards the mercury(ll) ion. As for the decrease in the absorption that occurs in the presence of anions ions, it is attributed to their behavior as masking agents [133].

(3-15) Effect masking agents [137].

(3-15-1) Limitation the best masking agent for the determination of the copper(II) and mercury(II) complexs.

Most of the cations overlap with the copper (II) and mercury (II)complexes formed, so a method must be proposed to remove this effect, and according to this, masking agent were chosen(6) to see the effect of the competition process between them and the reagent in interaction with the interfering ions And withholding them as this study was done by adding (1mL) from each masking agent, as shown in Tables (3-25) (3-26).

Table (3-25) The effect of masking agent on copper(II) ion absorption.

Seq	MasKing agent(0.1M)	Abs of Cu^{2+}
1	Without MasKing agent	0.711
2	Tartaric acid	0.255
3	Citric acid	0.088
4	Thiourea	0.766
5	KCl	0.598
6	Ascorbic acid	0.458
7	Formaldehyde	0.565

The results in Table (3-25) show that (Thiourea) has little effect on the absorption of the formed complex, so it can be used as a masking agent. The rest cannot be used as masking agents due to its dissociation with copper(II) ion.

Table (3-25)the effect of masking agent on mercury(II) ion absorption.

Seq	MasKing agent(0.1M)	Abs of Hg^{2+}
1	Without MasKing agent	0.523
2	Formaldehyde	0.518
3	Tartaric acid	0.424
4	Citric acid	0.412
5	Thiourea	0.195
6	KCl	0.437
7	Ascorbic acid	0.469

The results in Table (3-26) show that (Formaldehyde) has little effect on the absorption of the formed complex, so it can be used as a masking agent. The rest cannot be used as masking agents due to its dissociation with mercury (ll) ion .

(3-15-2) Use of a bast masking agent to determine the copper(ll)ion and mercury(ll) ion in the presence of cations interferers.

1- copper(ll) ion complexs.

To obtain the best estimate of the copper(ll) ion complex in the presence of interfering cationic ions, the best masking agent (Thiourea) described in the Paragrafe (3-15-1) was used.

Table (3-27)The effect of masking agent in the presence of cations on copper(II)ion absorption.

Foreign ions	Relative error E% after addition of cation (20µg) and addition masking agent (0.1M)
Absorbance without interferences	0.711
Fe^{+3}	0.094
Cr^{+3}	-0.292
Co^{+2}	-0.154
Ni^{+2}	0.097
Cd^{+2}	-0.122
Ba^{+2}	0.012
Pb^{+2}	-0.029

It is noticed from the tables (3-27) that the absorption values of the copper (ll) ion complex in the presence of interfering cations ions When adding a better masking agent, absorbance values close to the absorbance values are given before adding the interferers.

2- mercury(ll) ion complexs.

To obtain the best estimate of the mercury (ll) ion complex in the presence of interfering cationic ions, the best masking agent is (Formaldehyde).

Table (3-28)the effect of masking agent in the presence of cations on mercury(II)ion absorption.

Foreign ions	Relative error E% after addition of ions (40µg) and addition masking agent (0.1M)
Absorbance without interferences	0.523
Fe^{+3}	-0.051
Cr^{+3}	0.078
Co^{+2}	0.982
Ni^{+2}	0.889
Cd^{+2}	0.902
Ba^{+2}	0.212
Pb^{+2}	0.108

It is noticed from the tables (3-28) that the absorption values of the mercury(II) ion complex in the presence of interfering cations ions When adding a better masking agent, absorbance values close to the absorbance values are given before adding the interferers.

(3-16) Precision and accuracy of the proposed method.

The precision of the method represented by the relative standard deviation (RSD%) and the accuracy of the method represented by the relative recovery of the copper(II) ion and mercury(II) ion complexes with the reagent (BMTI) under study were studied, by studying the absorption of three different concentrations at a rate of four readings for each concentration . The results are summarized in the table (3-29) for the copper(ll) ion, and Table (3-30) for the mercury(ll) ion.

Table (3-29)The Precision and accuracy of the copper(II)ion complex.

Conc.of Cu^{+2} present[M]	Conc.of Cu^{+2} found[M]	RSD%	Recovery%	Error%
1.574×10^{-5}	1.635×10^{-5}	1.827	103.930	-3.875
4.724×10^{-5}	4.527×10^{-5}	0.720	95.829	4.170
9.440×10^{-5}	9.188×10^{-5}	2.110	97.330	2.669

Table (3-30)The Precision and accuracy of the mercury(II)ion complex.

Conc.of Hg^{+2} present[M]	Conc.of Hg^{+2} found[M]	RSD%	Recovery%	Error%
9.970×10^{-6}	9.741×10^{-6}	1.420	97.703	2.297
1.994×10^{-5}	1.978×10^{-5}	1.010	99.197	0.803
3.988×10^{-5}	3.918×10^{-5}	0.710	98.244	1.755

Where it was found from the results obtained, it can be inferred that the analytical method used for measuring using the reagent (BMTI) has high accuracy and precision [140].

(3-17) Calculation of sensitivity of the spectral method for estimating ionic copper(II) and mercury(ll) ions.

The term "Detection Limit" is used to denote the sensitivity of the spectral method used to estimate the copper(II) and mercury(ll) ions, where the detection limit crosses the determination of the lowest concentration that can be determined in this spectral method, where the minimum concentration of the copper(II) ion is (1.795x10^{-7} M) equivalent to (0.0114 µg/mL) while the lowest concentration of mercury ion (I) is (1.435x10^{-7} M) equivalent to (0.0288µg/mL), and this indicates that the method used has high sensitivity and is successful in Determination of the ionic copper (II) and mercury (ll), as shown in the following relationship for the calculation of (D.L).

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

SD = standard deviation

$\bar{x}$ = Average

(3-18) Preparation of solid complexes.

The best conditions that were reached in this study of acidity function, reagent size, temperature, molar ratios ..... etc. were used in preparing the two ion complexes under study with the reagent (BMTI) This was done by mixing the aqueous solution of the metal ionic (Cu^{+2} , Hg^{+2}) separately with the reagent (BMTI) dissolved in ethanol, where it was observed that a precipitate appeared during mixing the solutions and after cooling them The solutions were left to complete precipitation, were filtered and re-crystallized, and a number of physical properties of the two solid complexes were studied.

(3-19) Solubility reagent and the solid complexes.

The solubility of the reagent and the two solid complexes was tested in a number of polar and non-polar solvents in addition to water. The results of this study are shown in Table (3-31).

Table (3-30) Solubility reagent and the solid complexes.

Solvant	Reagent (MPAI)	Complex of Cu^{2+}	Complex of Hg^{+2}
Chloroform	+	+	+
Ether	÷	÷	-
Hexane	-	-	-
CH_3OH	+	+	+
C_2H_5OH	+	+	+
H_2O	-	-	-
DMSO	+	+	+
DMF	+	+	+

Soluble (+), insoluble (-), poorly soluble(÷)

(3-20) Measurement of the melting point of the complexes and the reagent.

When determining the melting point of the copper(II) and mercury(II) ions complexes with the reagent under study, it was found that the copper(II) complex melts at a temperature between (145-148 ^{o}C), while the mercury(II) complex melts at a temperature between (150-152 ^{o}C), while the values of the reagents melting point range between

(174-178 °C) that the difference in the values of the degree of melting point between the reagent and two complexs Evidence of new complex formation .

(3-21) Measurements of molar conductivity of copper(ll) and mercury(ll) complexes.

The degree of electrical conductivity is directly proportional to the number of charged ions in the solution that have the ability to carry electric current, and sometimes it takes low values that may approach zero when the complex does not have any ionic characteristic in its solution[145]. Therefore, the molar conductivity of the metal ion complexes under study with the reagent (BMTI) was measured at a concentration of ($1x10^{-3}$M) at room temperature using ethanol, and the table (3-32) indicates the molar conductivity values of the two copper(II) and mercury(Il) complexes with the reagent. Under study, and from the obtained results, it is clear that the copper(II) and mercury(Il) complexes with the reagent do not have ionic character .

Table (3-32) The molar conductivity values of the two solutions of copper(ll) and mercury(ll) complexs, prepared with a concentration of ($1x10^{-3}$M) in ethanol at laboratory temperature.

No	Complex	Λ_m(µs/cm)
		In Ethanol
1	$[Cu(BMTI)_2(NO_3)_2]$	7.92
2	$[Hg(BMTI)_2 (NO_3)^2]$	9.69

(3-22) Applications.

The analytical method used in the research was applied to estimate copper(II) ions in samples from tea leaves, from tooth filling and tap water, and to estimate mercury(ll) ion in samples from well and tap water to know the concentration of ions in these models. The results were obtained and compared with the results calculated by the Flame atomic absorption .

(3-22-1) Determination of copper(ll) ion in samples.

1- Determination of copper(ll) ion in sample from tea leaves and tap water.

The copper(II) ion was estimated in a sample from tea leaves, after applying the method of work in paragraph (2-19 -2), and Table (3-33) that shows the results obtained for the mentioned ion estimated at μg/mL. The ion in the same sample using the method under study using the reagent (BMTI), and the results mentioned in the table were obtained by comparing the values obtained by the Flame atomic absorption, as it was found that this method using a reagent (BMTI) has high sensitivity and can be used in Estimation of the copper(ll) ion in different forms, for ease of implementation and speed, as well as accuracy. Copper(ll) ion was estimated in a sample of tap water by the spectrophotometer method under study.

Table (3-33) Determination of the copper(II)ion in samples.

Sample	**Spectrophotometric method mol / L**	**Flam atomic absorption mol / L**
Tap water	**3.965×10^{-6}**	**4.021×10^{-6}**
Tea leaves **(type Apple tea)**	**6.867×10^{-6}**	**7.222×10^{-6}**

The results shown in the above table confirm the success of the proposed spectral method in estimating copper (II), where the result of the analytical spectral method is close to the result obtained using the flame atomic absorption technique, which indicates the possibility of using this method in spectral estimation in models from Tea leaves and Tap water.

2- Determination of copper(II) ion in dental filling.

The method was applied to a model of dental filling, to estimate the ratio of copper(II) ion in this model, and after applying the method of work in paragraph (2-19-3) to prepare the model for the purpose of analysis, where the copper(II) ion in the aforementioned model was estimated by the spectral method under Study Table (3-34) shows the results obtained in unit (µg/mL). By using the reagent (BMTI), and when comparing this method with the spectrophtometer method used to estimate the copper(II) ion, it was found that it has good sensitivity and can be used in estimating the mentioned ion for ease and speed of implementation in addition to that accuracy.

Table (3-34) Determination of the copper(II)ion in dental filling.

Sample	Relative% Cu^{+2}
dental filling	**30.03%**

The filling is supplied by (Australia by SDI limited), and the proportions of ingredients are (Ag = 41.0%, Cu = 28.7%, Sn = 30.3%).

(3-22-2) Determination of mercury(II) ion in Wells Water.

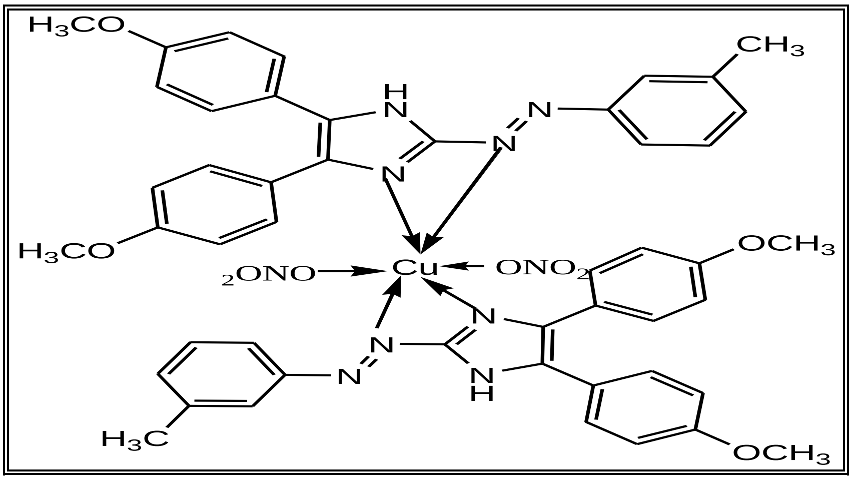
A number of well water samples were collected from different regions and a sample of tap water, and the results of mercury concentration in these samples are shown in the following table.

Table (3-35) Determination of the mercury(II) ion in samples.

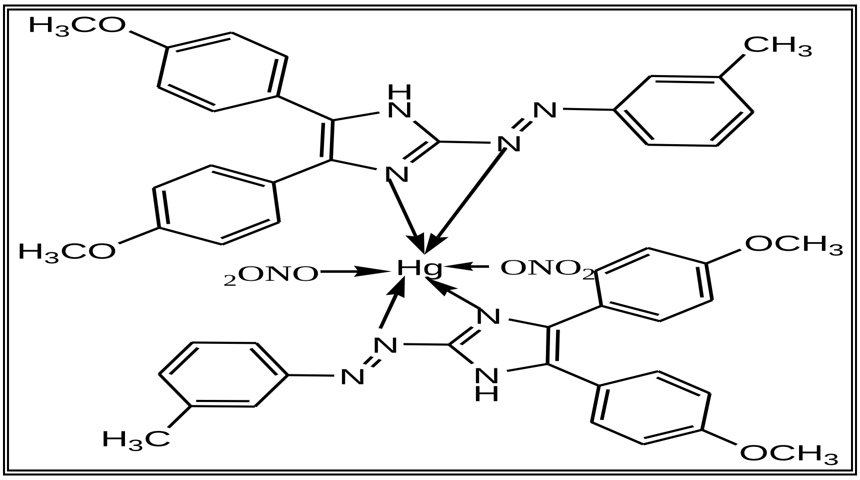
Sample	Spectrophotometric method Hg^{+2} mol / L	Cold atomic absorption Hg^{+2} mol / L
Tap water	2.891×10^{-6}	1.330×10^{-6}
Ain al tamer	10.80×10^{-6}	6.281×10^{-6}
Al-gadwal gharbi	24.27×10^{-6}	18.899×10^{-6}

(3-23) The suggested structuer of the complexes.

Through the study of paragraph (3-21), it was found that the copper(II) and mercury(II) complexs is not charged, where the steric structure of the copper(II) and mercury(II) complexs has an octahedral shape and sp^3d^2 hybridization, because the copper(II) and mercury(II) ions tend to form hexagonal complexes more than their tendency to form four-coordinated complexes.



Figure(3-21). The suggested structure for the Copper(ll)complex.



Figure(3-22). The suggested structure for the Mercury(ll)complex.

(3-24) Conclusions.

1- The possibility of preparing the new reagent (BMTI) through conventional nitrogenation of the compound diazonium salt (m-toluidine).

2-The possibility using the (BMTI) spectrophotomitric in estimating micro amounts of Cu(ll) and Hg(ll) ions as it has colored complexes. These complexes have maximum absorption peaks. .

3- The method for determining copper(II) and mercury(ll) ions with the prepared reagent is a quick and simple method after fixing the optimum conditions of the acidic function, the volume of the reagent, the sequence of addition and the temperature, as compliance with the Lambert-Beer law gives a wide range of concentrations.

4- The results of the determination of the equivalence of the two complexes by the method of molar ratios, the job's method and the Mollard method show that the ratio of the reagent to the ion are (1: 2) for each of the copper(II) and mercury(ll) complexs.

5- The reagent behaves Bidentate in a Coordination process with the copper ion and mercury(ll) complexs.

6- The results of the effect of masking agent indicate that (Thiourea) does not affect the process of estimating copper (II), so it can be used as a masking agent. As for the mercury(ll) complex , the results indicated that (Formaldehyde) does not affect the process of estimating the mercury(ll) ion and it can be used as a masking agent for mercury(ll) ion.

7- The results of the thermodynamic functions show that the negative values of (ΔH, ΔG) and values ΔS for the copper(II) complex with the reagent are evidence of the spontaneity of the reaction at low temperature, and that this reaction is an exothermic reaction, either the negative value of (ΔG) and the positive value of (ΔS , ΔH) for the mercury (ll) complex with the reagent is evidence of the spontaneous reaction at high temperature and that these reactions are endothermic.

8- Through the results of the stability constant values of the copper(II) and mercury(ll) complexes, the mercury(ll) complex with the reagent (BMTI) is more stable than the copper(ll) complex with the reagent.

9- By studying the effect of the Interference cations and anions ions on the spectroscopic estimation process for copper(II) and mercury(ll) ions under study, it was found that there is a differential effect of these cations and anions ions on the estimation process.

10- The study of determining the charge of the copper(II) and mercury(ll) complexes, as the study of the molar conductivity of the two complexes, showed that the two complexes are not charged.

11- The results of the calculation of the values of the relative standard deviation and the relative error of percent showed that the spectral method under study is of high sensitivity, easy, fast, and with high accuracy and precision as well as that it does not need any complications or prior preparations such as separation, ion exchange ... etc.

12- The possibility of using the prepared reagent (BMTI) in estimating the trace quantities of copper and mercury present in samples of water, tea leaves model and a sample of dental filling.

(3-25) Recommendations.

1- Study the possibility of using the reagent (BMTI) to estimats of other ions in different media.

2- Preparing new derivatives of the reagent itself for the purpose of improving the selectivity and characteristics as well as the possibility of using it in the estimation of other elements.

3- The possibility of using the prepared reagent in the study of extracting some elements of the transition due to its ability to be consistent with many of these ions.

4-Study the effect of the perpared reagent (ll) on biological activity due to the great importance of azo compound in inhibiting biological activity.

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Appendlx.

1- Statistical treatment.

-Calculation of the Relative standard deviation.

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

Table (1) Calculation of the %RSD of the copper(ll) ion at concentration 1.635x10^{-5}M.

N0	Abs (Xi)	Mean (x')	(xi-x')	Σ(xi-x')^2	$S.D=\sqrt{\frac{\Sigma(xi-x')^2}{N-1}}$	$\%RSD=\frac{SD}{X'}X100$
1	0.179	0.18075	-0.00175	3.275x10^{-5}	0.003304	1.827%
2	0.177		-0.00375			
3	0.183		0.00225			
4	0.184		0.00325			

Table (2) Calculation of the %RSD of the copper(ll) ion at concentration 4.540x10^{-5}M.

N0	Abs (Xi)	Mean (x')	(xi-x')	Σ(xi-x')^2	$S.D=\sqrt{\frac{\Sigma(xi-x')^2}{N-1}}$	$\%RSD=\frac{SD}{X'}X100$
1	0.501	0.50025	0.00075	3.875x10^{-5}	0.003594	0.72%
2	0.498		0.00475			
3	0.497		-0.00325			
4	0.505		-0.00225			

Table (3) Calculation of the %RSD of the copper(ll) ion at concentration 9.188x10^{-5}M.

N0	Abs (Xi)	Mean (x')	(xi-x')	Σ(xi-x')^2	$S.D=\sqrt{\frac{\Sigma(xi-x')^2}{N-1}}$	$\%RSD=\frac{SD}{X'}X100$
1	1.001	1.01525	-0.01425	1.328x10^{-3}	0.02146	2.11%
2	1.043		0.02775			
3	1.020		0.00475			
4	0.997		-0.01825			

2- Statistical treatment and calculation of %RSD values for mercury(II) ion.

Table (4) Calculation of the %RSD of the mercury(ll) ion at concentration 9.465x10^{-6}M.

N0	Abs (Xi)	Mean (x')	(xi-x')	Σ(xi-x')^2	$S.D=\sqrt{\frac{\Sigma(xi-x')^2}{N-1}}$	$\%RSD = \frac{SD}{X'}X100$
1	0.122	0.12475	-0.00275	6.031x10^{-5}	0.002217	1.77%
2	0.126		0.00125			
3	0.127		0.00225			
4	0.124		-0.00075			

Table (5) Calculation of the %RSD of the mercury(ll) ion at concentration 1.915x10^{-5}M.

N0	Abs (Xi)	Mean (x')	(xi-x')	Σ(xi-x')^2	$S.D=\sqrt{\frac{\Sigma(xi-x')^2}{N-1}}$	$\%RSD = \frac{SD}{X'}X100$
1	0.255	0.2525	0.0025	1.100x10^{-5}	0.001915	0.75%
2	0.251		-0.0015			
3	0.253		0.0005			
4	0.251		-0.0015			

Table (6) Calculation of the %RSD of the mercury(ll) ion at concentration 3.918x10^{-5}M.

N0	Abs (Xi)	Mean (x')	(xi-x')	Σ(xi-x')^2	$S.D=\sqrt{\frac{\Sigma(xi-x')^2}{N-1}}$	$\%RSD = \frac{SD}{X'}X100$
1	0.519	0.5165	0.0025	4.100x10^{-5}	0.003697	0.71%
2	0.512		-0.0045			
3	0.515		-0.0015			
4	0.520		0.0035			

- Calculation of Detection limit .

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

Table (7) Calculation of the D.L of the copper(ll) ion at concentration $6.299x10^{-5}$M.

N0	Abs (Xi)	Mean (x')	(xi-x')	Σ(xi-x')^2	$S.D = \sqrt{\frac{\Sigma(xi - x')^2}{N - 1}}$	$D.L = \frac{3x\ conc\ x\ S.D}{\bar{x}}$
1	0.711	0.71275	-0.00175	$3.275x10^{-5}$	0.003304	0.0114
2	0.715		0.00225			
3	0.716		-0.00325			
4	0.709		-0.00375			

2- Statistical treatment and calculation of D.L values for mercury(II) ion.

Table (8) Calculation of the D.L of the mercury(ll) ion at concentration $2.991x10^{-5}$M.

N0	Abs (Xi)	Mean (x')	(xi-x')	Σ(xi-x')^2	$S.D = \sqrt{\frac{\Sigma(xi - x')^2}{N - 1}}$	$D.L = \frac{3x\ conc\ x\ S.D}{\bar{x}}$
1	0.402	0.405	-0.003	$3.000x10^{-5}$	0.003163	0.0288
2	0.409		0.004			
3	0.406		0.001			
4	0.403		-0.002			

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة كربلاء

كلية العلوم- قسم الكيمياء

التقدير الطيفي لكميات ضئيلة لايوني النحاس(II) والزئبق(II) باستخدام مشتق (ازو) جديد ودراسة دوالها الثرموديناميكية وتطبيقاتها التحليلية

رسالة مقدمة الى

كلية العلوم – جامعة كربلاء

كجزء من متطلبات نيل درجة الماجستير

في علوم الكيمياء

من قبل

مصطفى حامد عطية

بكالوريوس علوم كيمياء – جامعة واسط (2016)

بأشراف

الاستاذ الدكتور

علاء فراك حسين

1441هـ 2021م

بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ

وَمَن يَتَّقِ اللَّهَ يَجْعَل لَّهُ مَخْرَجًا وَيَرْزُقْهُ مِنْ حَيْثُ لَا يَحْتَسِبُ
وَمَن يَتَوَكَّلْ عَلَى اللَّهِ فَهُوَ حَسْبُهُ إِنَّ اللَّهَ بَالِغُ أَمْرِهِ قَدْ
جَعَلَ اللَّهُ لِكُلِّ شَيْءٍ قَدْرًا

صدق الله العلي العظيم

(سورة الطلاق /3,2)

الخلاصة

اشتملت الدراسة على تحضير وتشخيص ليكاند ازو جديد **4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazol**وهو أحد مركبات Azo المحضر باستخدام طريقة الازوتة التقليدية طريق تفاعل الديازونيوم بواسطة تفاعل ملح مركبm-toluidine مع مشتق الأميدازول وإجراء دراسة أولية باستخدام (9) أيونات فلزية و دراسة التحليل الطيفي لها وقد تم اختيار ايوني النحاس والزئبق للدراسة ا باستخدام الكاشف المذاب في الإيثانول حيث اعطا محلول الكاشف اعلى امتصاص باستخدام تقنية UV-vis (λ max = 446.5nm) . تم دراسة معقدات النحاس (II) والزئبق (II) المتكونة مع الكاشف ، بالإضافة إلى ذلك ، تمت دراسة الضروف الفضلى لتفاعل هذه الأيونات مع الكاشف ، مثل الدالة الحامضية ، وحجم وتركيز الكاشف ، وزمن الاستقرار للمعقدات ، درجة الحرارة . تم دراسة منحني المعايرة لكل من هذه الأيونات مع الكاشف ، بحيث يكون معقد النحاس (II) ضمن مدى من التركيز ($3.14x10^{-7}$-$1.889x10^{-5}$ M) و معامل الخطية (R^2 = 0.9989) وقيمة الامتصاصية المولارية (ε) تساوي ($L.moL^{-1}$ .cm^{-1} $1.110x10^{4}$) وحساسية Sandel تساوي (0.00588 ميكروغرام / سم ^{2}) ، بينما كان ايون الزئبق (II) يقع في مدى من التركيز ($1.994x10^{-7}$-$8.973x10^{-6}$ M) ومعامل الخطية (R^2 = 0.9988). قيمة الامتصاصية المولارية (ε) = ($1.310x10^{4}L.moL^{-1}.cm^{-1}$) , تساوي حساسية ساندل (0.00153 ميكروغرام / سم ^{2}) ، وتمت دراسة تكافؤ ية المعقدات المحظرة من خلال إيجاد نسبة أيون الفلز إلى الكاشف (M: L) باستخدام طريقة التغييرات المستمرة والنسبة المولية وطريقة Mullard لمعقدات النحاس (II) والزئبق (II) ووجدت نسبة الليكاند للايون 2-1 مول. تم دراسة ثابت الاستقرار (K) للمعقدين وكانت قيمته لمركب النحاس (K =$2.649x10^{10}$) ولمركب الزئبق (K = $1.460x10^{9}$). بالإضافة إلى ذلك ، تم حساب الدوال الثرموديناميكية للمعقدات المحضرة (ΔH ،ΔG ،ΔS) ، حيث أشارت النتائج إلى أن التفاعل الناتج من تكوين معقد النحاس (II) باعث للحرارة ومركب الزئبق (II) ماص للحرارة. تم دراسة تأثير وجود الايونات السالبة والموجبة على المعقدات المحضرة ، كما تمت دراسة إضافة عوامل الحجب لتقليل تاثير تداخل الايونات المتداخلة في المحلول ، حيث وجد أن هذه الأيونات تتفاعل بدرجات متفاوتة حسب طبيعة وتركيز الأيونات المتداخلة . ، تم تحديد شحنة المعقدات الصلبة المحضرة الذائبة في الايثانول عن طريق قياس توصلية المعقدات ، حيث اظهرت النتائج انها غير مشحونة. تم تحديد دقة وتوافقية الطريقة التحليلية المستخدمة باستخدام ثلاثة تراكيز مختلفة لكل أيون ، فتراوحت قيم النسبة المئوية للانحراف المعياري النسبي لأيون النحاس (II) بين (0.720-2.110٪) وتراوح نسبة التوافقية بين (95.829٪ -103.930٪) أما بالنسبة للزئبق فقد تراوحت الانحراف المعياري النسبي بين (0.710-1.420٪) ونسة التوافقية تتراوح بين (97.703٪ - 99.197٪) . تم حساب حد الكشف لأيون النحاس وكان ($3.590x10^{-8}$M) اي ما يعادل (0.0114 ميكروغرام / مل) اما حد الكشف لأيون الزئبق (II) فيساوي ($1.435X10^{-7}$)، أي ما يعادل (0.0288 ميكروغرام / مل) ، مما يدل على ان الطريقة الطيفية ذات حساسية عالية باستخدام الكاشف (BMTI). تم دراسة بعض الخصائص الفيزيائية مثل درجة الانصهار والذوبانية والتوصلية المولارية . تم تطبيق الطريقة على المحاليل المحضرة مختبريا وعلى

عينات من صناعية وطبيعية مثل اوراق الشاي وحشوة الانسان ومياه الحنفية لتقدير النحاس في هذه العينات ايضا طبقة الطريقه لتقدير الزئبق في عينات من مياة الحنفية ومياة الابار ووجد ان الطريقة المتبعة في التقدير ذات حساسية ودقة عالية.